Measuring the triple \( O_2 \) isotopic composition of air trapped in ice cores and quantifying the causes of \( \delta^{18}O_{atm} \) millennial scale variations

PhD thesis
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Haraka haraka haina baraka

Swahili Proverb
Abstract

Owing to its 1200 yr lifetime, atmospheric oxygen (O₂) is a global tracer of biological and hydrological processes. The dominant source of O₂ is located in the the low latitudes, where most of the O₂ production/uptake occurs. Atmospheric O₂ can therefore provide valuable information on the tropics, a region of the world which still lacks of climatic reconstructions and whose role is widely debated in the context of millennial-scale climate variations. Atmospheric O₂ is enriched in heavy isotopologues (δ¹⁷O, δ¹⁸O) relative to O₂ in ocean water, the ultimate source of O₂ for photosynthesis. The processes causing enrichment of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O isotope ratios involve the biological cycle, the water cycle, global ice volume/sea-level variations, climatic conditions and stratospheric photochemistry. It is thus essential to estimate the relative importance of these processes to unleash the potential of O₂ isotopologues as global tracers of past changes in the climate system.

The evolution of the past atmosphere can be retrieved from the air bubbles occluded in polar ice cores back to 800 kyr. However, elemental and isotopic fractionation processes alter O₂ isotope ratios during the transport and entrapment of air in the porous layer (firn) on top of the ice sheets, during storage and during the experimental analysis. An understanding of these non-climatic mechanisms is a prerequisite for a correct interpretation of gases preserved in ice cores.

The work presented in this thesis focuses on the past evolution of stable isotopes of atmospheric oxygen from the technical aspects of the measurements of O₂ isotope ratios to the interpretation of their past variations. First, we present the O₂ cycle and describe the results of process-based modeling studies aiming at reproducing the observed enrichment in atmospheric δ¹⁸O and ¹⁷Δ (¹⁷Δₐₜₘ = ln(δ¹⁷Oₐₜₘ + 1) − 0.516 · ln(δ¹⁸Oₐₜₘ + 1)). We review the current understanding of past orbital and millennial time-scale variations of atmospheric O₂ isotopes. We also give a description of air transport and associated processes in the firn, which alter the climatic signal preserved in ice core bubbles.

Second, a very high analytical precision and accuracy is required to measure the past variations of δ¹⁸Oₐₜₘ and especially ¹⁷Δₐₜₘ preserved in ice core bubbles. One must primarily have the ability to measure variations as small as 10 permeg (0.001 ‰), corresponding to the millennial-scale changes observed in ¹⁷Δₐₜₘ. O₂ needs to be separated from other atmospheric constituents to achieve such a level of precision. This motivated us to develop a new method of O₂ separation, based on membrane
technology. We verify its 100 % selectivity to $O_2$, and estimate its $O_2$ permeability. This method is currently not applicable to $^{17}\Delta_{atm}$ measurements due to sealing issues and variable isotope fractionation during $O_2$ permeation across the membrane.

Third, a semi-automated, offline experimental setup for $\delta^{18}O_{atm}$ and $^{17}\Delta_{atm}$ measurements was build up from scratch as an alternative, based on the conventional method relying on gas chromatograph (GC) separation of $O_2$ and nitrogen ($N_2$). It includes air extraction from ice, standard introduction and cryo-collection at 12 K (with a closed Helium cooler) of an $O_2$/Argon (Ar) mixture, after separation from water ($H_2O$), carbon dioxide ($CO_2$) and $N_2$. The GC unit can be bypassed for $\delta^{18}O_{atm}$ measurements in a dried and $CO_2$-free air mixture. We give an overview of the units and controls of the experimental setup, and detail the developed procedure to extract, purify and collect atmospheric $O_2$ from ice core samples.

Fourth, the external precision of the setup, or the reproducibility of ice core $\delta^{18}O_{atm}$ measurements is estimated with 21 Late Holocene Neem (Greenland) ice core samples from the same depth. A melt-extraction method is applied on these large samples ($\sim 30$ g) and $\delta^{18}O_{atm}$, $\delta O_2/N_2$ and $\delta^{15}N$ are measured in an $O_2/N_2$/Ar mixture by isotope ratio mass spectrometry in Dual Inlet (di) mode. We describe the automation of a measurement sequence of up to 10 ice core samples. The scatter observed in the raw $\delta^{18}O_{atm}$ and $\delta O_2/N_2$ underlines the occurrence of gas loss fractionation processes in ice core samples. We detail the method of data-processing, its associated uncertainty and the strategy employed to correct for non climatic effects. Based on zero-enrichment tests, the internal precision of di measurements of $\delta^{18}O$ and $\delta^{15}N$ is 0.008 %o ($1\sigma$) and 0.005 %o ($1\sigma$). A similar precision is reached with individual ice core sample measurements. Based on the 21 Neem ice core samples, the ability of the analytical system to reproduce $\delta^{18}O_{atm}$ and $\delta O_2/N_2$ is estimated as 0.028 %o ($1\sigma$) and 0.021 %o ($1\sigma$), respectively.

Fifth, thanks to improving isotope measurement techniques, millennial scale variations of $\delta^{18}O_{atm}$ and $^{17}\Delta_{atm}$ preserved in polar ice cores have been revealed. In particular, a systematic $\delta^{18}O_{atm}$ increase is recorded during Heinrich stadials (Greenland stadials during which a Heinrich event occurs). Because of its global character, $\delta^{18}O_{atm}$ provides added value compared to the different local records of hydrological cycle variations in different continental and marine archives. However, until now, no quantitative, robust interpretation of past variations in $\delta^{18}O_{atm}$ has been established, which limits the use of $\delta^{18}O_{atm}$ as a quantitative indicator for past biospheric production or variations of the hydrological cycle. Here, we quantify the response of $\delta^{18}O_{atm}$ to such millennial events using a freshwater hosing simulation performed under glacial boundary conditions. Our $O_2$ isotope mass balance model takes into account the latest estimates of isotope fractionation factors for respiratory and photosynthetic processes, and makes use of atmospheric water isotope and vegetation changes obtained with the general circulation model IPSL-CM4. The atmospheric component of IPSL-CM4 is fitted with a water isotope module (LMDZ4), and its land component, the dy-
dynamic global vegetation model ORCHIDEE, is run offline. Our modeling approach reproduces the main observed features of a Heinrich stadial in terms of climatic conditions, vegetation distribution and $\delta^{18}O$ of precipitation. We use it to decipher the relative importance of the different processes behind the observed changes in $\delta^{18}O_{atm}$. Our results highlight the dominant role of hydrology on $\delta^{18}O_{atm}$ and confirm that $\delta^{18}O_{atm}$ can be seen as a global integrator of hydrological changes over vegetated areas. This work has been published in Climate of the Past in 2015 under the title Quantifying molecular oxygen isotope variations during a Heinrich stadial.
Med sin atmosfæriske levetid på 1200 år er atmosfærisk ilt ($O_2$) en global markør, der hovedsagligt opstår på de lave breddegrader idet signalet integrerer biologiske og hydrologiske ændringer i områder med vegetation. Det kan derfor indeholde værdifulde oplysninger om klimaændringerne i troperne, en region som stadig mangler klimatiske rekonstruktioner, og hvis rolle i forbindelse med tusindårige klimaversioner ikke er klarlagt. Atmosfærisk $O_2$ er beriget i tunge isotopologer ($\delta^{17}O, \delta^{18}O$) i forhold til $O_2$ i havvand, der er den oprindelige kilde af $O_2$ fra fotosyntese. De processer, som forårsager en berigelse af $^{17}O/^{16}O$ og $^{18}O/^{16}O$-isotopforholdene er den biologiske cyklus, vandets kredsløb, ændringer i globalt is-mængde/hav-niveau, klimatiske forhold og fotokemiske processer i stratosfæren. For at benytte $O_2$ isotopologer til at sige noget om de klimatiske ændringer er det derfor vigtigt at kende den relative betydning af disse processer. Udviklingen i sammensætningen af fortidens atmosfære gennem de sidste 800.000 år kan bestemmes ud fra luftbobler i de polare iskerner. Under transport og indeslutning af luft i et porøst is-lag (fîrn) på iskappernes overflade, samt under lagring og analysering, foregår stof- og isotop-fraktionerings-processer, som ændrer isotopforholdet af $O_2$. En forståelse af disse ikke-klimatiske processer er en forudsætning for en korrekt fortolkning af de gasser, som er bevaret i iskerneren.

Denne afhandling fokuserer på ændringerne af de stabile isotop der atmosfærisk ilt, fra tekniske aspekter af måling af $O_2$ isotopforhold til klimatiske fortolkning af deres tidslige variationer. Først præsenteres cyklussen for $O_2$, og vi beskriver resultater af proces-baserede modellerings-studier, som søger at reproduceres den observerede berigelse af atmosfærisk $\delta^{18}O$ og $\delta^{18}C$. Vi gennemgår den nuværende forståelse af fortidens variation af atmosfæriske $O_2$-isotoper. Vi beskriver også de processer forbundet med lufttransport i firnen, som ændrer det klimatiske signal i iskernernes luftbobler.

Det kræver meget høj analytisk præcision og nøjagtighed at måle fortidens variationer af $\delta^{18}O_{atm}$ og især $\Delta^{17}O_{atm}$ bevaret i iskernernes luftbobler. Dette gennemgåes i del 2. Først og fremmest skal man kunne måle meget små variationer på ned til 10 permeg (0,01 %), hvilket svarer til de observerede ændringer i $\Delta^{17}O_{atm}$ gennem de tusindårige klimaændringer. For at opnå denne grad af præcision er det nødvendigt at adskille $O_2$ fra de øvrige atmosfæriske bestanddele. Dette motiverede os til at udvikle en ny metode til $O_2$-adskillelse, baseret på membranteknologi. Vi bekræftede, at membranen har 100 % selektivitet til $O_2$, og vi har anslået dens $O_2$-permeabilitet,
men metoden er endnu ikke anvendelig for \(17 \Delta_{\text{atm}}\)-målinger grundet problemer med forsegling og variabel isotop-fraktionering under \(O_2\)'s bevægelse gennem membranen.

I afhandlingen tredje del gennemgås en semi-automatisk, offline forsøgspostilling for \(\delta^{18}O_{\text{atm}}\) og \(17 \Delta_{\text{atm}}\) målinger, som vi byggede op fra bunden som en alternativ metode, baseret på den konventionelle metode der bygger på adskillelse af \(O_2\) og kvælstof \((N_2)\) i en gaskromatograf \((GC)\). Metoden omfatter ekstraktion af luft fra is, introduktion af en standard og cryo-opsamling ved 12 K (med en lukket helium afkøler) af en \(O_2\)-Argon (Ar) blanding, efter adskillelse fra vand \((H_2O)\), kulloxid \((CO_2)\) og \(N_2\). GC enheden kan bypasses for \(\delta^{18}O_{\text{atm}}\) målinger i en tør og \(CO_2\)-fri luftblanding. Vi giver et overblik af enhederne og kontrol af forsøgspostillingen, og beskriver den udviklede procedure at udtrække, rense og indsamle den atmosfæriske \(O_2\) fra iskerneprøverne.

I afhandlingens fjerde del bekræftes vi forsøgspostillingens reproducerbarhed ved måling på 21 iskerneprøver fra NEEM iskernen (Grønland) taget fra den samme dybde, fra den sene del af Holocæn. Vi anvendte en smeltvands-ekstraktions metode på disse store prøver \((>30 g)\), og målte \(\delta^{18}O_{\text{atm}}\), \(\delta O_2/N_2\) og \(\delta^{15}N\) i en \(O_2\)-\(N_2\)-Ar-blanding med isotopforholds massespektrometri i Dual Inlet (di) tilstand. Vi beskriver automatisering af en målingssekvens på 10 iskerneprøver. En vis spredning i de rå \(\delta^{18}O_{\text{atm}}\) og \(O_2/N_2\) målinger understreger forekomsten af gastab ved fraktioneringsprocesser i iskerneprøverne. Vi beskriver metoden til databehandling, dens tilhørende usikkerhed og den strategi vi har anvendt til at korrigere for ikke-klimatiske effekter. Baseret på nul-berigelse tests findes den interne præcision af di-målinger af \(\delta^{18}O\) og \(\delta^{15}N\) til at være 0.008 \(\%\) (1 \(\sigma\)) og 0.005 \(\%\) (1 \(\sigma\)). En tilsvarande præcision er nået med individuelle målinger af iskerneprøverne. Baseret på de 21 prøver fra NEEM iskernen anslås reproducerbarheden af \(\delta^{18}O_{\text{atm}}\) og \(\delta O_2/N_2\) af det analytiske system til at være henholdsvis 0.028 \(\%\) (1 \(\sigma\)) og 0.021 \(\%\) (1 \(\sigma\)).

Den forbedrede måleteknik for isotopmålinger har afsløret tusindårige variationer af \(\delta^{18}O_{\text{atm}}\) og \(17 \Delta_{\text{atm}}\) (del 5). Især ses en systematisk stigning i \(\delta^{18}O_{\text{atm}}\) under Heinrich stadials. På grund af sin globale karakter giver \(\delta^{18}O_{\text{atm}}\) en merværdi i forhold til lokale data-arkiver af de hydrologiske ændringer i forskellige kontinentale og marine arkiver. Men der findes endnu ikke nogen kvantitativ, robust fortolkning af fortidens variationer i \(\delta^{18}O_{\text{atm}}\), hvilket begrænser anvendelsen af \(\delta^{18}O_{\text{atm}}\) som en kvantitativ indikator for fortidige ændringer i den biosfæriske produktion eller den hydrologiske cyklus. Vi har her kvantificeret reaktionen af \(\delta^{18}O_{\text{atm}}\) til sådanne tusindårige klima-begivenheder ved hjælp af en klimamodel med en ferskvands-spuling simulering under glaciale randbetingelser. Vores \(O_2\) isotop-massebalance model tager højde for de seneste estimer for isotop-fraktioneringsfaktorer for respiratoriske og fotosyntetiske processer, og den gør brug af ændringerne i vegetation og atmosfærisk vandisotop-forhold fundet med den generelle cirkulationsmodel IPSL-CM4. Den atmosfæriske komponent i IPSL-CM4 er tilført et vandisotop-modul (LMDZ4), og dens
terrestriske komponent, den dynamiske globale vegetations model ORCHIDEE, køres offline. Vores modellering producerer de vigtigste observerede elementer i et Heinrich stadial, såsom de klimatiske forhold, vegetationsforhold og nedbørens $\delta^{18}O$. Vi bruger disse resultater til at afkode den relative betydning af de forskellige processer bag de observerede ændringer i $\delta^{18}O_{atm}$. Vores resultater påviser, at hydrologiske forhold er den dominerende faktor bag ændringerne i $\delta^{18}O_{atm}$, og de bekræfter, at $\delta^{18}O_{atm}$ kan ses som en globalt integreret markør af de hydrologiske ændringer i områder med vegetation. Dette arbejde er blevet publiceret i Climate of the Past (2015) under titlen Quantifying molecular oxygen isotope variations during a Heinrich stadial.
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List of commonly-used abbreviations and physical constants

DI  Dual Inlet
CF  Continuous Flow
MS  Mass Spectrometer
IRMS Isotope-Ratio Mass Spectrometry
GC  Gas Chromatograph
LIZ Lock-in-zone
BFI  bubble-free ice
MIEC mixed ionic/electronic conducting (ceramic membranes)
BCFZO $BaCo_xFe_yZr_{1-x-y}O_{3-d}$
SST  stainless steel
IT  identical treatment
AC  alternating current
DC  direct current
NEEM North Greenland Eemian Ice Drilling (Greenland, 77.4°N 51.1°W, 2484 m)
NGRIP North Greenland ice core project (Greenland, 75.10°N and 42.32°W, 2917 m)
RICE Roosevelt Island Climate Evolution (Antarctica, 79.21°S, 161.42°W, 560 m)
EDC EPICA Dome C (Antarctica, 75.1°S 123.4°E, 3233 m)
EPICA European Project for Ice Coring in Antarctica
GS  Greenland stadial
GI  Greenland interstadial
HE  Heinrich event
HS  Heinrich stadial
DO  Dansgaard-Oeschger (event)
ITCZ Intertropical convergence zone

e = 1.6022 \cdot 10^{-19} \text{ C} \quad \text{elementary charge}

N_A = 6.02214179 \cdot 10^{23} \text{ mol}^{-1} \quad \text{Avogadro number}

R = 8.31451 \text{ J} \cdot \text{ K}^{-1} \cdot \text{ mol}^{-1} \quad \text{gas constant}

k = 1.3807 \cdot 10^{-23} \text{ J} \cdot \text{ K}^{-1} \quad \text{Boltzmann constant}

k = 8.6175 \cdot 10^{-5} \text{ eV} \cdot \text{ K}^{-1} \quad \text{Boltzmann constant}
1 Introduction

1.1 Preamble

This thesis focuses on the past variations of three stable isotopes of atmospheric oxygen preserved in polar ice cores, reflecting a global climatic signal. In order to retrieve the climatic information, the isotopic composition of \( \text{O}_2 \) occluded in ice core bubbles need to be measured with very high precision/accuracy and corrected for all the processes - in the firn, during coring, during storage and during the analytical measurements - that alter its composition and add uncertainties. The experimental part of my thesis focuses on these aspects and includes the building of an analytical system to extract and measure the three isotopes of \( \text{O}_2 \) in ice core samples. Once the "true" isotopic composition of ancient atmospheric \( \text{O}_2 \) is obtained, the interpretation of its past variations remains complex because the oxygen cycle includes various biological, hydrological and photochemical processes that cause oxygen isotope fractionation. It is therefore critical to estimate the relative contribution of these processes to give a correct interpretation of past oxygen isotope variations. The modeling part of this thesis quantifies the latter during abrupt climatic events of the last glacial period.

Disentangling of the measured \( \text{O}_2 \) isotopic signal (\( \delta^{18}O_{\text{atm}} \), \( \Delta^{17}O_{\text{atm}} \)) can thus be seen as the Ariadne's thread of this thesis:

- From an experimental standpoint, this implies (1) to design and build a high-purity \( \text{O}_2 \) extraction line, (2) to develop an analytical procedure in agreement with the international standards in isotope-ratio mass spectrometry (noted IRMS hereafter) measurements, in particular in terms of precision and accuracy, (3) to correct for isotope fractionation caused by processes in the firn and gas loss processes during coring and storage, and (4) to correct for isotope fractionation processes occurring in the experimental setup during the handling, extracting, separating, collecting or measuring steps undergone by the ice core sample.

- From a modeling perspective, unraveling the signal requires (1) to understand the factors driving the isotopic composition of atmospheric oxygen, (2) to model the processes at play in the \( \text{O}_2 \) cycle, and (3) to quantify the relative contribution of these processes so as to give a consistent interpretation of the observed past variations.

The present PhD thesis is part of the Initial TRAining network on Mass Independent Fractionation (INTRAMIF) project (project No:237890). The scientific objectives of this European project were to "investigate processes which include signatures of Mass Independent Fractionation (MIF)" in several O-bearing compounds in the Earth's system. This was carried out in 13 individual Early Stage Researchers projects.

My original project, ESR 11, was entitled Mass independent fractionation in tropospheric \( \text{O}_2 \): a tracer for past total oxygen production. The initial goal of this thesis
was mainly experimental: it represented the development of a new method for oxygen separation (Chapter 2), along with the building of an improved extraction and collection system to measure the triple isotope composition of past oxygen in air bubbles occluded in ice cores (Chapter 3). The aim was to obtain a very high precision record of MIF over several glacial-interglacial cycles by extending measurements back to 850 kyr on Antarctic ice core, to track back the past global productivity of the vegetation. However, multiple challenges and delays faced throughout the PhD thesis on the experimental side required modifications to this approach. The oxygen line built during this thesis can currently measure $\delta^{18}O_{\text{atm}}$ with a reasonable ice reproducibility (Chapter 4), but has not been yet validated for $\Delta^{17}O_{\text{atm}}$ analysis.

(a)

(b)

Figure 1.1 – The interdisciplinary character of the present thesis, ESR 11 project, is illustrated in this two graphs. (a) The different research centers involved in the INTRAMIF project. ESR 11 project is based at the Center for Ice and Climate (CIC), Denmark. (b) Interpreting the isotope composition of atmospheric $O_2$ is at the heart of the climate system (ocean, ice, atmosphere), requiring knowledge on the biospheric processes, the hydrological cycle and the stratospheric photochemistry.

Instead, a modeling part is included in my PhD, in collaboration with the Laboratoire des Sciences du Climat et de l’Environnement (LSCE). This work focuses on the millennial scale variations of atmospheric $O_2$ isotope composition over the last glacial period, and has been published in Climate of the Past in 2015 under the title "Quantifying molecular oxygen isotope variations during a Heinrich stadial" (Reutenauer et al., 2015). The paper is reproduced in Chapter 5.

Additionally to its interdisciplinary character (Fig. 1.1), a strong added value of this project was the opportunity to be involved in all the steps required to extract valuable climatic information from an ice core sample: from the ice sheet to the mass spectrometer (experimental side), and from the measured data to their interpretation, using models to disentangle the processes at play (modeling side). This section starts with an overview of the $O_2$ cycle, including a review of the processes influencing its isotope composition (Sect. 1.2). Section 1.3 describes the past variations of the three isotope logues of atmospheric $O_2$ over the last 800 kyr, documented by ice core archives, and
presents the current understanding of its orbital and millennial time-scale changes. To correctly interpret the past variations of atmospheric $O_2$ isotopologues preserved in air bubbles occluded in polar ice cores, it is critical to understand how the air is entrapped in the ice during the transformation of snow to ice, as these processes affect the elemental and isotope composition of $O_2$ (Sect. 1.4). Note that other artifactual gas loss processes cause isotope fractionation of $O_2$, during ice core recovery, storage and/or during the ice core sample measurements, and they are discussed in Chapter 4. Finally, the organization of the manuscript is presented in Sect. 1.5.

### 1.2 The isotopic composition of atmospheric oxygen

Oxygen is the third most abundant element in the universe (with hydrogen and helium), and second most abundant species (with $N_2$) in atmospheric air (20.8%). It is also abundant in surface waters, the mantle and the crust, and biological reservoirs. $CO_2$ plays an important role in the transfer of oxygen between these reservoirs (Thiemens, 2012). The cycle of $O_2$ represents the largest biogeochemical cycle on Earth, with $\approx 3 \cdot 10^{16}$ moles of $O_2$ produced and consumed. As oxygen is produced by photosynthesis and consumed by respiration, a record of oxygen concentration in the past should help constrain these two major biospheric fluxes on Earth and potentially provide information on their link with the carbon cycle. Besides, gathering knowledge on the past vegetation is important, as biosphere - atmosphere interactions affect global climate through various feedbacks, via the role of the biosphere in the hydrological cycle or terrestrial albedo change, emission and consumption of greenhouse gases (Bender, 2003).

#### 1.2.1 Focusing on $O_2$ isotopes rather than $O_2$ mixing ratio

Changes in the $O_2/N_2$ ratio can be measured in air trapped in ice cores back to 800 kyr (Bender, 2002; Kawamura et al., 2007; Landais et al., 2012). Unfortunately the $O_2/N_2$ ratio in ice cores does not provide a direct information on the true atmospheric variations because it is affected by permeation\(^1\) through the ice lattice during bubble formation at pore close-off, roughly 100 m below the ice sheet surface, and by gas loss during ice core recovery and storage (Sect. 1.4). Orbital tuning of ice core chronologies has nonetheless been achieved based on the magnitude of $\delta O_2/N_2$ fractionation at bubble close-off, considered as a proxy for local summer insolation (Bender, 2002; Kawamura et al., 2007; Landais et al., 2010). While they affect the elemental composition of ice core samples, these processes have fortunately less impact on oxygen isotopologues ($\delta^{18}O$, $\delta^{17}O$), the diameter of which are of similar size (see Sect. 1.4.1.3). Oxygen isotope ratios have thus been explored as possible constraints on biospheric productivity (e.g. Luz et al., 1999).

\(^1\)Permeation is the transport of a fluid through the interconnected pore space (interstitial space) of a porous medium.
1.2.2 Definitions

Molecular oxygen has three stable isotopologues, the most abundant being $^{16}$O$^{16}$O (mole fraction: 0.99757(16)) and the two rarer $^{17}$O$^{16}$O (3.8(1) · 10$^{-4}$) and $^{18}$O$^{16}$O (2.05(14) · 10$^{-3}$). When dealing with oxygen isotopes, it is standard to use the isotope ratio, $R$, defined as the fraction of the abundance of the rare isotope over the dominant one in a substance:

$$iR = R(i/O^{16}O) = \frac{iO}{16O}, \quad (1.1)$$

where $i$ can either be 18 or 17. Indeed, $^{34}R = 2 \cdot 18$ and $^{33}R = 2 \cdot 17$ are good approximations (Young et al., 2014). In this thesis, $O_2$ isotopologues are measured by IRMS, where the ratio of the ion currents, that is the number of ions collected in the Faraday cups (refer to chapter 4 for details), represents the quantity $R$ (Coplen, 2011).

For $O_2$ isotopologues, the ratio of the ion current measured on the $m/z$ 34 (mass (m) to charge (z) ratio) or $m/z$ 33 collector to the ion current measured on $m/z$ 32 collector is:

$$^{34}R = ^{34/32}R = \frac{N^{(18}O^{16}O)}{N^{(16}O^{16}O)} \quad (1.2)$$

and

$$^{33}R = ^{33/32}R = \frac{N^{(17}O^{16}O)}{N^{(16}O^{16}O)} \quad (1.3)$$

where $N^{(18}O^{16}O)$, $N^{(17}O^{16}O)$ and $N^{(16}O^{16}O)$ are, respectively, the $^{18}O^{16}O^+$, $^{17}O^{16}O^+$ and $^{16}O^{16}O^+$ number of ions collected on $m/z$ 34, $m/z$ 33 and $m/z$ 32 collectors.

Since changes in isotope ratios through natural processes are very small, the isotope delta, or relative difference in isotopic ratios is expressed in relation to a standard using the $\delta$ notation. In the case of $O_2$ isotopes:

$$\delta^iO = \frac{iR_{\text{sample}}}{iR_{\text{standard}}} - 1, \quad (1.4)$$

where $i$ can either be 18 or 17. As $\delta$ values are very small, it is standard to multiply them by a factor of 1000 and express them in ‰. Present-day atmospheric $O_2$ is used as a primary standard for atmospheric $O_2$ (e.g. Barkan and Luz, 2003) as it is spatially homogeneous because of its long residence time in the atmosphere ($\simeq 1200$ yr) compared to the interhemispheric mixing time ($\simeq 1$ yr). Additionally, its isotopic composition has not significantly changed over the last 50 years (corresponding to the period where it has been measured).

The partitioning of isotopes which occurs during most of physical and chemical processes on Earth is mass-dependent. It results from equilibrium and kinetic reactions between two substances (e.g. carbon dioxide into plant organic carbon), or phases (e.g. liquid water to water vapor). Isotopes of an element have indeed slight differences in
chemical and physical properties due to their mass difference (due to a different number of neutrons). As a result of fractionation processes, the isotope ratio of the considered substance is often unique and may inform on the source of the substance or the nature of the processes at play. The increased level of precision obtained through continuous improvements in IRMS measurements and analytical procedures enable at present to distinguish equilibrium and kinetic fractionation processes (Young et al., 2002).

Equilibrium isotope fractionation is expressed with the isotope fractionation factor \( \alpha \). It is defined as the ratio of the isotope ratios between the two substances, or phases A and B at equilibrium. It is equivalent to the equilibrium constant between compounds A and B for the isotope substitution reaction

\[
A + hB \rightleftharpoons hA + B,
\]

where \( h \) indicates the compound containing the heavy isotope (\( ^{17}O \) or \( ^{18}O \) in the case of \( O_2 \)):

\[
K = \frac{[hA][B]}{[hB][A]} = \frac{[hA] / [A]}{[hB] / [B]} = \frac{hR_A}{hR_B} = h\alpha_{A/B} = h\alpha_{eq}.
\] (1.5)

For instance, let us consider equilibrium exchange of \( ^{18}O \) of \( H_2O \) between liquid (liq) and vapor (vap) phases. \( R_A \) and \( R_B \) are the oxygen isotope ratios \( ^{18}R_{liq} \) and \( ^{18}R_{vap} \), respectively. In that case, \( ^{18}\alpha_{eq} \) is greater than 1, in other words the \( O_2 \) isotopic composition of liquid water is heavier than the one of water vapor. Light isotopes have indeed a higher saturation pressure than heavy isotopes, and are therefore more abundant in the gas phase than in the liquid phase. The liquid phase is thereby enriched in heavy isotopes. In general, \( \alpha \) decreases with temperature, as the isotopic difference in binding energies decreases with increasing temperature (Lennard-Jones, 1931).

Unlike reversible equilibrium reactions, where forward and backward reaction rates are identical, kinetic processes represent irreversible, one way reactions, such as respiration or evaporation. Such reactions are dependent on the ratio of the masses of the isotopologues. Light isotopologues indeed are more reactive according to their kinetic energy:

\[
E_{kin} = kT = \frac{1}{2}mv^2,
\] (1.6)

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, \( m \) the mass and \( v \) the average molecular velocity. As shown by Eq. 1.6, the kinetic energy of a molecule is solely controlled by its temperature. This means that a heavier isotopologue will have a lower velocity than the light isotopologue. For atmospheric \( O_2 \), the molecule containing a \( ^{18}O \) atom will move at \( \sqrt{M_{18O}/M_{^{16}O}} = \sqrt{32/34} = 0.94\% \) of the speed of the light isotopologue. This speed difference explains why light isotopologues will (1) diffuse faster, and (2) undergo more collisions with other molecules, thus reacting more often and thereby depleting the products (in heavy isotopologues) while enriching the reactants. Kinetic isotope fractionation is expressed with the fractionation factor \( \alpha_{kin} \).

The relation between the quantities isotope fractionation factor \( \alpha \), isotope fraction-
ation $\varepsilon$, and isotope delta $\delta$ of compounds A and B is expressed as:

$$\varepsilon_{A/B} = \alpha_{A/B} - 1 = \frac{\delta_{A/\text{standard}} - 1}{\delta_{B/\text{standard}} - 1},$$

We’ve seen that the quantities $\varepsilon$ and $\alpha$ can refer to a thermodynamic equilibrium process or a kinetic process. It can also define an “apparent” distribution of isotopes between substances or phases in complex biogeochemical systems, having unknown pathways or combining several reactions.

1.2.3 The oxygen cycle and its associated isotope fractionations

In this section, we describe the cycle of oxygen (Fig. 1.2) and its associated processes causing isotopic fractionation\(^2\). Not only biological processes, but also the hydrological cycle or the stratospheric photochemistry cause oxygen isotope fractionation, which makes the interpretation of atmospheric $O_2$ isotope variations complex.

1.2.3.1 Biological processes: oxygen production

*Photosynthesis* Photosynthesis produces organic carbon from inorganic carbon ($CO_2$):

$$6CO_2 + 12H_2O + \text{light} \longrightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Tropospheric oxygen is produced through terrestrial and marine photosynthesis. According to estimates from Bender et al. (1994), Luz et al. (1999), Hoffmann et al. (2004), marine production ranges from 7.61 to 12 $Tmol \cdot yr^{-1}$ of $O_2$ ($1Tmol = 10^{15}$ mol), while terrestrial production causes $O_2$ fluxes from 16.7 to 20.4 $Tmol \cdot yr^{-1}$.

*Land* As photosynthesis produces $O_2$ from water, and ocean waters represents the ultimate source of oxygen, being the largest reservoir on Earth, one would not expect large differences between the isotopic composition of atmospheric $O_2$ and the one of ocean waters. At isotopic equilibrium between ocean water and air, $\delta^{18}O_{atm}$ would in fact be enriched by $6\%$ (Urey and Greiff, 1935; Young et al., 2014). However, more than 80 years ago, Dole (1935) and Morita (1935) observed a very large difference in the atomic weight of oxygen in air and in water, with air enriched in $^{18}O$. The review of Dole (1965) attributed this difference to isotope fractionation during photosynthesis (based on experiments of Dole and Jenks, 1944) and respiration (based on experiments from Lane and Dole, 1956). However, following observations (Guy et al., 1993) showed that no fractionation of oxygen isotopes occurred during photosynthesis (on spinach thylakoids, cyanobacteria, and diatoms). Instead, Dongmann et al. (1972); Dongmann (1974) proposed that evapotranspiration of the substrate water for photosynthesis - at the site of oxygen production - would enrich newly produced $O_2$ by $8\%$, a value refined since then (Sect. 1.2.3.3). This is an important contribution to

\(^2\)An exhaustive review can be found in Luz et al. (2014), with a detailed description of the experimental studies done to determine isotope fractionation of biological processes.
Figure 1.2 – Scheme of sources and sinks related to the oxygen cycle. Fluxes of water (blue), and fluxes of oxygen (green) are associated with mass-dependent fractionation, while fluxes of oxygen between the troposphere and the stratosphere (red) are associated with mass-independent fractionation. All these processes must be accounted for when calculating the isotopic balance of oxygen in the troposphere (Chapter 5).

the understanding of $\delta^{18}O_{atm}$ variations as $\delta^{18}O$ enrichment during photosynthesis on land is primarily driven by hydrological processes (Sect. 1.2.3.3), rather than biological ones.

In the last 20 years, new experiments have confirmed that assuming no isotope fractionation during oxygen production (Guy et al., 1993) is likely to be correct for land photosynthesis (Luz and Barkan, 2005), but have also revealed that marine photosynthetic production of $O_2$ by phytoplankton causes enrichment of the produced $O_2$ up to 6 % with respect to the substrate water (Eisenstadt et al., 2010), at the exception of cyanobacteria (Helman et al., 2005), where no fractionation is observed.

### 1.2.3.2 Biological processes: oxygen uptake

#### 1.2.3.2.1 $^{18}\alpha_{\text{resp}}$

10 years later, Rabinowich (1945) first proposed that respiration was responsible for the isotopic enrichment observed in atmospheric $O_2$. Indeed, respiratory processes consume preferentially light isotopologues of $O_2$, leaving the remaining gas - the atmosphere - enriched in heavy isotopologues. Dole (1965) confirmed in a review that respiration by various organisms was causing isotopic fractionation.

In land, the isotope fractionation factor associated with oxygen uptake can be expressed in terms of dark (mitochondrial) respiration, Mehler reaction and photoreso-
expiration fractions, each of these respiratory processes being associated with a specific fractionation:

\[ 18\alpha_{\text{resp}} = 18\alpha_{\text{photo}} \cdot f_{\text{photo}} + 18\alpha_{\text{Mehler}} \cdot f_{\text{Mehler}} + 18\alpha_{\text{dark}_\text{soil}} \cdot f_{\text{dark}_\text{soil}} + 18\alpha_{\text{dark}_\text{leaves}} \cdot f_{\text{dark}_\text{leaves}} \]  \hspace{1cm} (1.9)

The latest estimations - and associated references - of the isotope fractionation factors \(18\alpha_{\text{resp}}, 18\alpha_{\text{Mehler}}, 18\alpha_{\text{photo}}, 18\alpha_{\text{dark}_\text{leaves}}\) and \(18\alpha_{\text{dark}_\text{soil}}\) can be found in Table 1.1. Corresponding \(O_2\) uptake fluxes are represented by \(f_{\text{Mehler}}, f_{\text{photo}}, f_{\text{dark}_\text{leaves}}\) and \(f_{\text{dark}_\text{soil}}\), whose sum equals 1. The Mehler reaction fraction, \(f_{\text{Mehler}}\), is assumed to represent 10% of global respiration (Badger et al., 2000). GCMs are required to precisely estimate the fraction of photorespiration \(f_{\text{photo}}\), (e.g. Hoffmann et al., 2004; Landais et al., 2007a; Reutenauer et al., 2015). The fractions \(f_{\text{dark}_\text{soil}}\) and \(f_{\text{dark}_\text{leaves}}\) can be estimated based on Schlesinger and Andrews (2000), who found that global carbon fluxes from soils represent 62% of the global Gross Primary Production (GPP).

Figure 1.3 – The dependence of the isotope fractionation of terrestrial respiration on that of two of the main \(O_2\) uptake processes, soil respiration and photorespiration. Values are calculated from GPP computed by the global dynamic vegetation model ORCHIDEE for the LGM Control simulation (refer to Chapter 5). Each value correspond to a grid cell in the model. While the fraction of photorespiration \(f_{\text{photo}}\) is variable but its associated isotope fractionation constant, the fraction of soil respiration \(f_{\text{dark}_\text{soil}}\) is almost constant but its associated isotope fractionation \(18\epsilon_{\text{dark}_\text{soil}}\) variable. The triangle shape is due to the fact that \(\epsilon_{\text{dark}_\text{soil}}\) associated with temperate and boreal soils is of similar magnitude as \(\epsilon_{\text{photo}}\), such as variations of \(f_{\text{photo}}\) in mid to high latitudes have only a moderate impact. In contrast, \(\epsilon_{\text{dark}_\text{soil}}\) is much weaker in tropical soils and compensates for the strong isotope fractionation of photorespiration.
Table 1.1 – Isotope fractionation $^{18}\varepsilon$ and mass-dependent fractionation slope $\lambda \left( \frac{\ln(17\varepsilon)}{\ln(18\varepsilon - 1)} \right)$ during $O_2$ uptake processes. Uncertainties are indicated if available

<table>
<thead>
<tr>
<th>parameter</th>
<th>$O_2$ uptake process</th>
<th>$10^4 \cdot 18\varepsilon$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{18}\varepsilon_{\text{dark leaves}}$</td>
<td>dark respiration in leaves (90% COX, 10% AOX) through cytochrome oxidase pathway (COX)</td>
<td>19 ± 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.516 ± 0.001&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>alternative oxidase pathway (AOX)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.4 to 19.9&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.516&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.1 to 26.2&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.514&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$^{18}\varepsilon_{\text{dark soil}}$</td>
<td>dark soil respiration including tropical</td>
<td>15.6 ± 0.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.516 ± 0.001&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>temperate</td>
<td>17.8 ± 1.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>boreal</td>
<td>22.5 ± 3.6&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$^{18}\varepsilon_{\text{Mehler}}$</td>
<td>Mehler reaction</td>
<td>10.8 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.525 ± 0.002&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>$^{18}\varepsilon_{\text{photo}}$</td>
<td>photosynthesis</td>
<td>21.4 ± 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.509 ± 0.001&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>a two step process</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>rubisco oxygenase</td>
<td>21.3 to 21.8&lt;sup&gt;g,h&lt;/sup&gt;</td>
<td>0.517&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>glycolate oxidase</td>
<td>21.5 to 22.7&lt;sup&gt;g,h&lt;/sup&gt;</td>
<td>0.501&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>$^{18}\varepsilon_{\text{resp}}$</td>
<td>global terrestrial respiration</td>
<td>17.4 ± 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.5145 ± 0.000&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Landais et al., 2007a.  
<sup>b</sup>Angert et al., 2003a.  
<sup>c</sup>Angert et al., 2003b.  
<sup>d</sup>Luz and Barkan, 2005.  
<sup>e</sup>Guy et al., 1989.  
<sup>f</sup>Guy et al., 1992.  
<sup>g</sup>Helman et al., 2005.  
<sup>h</sup>Guy et al., 1993.

1.2.3.2.2 Dark respiration

Mitochondrial respiration takes place in the cell of a living organism. It includes various pathways of substrate oxidations, involving glycolysis, Krebs’ cycle and oxidative phosphorylation, that releases usable energy in the form of ATP. This process yields $CO_2$ and $H_2O$ from oxygen and sugars:

$$6O_2 + C_6H_{12}O_6 \rightarrow 6CO_2 + 6H_2O + ATP(\text{energy})$$,  \hspace{1cm} (1.10)

Mitochondrial respiration is the dominant oxygen uptake mechanism, which is assumed to be similar under dark and light conditions (e.g., McCree and Amthor, 1982; van Iersel and Bugbee, 2000). It is also called dark respiration as it does not require sunlight to consume $O_2$ and release $CO_2$, in contrast with photosynthesis or the Mehler reaction. McCree et al. (1970) first proposed the empirical partitioning of dark respiration into two physiological components: a growth and a maintenance component. Growth respiration is dedicated to the synthesis of new biomass while maintenance respiration is defined as the respiration needed to provide the energy for all plant processes that do not result in a net gain in plant biomass, but maintain
existing organs and normal activities of living cells. Quantifying their contribution is essential as variations in their ratio may significantly alter the carbon balance of the plants. Indeed, the amount of carbon incorporated into dry matter represents 50% to 70% of the total amount of carbon fixed in the photosynthetic process (Amthor, 2012), which means that up to 50% of the carbohydrates are respired by the plants.

Dark respiration occurs through two pathways, the cytochrome oxidase pathway (denoted COX hereafter) and the cyanide resistant alternative oxidase pathway (denoted AOX hereafter). In most of the plants, the COX pathway dominates, and a value for $^{18}\varepsilon_{\text{dark leaves}}$ of 0.981‰ (Landais et al., 2007a; Blunier et al., 2002) is estimated when assuming that only 10% of dark respiration in leaves occurs through the AOX pathway, hence 90% through the COX pathway.

1.2.3.2.3 Dark respiration in soils

A significant proportion of terrestrial respiration (30 to 40%) occurs below the surface (Raich and Potter, 1995) with varying fractionation values (Table 1.1). Indeed, isotope fractionation associated with tropical (10.1‰), temperate (17.8‰) and boreal soils (22.5‰) exhibit significant differences, due to different diffusion pathways (Angert et al., 2003a), increasing with colder temperatures, hence causing a high zonal contrast. The nature of the soils thus need to be considered to correctly estimate $^{18}\varepsilon_{\text{dark soil}}$ (Sect. 5).

Additionally to the nature of the soils, diffusion limitations in soils modify the magnitude of the effective $^{18}\varepsilon_{\text{dark soil}}$. This phenomenon was observed by Guy et al. (1989), who noted that when O$_2$ diffusion to the consumption site is slow, the effective $^{18}\varepsilon_{\text{dark soil}}$ is not only dependent on the isotope fractionation of the O$_2$ consuming process, but also on the isotope fractionation of the O$_2$ diffusion and the relative rate of diffusion and consumption (Angert et al., 2001). Farquhar et al. (1982) describes it for CO$_2$ uptake by leaves:

$$^{18}\varepsilon_{\text{eff}} = ^{18}\varepsilon_{\text{diff}} + (^{18}\varepsilon_{\text{uptake}} - ^{18}\varepsilon_{\text{diff}}) \frac{C_i}{C_a},$$

where $\varepsilon_{\text{eff}}, \varepsilon_{\text{diff}}, \varepsilon_{\text{uptake}}$ are respectively the effective, diffusion, uptake isotope fractionation.

It is interesting to mention here the role of soil respiration in Biosphere 2, an enclosed (airtight) experimental ecosystem located in southern Arizona, occupied by a few humans (e.g Broecker, 2000; Severinghaus, 1995): a sharp decrease in O$_2$ concentration (from 21% to 14%) was experienced within Biosphere 2 over the first 16 month. The O$_2$ loss was higher during winter, as photosynthesis was reduced at time of low luminosity. It turned out that soils were too rich in organic matter, causing respiration fluxes to be two times higher than photosynthetic ones. It took some time to validate this hypothesis because the increase in CO$_2$ concentration was too low with respect to the O$_2$ loss. Indeed, during microbial oxidation of organic matter, one mole of CO$_2$ is produced for each mole of O$_2$ consumed. The mystery was unfold when Severinghaus (1995) proved that uptake of carbon by concrete (walls material) to form calcium carbonate was responsible for the discrepancy. This story illustrates the important contribution of soil respiration to total respiration, but an analogy to the real world is not possible, as these soils were extremely rich in organic matter, in particular compost (Severinghaus, 1995).
ation, and Ca and Ci are the substrate concentrations in the ambient air and in the reaction site, respectively. In the case of very slow diffusion, any $O_2$ reaching the site of respiration is entirely consumed, and the effective $O_2$ soil isotope fractionation is only due to diffusion. When diffusion is rate limiting, higher clay content or water content in soils weakens the effective $^{18}\varepsilon_{\text{dark Soil}}$ by switching the mode of $O_2$ diffusion from diffusion in gas to diffusion in liquid phase, much lower (Farquhar and Lloyd, 1993). Consequently, water saturated soils are very poor at transmitting oxygen from the sites of respiration back to the atmosphere (Angert et al., 2001), while dry soils, well aerated, have an effective isotope fractionation similar to the one of the $O_2$ uptake process. In other words, a high-moisture content in soils, by preventing or dampening the back flux of isotopically enriched $O_2$, the residual left over after partial respiratory consumption, to the atmosphere, weakens the effect of $^{18}\varepsilon_{\text{dark Soil}}$ on $^{18}\varepsilon_{\text{resp}}$.

In the context of millennial scale variability during the last glacial period, soil aeration is of great importance. Indeed, during HSs, NH tropical soils generally became less waterlogged, as inferred from the lower atmospheric nitrous oxide concentration and its isotopic composition during HS1 (Schilt et al., 2014). This should cause a stronger $^{18}\varepsilon_{\text{dark Soil}}$, which could play a role in the $\delta^{18}O_{\text{atm}}$ increase over HSs. A rough attempt to account for soil water content variations on millennial time scale can be found in Chapter 5. Additionally, the influence of soil moisture on $^{18}\varepsilon_{\text{dark Soil}}$ strengthens the link between $\delta^{18}O_{\text{atm}}$ and the low latitude hydrological cycle, as already proposed by e.g. Bender et al. (1994) and Severinghaus et al. (2009) on orbital and millennial time scale, respectively.

### 1.2.3.2.4 Photorespiration

Photorespiration is associated with a strong isotope fractionation, with $^{18}\varepsilon_{\text{photo}} = 21.4\%$ (Helman et al., 2005). It is therefore important to estimate the variations of its associated $O_2$ uptake flux as even small changes can significantly affect $\delta^{18}O_{\text{atm}}$ (Fig. 1.3). Photorespiration fraction $f_{\text{photo}}$ is calculated from the proportion of C4 vs C3 plants, the Plant Functional Type (noted PFT hereafter, see Table 1 of Chapter 5 for details), the temperature and $CO_2$ level as depicted in the biochemical model of photosynthesis from Farquhar et al. (1980), and already implemented in the studies of Hoffmann et al. (2004) and Landais et al. (2007a). Low $CO_2$ level, high temperature, conditions of hydric stress lead to an increased rate of photorespiration.

In the following, we describe the parameters controlling $f_{\text{photo}}$. All types of C3 plants photorespire, but in different proportions, while C4 plants do not, owing to a $CO_2$ concentration mechanism allowing them to operate at high chloroplast $CO_2$ partial pressures and thereby to inhibit the oxygenation reaction (Von Caemmerer, 2000). As $CO_2$ assimilation rate and evapotranspiration rate are linked through stomatal conductance (Eq. 1.19), C4 plants resist better to hydric stress than C3 plants. Indeed, they do not need to open their stomata as much as C3 plants do to compensate for the low $CO_2$ level, and thereby limit their evapotranspiration. During photosynthesis, in
Figure 1.4 – Isotopic fractionation and location of various respiratory pathways involved in the oxygen cycle. This graphic is intended to give a qualitative overview of the processes to consider when calculating the global terrestrial isotope fractionation during oxygen uptake. Fractions and isotope fractionation can vary depending on vegetation distribution and climate conditions, in particular the fraction of photorespiration and $\delta^{18}O_{\text{dark}}$ through its soil contribution $\delta^{18}O_{\text{dark,soils}}$. Please refer to text for details and Table 1.1 for references.

(a) Fraction of respiratory processes. Photorespiration fraction primary depends on the C3/C4 ratio (Sect. 1.2.3.2.4) and thus requires the use of vegetation models. Here $f_{\text{photo}}$ has been estimated under Last Glacial Maximum conditions with outputs of the global dynamic vegetation model ORCHIDEE (Sect. 5). (b) The total $\delta^{18}O_{\text{resp}}$ represents the $O_2$ consumption weighted average of $\delta^{18}O_{\text{Mehler}}, \delta^{18}O_{\text{photo}}$ and $\delta^{18}O_{\text{dark}}$. (c) This figure represents the soil, dark and stem fraction of dark respiration, that is without considering photorespiration and Mehler reaction, which do not occur in soils as they require sunlight. Note that in Reutenauer et al. (2015), stem respiration (Angert et al., 2012) is not considered as the estimation of both its fraction and associated isotope fractionation are uncertain.

The chloroplast stroma of C3 plants, there is competition between carboxylation and oxygenation of the Ribulose-1,5-biphosphate- carboxylase-oxygenase (Rubisco), the enzyme responsible for carbon fixation during the Calvin cycle (Tamiya and Huzisige, 1993).
The rate of carboxylation, $V_c$, and of oxygenation, $V_o$, are related by $\eta = \frac{V_o}{V_c}$. During the photosynthetic carbon reduction (PCR) cycle, 1 mol of $CO_2$ consumed produces 1 mol of $O_2$. During the photorespiratory carbon oxidation (PCO) cycle, 0.5 mole of $CO_2$ is released for 1 mol of $O_2$ consumed. In terms of carbon production and oxygen production:

$$C_{\text{prod}} = V_c - 0.5 \cdot V_o = V_c(1 - 0.5 \cdot \eta) \quad (1.12)$$

and

$$O_{2\text{prod}} = V_c + V_o = V_c(1 + \eta). \quad (1.13)$$

From the stoechiometry of the photorespirative reaction, it follows that $P_{\text{photo}}$ for C3 plants, expressed in terms of carbon and oxygen production (Von Caemmerer, 2000; Hoffmann et al., 2004):

$$P_{\text{photo}} = f_{\text{photo}} + 1 = \frac{V_c(1 + \eta)}{V_c(1 - 0.5 \cdot \eta)}. \quad (1.14)$$

From Eq. 1.12 it can be seen that the $CO_2$ compensation point $\tau$ (Laisk, 1977; Laisk and Oja, 1998), defined as the chloroplast $CO_2$ partial pressure when carboxylation equates oxygenation in absence of dark respiration or, in other words, when there is no net $CO_2$ assimilation, is reached when $\eta = 2$. Equations (2.16) and (2.17) from Von Caemmerer (2000) show that:

$$\eta = \frac{V_o}{V_c} = \frac{1}{S_{\text{c/o}}} \cdot \frac{O_i}{C_i}, \quad (1.15)$$

where $S_{\text{c/o}}$ is the relative specificity of Rubisco, and $O_i$ and $C_i$ are the leaf intercellular mixing ratio - or chloroplastic partial pressure - of $O_2$ and $CO_2$, respectively. At $CO_2$ compensation point, Eq 1.15 becomes:

$$2 = \frac{1}{S_{\text{c/o}}} \cdot \frac{O_i}{\tau}, \quad (1.16a)$$

hence

$$S_{\text{c/o}} = \frac{O_i}{2 \cdot \tau}. \quad (1.16b)$$

Rearranging Eq. 1.15 using Eq. 1.16,

$$\eta = \frac{V_o}{V_c} = 2 \cdot \frac{\tau}{C_i}. \quad (1.17)$$

Rearranging Equation 1.14 by substituting $\eta$ with $2 \cdot \frac{\tau}{C_i}$:

$$P_{\text{photo}} = \frac{C_i + 2 \tau}{C_i - \tau}. \quad (1.18)$$

In their study, Lloyd and Farquhar (1994) estimate $\tau = 2 \cdot T_p$, where $T_p$ is the temperature at the time of photosynthesis.
The dependence of \( P_{\text{photo}} \) on PFT is due to \( C_i \), as detailed in the following. Indeed, each PFT optimizes its stomatal behaviour (Cowan, 1977; Cowan and Farquhar, 1977) by varying its stomatal conductance in order to keep constant \( \Lambda \) (\text{mol.mol}^{-1}) the PFT specific biome marginal water cost of plant carbon gain (Lloyd and Farquhar, 1994). \( \Lambda \) is expressed as follows:

\[
\Lambda = \frac{\partial E}{\partial A} = \frac{\partial E}{\partial A},
\]

where \( E \) is the transpiration rate, \( A \) the rate of carbon assimilation, \( g_s \) the stomatal conductance. \( C_i \) calculates to:

\[
C_i = C_a - \sqrt{1.6 \cdot D \cdot (C_a - \tau)},
\]

where 1.6 relates to how much faster than \( \text{CO}_2 \) water vapor pass through stomata pore, \( C_a \) denotes ambient \( \text{CO}_2 \) mixing ratio and \( D \) the leaf to air vapour mole fraction deficit during photosynthesis (biome values can be found in Lloyd and Farquhar, 1994). \( C_i \) depending on \( \Lambda \), it follows that \( f_{\text{photo}} \) is PFT dependent. A detailed simulated vegetation cover is therefore required to assess \( f_{\text{photo}} \), hence the global terrestrial biosphere’s oxygen fluxes.

From Eq. 1.28 (Sect. 1.2.4) and Eq. 1.18, we can extract the following relationship relating photorespiration fraction to \( T \), \( C_i \), and \( C_4 \) fraction, \( f_{C_4} \):

\[
f_{\text{photo}} = (1 - f_{C_4})(1 - f_{\text{Mehler}})(1 - \frac{C_i - 2T_p}{C_i + 4T_p}),
\]

The first term shows that an increased \( C_4/C_3 \) ratio will decrease \( f_{\text{photo}} \), while the third term expresses both the positive relationship between \( f_{\text{photo}} \) and \( T_p \) (Fig. 1.5), and the relationship between \( f_{\text{photo}} \) and \( C_i \), controlled by PFT, \( C_a \) and \( T_p \) (Eq. 1.20). Obviously \( \text{CO}_2 \) also has an impact on photorespiration. Increase in \( \text{CO}_2 \) would reduce the photorespiration fraction, thus lowering \( ^{18} \epsilon_{\text{resp}} \), but replacement of \( C_4 \) plants by \( C_3 \) plants favored by higher \( \text{CO}_2 \) level would lead to an opposite effect. It is thus complex to assess the impact of a change in \( \text{CO}_2 \) concentration on the photorespiration fraction.

### 1.2.3.2.5 Mehler reaction

Like photorespiration, the Mehler reaction can be seen as an alternative electron sink during plant photosynthesis. During the Mehler reaction (Mehler, 1951), \( O_2 \) is ultimately reduced to \( H_2O \) using light. First, superoxide \( O_2^- \), which results from the reduction of \( O_2 \) in the photosystem 1 complex, is dismutated to \( H_2O_2 \), which is subsequently reduced to \( H_2O \) by ascorbate peroxidase in the chloroplast (Rebeiz et al., 2010). Despite the weak contribution of the Mehler reaction to global \( O_2 \) uptake fluxes, \( \sim 10\% \)

\( ^* \)such as \( f_{C_3} + f_{C_4} = 1 \)
Figure 1.5 – The control of temperature and $C_3/C_4$ ratio on the fraction of photosynthesis $f_{\text{photo}}$ based on Equation 1.21. A decrease in $C_4$ fraction as well as an increase in temperature cause a higher $f_{\text{photo}}$. Below 15-20 °C, temperature controls $f_{\text{photo}}$, while above 20 °C, $f_{\text{photo}}$ is strongly dependent on the $C_4$ fraction, regardless of the temperature. Here outputs of the global dynamic vegetation model ORCHIDEE run under Last Glacial Maximum conditions are used (Sect. 5).

(Badger et al., 2000), interest in this respiratory pathway grew in recent years because in its role in the generation of reactive oxygen species, essential for the control of different cell processes, and in stress resistance, through the involvement of $H_2O_2$ in stomata closure and movement (Strizh, 2008). $^{18}\epsilon_{\text{Mehler}}$ is very weak (10.8 %) relative to other respiratory processes (Helman et al., 2005) and therefore attenuates the magnitude of the global terrestrial respiratory isotope fractionation $^{18}\epsilon_{\text{resp}}$ (Table 1.1).

1.2.3.2.6 Uptake processes in the ocean

Global respiratory isotope fractionation in the ocean $^{18}\epsilon_{\text{resp, mar}}$ is estimated in a global way as most of the $O_2$ uptake occurs in the euphotic zone ($f_{\text{euph}} \approx 90\%$, Luz et al., 2014). Isotope respiratory fractionation in the euphotic zone, $^{18}\epsilon_{\text{resp, euph}}$, is estimated to range from 20 % to 26 % (Kiddon et al., 1993; Quay et al., 1993; Luz et al., 2002; Hendricks et al., 2004). Marine respiration also occurs below the surface, associated with a weaker $^{18}\epsilon_{\text{resp, deep}}$ (Levine et al., 2009; Bender, 1990; Kroopnick and Craig, 1976; Rakestraw et al., 1951). As for soil respiration, $^{18}\epsilon_{\text{resp, deep}}$ is not only dependent on the isotope fractionation of the $O_2$ consuming process, but also on the isotope fractionation of the $O_2$ diffusion and the relative rate of diffusion and consumption (cf. Eq.
1.11). An effective respiratory isotope fractionation of $19.4 \pm 0.5$ in the subphotic zone has been derived by (Luz and Barkan, 2011) and can be taken as a representative value for $\varepsilon_{\text{resp, deep}}$. The fraction of respiration in the deep ocean $f_{\text{deep}}$ is about 11%, according to the most recent estimation (Luz et al., 2014). Previous ones ranged from 5% (Bender et al., 1994) to 20% (Hoffmann et al., 2004) (Table 1.2).

1.2.3.3 Hydrological processes

The water consumed by the terrestrial biosphere serves as substrate water for photosynthesis and is largely responsible for isotope fractionation associated with oxygen production processes (Sect. 1.2.3.1). This substrate water, commonly called leaf water, is not homogenous worldwide and shows strong variations with the latitude and climate. Indeed, Rayleigh distillation associated with transport of meteoric water from the evaporative region to the source of precipitation causes a depletion of $H_2O$ in $^{18}O$ and $^{17}O$, increasing with latitude. Besides, changes in isotope composition of meteoric $H_2O$ depends on the composition of the moisture source region, rainfall amount and the amount of evaporation, changes in past atmospheric circulation patterns and the ratio of summer to winter precipitations (Yuan et al., 2004; Johnson et al., 2006; Clemens et al., 2010; Dayem et al., 2010; Pausata et al., 2011; Tan, 2014). Integrating this combination of processes along air mass trajectories for each grid square can thus only be done with an AGCM (Risi et al., 2012).

In contrast, evapotranspiration at the site of land photosynthesis causes an enrichment of leaf water in heavy $O_2$ isotopes which is function of the relative humidity (Gonfiantini, 1965). The cause of the $^{18}O$ enrichment in leaf water is similar to that of evaporation from small water bodies and is controlled by the liquid-water isotopic equilibrium and the isotope fractionation during the diffusion of water vapor in air. Although measurements of $\delta^{18}O_{lw}$ have been used to calculate a global value of $6.5 \pm 2.1\%$ (West et al., 2008), it is complex to estimate the global isotopic composition of leaf water, because it is strongly affected by the spatial distribution and temporal variations of the isotopic composition of precipitation and of climate conditions (relative humidity and temperature) in the lowest layer of the atmosphere. GCMs fitted with water isotopes (Hoffmann et al., 2004; Landais et al., 2007a) are therefore required to model the worldwide isotopic composition of leaf water (See Chapter 5). The global isotopic composition of leaf water can be then computed from the spatial and temporal integration of local (grid cell in a model) $\delta^{18}O_{lw}$ and associated photosynthetic $O_2$ fluxes (e.g. Landais et al., 2007a). Local $\delta^{18}O_{lw}$ of leaf water is computed through the Craig and Gordon (1965) equation of evaporation from large bodies of water applied to leaf transpiration, including effects of diffusion through stomata and leaf boundary layer effects (Dongmann, 1974):

$$\delta^{18}O_{lw} = h \cdot \left( \delta^{18}O_{\text{vap}} + ^{18}\varepsilon_{eq} \right) + (1 - h) \cdot \left( \delta^{18}O_E + ^{18}\varepsilon_{eq} + ^{18}\varepsilon_{\text{kin}} \right), \quad (1.22)$$

where $h$ is the relative humidity at the site of photosynthesis, $^{18}\varepsilon_{eq}$ is the liquid vapor equilibrium isotope effect, temperature dependent, $^{18}\varepsilon_{\text{kin}}$ is the kinetic isotope effect occurring when humidity is below saturation, $\delta^{18}O_{\text{vap}}$ is the water vapor $\delta^{18}O$ in the
first layer of the troposphere, and $^{18}O_{gw}$ stands for soil water, but is stricto sensu the isotopic composition of the transpired water, that must be close to the one of the source (soil) water in steady state (Farquhar et al., 2007). $\delta^{18}O_{gw}$ and the $\delta^{18}O$ of meteoric waters at the site of $O_2$ production can be considered identical at first order. From Eq. 1.22, it follows that leaf water is usually $^{18}O$ enriched, as both equilibrium and kinetic fractionation tend to discriminate against heavy isotopologues. The former due to higher partial vapor pressure of the heavier isotopologue $H^{18}O$, the latter due to lower binary diffusivity in air for $H^{18}O$ water vapor (Farquhar et al., 2007).

Under moist conditions, just after rain, $\delta^{18}O_{lw}$ enrichment will be very small, while the maximum isotope effect occurs when atmospheric humidity is very low, and can be approximated as the sum of kinetic and equilibrium fractionation terms (refer to Farquhar et al., 2007 for details).

![Figure 1.6](image.png)

**Figure 1.6 –** Leafwater as a function of relative humidity and precipitation. Here outputs of the global dynamic vegetation model ORCHIDEE and LMDZ run under Last Glacial Maximum conditions are displayed (Chapter 5)

### 1.2.3.3.1 Lower $\delta^{18}O_{lw}$ enrichment in observations

Several studies have found that $\delta^{18}O_{lw}$ enrichment predicted by the Craig and Gordon equation (Eq. 1.22) was more enriched than observed $\delta^{18}O_{lw}$ (e.g. Allison et al., 1985; Bariac et al., 1989; Flanagan et al., 1994; Wang et al., 1998. Here we present a few hypothesis to explain why.
• A too strong kinetic fractionation at leaf surface?

Several values for the ratio $^{18}H^2O/^{16}H^2O$ can be found in the literature (Merlivat, 1978; Cappa et al., 2003; Luz et al., 2009), varying from 1.028 to 1.032. For leaf water transpiration, various studies suggest that kinetic fractionation is very heterogeneous (e.g. Yakir et al., 1989) and many of them have reported finding lower enrichment in $\delta^{18}O_{lw}$ than that predicted by Eq. 1.22. An explanation for the varying $^{18}\varepsilon_{kin}$ focused on the relative strength of either stomatal or boundary layer resistances (Farquhar et al., 2007). In 1989, Farquhar et al. suggested that kinetic fractionation at leaf surface could be expressed as:

$$^{18}\varepsilon_{kin} = \frac{32rs + 22rb}{rs + rb}/1000,$$

(1.23)

where $rs$ and $rb$ are the stomatal resistances (reciprocal of conductances $gs$ and $gb$) of the stomata and the boundary layer to diffusion of water vapor, respectively. Here 32/1000 represents the fractionation during diffusion (Cappa et al., 2003), while 22/1000 comes from 1.032$^{2/3}$ (Farquhar et al., 2007). In moist conditions, stomatal resistance $rs$ is low. Thus fractionation caused by $rb$ dominates, and it is follows from Eq. 1.23 that $^{18}\varepsilon_{kin}$ becomes weaker, closer from 22‰ than 32‰. Besides, stomatal opening and increased evapotranspiration increases the latent heat flux out of the leaves and thereby reduce leaf temperature, increasing relative humidity and in turn weakening $\delta^{18}O_{lw}$ enrichment (Farquhar et al., 2007). Accordingly, we have imposed a mean value of 20‰ for $^{18}_k\varepsilon_{kin}$ in the model presented in Chapter 5.

• How does plant transpiration relate to $\delta^{18}O_{lw}$ enrichment?

Plants must solve the dilemma of adjusting stomatal apertures to allow sufficient $CO_2$ uptake for photosynthesis while preventing excessive water loss, that is $E$ (cf. Eq. 1.19). As pointed out by Farquhar et al. (2007), the relation between $\delta^{18}O_{lw}$ enrichment and the transpiration rate $E$ is not straightforward. $E$ is defined as:

$$E = gw \cdot v,$$

(1.24)

where $gw$ is the conductance to diffusion of water vapor to the atmosphere from the sites of evaporation within the leaf, combining stomatal and boundary layer conductances, and $v$ is the leaf-to-air water vapor concentration difference. According to Eq. 1.22, $\delta^{18}O_{lw}$ enrichment is increased with lower relative humidity $h$, thus with a higher $E$, while Eq. 1.23 shows that $^{18}_k\varepsilon_{kin}$, hence $\delta^{18}O_{lw}$, is increased with a stronger $rs$, thus with a lower $E$. It follows that estimating $\delta^{18}O_{lw}$ with the Craig and Gordon equation may be incomplete, as it only considers the positive relationship between $\delta^{18}O_{lw}$ and $E$.

\*\*with the measured values from Merlivat (1978), $rs = 28%$ and $rb = 19%$.\*\*
Spatial heterogeneity of $\delta^{18}O_{lw}$ within a single leaf.

Applying Craig and Gordon model to leaves assumes two major assumptions, as noted by Helliker and Ehleringer (2002): one assumption is that the leaf is at isotopic steady-state, where the isotopic composition of the transpiration flux is identical to the one of the water entering the leaf through its bases (Helliker and Ehleringer, 2002), and the second one is that the leaf represents a single homogeneous pool of water from the base to the tip, with the substrate water entering from the petiole and exiting solely by evapotranspiration. Various studies have shown isotopic inhomogeneities in leaf water (e.g. Yakir et al., 1989, 1990), whose main feature is a progressive enrichment from the bases to the tips of the leaves (Farquhar et al., 2007). There have been two main approaches taken to represent this pattern. The ”pools of water” model (Yakir et al., 1989) is based on isolated water pools in the leaf, a few of them - at least 10 % - with no enrichment, while the second model is based on $\delta^{18}O$ gradient within the leaf, due to the opposing effect of convection of unenriched vein waters pumped from the roots and back diffusion of enriched evaporative water (the Peclet effect, Farquhar and Lloyd, 1993). According to the Peclet model, $\delta^{18}O_{lw}$ enrichment occurs if transpiration rate decreases.

1.2.3.3.2 Link to $\delta^{18}O$ of $CO_2$

The oxygen isotopic composition of $CO_2$ depends on interactions between $CO_2$ and ocean waters, soil water and leaf water (Francey and Tans, 1987; Farquhar et al., 1993). There is no exchange of $O_2$ isotopes with oxygen of water vapor. When $CO_2$ dissolves in liquid water, oxygen atoms are exchanged (Mills and Urey, 1940) through hydration/dehydration of $CO_2/HCO_3^-$

$$
CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-,
$$

(1.25)

where $H_2CO_3$ is carbonic acid and $HCO_3^-$ is bicarbonate. It takes $\simeq 30$ s (up to a few minutes according to Luz et al. (2014)) for dissolved $CO_2$ to reach isotopic equilibrium with water, similar to the time required for hydration (Keeling, 1995). Exchange of $O_2$ isotopes of $CO_2$ with soil water is caused by diffusion into the atmosphere of $CO_2$ respired by the soils. It is assumed to vary with the $\delta^{18}O$ of precipitation, depleted polewards through Rayleigh fractionation. Exchange with ocean waters occurs through exchange of $CO_2$ across the air-sea interface (Keeling, 1995). As ocean is the dominant reservoir of water on Earth, it was long believed that $\delta^{18}O$ of $CO_2$ was driven by the $\delta^{18}O$ of ocean waters, until Francey and Tans (1987) found that the former was affected by $\delta^{18}O_{lw}$, despite the small size of the leaf water reservoir. Indeed, the $CO_2/H_2O$ equilibration is very fast in leaves, due to the presence of carbonic anhydrases (noted CA hereafter). CA are zinc-containing enzymes that catalyze the reversible reaction between carbon dioxide hydration and bicarbonate dehydration. Hence isotopic exchange occurs in spite of the small residence time (< 1 s) of $CO_2$ within the leaves (Keeling, 1995). Consequently, Farquhar et al. (1993) developed a global model
for $\delta^{18}O$ of atmospheric $CO_2$ including the rapid $CO_2/H_2O$ equilibration within leaves. To close the budget of $\delta^{18}O$ of $CO_2$, their model calculated a value of 4.4 $\%e$ for global $\delta^{18}O_{lw}$, much weaker than the value of 8 $\%e$ needed by Dongmann (1974) or Bender et al. (1994) to balance their budget of the Dole Effect (Table 1.2).

The $O_2$ isotope composition of leaf water influences both $\delta^{18}O_{atm}$ and $\delta^{18}O$ of atmospheric $CO_2$ because at the time of photosynthesis, leaf water, that is the substrate water for the newly produced $O_2$, instantaneously equilibrates with $CO_2$, a fraction of which is not assimilated and diffuses back in the atmosphere (Keeling, 1995; Luz et al., 2014). The difference observed between the $O_2$ (e.g. Bender et al., 1994) and $CO_2$ (Farquhar et al., 1993) based $\delta^{18}O_{lw}$ may be due to an incomplete equilibration (≤80 $\%$) between $CO_2$ and leaf water (Gillon and Yakir, 2001), resulting in an underestimation of $\delta^{18}O_{lw}$ in Farquhar et al.’s model. Another possibility arises from the fact that over night, if stomata are open, $CO_2$ can exchange isotopically with leaf water without involving photosynthesis (Cernusak et al., 2004).

### 1.2.3.4 Photochemistry in the stratosphere

Stratospheric $CO_2$ is enriched in heavy isotopes (e.g. Boering et al., 2004; Lammerzahl et al., 2002; Gamo et al., 1989). This results from mass-independent transfer of $^{18}O$ and $^{17}O$ from $O_2$ to ozone ($O_3$) and then to $CO_2$ (e.g. Thiemens, 1999). The stratospheric isotope exchange reaction can be described by the following set of reactions:

$$O_2 + h\nu \longrightarrow 2O,$$  
(1.26a)

$$O + O_2 \longrightarrow O_3,$$  
(1.26b)

$$O_3 + h\nu \longrightarrow O_2 + O(^1D),$$  
(1.26c)

$$CO_2 + O(^1D) \longrightarrow CO_3,$$  
(1.26d)

$$CO_3 \longrightarrow CO_2 + O,$$  
(1.26e)

$$O + O \longrightarrow O_2,$$  
(1.26f)

Eq. 1.26a represents the ultraviolet photodissociation of $O_2$, splitting the $O_2$ molecule in 2 atoms, while Eq. 1.26b describes the formation of $O_3$, whose ultraviolet photolysis produces $O(^1D)$ (Eq. 1.26c). The electronically excited oxygen atom reacts with $CO_2$ (Eq. 1.26d) to form carbon trioxide, which decays spontaneously to $CO_2$ and $O_2$ (Eq. 1.26e) (lifetime << 60s). The $^{17}O$ excess is transferred from $O_2$ to $O(^1D)$ and then to $CO_2$ (e.g. Shaheen et al., 2007)
From Eq. 1.26, we can thus see that stratospheric $O_2$, the largest oxygen reservoir, is the ultimate source of oxygen in stratospheric $CO_2$ via the transfer of oxygen to $O_3$ then $O(^{1}D)$. Mass independent fractionation occurs during ultraviolet photolysis of $O_3$ (e.g. Thiemens and Jackson, 1987) producing $O_2$ and $O(^{1}D)$ (Eq. 1.26c). Bender et al. (1994) proposed that the mass-independent enrichment in heavy isotopes observed in stratospheric $CO_2$ should be accompanied by a mass-independent $O_2$ depletion in $^{18}O$ and $^{17}O$, through an isotopic exchange between $CO_2$ and $O(^{1}D)$ (Eq. 1.26d and 1.26e). No $CO_2$ enrichment in the atmosphere is observed as the $CO_2$ turnover time is very short (1 yr), resulting from isotope exchange between $CO_2$ and liquid water in leaves (rapid exchange because of the presence of a catalyst, cf. Sect. 1.2.3.3.2) and ocean waters. In contrast, atmospheric $O_2$ has a long lifetime (1.2 kyr), and the $^{17}O$ depletion is only removed through respiration and photosynthesis. Bender et al. (1994) estimated that photochemical reactions in the stratosphere were causing a depletion of tropospheric $\delta^{18}O_{atm}$ of $0.4 \%$, refined to $0.3 \%$ (Luz et al., 1999), which is very small compared to the effect of hydrological and biological processes on $\delta^{18}O_{atm}$ (Table 1.2). However, the role of the stratospheric mass-independent fractionation has some important consequences when studying the past variations of the three stable isotopes of atmospheric $O_2$ (Sect. 1.2.5).

1.2.3.5 Estimating biospheric $O_2$ fluxes

To estimate the isotopic composition of atmospheric $O_2$, on millennial to orbital timescales, at which the concentration of atmospheric $O_2$ remains almost constant, a system in biological steady state is considered, with equal fluxes of $O_2$ production and uptake (e.g. Bender et al., 1994; Hoffmann et al., 2004; Landais et al., 2007a):

$$F_{O_2}^{\text{photosynthesis}} = F_{O_2}^{\text{resp}},$$

(1.27)

where $F_{O_2}^{\text{resp}}$ stands for $O_2$ respiratory fluxes. The terrestrial ($F_{O_2}^{\text{ter}}$) and marine ($F_{O_2}^{\text{mar}}$) components are estimated similarly, but separately.

Marine fluxes can be assessed with models computing the oceanic productivity. Terrestrial biospheric $O_2$ fluxes are usually derived from Gross Primary Production (GPP), computed for different PFTs by global vegetation models (e.g. Landais et al., 2007a). Simulated carbon molar fluxes ($molC \cdot m^{-2} \cdot yr^{-1}$) for each PFTs are converted to oxygen molar fluxes ($molO_2 \cdot m^{-2} \cdot yr^{-1}$), based on the biochemical model of photosynthesis from Farquhar et al. (1980). The model accounts for fraction of photorespiration, which is PFT and temperature dependent (Sect. 1.2.3.2.4), and the photosynthetic quotient (PQ), representing the net $O_2$ to $CO_2$ exchange with the ecosystem, and estimated as $1.1 \pm 0.5$ (Keeling, 1988; Severinghaus, 1995). Biospheric $O_2$ uptake fluxes for each PFT are expressed in terms of dark respiration, Mehler respiration and photorespiration:

$$F_{O_2}^{\text{resp}} = F_{Mehler}^{O_2} + F_{\text{dark}}^{O_2} + F_{\text{photo}}^{O_2}$$

(1.28a)

$$= \frac{GPP \cdot PQ \cdot (1 + f_{photo})}{1 - f_{Mehler}},$$

(1.28b)
With,

\[
F_{\text{photo}}^{O_2} = (1 - f_{\text{Mehler}}) \cdot (F^{O_2} - PQ \cdot GPP) \tag{1.28c}
\]

\[
F_{\text{photo}}^{O_2} = (1 - f_{\text{Mehler}}) \cdot PQ \cdot GPP \cdot f_{\text{photo}}, \tag{1.28d}
\]

where \( f_{\text{Mehler}} \) represents 10% of total respiration (Badger et al., 2000), that is 0.1 \( \cdot F_{\text{resp}}^{O_2} \).

Underestimation of \( f_{\text{photo}} \) may arise from uncertainties related to the time of photosynthesis. In the real world, plants must reduce their \( CO_2 \) uptake under water stress, as stomata close to preclude water loss (See Eq. 1.19). This may lead to a higher proportion of photorespiration, not necessarily considered during experiments performed under ideal hydric conditions (pers. comm., Severinghaus, 2015), whose results are used in the classical Farquhar parameterization (Farquhar et al., 1980).

1.2.4 The global budget of \( \delta^{18}O_{\text{atm}} \)

1.2.4.1 The Dole Effect

Previous sections showed that \( \delta^{18}O_{\text{atm}} \) is a complex signal, which results from biospheric (influenced by the hydrological cycle) and stratospheric fluxes associated with different isotope fractionations. Additionally, \( \delta^{18}O_{\text{atm}} \) is also dependent on the volume of ice sheets. Indeed, ice sheets are highly depleted in \(^{18}O\), due to Rayleigh distillation during transport and condensation of water vapor from the warm tropics to the cold poles. By storing more depleted \( H_2O \), an increase of the ice sheet volume causes a sea-level decrease associated with an enrichment of ocean waters \( \delta^{18}O \), to balance the water isotopic budget. Waelbroeck et al. (2002) estimated a 1% increase of ocean waters at the Last Glacial Maximum (LGM, 21 kyr B.P.) based on the isotopic composition of benthic foraminifera. As ocean is the substrate water for photosynthesis, variations in mean ocean waters \( \delta^{18}O \) are transmitted to \( \delta^{18}O_{\text{atm}} \). To remove the influence of sea level variations, it is common to use the difference between \( \delta^{18}O_{\text{atm}} \) and mean ocean water’s \( \delta^{18}O \) (called \( \delta^{18}O_{sw} \) hereafter), called the Dole Effect. The most recent estimate of the present-day DE measures to 23.88 ± 0.02%0 (Barkan and Luz, 2005). Note that for present-day, the DE and \( \delta^{18}O_{\text{atm}} \) are identical, as the value of present-day \( \delta^{18}O_{sw} \) is by convention 0%0 in the VSMOW scale.
Table 1.2 – evolution of the estimation of the DE budget in the last 20 years. It has been refined with new observations, more precise thanks to improvements in isotopic measurements. Bender et al. (1994) divided the DE in a marine and terrestrial component. It includes O$_2$ isotope fractionation during terrestrial photosynthesis (Dongmann, 1974), with a value of 4.4‰ for δ18O$_{lw}$ based on Farquhar et al. (1993). The budget takes account of new or more precise measurements on oxygen isotope fractionation associated with respiratory processes (Guy et al., 1989, 1993; Kiddon et al., 1993; Bender, 1990), and estimates of O$_2$ consumption on land and in the ocean (Farquhar et al., 1980; Guy et al., 1993; Keeling and Shertz, 1992). With respect to Bender et al. (1994), Hoffmann et al. (2004) obtain a higher δ18O$_{lw}$ but the increase in the terrestrial DE is counterbalanced by a decrease in the marine DE caused by a larger fraction of deep marine respiration (20% against 5% for Bender et al., 1994), which is associated with a weak isotope fractionation. Luz et al. (2014) additionally consider isotope fractionation in marine photosynthesis and attenuated fractionation in soil respiration in their work.

The Dole effect can be divided in a marine and terrestrial component (Bender et al., 1994):

\[
DE = \delta^{18}O_{atm} - \delta^{18}O_{sw} = \frac{F_{O_2}^{\text{terr}}}{F_{O_2}^{\text{tot}}} \cdot DE_{\text{terr}} + \frac{F_{O_2}^{\text{mar}}}{F_{O_2}^{\text{tot}}} \cdot DE_{\text{mar}} - 18 \varepsilon_{\text{strat}}, \tag{1.29}
\]

where \(F_{O_2}^{\text{tot}} = F_{O_2}^{\text{terr}} + F_{O_2}^{\text{mar}}\). Air exchange between the troposphere and the stratosphere results in a δ18O depletion of 0.3 permil (18ε$_{\text{strat}}$) in tropospheric O$_2$ (Sect. 1.2.3.4). The latest estimations of DE$_{\text{terr}}$ and DE$_{\text{mar}}$ can be found in Table 1.2 for different studies. Most recent estimates of present-day DE$_{\text{terr}}$ and DE$_{\text{mar}}$ are 23.5 ± 2.3 and 24.3 ± 2.0, respectively (Luz et al., 2014).
1.2.4.2 $DE_{\text{mar}}$

$DE_{\text{mar}}$ is estimated following Bender et al.’s (1994) approach:

$$DE_{\text{mar}} = f_{\text{euph}} \cdot DE_{\text{euph}} + f_{\text{deep}} \cdot DE_{\text{deep}},$$

where $f_{\text{euph}}$ (89 %) and $f_{\text{deep}}$ (11 %) are the fraction of $O_2$ uptake in the euphotic zone and in the deep ocean, respectively (Sect. 1.2.3.2.6). $DE_{\text{euph}}$ has been recently reestimated as 24.4 ± 1.1‰ (see Table 1.2) by (Luz and Barkan, 2011; Luz et al., 2014), after Eisenstadt et al. (2010) found photosynthetic enrichment up to 6 %‰ in marine phytoplankton. The combined effect of isotope fractionation due to photosynthesis and respiration ($^{18}\epsilon_{\text{bio, euph}}$) in the euphotic zone was estimated as 25.2 ± 1.9‰ from the mass balance of $^{18}O$ dissolved in $O_2$ (Luz et al., 2014). Additionally, the equilibrium isotope fractionation $^{18}\epsilon_{eq}$ of dissolved $O_2$ in seawater with respect to atmospheric $O_2$ causes dissolved $O_2$ to be slightly enriched in $^{18}O$ by 0.75 ‰ with respect to $\delta^{18}O_{\text{atm}}$ (Benson and Krause, 1984). $DE_{\text{euph}}$ is therefore calculated as:

$$DE_{\text{euph}} = ^{18}\epsilon_{\text{bio, euph}} - ^{18}\epsilon_{eq} = 25.2 \pm 1.9\% - 0.75\% = 24.4\%,$$  

(1.31)

1.2.4.3 $DE_{\text{terr}}$

$DE_{\text{terr}}$ is estimated in the following way:

$$DE_{\text{terr}} = \delta^{18}O_{\text{lw}} + ^{18}\epsilon_{\text{resp}} - \delta^{18}O_{\text{sw}}$$

(1.32)

where $^{18}\epsilon_{\text{resp}}$ is the respiratory isotope fractionation caused by terrestrial $O_2$ uptake (refer to Eq. 1.9 and Table 1.1), and $\delta^{18}O_{\text{lw}}$ the isotope composition of leaf water (refer to Eq 1.22). Last estimate of $DE_{\text{terr}}$ by Luz et al. (2014) is 23.5 ± 2.3‰, 0.38 ‰ lower than the observed value of 23.88 ‰ (Barkan and Luz, 2005).

1.2.4.4 What processes influence $\delta^{18}O_{\text{atm}}$?

In this section we summarize all the factors that can cause a $\delta^{18}O_{\text{atm}}$ enrichment:

- a $\delta^{18}O_{\text{sw}}$ enrichment because of a sea level decrease/ ice sheet volume increase. Note that this would not affect the DE, by definition.
- a $\delta^{18}O_{\text{lw}}$ enrichment, driven by:
  - a decrease in relative humidity (due to increased temperature or reduced water vapor content), causing kinetic fractionation to dominate over equilibrium fractionation during plant transpiration.
  - a $\delta^{18}O$ enrichment of the meteoric water consumed by the plants
  - stomata closure and associated decrease of transpiration, according to the Peclet effect (Farquhar and Lloyd, 1993).
- an increase of the photorespiration fraction, driven by:
- a decrease of the ratio of C4/C3 plants, driven by a higher CO₂ concentration or more humid conditions
- a higher temperature at the site and time of photosynthesis
- a decrease in CO₂ concentration. Note that it is difficult to assess the net effect of a CO₂ decrease on δ¹⁸O atm, as it also leads to replacement of C3 plants by C4 plants, hence to a reduction of the photorespiration fraction, causing δ¹⁸O atm depletion.

- a decrease in soil respiratory isotope fractionation, driven by:
  - an increase in the fraction of tropical soils (with respect to temperate and boreal soils), associated with a weak isotope fractionation during O₂ uptake.
  - well-aerated soils, i.e. a lower water content in the soils, increasing the back flux from the site of respiration to the atmosphere of the remaining fraction of O₂ isotopically enriched after partial respiration. As explained in Sect. 1.2.3.2.3, the presence of water causes diffusion to be rate-limiting. As a result, instead of an effective soil respiratory fractionation reflecting the isotope fractionation of the O₂ uptake process (case of well-aerated soils), it reflects the isotope fractionation associated with diffusion of O₂ in water.

- a relative increase of the marine O₂ production (or uptake) F^O₂ mar, considering the latest estimations of DE_terr and DE_mar (Table 1.2). However, they are identical within the uncertainties (± 2‰) of their estimations. Luz and Barkan (2011) thus suggest that changes in the land-to-sea ratio O₂ production should not affect the global DE.

1.2.5 Three isotopes of oxygen

Numerous factors affect the DE (Sect. 1.2.4.4), so that even with a detailed quantitative approach (Chapter 5), it is difficult to assess the relative importance of the factors responsible for the DE. The triple isotope composition of atmospheric O₂ provides additional information on the O₂ cycle. Luz et al. (1999) indeed showed that past changes in global O₂ productivity could be inferred from the relation between ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios. Moreover, studying the relative variations of the two heavy O₂ isotopologues through time should bring to light the driving processes of each isotopic change.

1.2.5.1 Definitions

On Earth, most of the isotopic variations observed in elements with at least three stable isotopes are strongly correlated with the isotopic mass differences. Let us consider the partitioning of O₂ isotopes between two compounds A and B. The mass-dependent relationship that relates isotope fractionation factors of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O
can be expressed as follows (Mook and De Vries, 2000):

\[ {^{17}}\alpha_{A/B} = {^{18}}\alpha_{A/B}^{\lambda}. \quad (1.33) \]

In nature, most isotope fractionation processes cause the \( {^{17}}O/{^{16}}O \) ratio of \( O_2 \) -bearing compounds to be approximately one half of the \( {^{18}}O/{^{16}}O \) ratio, with a value of \( \lambda \), the exponent relating the fractionation factors for two isotope ratios (the slope in the \( {^{17}}O/{^{18}}O \) relationship), around 0.52. However, the improved analytical precision of stable isotope ratio measurements, allowing to determine \( \lambda \) with precision in the third decimal place (e.g. Barkan and Luz, 2003; Luz and Barkan, 2005) showed that on Earth, slight differences in the magnitude of the mass-dependent fractionation exist. In theory, isotope fractionation resulting from equilibrium or kinetic processes can explain such variations (Matsuhisa et al., 1978; Young et al., 2002). In the case of equilibrium exchange (depending solely on the atomic mass Young et al., 2002) of \( O_2 \) isotopes between two compounds A and B, \( \lambda \) is expressed such that:

\[ \lambda = \frac{\left( \frac{1}{16} - \frac{1}{17} \right)}{\left( \frac{1}{16} - \frac{1}{18} \right)} \simeq 0.5294. \quad (1.34) \]

In the case of a kinetic process:

\[ \lambda = \frac{\ln(M_1)}{\ln(M_3)}, \quad (1.35) \]

where \( M_1, M_2 \) and \( M_3 \) are atomic, molecular or reduced masses, and \( M_1 < M_2 < M_3 \). Atomic or molecular masses apply for transport processes, while reduced masses apply for breaking bonds (Young et al., 2002). Using atomic or molecular masses bring a \( \lambda \) value of 0.5147 or 0.5076, respectively. Thus, according to theory, \( \lambda \) can vary between 0.501 (kinetic) and 0.531 (steady state) (e.g. Matsuhisa et al., 1978; Kaiser, 2008). As a matter of fact, various relations between \( {^{17}}O/{^{16}}O \) and \( {^{18}}O/{^{16}}O \) ratios have been observed in nature. \( \lambda \) has a value of 0.525 ± 0.001 in rocks (Miller, 2002), suggesting the domination of equilibrium processes during rock formation. The value of
0.528 ± 0.002 in meteoric waters (Meijer and Li, 1998; Landais et al., 2008; Luz and Barkan, 2010) can result from dominant equilibrium fractionation processes, but also from kinetic ones, as \( \lambda \) calculated with the reduced masses of H-OH bonds or O-H bonds varies from 0.5270 to 0.5286 (Young et al., 2002).

In Figure 1.7, atmospheric \( O_2 \) stands out among Earth’s oxygen pools by its \( ^{17} \Delta \) signature, (calculated with \( \lambda = 0.528 \)), or, in other words, by the low value of its slope \( \lambda \) compared to \( \lambda \) for rocks or \( \lambda \) for waters (e.g. Young et al., 2014). The depletion is caused in part by the biologic origin of atmospheric \( O_2 \). Indeed, close to the value predicted by theory for kinetic fractionation \( (\lambda = 0.515) \), Helman et al. (2005) and Luz and Barkan (2005) determined \( \lambda \) as 0.518 for dark respiration (the dominant respiratory process on Earth) in a number of organisms. Besides, as mentioned in Sect. 1.2.3.4 the deficit in \( ^{17}O \) in the atmosphere also originates from stratospheric photochemistry (Yung et al., 1991; Bender et al., 1994; Luz et al., 1999).

When studying the three stable isotopes of \( O_2 \), the general practice (Miller, 2002; Luz and Barkan, 2005) is to use a modified \( \delta \), noted \( \delta’ \). (Hulston and Thode, 1965):

\[
\delta’ = \ln(\delta + 1) = \ln\left(\frac{R}{R_{ref}}\right),
\]

where \( R_{ref} \) refers to the isotope ratio of a reference state, another phase or to initial conditions. This “delta-prime” notation is convenient because of the linear relationship between \( \ln(17\alpha) \) and \( \ln(18\alpha) \) (Young et al., 2014):

\[
\delta’^{17}O = \lambda \cdot \delta’^{18}O - (\delta’^{17}O_{ref} - \lambda \cdot \delta’^{18}O_{ref}),
\]

Indeed, fractionation lines are straight in \( \delta^{18}O \) vs. \( \delta’^{17}O \) plots, while they are curved in conventional \( \delta^{18}O \) vs. \( \delta^{17}O \) plots. In contrast, mixing lines are straight in a conventional three isotope plot but curved using the modified \( \delta’ \) space. Consequently, mixing laws are an approximation in this definition of \( ^{17} \Delta \) (Kaiser et al., 2004). Figure 1.8 illustrates the previous point for gaseous \( O_2 \) only affected by biologic fluxes, that is a system at steady-state between respiratory consumption and photosynthetic production: while respiratory fractionation processes, which can be determined with Rayleigh experiments (Luz et al., 2014), increase \( \delta^{18}O \) and \( \delta^{17}O \) along straight lines, photosynthesis leads to mixing of fractionated \( O_2 \) with new photosynthetic \( O_2 \) along curved lines (Luz and Barkan, 2005). Note that in general, the last term of Eq. 1.37, \( \delta’^{17}O_{ref} - \lambda \cdot \delta’^{18}O_{ref} \), cancels out as the reference value can be taken to origin (Young et al., 2014).

\( ^{17} \Delta_{atm} \) represents the deviation from the specified mass-dependent isotopic fractionation relationship between \( \delta^{17}O_{atm} \) and \( \delta^{18}O_{atm} \), denoted as the anomaly \( ^{17} \Delta_{atm} \) (Luz et al., 1999) and expressed in per meg \((10^{-6})\) as variations are very small:

\[
^{17} \Delta_{atm} = \ln(\delta^{17}O_{atm} + 1) - \lambda \cdot \ln(\delta^{18}O_{atm} + 1) = \ln(\alpha_{atm}^{17}) - \lambda \cdot \ln(\alpha_{atm}^{18}).
\]
The standard of reference for $O_2$ gas is atmospheric $O_2$. As the latter defines the origin of the isotopic scale, it follows that $\delta^{18}O_{atm}$, $\delta^{17}O_{atm}$ and $17\Delta_{atm}$ have a value of 0‰. $\lambda$, as mentioned previously, is the slope of the mass-dependent isotopic fractionation line (or reference line) between the two heavy stable isotopologues of atmospheric $O_2$. It should be mentioned that the value of $\lambda$ is independent on the choice of isotopic reference (e.g. VSMOW or atmospheric $O_2$) (Miller, 2002). In contrast, Equation 1.38 shows that $17\Delta_{atm}$ is strongly dependent on the chosen value of $\lambda$, but also on the choice of the standard of reference, as variations in $\delta^{18}O$ alone cause apparent variations in $17\Delta$. A consistent selection of the two is therefore critical for a correct interpretation of $17\Delta$ variations. We underline below why the choice of $\lambda$ is critical, but the reader is invited to refer to Miller (2002); Young et al. (2014) or Luz and Barkan (2005) for more details on the selection of the optimal primary standard and relevant reference fractionation line with respect to the system under investigation.

1.2.5.1.1 Choice of $\lambda$

The symbol $\lambda$ is empirically chosen to reflect a predicted or observed mass-dependent relationship between $^{17}O^{16}O$ and $^{18}O^{16}O$ isotope ratios (Meijer and Li, 1998; Li and Meijer, 1999). Because of the biologic origin of atmospheric $O_2$, $\lambda$ must be representative of equilibrium fractionation during $O_2$ uptake, whose most dominant process is dark respiration (Angert et al., 2003b; Helman et al., 2005). The dark respiration slope was determined by Helman et al. (2005) in closed-system experiments where only $O_2$ consumption took place, without $O_2$ production. In this case, the change in oxygen isotopic composition of the remaining fraction can be expressed with the Rayleigh fractionation equation (e.g. Young et al., 2014; Angert et al., 2003b; Helman et al., 2005):

$$\frac{iR}{iR_{init}} = f^i,$$

(1.39)

where $iR_{init}$ represents the initial isotope ratio $^{i}O^{16}O/^{16}O$, with $i$ standing either for 17 or 18. $f^i$ represents the remaining $^{16}O^{16}O$ fraction. This expression is equivalent to:

$$\ln(\delta^iO + 1) - \ln(\delta^iO_{init} + 1) = i\cdot\epsilon \cdot \ln(f),$$

(1.40)

It follows that the fractionation law relating the two heavy isotopologues of $O_2$ in a Rayleigh process can be expressed as (e.g. Blunier et al., 2002; Helman et al., 2005):

$$\lambda = \gamma = \frac{\ln(17R/17R_{init})}{\ln(18R/18R_{init})} = \frac{\ln(\delta^{17}O + 1) - \ln(\delta^{17}O_{init} + 1)}{\ln(\delta^{18}O + 1) - \ln(\delta^{18}O_{init} + 1)} = \frac{17\epsilon}{18\epsilon},$$

(1.41)

where $\gamma$ represents the mass-dependent relationship between $^{18}O^{16}O$ and $^{17}O^{16}O$ during a Rayleigh fractionation process. A value of $\gamma = 0.518$ was defined for dark respiration. Note that in this limiting case, the value of 0.518 represents the effective value of the three-isotope exponent $\gamma$, that is the effect of the process of interest (here $O_2$ consumption, characterized by its intrinsic fractionation) together with
Table 1.3 – Table describing the difference between the symbols $\beta$, $\beta_{\text{eff}}$, $\gamma$ and $\eta$ symbols used in literature for triple isotope exponent $\lambda$. Equations and terminology are based upon Young et al. (2014). Experimental conditions can differ: (i) steady-state or $O_2$ removal only (Rayleigh-type fractionation) in a closed system of 2 reservoirs, or (ii) a system where one reservoir provides an infinite amount of reactant (e.g. $\delta^{18}O_{sw}$ remains constant despite photosynthesis), its isotope composition thereby being not affected by a change of $O_2$ amount in the reservoir. Determination of $\lambda$ from the best fit of a triple isotope plot ($\delta^{17}O$ vs $\delta^{18}O$) does not necessarily represent the process at play, due to the fact that reservoirs influence each other in a closed system. As an illustration, applying Young et al.’s simple 2-box model for $O_2$ photosynthesis from $H_2O$ and $O_2$ respiration, $\beta_{\text{eff}}$ is given when $^{18}\alpha_{\text{resp}} = 17.4 \%e$, $\beta = 0.516$ and $k = F_{\text{respiration}}/F_{\text{photosynthesis}} = 0.9$. $\lambda$ varies from 0.514 to 0.516, Note that in several studies, including this thesis and Reutenauer et al. (2015), $\theta$ corresponds to $\beta$.

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>exponent</th>
<th>condition?</th>
<th>reservoir effects?</th>
<th>equation</th>
<th>$\frac{\ln(\delta^{14}O)}{\ln(\delta^{18}O)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta^a$</td>
<td>intrinsic exponent</td>
<td>infinite reservoir</td>
<td>$\beta_{\text{eff}} = \beta$</td>
<td>$0.516$</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>steady-state exponent</td>
<td>steady-state</td>
<td>yes</td>
<td>$\beta_{\text{eff}} = \eta$</td>
<td>$0.515$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Rayleigh exponent</td>
<td>$O_2$ removal alone</td>
<td>yes</td>
<td>$\beta_{\text{eff}} = \gamma = \frac{\alpha_{\text{light}} \cdot 1}{\alpha_{\text{dark}} - 1}$</td>
<td>$0.514$</td>
</tr>
</tbody>
</table>

*a: called $\theta$ in this thesis as in e.g. Angert et al., 2003b; Helman et al., 2005; Landais et al., 2007a. $\theta$ results only from the process of interest, and is not affected by mass balance considerations.

mass-balance effects (referred as ”reservoir effects” by Young et al., 2014). The slope $\gamma$ can be derived from the best fit of a $\delta^{17}O$ vs $\delta^{18}O$ plots.

The triple isotope exponent $\gamma$, characterizing a Rayleigh process, is not adapted for global mass balance calculations of triple isotope ratios of atmospheric $O_2$ in biological steady-state (combination of $O_2$ uptake and mixing with photosynthetic $O_2$ ), which is another limiting case where the mass-dependent relationship between $^{18}O$/$^{16}O$ and $^{17}O/^{18}O$ can be predicted. A slope $\lambda = \theta$ of 0.516 (Table 1.4), which reflects the expected relationship between the two heavy $O_2$ isotopologues for dark respiration (most common respiratory process) fractionation in steady-state with production, is used instead and defined as (Blunier et al., 2002; Angert et al., 2003b; Helman et al., 2005; Luz and Barkan, 2005; Young et al., 2014):

$$\lambda = \theta = \frac{\ln(\alpha')}{{\ln(\alpha')}} = \frac{\ln(y \cdot \alpha' - y + 1)}{{\ln(\alpha')}} = \frac{\ln(y \cdot \alpha + 1)}{{\ln(\alpha' + 1)}}$$  \hspace{1cm} (1.42)

This equation is convenient as it enables calculation of $\theta$ from $\gamma$, which can be easily derived from a Rayleigh fractionation experiment. Note that according to Young et al. (2014), $\theta$ in Eq. 1.42 does not define a situation of steady-state, but the intrinsic triple isotope exponent $\beta$ (see Table 1.3), obtained when reservoir effects are eliminated. Young et al. (2014) indeed shows that $^{18}\alpha$ and $^{17}\alpha$ are not modified when the exchange of isotopes between two reservoirs is not reciprocal, and in this case, the effective value of the slope $\lambda$ is identical to the intrinsic value of the single process at play (as expressed in Eq. 1.35). Atmospheric $O_2$ can be considered free of reservoir ef-
fects because the ultimate source of atmospheric $O_2$, seawater, represents an infinite reservoir of $O_2$, and thereby its oxygen isotope composition, which mainly controls the one of the photosynthetic $O_2$, is unaffected by the exchange between the reservoirs. On the contrary, in steady-state between respiration and photosynthesis in a closed system, isotope fractionation factors $^{18}\alpha$ and $^{17}\alpha$ arise from the weakening of the intrinsic fractionation in one direction (respiration) by the lack of fractionation in the other direction (photosynthesis), and the impact of isotopic exchange on both reservoirs (reciprocity) (Young et al., 2014).

Figure 1.8 – Original Figure 2 from Luz and Barkan (2005). This figure schematizes the effect of biospheric fluxes on the triple isotope composition of gaseous $O_2$ at steady state (production = respiration). It depicts how the enrichment observed in gaseous $O_2$ compared to the substrate water is the product of two processes. Oxygen consumption through respiration, a one-way kinetic process, enriches gaseous $O_2$ as it tends to leave behind heavy isotopes, and appears as a straight line in a $\delta^{18}O$ vs. $\delta^{17}O$ plot. $O_2$ produced through photosynthesis, with the isotope composition of the substrate water (see below), depletes the enriched $O_2$ via mixing, whose graphical representation is a curved line. The dashed line connecting the points representing the isotopic composition of substrate water and gaseous $O_2$ in steady state, whose slope $\theta = 0.516$, does not represent a single fractionating process, but results from the combination of the two biologic processes (respiration and photosynthesis) (Luz and Barkan, 2005). The insert represents a zoom on the first cycle. Note that it is here assumed that photosynthesis does not fractionate $O_2$ isotopes, a view which has been recently challenged for marine photosynthesis in phytoplankton (Eisenstadt et al., 2010). Hence the newly produced $O_2$ bears the same isotopic composition as the substrate water.
1.2.5.2 Why is atmospheric $O_2$ depleted in $^{17}O$ relative to biological steady-state $O_2$?

In 1999, an experiment by Luz et al. (1999) revealed that atmospheric $O_2$ was depleted in $^{17}O$ versus biological steady state $O_2$. The experiment took place in an airtight and illuminated terrarium containing Philodendron plants, soil and natural water (Luz et al., 1999). At the beginning of the experiment, the terrarium was filled with ambient air, with a $^{17}\Delta_{atm}$ value of 0 permeg by definition. Then mixing of fractionated $O_2$ by partial respiration with newly produced photosynthetic $O_2$ caused $^{17}\Delta$ in the terrarium to increase over several weeks. Once all the $O_2$ in the terrarium was of biological origin alone, $^{17}\Delta$ reached a stable value, denoted $^{17}\Delta_{bio}$ hereafter, enriched by $\approx 155$ permeg (updated to 166 permeg by Luz et al., 2014) relative to atmospheric $O_2$, which conversely means that ambient $O_2$ is anomalously depleted in $^{17}O$ relative to $O_2$ of biological origin alone. Following (Bender et al., 1994) suggestion, they attributed this effect to stratospheric photochemistry (Sect. 1.2.3.4). Indeed, as $CO_2$ is preferentially enriched in $^{17}O$, stratospheric isotope transfer reaction between $O_2$ and $CO_2$ via $O_3$ involves preferential depletion of atmospheric $O_2$, the largest oxygen reservoir, in $^{17}O$ relative to biological steady state $O_2$.

1.2.5.3 $^{17}\Delta_{atm}$, a tracer of past global $O_2$ productivity

Taking profit of the $^{17}\Delta$ stratospheric signal, Luz et al. (1999) and Blunier et al. (2002) interpreted $^{17}\Delta_{atm}$ measured in air preserved in ice cores as a tracer of past changes of global photosynthetic rate. Indeed, the triple isotope composition of tropospheric $O_2$ reflects the isotopic balance between (1) the oxygen flux between the biosphere and the troposphere associated with mass dependent fractionation, and (2) the oxygen flux between the stratosphere and the troposphere associated with mass independent fractionation (Luz et al., 1999):

$$F_{bio} \cdot (^{17}\Delta_{bio} - ^{17}\Delta_{atm}) = F_{strat} \cdot (^{17}\Delta_{strat} - ^{17}\Delta_{atm}), \quad (1.43)$$

where $^{17}\Delta_{strat}$ and $^{17}\Delta_{bio}$ are the deviations from the reference line of slope $\lambda = 0.516$ of the stratospheric $O_2$ flux ($F_{strat}$) and the biospheric $O_2$ flux ($F_{bio}$), respectively.

Knowing the stratospheric contribution thus enables in theory to access the past global productivity. To estimate the production rate of mass-independently fractionated $O_2$ in the stratosphere, $F_{strat} \cdot (^{17}\Delta_{strat} - ^{17}\Delta_{atm})$, Luz et al. (1999) assume that it is proportional to $CO_2$ concentration. It is then possible to compare the $O_2$ productivity of the biosphere between two periods of time $t_1$ and $t_2$, with known $^{17}\Delta_{atm}$ and $CO_2$ concentration (Landais et al., 2007a):

$$\frac{F_{bio,t_2}}{F_{bio,t_1}} = \frac{[CO_2]_{t_2} \cdot (^{17}\Delta_{bio,t_1} - ^{17}\Delta_{atm,t_1})}{[CO_2]_{t_1} \cdot (^{17}\Delta_{bio,t_2} - ^{17}\Delta_{atm,t_2})}, \quad (1.44)$$

*if $O_2$ uptake is complete, respiration causes no fractionation as expected from a Rayleigh process*
where $[\text{CO}_2]$ is the atmospheric concentration of $\text{CO}_2$. Based on Eq \ref{eq:1.44}, the global oxygen biospheric productivity of the LGM was evaluated to be 60-85% of the present value (Blunier et al., 2002; Landais et al., 2007a).

1.2.5.4 Evaluating $17\Delta_{atm}$ budget

Rearranging Eq. \ref{eq:1.44}, the temporal evolution of $17\Delta_{atm}$ can be expressed as:

$$17\Delta_{atm,t2} = 17\Delta_{bio,t2} - \frac{[\text{CO}_2]_{t2}}{[\text{CO}_2]_{t1}} \cdot \frac{F_{bio,t1}}{F_{bio,t2}} \cdot (17\Delta_{bio,t1} - 17\Delta_{atm,t1}). \quad (1.45)$$

Equation \ref{eq:1.45} reveals that $17\Delta_{atm}$ depends on $[\text{CO}_2]$, $F_{bio}$ and $17\Delta_{bio}$. It should be emphasized that a precise estimation of $17\Delta_{bio}$ remains difficult as mass-dependent relationships between $18O/16O$ and $17O/16O$ (i.e. $\lambda$) differ depending on the processes at play during the $O_2$ cycle (Table 1.4).

Table 1.4 – Mass-dependent fractionation slopes ($\gamma = \frac{\delta^{17}O}{\delta^{18}O}$ and $\theta = \frac{\ln(\delta^{17}O)}{\ln(\delta^{18}O)}$) during $O_2$ uptake processes and hydrologic processes. Values and uncertainties are indicated if available. The slope $\gamma$ is optimal for describing the mass-dependent relationship between $18O/16O$ and $17O/16O$ in a Rayleigh process system, where only uptake takes place (e.g. fractionation of water during the hydrological cycle, or respiration). To deal with a system at steady state (combination of $O_2$ uptake and mixing with photosynthetic $O_2$), $\theta$ is preferred (Luz and Barkan, 2005).

<table>
<thead>
<tr>
<th>Process</th>
<th>$10^3 \cdot \gamma$</th>
<th>$10^3 \cdot \theta$</th>
<th>$\gamma$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark respiration in leaves</td>
<td>-19.0±1.8</td>
<td>-9.84±1.8</td>
<td>0.518±0.001</td>
<td>0.516±0.001</td>
</tr>
<tr>
<td>Dark respiration in soils</td>
<td>-15.6±0.5</td>
<td>-8.68±0.5</td>
<td>0.518±0.001</td>
<td>0.516±0.001</td>
</tr>
<tr>
<td>Mehler reaction</td>
<td>-10.8±0.2</td>
<td>-5.68±0.2</td>
<td>0.526±0.002</td>
<td>0.525±0.002</td>
</tr>
<tr>
<td>Photosynthesis</td>
<td>-21.4±0.1</td>
<td>-10.96±0.1</td>
<td>0.512±0.001</td>
<td>0.509±0.001</td>
</tr>
<tr>
<td>Global Meteoric Water Line (GMWL)</td>
<td>0.528±0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor-liquid equilibrium $\delta_{v0}$ (o to 30 °C)</td>
<td>1.0118±1.00894</td>
<td>1.0062±1.00472</td>
<td>0.529±0.001</td>
<td></td>
</tr>
<tr>
<td>Diffusive transport of water vapor in air $\theta_{air}$</td>
<td>9.6±1.8</td>
<td>4.96±1.8</td>
<td>0.518±0.002</td>
<td></td>
</tr>
<tr>
<td>Evapotranspiration ($\lambda_{trans}$)</td>
<td></td>
<td>(-0.0078±0.0026)·h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Landais et al., 2007a; Angert et al., 2003a; Angert et al., 2003b.
\*\*derived from $\gamma$ and $\theta$ from Helman et al. (2005) such as $\delta^{17}O/\delta^{18}O = \gamma \cdot \delta^{18}O$.
\*\*\*Helman et al., 2005; Meijer and Li, 1991; Landais et al., 2008; Luz and Barkan, 2010.
\*\*\*\*Horita and Wesolowski, 1994
\*\*\*\*\*derived from $\gamma$ and $\theta$ such as $\delta^{17}O/\delta^{18}O = \gamma \cdot \delta^{18}O$.
\*\*\*\*\*relative humidity at the site of photosynthesis.
\*\*\*\*\*\*Landais et al., 2006a; Barkan and Luz, 2007.

1.2.5.4.1 Estimating $17\Delta_{bio}$

Similar to the approach taken to evaluate $\delta^{18}O_{atm}$ (Eq. \ref{eq:1.29}), the marine $17\Delta_{mar}$ and terrestrial $17\Delta_{terr}$ contributions to $17\Delta_{bio}$ are estimated separately, that is by considering the $O_2$ fluxes and associated isotope effect of marine (terrestrial) photosynthesis and respiration in a system at equilibrium between the atmosphere and the marine (terrestrial) component only. Here we summarize the current understanding of $17\Delta_{bio}$.
composition of leaf water, transferred to newly produced $O_2$ through photosynthesis. $^{17}\Delta_{\text{terr}}$ is expressed relative to atmospheric $O_2$ (Landais et al., 2007a):

$$^{17}\Delta_{\text{terr}} = \ln\left(\frac{^{17}R_{\text{terr}}}{^{17}R_{\text{atm}}}\right) - 0.516 \cdot \ln\left(\frac{^{18}R_{\text{terr}}}{^{18}R_{\text{atm}}}\right),$$  

(1.46)

where $^{17}R_{\text{atm}}$ and $^{18}R_{\text{atm}}$ represent the isotopic ratios of atmospheric $O_2$ (primary standard), and $^{17}R_{\text{terr}}$ and $^{18}R_{\text{terr}}$ the isotopic ratios of $O_2$ produced by the terrestrial biosphere, respectively. $iR_{\text{terr}}$ is estimated as follows:

$$iR_{\text{terr}} = \frac{iR_{\text{lw}}}{i\alpha_{\text{resp}}},$$  

(1.47)

where $i$ denotes either 17 or 18, and $iR_{\text{lw}}$ stands for the global isotope ratio of leaf water. The global effective respiratory isotope fractionation factors $i\alpha_{\text{resp}}$ are estimated as described in Eq. 1.9, with the fractionation factors $^{17}\alpha_{\text{darkLeaves}},^{17}\alpha_{\text{darkOils}},^{17}\alpha_{\text{Mehler}},^{17}\alpha_{\text{photo}}$ calculated according to the fractionation law described by Eq. 1.33, i.e. $^{17}\alpha = ^{18}\alpha \lambda$, using the appropriate slope $\lambda$ (refer to Table 1.4 for values and associated references) depending on the process at play (Landais et al., 2007a). The mass-dependent relationship between $\delta^{18}O$ vs. $\delta^{17}O$ can then be expressed as:

$$^{17}\alpha_{\text{resp}} = ^{18}\lambda_{\text{resp}},$$  

(1.48)

with:

$$\lambda_{\text{resp}} = \frac{\ln(^{17}\alpha_{\text{resp}})}{\ln(^{18}\alpha_{\text{resp}})},$$  

(1.49)

where $\lambda_{\text{resp}}$ is obtained by weighting it with the relative proportion of the various terrestrial respiratory processes. For instance, an increase of the photorespiration fraction, associated with a slope $\lambda$ of 0.509, would lower $^{17}\alpha_{\text{resp}}$, hence $^{17}\Delta_{\text{terr}}$, the latter expressing the $^{17}O$ deviation from the biological steady-state fractionation line of slope $\lambda = 0.516$ (from D to E on Fig. 1.9 f). It is interesting to note that the opposite effect is observed on $\delta^{18}O_{\text{terr}}$, which is enriched with increasing fraction of photorespiration. This opposite sensitivity of $\delta^{18}O$ and $^{17}\Delta$ to the photorespiration fraction underscores the value of an additional tracer of the $O_2$ cycle as the relative variations of the two heavy isotopologues of $O_2$ should help constrain the processes at play.

$\delta^{18}O_{\text{lw}}$ is estimated following Eq. 1.22 and is enriched relative to $\delta^{18}O_{\text{gw}}$ (Sect. 1.2.3.3) while $\delta^{17}O_{\text{lw}}$ is evaluated as follows$^7$ (Landais et al., 2006a, 2007a):

$$\delta^{17}O_{\text{lw}} = \delta^{17}O_{\text{mw}} + (\delta^{18}O_{\text{lw}} - \delta^{18}O_{\text{mw}}) \cdot \lambda_{\text{transp}},$$  

(1.50)

where $\lambda_{\text{transp}}$ is the slope of the evapotranspiration process, measured by Landais et al. (2006a), and decreases linearly as relative humidity $h$ increases, which may seem counterintuitive as a higher humidity causes less kinetic fractionation - associated with a

$^7$Please remind that $\delta' = \ln(\delta + 1)$
Table 1.5 – A few $^{17}\Delta_{atm}$ values calculated using the specified exponent $\lambda$ and standard.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>$10^6 \cdot 17\Delta$</th>
<th>$\lambda$</th>
<th>standard</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{17}\Delta_{photo,mar}$</td>
<td>26</td>
<td>0.518</td>
<td>VSMOW</td>
<td>Barkan and Luz, 2011</td>
</tr>
<tr>
<td>$^{17}\Delta_{mw}$</td>
<td>33</td>
<td>0.528</td>
<td>VSMOW</td>
<td>Barkan and Luz, 2011</td>
</tr>
<tr>
<td>$^{17}\Delta_{aw}$</td>
<td>223 ± 4</td>
<td>0.516</td>
<td>air $O_2$</td>
<td>Barkan and Luz, 2011</td>
</tr>
<tr>
<td>$^{17}\Delta_{mar}$</td>
<td>249 ± 15</td>
<td>0.516</td>
<td>air $O_2$</td>
<td>Luz and Barkan, 2000; Barkan and Luz, 2011</td>
</tr>
<tr>
<td>$^{17}\Delta_{terr}$</td>
<td>117 ± 35</td>
<td>0.516</td>
<td>air $O_2$</td>
<td>Landais et al., 2007a; Luz et al., 2014</td>
</tr>
<tr>
<td>$^{17}\Delta_{bio}$</td>
<td>166 ± 51</td>
<td>0.516</td>
<td>air $O_2$</td>
<td>Luz et al., 2014</td>
</tr>
<tr>
<td>$^{17}\Delta_{atm}$</td>
<td>0</td>
<td>0.516</td>
<td>air $O_2$</td>
<td></td>
</tr>
<tr>
<td>$^{17}\Delta_{airO_2}$</td>
<td>−463$^a$</td>
<td>0.528</td>
<td>VSMOW</td>
<td>Kaiser, 2008</td>
</tr>
<tr>
<td>$^{17}\Delta_{airO_2}$</td>
<td>−506$^b$ ± 4</td>
<td>0.528</td>
<td>VSMOW</td>
<td>Barkan and Luz, 2011</td>
</tr>
<tr>
<td>$^{17}\Delta_{airO_2}$</td>
<td>−453$^c$ ± 10</td>
<td>0.528</td>
<td>VSMOW$^d$</td>
<td>Young et al., 2014</td>
</tr>
</tbody>
</table>

$a$ value obtained by renormalizing prior values to VSMOW.

$b$ $−454 ± 10$ permeg obtained with values from Barkan and Luz (2005).

$c$ Adjusted value to accommodate for a $^{17}\Delta$ offset of $−80$ permeg in San Carlos olivine. Non corrected value is $−373 ± 5$ permeg.

$d$ Indirect measurement, as they measured air $O_2$ against their rock reference, San Carlos olivine.

lower $\lambda$ (0.518) than equilibrium fractionation (0.529) - hence a higher $\lambda_{trans}$, but the higher isotopic exchange between leaf water and surrounding atmospheric water vapor causes a decrease of $\lambda_{trans}$ with higher humidity (see Fig. 1.9e and details in Landais et al., 2006a):

$$\lambda_{trans} = 0.522 - h \cdot 0.008,$$  \hspace{1cm} (1.51)

when $h$ ranges from 32 to 100 %, and $\lambda_{trans}$ ranges from 0.5194 to 0.514 accordingly. When $h < 32\%$, $\lambda = 0.519$ (Landais et al., 2006a). A global value of 0.517 for $\lambda_{trans}$ has been estimated by Landais et al. (2007a) for present-day. $\lambda_{trans}$ being much lower than the global meteoric water line slope $\lambda_{mw} = 0.528$ (refer to Table 1.4 for references), the isotope effect of evapotranspiration causes a decrease of the $^{17}O_{excess}$ of leaf water. However, as mentioned previously, a mass-dependent relationship between $\delta^{18}O$ and $\delta^{18}O$ with the slope $\lambda = 0.516$ must be used for evaluation of the global isotopic budget of atmospheric $O_2$. As a result, plant transpiration only causes a slight increase in $^{17}\Delta_{terr}$, amplified in dry conditions.

In contrast, $^{17}\Delta_{terr}$ is much more affected by changes in the isotope composition of meteoric waters ($\delta^{17}O_{mw}$ and $\delta^{18}O_{mw}$) from the site of evaporation to the site of precipitation. These processes cause indeed a spatially heterogenous depletion in $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios along the meteoric water line of slope $\lambda_{mw} = 0.528$. As mentioned previously, because of different fractionation slopes, shifts in $\delta^{18}O$ alone cause apparent shifts in $^{17}\Delta$ relative to the slope $\lambda$ of reference. Consequently, as $\lambda_{mw}$ is higher than 0.516, a decrease in $\delta^{18}O_{mw}$ of say 5 $\%_o$ causes a $^{17}\Delta$ depletion of 60 permeg:

$$\Delta^{17}\Delta = (\lambda_{mw} - 0.516) \cdot \ln(\Delta^{18}O + 1) = 0.012 \cdot -0.005 = -0.006$$  \hspace{1cm} (1.52)
Besides, Luz and Barkan (2010) observed a $^{17}O_{\text{excess}}$ of 33 per meg in meteoric waters (with respect to VSMOW) from various locations, such as:

$$\delta^{17}O_{\text{mw}} = 0.528 \cdot \delta^{18}O_{\text{lw}} + 0.00033. \quad (1.53)$$

The $^{17}O_{\text{excess}}$ is caused by (i) evaporation of ocean water into the atmosphere, increasing with decreasing humidity, hence more kinetic fractionation associated with a slope $\lambda = 0.518$ (from A to B on Fig. 1.9c) and (ii) by equilibrium fractionation between water vapor and precipitation, associated with a slope $\lambda = 0.529$ (from B to C on Fig. 1.9 d). By accounting for the combination of all the aforementioned terrestrial isotope effects, Landais et al. (2007a) estimated $^{17}\Delta_{\text{terr}}$ as $110 \pm 35$ permeg with respect to atmospheric $O_2$ for present-day. This value was recently refined to $117 \pm 35$ after accounting for (i) the correction of the value of $^{17}\Delta_{\text{sw}}$ (identical to VSMOW within the uncertainty of the measurements) with respect to atmospheric $O_2$ from 173 to 223 per meg (Barkan and Luz, 2011), and (ii) the $^{17}O_{\text{excess}}$ of 33 per meg in meteoric waters.

$^{17}\Delta_{\text{mar}}$ is estimated as $249 \pm 15$ permeg (Barkan and Luz, 2011) with respect to atmospheric $O_2$. It consists of two components, $^{17}\Delta_{\text{sw}}$, the $^{17}O$ excess of seawater with respect to atmospheric $O_2$, and $^{17}\Delta_{\text{photo\_mar}}$, the $^{17}O$ excess of photosynthetic $O_2$ with respect to its substrate water.

- 15 years ago, Luz and Barkan (2000) obtained $^{17}\Delta_{\text{mar}}$ as 249 permeg from laboratory measurements of the isotopic composition of dissolved oxygen $^{17}\Delta_{\text{diss}}$, which depends on the rate of air-water gas exchange and the rate of in situ $O_2$ production through photosynthesis (Luz and Barkan, 2000). Respiration does not affect $^{17}\Delta_{\text{diss}}$ because it fractionates the two heavy isotopes of oxygen along a line of slope $\lambda_{\text{diss}} = 0.518$ (Fig. 1.9b), used for $^{17}\Delta_{\text{diss}}$ calculations (Barkan and Luz, 2011). Measurements were performed once the dissolved $O_2$ was solely of biological origin, the $O_2$ reservoir (overhead of the flask) being recycled through respiration and photosynthesis of various marine organisms in airtight flasks experiencing several dark-light cycles (without UV radiations). At this time, photosynthesis was believed to cause no $O_2$ isotopic fractionation of its substrate water, and the obtained $^{17}\Delta_{\text{diss}}$ was thus believed to represent $^{17}\Delta_{\text{sw}}^\text{8}$, but subsequent measurements on phytoplankton contradicted this assumption, at least for the marine realm (Eisenstadt et al., 2010). Isotope fractionation during photosynthesis was later confirmed by Barkan and Luz (2011), who found an average $^{17}\Delta_{\text{photo\_mar}}$ value of 26 permeg ($\lambda_{\text{diss}} = 0.518$) for photosynthetic $O_2$ with respect to the substrate water in experiments similar to the one carried out in 2000, even when respiration was prevented.

- Since 2005, the ability to measure at very high precision the triple isotope composition in water, using a method of water fluorination to produce $O_2$ (Barkan and Luz, 2005), made possible to measure the oxygen isotope composition of VSMOW (identical to the one of seawater within the experimental error, Luz

---

*or $^{17}\Delta_{\text{mar}}$ (of biological origin alone as as $O_2$ uptake processes do not modify $^{17}\Delta_{\text{diss}}$ and photorespiration was believed to causes no isotope fractionation back in 2000.*
with respect to atmospheric $O_2$. The most recent estimates of $\delta^{18}O_{sw}$ and $\delta^{17}O_{sw}$ are $-23.324\%e$ and $-11.883\%o$, respectively Barkan and Luz (2011). This translates into a $^{17}\Delta_{sw}$ of 223 permeg.

$^{17}\Delta_{bio}$ $^{17}\Delta_{terr}$ and $^{17}\Delta_{mar}$ ($\lambda = 0.516$) have been estimated as 117 ± 35 permeg and 249 ± 15 permeg, respectively. Depending on the relative proportion of terrestrial and marine $O_2$ production - for present-day conditions the various ocean and land biosphere models give an ocean to land $O_2$ production ratio that varies from 0.45 to 0.59 (Bender et al., 1994; Blunier et al., 2002; Hoffmann et al., 2004) -, the global $^{17}\Delta_{bio}$ calculates as 166 ± 51 permeg. Despite its large uncertainty, $^{17}\Delta_{bio}$ has been used with Eq. 1.44 to gain insight in past changes in biosphere productivity (e.g. Blunier et al., 2002, 2012; Landais et al., 2007a; Luz et al., 1999).

1.2.5.5 What processes influence $^{17}\Delta_{atm}$?

Figure 1.9 summarizes the various $\lambda$ associated with the $O_2$ cycle. An increase of $^{17}\Delta_{atm}$ can be caused by:

- a $\delta^{18}O_{sw}$ enrichment as $\lambda_{sw} = 0.528$, because of a global ice volume increase
- a $\delta^{18}O$ enrichment of the meteoric water consumed by the plants
- an increase of $\lambda_{trans}$, driven by a decrease in relative humidity as shown by Eq. 1.51 (from C to D on Fig 1.9)
- a decrease of the $CO_2$ concentration, which scales the stratospheric depletion (causing $I$ to move toward $H$ on Fig 1.9). Young et al. (2014) details the possible stratospheric-related causes of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ variations:
  - rates of $O_3$ formation and destruction in the stratosphere
  - rates of formation and quenching of excited-state atomic oxygen, $O(^1D)$, in the stratosphere
  - rate of transfer of $O_2$ isotopes from $O(^1D)$ to $CO_2$ in the stratosphere
  - AIR fluxes between stratosphere and troposphere
  - rate of $CO_2$ exchange with $H_2O$ at the surface
- an increase of total photosynthetic and respiratory fluxes, as shown by Eq. 1.45, or a relative increase of $O_2$ oceanic production, associated with a higher $^{17}\Delta_{atm}$, with respect to the $O_2$ production on land (from $E$ and $G$ to $H$ on Fig 1.9)
- a decrease of the photorespiration fraction, associated with a low $\lambda = 0.509$ (causing $\lambda_{terr,resp}$ to increase from $D$ to $E$ on Fig 1.9). Note however that a reduced photorespiration fraction may be caused by an increased $CO_2$ concentration, which would lead to a decrease in $^{17}\Delta_{atm}$
Figure 1.9 – A schematic representation of all the processes causing $^{17}\Delta_{atm}$ variations. Not to scale. Refer to text for details.
1.3 Past variations of the three $O_2$ isotopes in ice cores

Ice core archives represent the medium from which numerous tracers of the evolution of the climate in the past 800 kyr are retrieved. In particular, the past triple isotopic composition of atmospheric $O_2$ is obtained from fossil air preserved in ice core bubbles. This section describes the past orbital (Sect. 1.3.1) and millennial (Sect. 1.3.2) timescale variations of $\delta^{18}O_{atm}$ and $\Delta_{atm}$ over the last 800 kyr and 400 kyr, respectively, and the current understanding of these changes.

1.3.1 Orbital scale variations during the Quaternary Period

The Quaternary period, including the Pleistocene (from 2.588 Myr to 11700 yr B.P.) and Holocene period (from 11700 yrs), is characterized by a series of long-lasting glacial and shorter interglacial periods (Fig. 1.10). While ice started to accumulate in Antarctica over 20 Myr ago, major ice sheets in the Northern Hemisphere only started to build 2.5 Myr ago (e.g. Williams et al., 1997). During glacial periods, ice sheets covered an important part of Eurasia and North-America north of 40-50 °N, while only Antarctica and Greenland were ice covered during interglacial periods. These large-scale environmental changes caused a transfer of large amounts of water between oceans and ice sheets, leading to global sea level change up to $\pm 120$ m (Waelbroeck et al., 2002; Lambeck et al., 2002; Bintanja et al., 2005). The Quaternary climate oscillations are recorded in archives like speleothems, marine or lake sediments (e.g. McDermott, 2004; Imbrie et al., 1984) and Antarctic ice cores (see Fig 1.10) for the last 800 kyr (e.g. Jouzel et al., 2007; Lüthi et al., 2008). Archives show that Pleistocene climatic oscillations varied with a period of 41 kyr until 1 Myr, then with a period of mean $\approx 100$ kyr to present day. The reason of this frequency shift is still not fully understood. For instance, Ruddiman (2003) suggests that the 100 kyr cycle began 0.9 Myr ago because of a gradual global cooling trend allowing ice sheets to survive during weak precession insolation maxima and grow large enough during 41 kyr-ice-volume maxima to generate strong positive $CO_2$ feedback. As proposed by Milankovitch (1941), reduction of summer insolation in the mid-latitudes of the Northern Hemisphere causes onset of glaciations. Changes in insolation are driven by variations in the orbital parameters of the Earth, namely precession, obliquity and eccentricity (by modulating the precession signal). Milankovitch’s hypothesis was that summer insolation in the NH at the periods of obliquity (41 kyr) and precession (23 kyr) directly forces NH ice sheets through changes in summer ablation. The response of the climate system to change in insolation is however more complex, because several processes interact and cause positive feedbacks. Indeed, a decrease in insolation is amplified by a weaker albedo feedback, and a decrease in greenhouse gases mixing ratios (which control the radiative surface forcing of the atmosphere), sea ice increase (Khodri et al., 2001), or biospheric changes (de Noblet et al., 1996). For instance, during the Last Glacial Maximum (noted LGM hereafter), 21 kyr ago, greenhouse gases concentration of $CO_2$, $CH_4$ and $N_2O$ reached a minimum of 185 ppm, 350 ppb et 200 ppb, resp. (Monnin et al., 2001; Dällenbach et al., 2000; Flückiger et al., 1999), while
Comparison between two Late Pleistocene (last 800 kyr) records describing glacial interglacial cycles caused by orbital variations: the LR04 stack (benthic $\delta^{18}O$ records from 57 globally-distributed sites, Lisiecki and Raymo, 2005) on its own time-scale and $\delta$D from the EDC Antarctic ice core on EDC3 timescale (EPICA community members, 2004; Jouzel et al., 2007) present an excellent agreement. Benthic $\delta^{18}O$ is used as a proxy for global ice volume and deep ocean temperature, while $\delta$D variations indicate local surface temperature shifts.

reaching 280 ppm, 700 ppb et 270 ppb, resp., during the pre-industrial period (Fig. 1.11).

The past atmospheric concentrations and isotope composition of ancient atmosphere are retrieved from air bubbles occluded in polar ice sheets. Indeed, in the firn to ice transition, close to the surface of the ice sheet, atmospheric air gets sealed into air bubbles (see Sect. 1.4.1.3). The air bubbles are then advected with the surrounding ice through the ice sheet. The deeper the ice layer, the older the retrieved climatic information. Ice cores drilled in Antarctica and Greenland have thus been analysed to reconstruct the past atmospheric composition up to 800 kyr (120 kyr in Greenland) back in time. For instance, ice core analysis show variations of greenhouse gases at orbital timescales (Lüthi et al., 2008; Loulergue et al., 2008; Petit et al., 1999; Schilt et al., 2010) synchronous with temperature reconstructions (see Fig. 1.11), suggesting an amplifying role to orbital-scale climatic transitions as aforementioned. Not only past mixing ratios but also isotopic ratios of greenhouse gases and non-trace gases (e.g. $O_2$, $N_2$, Ar, Ne or Kr) are preserved in this irreplaceable natural archive, and provide valuable but complex information on the evolution of the past climate.

Precipitation in the form of snow falling each year is also preserved in the ice layers of the polar ice sheets. Water stable isotopes from Greenland (e.g NEEM members, 2013; NGRIP members, 2004) and Antarctic (e.g. Jouzel et al., 2007; EPICA community members, 2004; EPICA Community Members, 2006) ice cores are used to qualitatively define abrupt climatic transitions, while thermal fractionation of gases ($\delta^{15}N$, $^{40}Ar$) in the diffusive column of the firn (Sect. 1.4.1.2) provides in Greenland a
**1.3.1.1 Precession-driven variations of $\delta^{18}O_{\text{atm}}$**

$
\delta^{18}O_{\text{atm}}
$ from ice samples has been measured for the period of the past 800 kyr (Bazin et al., 2016; Bender et al., 1994; Malaize et al., 1999; Petit et al., 1999; Dreyfus et al., 2007) with a mean resolution of about 1000-1500 years (Landais et al., 2010 and references therein). Glacial-interglacial variation of $\delta^{18}O_{\text{atm}}$ mainly stems from $\delta^{18}O_{\text{sw}}$ variation (Bintanja et al., 2005), and reflects the role of ice sheet volume, forced by obliquity, on the ultimate source of atmospheric $O_2$, seawater. Indeed, removing the signal of $\delta^{18}O_{\text{sw}}$ from $\delta^{18}O_{\text{atm}}$, that is the definition of the Dole effect (Dole, 1935; Dole et al., 1954), enables to remove the obliquity component (see Fig. 1.12b) common to both signals (Landais et al., 2010).

At the orbital scale, $\delta^{18}O_{\text{atm}}$ is depicting clear variations at a 23 kyr periodicity (Jouzel et al., 1993, 1996; Malaize et al., 1999) also revealed a strong precessional periodicity (23 kyr) in Dole Effect ($\delta^{18}O_{\text{atm}} - \delta^{18}O_{\text{sw}}$) records, with a striking correspondence with summer insolation in the low latitudes.
Figure 1.12 – (a) Coherence wavelet analysis using Wavelet Analysis (Grinsted et al., 2004) reveals a strong covariation of Vostok $\delta^{18}O_{atm}$ (Petit et al., 1999) and Vostok $17\Delta_{atm}$ (Blunier et al., 2012) in the orbital frequencies. Both records were transferred to the orbitally tuned Vostok time scale from Suwa and Bender (2008). The most prominent feature is the variation of the coherence through time in the precession band. Covariation in obliquity mainly stems from $\delta^{18}O_{sw}$ signal. Black contours indicate significance on a 95% level assuming red noise. The transparent region outside the cone of influence should not be considered. (b) Figure from Landais et al. (2010) showing a spectral analysis of Dole effect (top), $\delta^{18}O_{atm}$ (Middle) and $\delta^{18}O_{sw}$ (Bottom) over the last 800 kyr with a 1000 kyr resolution. $\delta^{18}O_{atm}$ originates from EDC (Dreyfus et al., 2007) and Vostok (Sowers et al., 1991; Jouzel et al., 1993, 1996; Malaize et al., 1999; Petit et al., 1999) ice cores. Please note that according to the authors, the results do not depend on the chosen timescale (original timescales, or adjusted on precession (orbitally tuned)). Similar results are indeed obtained with the Vostok $\delta^{18}O_{atm}$ record in its original timescale GT4 (Glaciological Time Scale 4 cycles), built through glaciological modeling (Petit et al., 1999). (c) Cross correlation spectra of $\delta^{18}O_{atm}$ and $17\Delta_{atm}$ with $\delta^{18}O_{sw}$, Dole effect, $CO_2$, and insolation describe the influence of orbital parameters and associated mechanisms on the long term variations of those two records. Red bars represent the frequencies relevant for orbital parameters (from low to high frequency: excentricity (100 kyr), obliquity (41 kyr) and the two 23 kyr and 19 kyr peaks of precession).
of the Northern Hemisphere. This strong link with precession of both $\delta^{18}O_{atm}$ and the DE (Fig. 1.12b) is thus probably related to the variations of the hydrological cycle at low latitudes (Bender et al., 1994). Indeed, changes in precession, the timing of the seasons with respect to perihelion, affect the amplitude of the seasons and the intensity of the monsoons (Prell and Kutzbach, 1987). Variations related to the monsoon regime strongly imprint the isotopic composition of meteoric water as observed in speleothem records (e.g. Wang et al., 2008). They are easily transmitted to the isotopic composition of atmospheric oxygen because the major part of the biospheric productivity, hence photosynthesis, is occurring in the tropics and subtropics. Based on these observations, the DE is interpreted as a tracer of low latitude hydrological cycle on orbital timescale, hence of precession-driven monsoonal activity (e.g. Landais et al., 2010).

The dominant role of the low latitude hydrological cycle on $\delta^{18}O_{atm}$ orbital variations is corroborated by the striking correspondence between the calcite $\delta^{18}O$ record of a speleothem from Sanbao Cave (China, Wang et al., 2008) and $\delta^{18}O_{atm}$ from Vostok ice core. Indeed, both tropical speleothem's calcite $\delta^{18}O$, a tracer of monsoonal activity (e.g. Wang et al., 2001, 2008; Cruz et al., 2005), and $\delta^{18}O_{atm}$ bear a strong precession signal:

- Precession is believed to control the position of the InterTropical Convergence Zone (ITCZ) (Bender et al., 1994; Wang et al., 2008). During precession minima, the ITCZ and its associated tropical rain belt shift northwards, enhancing monsoonal activity on land. As a result, $\delta^{18}O_{mw}$ becomes depleted, through the amount effect, and it transmits the signal to $\delta^{18}O_{atm}$ through photosynthesis (Landais et al., 2010). The opposite effect occurs in the Southern Hemisphere, with less precipitation, characterized by enriched calcite $\delta^{18}O$ (e.g. Cruz et al., 2005). However, given the NH/SH land ratio, hence the biospheric $O_2$ production ratio, the imprint of the low latitudes of the NH on $\delta^{18}O_{atm}$ is dominant.

- The $\delta^{18}O$ of calcite, a local monsoon intensity tracer, is mostly influenced by land-sea thermal contrasts and local seasonal cycle, which are driven by precession. These processes influence $\delta^{18}O_{mw}$, hence calcite $\delta^{18}O$ (e.g. Braconnot and Marti, 2003).

Based on new $\delta^{18}O_{atm}$ and $\delta O_2/N_2$ (synchronous at first order with local summer insolation) records from EPICA Dome C (noted EDC hereafter, Fig. 1.13), Bazin et al. (2016) recently confirmed the occurrence of large variations (1 to 6 kyr) in the phase delay between $\delta^{18}O_{atm}$ and precession. While previous studies observed a 5 to 6 kyr lag between $\delta^{18}O_{atm}$ and precession over Termination I (e.g. Dreyfus et al., 2007) and Termination II (e.g. Landais et al., 2013), Bazin et al. (2016) found similar lags over Termination II (-5.5 kyr), MIS 8 (-5 kyr) and MIS 16 (-2 kyr), but also minimal lags ($\simeq$ 1 kyr) during periods characterized by intermediate sea-ice extent and high eccentricity levels (MIS 6-7, end of MIS 9, the transition MIS 14-15 and the end of MIS 17). As Termination 2, MIS 8 and MIS 16 are associated with large destabilizations of the Northern Polar ice sheets, they hypothesize that changes in the low latitude hydrolog-
ical cycle caused by weak NH monsoonal activity (associated with large freshwater input causing a southwards ITCZ shift) delay the $\delta^{18}O_{atm}$ response to precession peak (Sect. 1.3.2). The variation of the lag has also serious implications for orbital datation of ice cores assuming a constant phase relationship between $\delta^{18}O_{atm}$ and the precession parameter (Dreyfus et al., 2007), or an insolation curve (e.g. Jouzel et al., 1996; Petit et al., 1999; Bender et al., 1994; Malaize et al., 1999), in terms of uncertainty, and this method should thus be used with caution. On the other hand, the change in the lag does not affect the potential of $\delta^{18}O_{atm}$ to synchronize ice cores, as the $\delta^{18}O_{atm}$ signal is global.

Figure 1.13 – Original Figure from Bazin et al. (2016) with original caption: Top: EDC ice core record of water stable isotopes ($\delta D$, Jouzel et al., 2007). Middle: EDC record of $\delta O_2/N_2$ (black: Landais et al. (2012), green: Bazin et al. (2016)) and local summer solstice insolation (grey, reversed axis). Bottom: EDC record of $\delta^{18}O_{atm}$ (reversed vertical scale) (orange: Dreyfus et al. (2007, 2008); Landais et al. (2013), blue: Bazin et al. (2016)), precession parameter (grey, reversed axis) and 65 ° summer solstice insolation (dashed grey) both shifted younger by 5 kyr. All EDC records are presented on the orbitally tuned AICC2012 chronology (Bazin et al., 2013; Véres et al., 2013). The orbital parameters are calculated using the Laskar et al. (2004) solution, with the Analyseries software (Paillard et al., 1996). This figure depicts the orbital variations of water stable isotopes, $\delta O_2/N_2$ and $\delta^{18}O_{atm}$ of the EDC ice core, back to 800 kyr During periods of weak eccentricity (e.g. around 400 kyr and before 720 kyr), there is no clear correspondence between the variations of $\delta^{18}O_{atm}$ and precession, and the variations of $\delta O_2/N_2$ with local summer solstice insolation (Bazin et al., 2016; Dreyfus et al., 2007; Landais et al., 2012).

1.3.1.2 Long-term variations of $^{17}\Delta_{atm}$

Owing to the low abundance of $^{17}O$, accounting for 0.078 % of the total oxygen, and the subsequent very high precision required to obtain reliable datasets, only a few
studies have focused on past long term variations of $^{17}\Delta_{atm}$ (Luz et al., 1999; Blunier et al., 2002, 2012). $^{17}\Delta_{atm}$ has been measured back to 400 kyr with approximately 1000 years resolution (Blunier et al., 2002, 2012). $^{17}\Delta_{atm}$ also depict glacial-interglacial variation of around 40 permeg (Fig. 1.14), mainly driven by changes in $CO_2$ concentration. Such a strong dependence is mainly due to stratospheric photochemistry (Sect. 1.2.5.3) involving transfer of heavy isotopes of $O_2$ to $CO_2$ via $O_3$ (e.g. Thiemens, 1999), and scaling with $CO_2$ concentration. Timings of strong coherence between $\delta^{18}O_{atm}$ and $^{17}\Delta_{atm}$ occur during strong concomitant sea level and $CO_2$ variations, associated with a strong precession signal (Fig. 1.14).

Figure 1.14 – Bottom-Up: Precession parameter and eccentricity (Laskar et al., 2004); compiled $CO_2$ data from Vostok, Taylor Dome and Epica Dome C (Lüthi et al., 2008; Blunier et al., 2012); coherence in the precession band extracted from Fig. 1.12a; $\delta^{18}O_{sw}$ curve from Bintanja et al. (2005); $\delta^{18}O_{atm}$ from Vostok (Petit et al., 1999); $^{17}\Delta_{atm}$ from Blunier et al. (2002). Vertical shaded bars indicates periods of strong coherence between $\delta^{18}O_{atm}$ and $^{17}\Delta_{atm}$; approximate MISs timings are indicated on top. Note that all records are displayed on their original timescale adjusted to start in 2000.

1.3.2 Millennial scale climate variability

Beyond the large and valuable climate information that can be retrieved from the polar ice sheets, ice core are unique archives as they also provide high temporal resolution (which is function of the accumulation rate) and accurate datation*. For instance, the fine yearly data resolution of NGRIP (Northern Greenland Ice Core Project, Greenland) ice core sample enables annual layer counting down to a depth of 2430 m, which

*With the new technological developments, speleothems nonetheless challenge ice archives in terms of absolute datation, because they can be dated in calendar years with a precision approaching $\pm 0.5\% (2\sigma)$ (McDermott, 2004). McDermott (2004) actually predicts that the chronology of the Greenland ice-cores records will be increasingly refined with speleothem records.
corresponds to an age of 60 kyr (Svensson et al., 2008).

Millennial-scale climate variability is perhaps best known from the Greenland ice cores, where it is manifested in the stable water isotopes of ice. During the last glacial period, these cores show 25 Dansgaard-Oeschger (DO) events (NGRIP members, 2004). A DO event typically exhibits a sawtooth pattern: (i) a cold phase (Greenland stadial, noted GS hereafter) lasting from centuries to millennia, followed by a warm phase (Greenland interstadial, GI) starting with (ii) a rapid transition (a few decades) with an amplitude of up to $16 \pm 2.5^\circ$C (Landais et al., 2004a,b, 2006c; Huber et al., 2006b; Kindler et al., 2014), and ending with (iii) a gradual cooling before an abrupt decrease towards cold, stadial values. During the last glacial period, the presence of ice rafted debris (IRD, Ruddiman, 1977; Heinrich, 1988) in marine sediments from the North Atlantic region during the largest GS document episodes of massive iceberg release in the North Atlantic, mainly from the Laurentide and Fennoscandian ice sheets (Grousset et al., 1993; Guillevic et al., 2014 and references therein). Even though IRD are present in each GS (Elliot et al., 2002), not all GSs contain a Heinrich event. Only six major IRD, occurring within the Ruddiman band, between 40°N et 55°N, were defined as Heinrich events (Hemming, 2004). When a Heinrich event occurs during a GS, the latter is defined as a Heinrich stadial (HS) (Barker et al., 2009; Sanchez Goni and Harrison, 2010).

1.3.2.1 What drives abrupt climate changes?

Millennial-scale climate variations in Greenland are associated with abrupt climate changes in the mid to low latitudes as recorded in numerous terrestrial (speleothems, e.g. Fleitmann et al., 2009) and marine (e.g. Bond et al., 1993; Broecker, 2000) archives (read Clement and Peterson, 2008 for a review). As the tropics are the main source of heat and water vapor in the global climatic system (Clement and Peterson, 2008), and document major climatic impacts from millennial scale variability in terrestrial and marine paleoarchives (e.g. Voelker and workshop participants, 2002, and reference therein), hydrological reorganizations in low latitudes may have played a critical role (e.g. Peterson et al., 2000) in abrupt climatic events. Concomitant methane excursions in ice cores and variations in the isotopic composition of the calcite of speleothems in eastern Asia (e.g. Wang et al., 2001; Cheng et al., 2012) actually strongly support the fact that millennial scale variability is associated with major reorganization of the tropical water cycle and hence monsoon intensity in a relation with a shift in the ITCZ and its terrestrial equivalent, the tropical rain belt (Chappellaz et al., 2013; Wang et al., 2008; Pausata et al., 2011).

Each DO event has a corresponding Chinese Interstadial, as observed in $\delta^{18}O$ of calcite speleothems (e.g. Cheng et al., 2012). However, on shorter timescales, a decoupling is observed between the tropical and the polar regions. For instance, on-the-field continuous laser spectroscopy measurements of $CH_4$, at a very high temporal resolu-
tion, unveiled sub-millennial scale variations with no signal in Greenland water stable isotopes (Landais et al., 2015; Chappellaz et al., 2013). Details of the link between tropical and high latitude climate is widely discussed and partly hampered by the difficulty to synchronize timescales of archives of different nature (speleothems, marine cores, ice cores). Guillevic et al. (2014) avoid interarchives datation discrepancies by developing a multi-proxy approach based on the identification in polar ice cores of the fingerprint of HEs in the mid-to-low latitudes. This study, based on direct comparison between various ice core proxies (δ^{18}O_{atm}, CO_2, CH_4 mixing ratio, sulfuric acid (MSA)) sensitive to climate of different latitudes, also reveals a decoupling between Greenland temperatures and low latitude HE imprints (Heinrich event 4) during GS 9. These examples highlight the need for low latitude climate ice core proxies, on a common timescale and at high temporal resolution, for testing the mechanisms associated with millennial scale variability. Indeed, despite the variety of regional scale paleoarchives (ocean cores, lake sediments, speleothems, pollen, corals, paleosoils, tree rings) that unveil the imprint of climate instabilities at different latitudes in both hemispheres, assessing their spatial extent is challenged by (i) the dating uncertainties of low latitudes records, making difficult to obtain a precise chronology over archives of different types, and (ii) their spatial distribution, as most of the records are located in the North-Atlantic, with enormous spatial gaps elsewhere (Clement and Peterson, 2008; Voelker and workshop participants, 2002), and significance (Hemming, 2004; Wunsch, 2006; Severinghaus et al., 2009). Atmospheric O_2 helps address the spatial issue because it represents an integrated signal sensitive in particular to the low latitude hydroclimate.

### 1.3.2.2 Rapid changes in the composition of atmospheric O_2

At the millennial scale, δ^{18}O_{atm} is responding to the abrupt climate changes of the last glacial period. NGRIP δ^{18}O_{atm} high-resolution measurements (100 yrs step) covering MIS 4 and MIS 5 (Landais et al., 2007b, 2006c; Capron et al., 2008) and including 8 DO events indeed reveal a δ^{18}O_{atm} increase (decrease) over the cold (warm) phase of DO events (Fig. 1.15a). A clear illustration of this pattern can be found during DO 22 and 21. Superimposed to the general decreasing trend of δ^{18}O_{atm} by −0.6‰ (blue arrow on Fig. 1.15a), millennial scale variations, are observed (red arrows): during the warm phases of DO 22 and 21, δ^{18}O_{atm} decreases more abruptly, and remains stable during the cold stadial (Landais et al., 2010).

As mentioned in Sect. 1.3.1, among the cold phases (GSs) characterized by an increase in δ^{18}O_{atm} (Landais et al., 2007b; Severinghaus et al., 2009), some GSs are associated with major iceberg discharges and are designed as HSs. The δ^{18}O_{atm} signal is often stronger during the HSs than during the other GSs. These GSs and/or HSs are associated with strong variations in the monsoon regime in the low latitudes through southward shift of the ITCZ, more pronounced during HS (GS associated with a HE) than GS, as suggested by speleothem growth rate and calcite δ^{18}O (Kanner et al., 2012; Wang et al., 2007; Mosblech et al., 2012). It has
Figure 1.15 – (a) Based on Landais et al. (2010). Top: NorthGRIP water δ¹⁸O is displayed on the EDML1 Antarctic timescale (Ruth et al., 2007; Capron et al., 2010). The DO events are indicated. Middle: millennial scale variations of δ¹⁸O_{atm} on the EDML1 timescale (Landais et al., 2006a, 2007b; Capron et al., 2008) during MIS 5 and MIS4, increasing over GSs and decreasing over GIs. Are also shown in red variations of speleothem’s calcite δ¹⁸O from Sanbao, north-east Asia (Wang et al., 2008). Millennial forcings are superimposed to the precessional and/or ice-sheet-induced long-term δ¹⁸O_{atm} trend. Vertical dotted lines indicate the correspondence between δ¹⁸O_{atm}, water δ¹⁸O and calcite δ¹⁸O records. (b) Based on Landais et al. (2007b). Millennial scale variations of the three isotopes of O₂ over DO 19. NGRIP δ¹⁸O_{atm} was measured at very-high resolution (50 years) resolution, not ¹⁷Δ_{atm}. The blue dashed line symbolizes the sea-level gradual δ¹⁸O_{sw} enrichment due to growing ice-sheet (e.g. Bintanja et al., 2005).

thus been suggested that the driver of the global δ¹⁸O_{atm} millennial scale variations is the hydrological cycle of the low latitudes. For instance, Landais et al.’s study (2010) invokes changes in the low latitude hydrology and in terrestrial vegetation distribution, driven by ITCZ shifts, to explain δ¹⁸O_{atm} millennial scale variations observed in ice cores. Besides, Severinghaus et al. (2009) found a striking anti correlation between Chinese speleothems calcite δ¹⁸O (Wang et al., 2001, 2008) and δ¹⁸O_{atm} derived ε_{land} from Siple Dome, highlighting too the importance of the NH tropical hydology. To summarize, these studies underscore the influence of NH monsoonal activity on δ¹⁸O_{atm}, driven by ITCZ shifts on millennial timescales. Quantifying its past variations should provide valuable information on the low latitude hydroclimate and this work represents the scope of Chapter 5.

To my knowledge, only one study hitherto has combined very high resolutions measurements of the three isotopes of atmospheric O₂ (Landais et al., 2007b). 96 δ¹⁸O_{atm} measurements were performed over the period 80 to 60 kyr (DO 18, 19 and 20). In addition, ¹⁷Δ_{atm} measurements were done at 7 depth level over DO 19, where the largest temperature variation during MIS 4 occurs, to constrain the origin of the observed δ¹⁸O_{atm} variations (Fig. 1.15b). As already observed for δ¹⁸O_{atm} over other DO events, an imprint of millennial processes on the long-term trend of δ¹⁸O_{atm} is observed. Indeed, δ¹⁸O_{atm} should be steadily increasing from 76 kyr to 66 kyr B.P, driven by the increase in δ¹⁸O_{sw} (symbolized by the dashed blue line in Fig. 1.15b) due to a decreasing sea level (and more voluminous ice sheet) (Landais et al., 2007b). Instead,
it increases by more than 0.2 %/o over GS 20 with respect to its long-term increase, and decreases by the same amount during GI 19 (considering that $\delta^{18}O_{atm}$ should get enriched) (Landais et al., 2007b). The mean $17\Delta_{atm}$ decrease of 12 ± 10 permeg from GS 20 to GI 19 (Fig. 1.15) provides valuable information in the sense that the magnitude of its variation discards the possibility that rapid sea-level changes are driving $\delta^{18}O_{atm}$ variations over DO 19. Indeed, a 12 permeg decrease would require, according to Eq. 1.52, a 1 %/o decrease of $\delta^{18}O_{sw}$, hence $\delta^{18}O_{atm}$ over GI 19, corresponding to the observed variations in mean $\delta^{18}O_{sw}$ between LGM and present-day (Waelbroeck et al., 2002), around 120 m (Bintanja et al., 2005). The inter-comparison of $\delta^{18}O_{atm}$ and $17\Delta_{atm}$ relative variations over DO 19 by Landais et al. (2007b) confirms the view according to which the combined changes of hydrology and vegetation cover, rather than rapid sea-level changes, drives the triple isotopic composition of atmospheric $O_2$ on millennial time-scale.

The study of Landais et al. (2007b) illustrates the interest of combining very-high resolution measurements of $17\Delta_{atm}$ and $\delta^{18}O_{atm}$ to constrain the origin of their variations. Still, $17\Delta_{atm}$ measurements are challenging, requiring a very high precision (less than 10 permeg) to obtain a record with a reliable climatic signal. The quality of the record does not only depend on the quality of the analytical measurements, on the conditions of ice core recovery and storage, but also on our understanding of how the air is trapped in the ice. Indeed, the elemental and isotopic composition of the air occluded in ice core bubbles is different from the ancient atmosphere it represents, because of fractionating processes that occur in the firn, the porous top layer of the ice sheet where transformation of snow to ice occurs. Corrections are therefore unavoidable, and their quality reflects our understanding of these firn processes, which is reviewed in the next section.

1.4 Alteration of the composition of gases trapped in ice core bubbles

The previous section reviewed the current understanding of $\delta^{18}O_{atm}$ and $17\Delta_{atm}$, described their orbital and millennial time-scale variations observed in ice cores, and focused on the processes that affect the triple isotope composition of atmospheric $O_2$. In Chapter 5 we use a modeling approach to quantify the relative importance of the different processes behind the observed changes in $\delta^{18}O_{atm}$ over a Heinrich Stadial. However, this step requires first to reconstruct the original $\delta^{18}O_{atm}$, or $17\Delta_{atm}$ record preserved in air bubbles entrapped in ice cores. To do so, leaving aside the building and validation of an analytical system able to measure with high precision the triple isotopic composition of $O_2$ from fossil air (Chapter 3), it is necessary to understand the processes of air trapping in the firn, and how they alter the elemental and isotope composition of fossil air. While this section introduces the firn processes, Chapter 4 will detail the strategy adopted to correct ice core measurements for these effects, but also for the effects of coring and post-coring fractionation.
Figure 1.16 – Original figure 2-2 from Schmitt (2006). Scheme of physical processes occurring in the firm column with depth and age values for ice and gas representative for the drill site Kohnen station (Antarctica). This figure illustrates (1) the progressive compaction of snow to ice caused by the overburden pressure of successive precipitation, resulting in a gradual density increase from $\rho \approx 0.3 \pm 0.2 \, \text{g cm}^{-3}$ at the top to $0.8 \pm 0.05 \, \text{g cm}^{-3}$ ($\rho_{\text{ice}} = 0.92 \, \text{g cm}^{-3}$) at the bottom of the firm. (2) Firn densification causes the interstitial space between ice crystals, called porosity, to decrease with depth, and air to be gradually trapped in bubbles. (3) Firn can be divided in 3 distinct zones based on the mode of air transport: a convective zone, typically 1-15 m deep (Kawamura et al., 2006; Landais et al., 2006b) where the air has the same composition as the atmosphere due to rapid mixing; a diffusive zone characterized by molecular diffusion of gases, where mass dependent gravitational fractionation leads to enrichment of heavy isotopes with depth; and a lock-in-zone, or non diffusive zone, where air is advected with the ice matrix. Vertical diffusion stops at the lock-in-depth, on top of the locking zone. In other words, the lock-in-zone is isolated above from atmosphere, probably due to the presence of high density winter layers (Battle et al., 1996; Landais et al., 2006b) at the lock-in-depth that inhibit vertical gas transport (Buizert, 2011). The limit of the lock-in-zone is defined below by the firn to ice transition, where there are no more open pores. This zone is characterized by size-dependent fractionation, evidenced by e.g. Huber et al. (2006a); Severinghaus and Battle (2006), who observed strong enrichment of gas species with a small molecular diameter, such as He, Ar, Ne and $O_2$ (see text for details) (4) Finally, this figure shows how $\Delta \text{age}$ (the ice age - gas age difference) increases with depth. This is due to the fact that air in the firn continuously exchanges with the atmosphere until the lock-in-zone is reached. As a result, the air occluded in bubbles is younger than the surrounding ice (Schwander and Stauffer, 1984). Note that in the lock-in-zone, the age of the air is substantially older than in the diffusive zone, as air is advected downwards at the same pace as the ice matrix. This offers the possibility to retrieve large ancient air samples without the need of extracting them from ice core bubbles (Severinghaus and Battle, 2006). However, it is challenging to isolate the climatic signal as the air composition of the lock-in-zone depends on several factors (Sect. 1.4.1.3.4).
1.4.1 Diffusive Processes in Firn

Air bubbles trapped in ice cores have a different elemental and isotopic composition than the one of the past atmosphere they represent. This is caused by the presence of a 40-120 m thick porous snow layer at the top of the ice sheet (Fig. 1.16), called firn. Various processes modify the composition of the air traveling downwards until the air is occluded in the ice matrix at the bottom of the firn.

The firn column is usually divided in 3 zones, based on the $\delta^{15}N$ of $N_2$ (Sowers et al., 1992). Figure 1.17c shows that $\delta^{15}N$ has the same value as in the atmosphere in the upper 1-15 m of the firn column, where convective exchange (surface winds, thermal convection) with the atmosphere occurs. No diffusion occurs in this zone. The diffusive zone is mostly characterized by a gravitational enrichment of $\delta^{15}N$. In the lock-in-zone, the air is isolated from the atmosphere, which causes $\delta^{15}N$ enrichment to stop.

In the following sections we describe how the physical processes taking place in the firn column alter the elemental and isotopic composition of the air bubbles occluded in ice cores. Concentration gradients within the firn drive gas fluxes via molecular diffusion (Craig et al., 1988). They can originate from changes in the composition of the overlying atmosphere, gravitational settling (Craig et al., 1988) (Sect. 1.4.1.1), thermal diffusion (first observed in sand dunes, Severinghaus et al., 1996) (Sect. 1.4.1.2), and molecular size fractionation at close-off depth (Sect. 1.4.1.3), where all bubbles are closed Huber et al. (2006a).

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**Figure 1.17 – Original caption and figure 2.3 from Buizert (2011).** Firn characteristics at NEEM (North Eemian Drilling Project, Greenland, 77.4°N, 51.1°W). (a) Firn density and porosity using the parameterizations of Schwander (1989) (solid line) and Goujon et al. (2003) (dashed line). (b) Downward velocity of firn layers ($w_{\text{ice}}$) and of air in the open porosity ($w_{\text{air}}$). (c) Zonal division based on gravitational enrichment of $\delta^{15}N$ of $N_2$. Data are corrected for thermal fractionation.
1.4.1.1 Gravitational fractionation

Earth’s gravity field causes heavy isotopes to accumulate at the bottom of the firn air column in diffusive equilibrium. Gravitational enrichment increases with depth and the absolute mass difference between a pair of elements, or isotopes. Equilibrium is reached when the gravitational force balances the molecular diffusion driven by the gradient of concentration in the firn. The isotopic enrichment at the lock in depth caused by gravitational settling can be expressed by the barometric equation (Craig et al., 1988):

$$\delta_{\text{grav}} = e^{\frac{\Delta m g z}{RT}} - 1 \approx \frac{\Delta m g z}{RT},$$

(1.54)

with $\Delta m$ being the mass difference between the two considered isotopologues, $g$ the acceleration due to gravitation, $z$ the depth of the diffusive zone, $R$ the ideal gas constant, and $T$ the mean firn temperature in K. Because gravitational fractionation scales with the mass difference $\Delta m$ (Craig et al., 1988; Schwander, 1989), it is thus 2 times stronger for $^{18}O$ ($\Delta m = 34 - 32 = 2$) than for $^{15}N$ ($\Delta m = 29 - 28 = 1$).

1.4.1.2 Thermal fractionation

Thermal fractionation arises from temperature difference in the firn, leading to enrichment of heavy elements towards the bottom of the firn, colder than in the surface. This process is due to the sensitivity of intermolecular forces during collision of molecules and atoms (Severinghaus et al., 2001) and is determined empirically. To be significant, thermal gradients must be higher than 10 °C (Landais, 2004). Thermal fractionation is therefore stronger during abrupt climate changes, for instance during DO events: when a rapid temperature warming occurs at the surface, heavy isotopologues ($\delta^{15}N$, $\delta^{18}O$, $^{40}Ar$) migrate towards the bottom of the firn. As diffusion of gases is $\approx 10$ times faster than diffusion of heat (Paterson, 1994), it will take hundreds of years before temperature homogenize in the firn, causing in turn $\delta^{15}N$ to reach back its initial value. It follows that the thermal diffusion signal can fully develop until warm temperatures reach the bottom of the firn. This also means that the temperature change indicated by air isotopes is recorded at the same level than changes in trace gases like $CO_2$ or $CH_4$, while water isotopes register this change at the surface. As a consequence, a paleothermometry method based on $\delta^{15}N$ has been developed (see e.g. Severinghaus and Brook, 1999 or Kindler et al., 2014, who measured nGRIP $\delta^{15}N$ for the whole last glacial period from 10 to 120 kyr b2k (thousand years before 2000) including every DO event). This method offers the great advantage of avoiding the uncertainty caused by the depth difference $\Delta$ depth, hence age difference $\Delta$ age$^{10}$, between water isotopes and gas isotopes when interested in comparing temperature and greenhouse gases variations.

At equilibrium between thermal diffusion, in one direction, and molecular diffusion along a concentration gradient in the other direction, thermal fractionation can

$^{10}$The error associated with $\Delta$age is $\approx 10\%$, which corresponds to 100 yr in Greenland during the glacial period, and 1000 yr (or more) in Antarctica (Landais, 2004)
Indeed, in the shallow firn, large temperature gradients caused by the downward propagation of the seasonal surface temperature cycle, with a temperature minimum around 5 m depth here, lead to a local enrichment in heavy isotopes of \( \text{N}_2 \) and Ar. \( \delta^{40}\text{Ar} \) is divided by 4 to display the gravitational enrichment in terms of unit of mass difference. Sampling was done in summer as the temperature is higher at the surface than in depth.

be expressed as (Severinghaus et al., 1998):

\[
\delta_{\text{therm}} = \left( \frac{T_t}{T_b} \right)^{\alpha_T} - 1 \approx \alpha_T \cdot \frac{\Delta T}{T_b} \approx \Omega \Delta T, \tag{1.55}
\]

where \( \Delta T \) represents the temperature difference between the top \( (T_t) \) and the bottom \( (T_b) \) of the diffusive zone, \( \alpha_T \) stands for the thermal diffusivity constant, \( \Omega \) stands for the thermal diffusion sensitivity (\( \% \cdot \text{K}^{-1} \)).

The influence of thermal diffusion can be corrected with isotope ratios of \( \text{N}_2 \) and Ar. The effect of gravitation can indeed be separated from thermal diffusion by using the thermal diffusion constants of considered gases (Severinghaus et al., 2001). These two effects can be quantified by \( \text{N}_2 \) and Ar isotope measurements on the same air sample. The gravitational signal of \( \delta^{15}\text{N} \) and \( 40\text{Ar}/4 \) is identical, but their thermal diffusivities are different. Hence, the temperature gradient in the firn is proportional to:

\[
\delta^{15}\text{N}_{\text{excess}} = \delta^{15}\text{N} - \delta^{40}\text{Ar}/4. \tag{1.56}
\]

By measuring both parameters, \( \delta^{15}\text{N} \) and \( 40\text{Ar}/4 \), on air extracted from Greenland ice
cores, the gradient of temperature in the firn can be estimated in the following way:

\[
\Delta T = \frac{\delta^{15}N_{\text{excess}}}{(\alpha_{\text{Ar}} - 4 \cdot \alpha_N)}
\]  

(1.57)

To assess the magnitude of abrupt temperature changes at the surface, which are higher than \(\Delta T\), a firn model is needed to inverse the gradient of temperature \(\Delta T\), by accounting for the thickness and structure of the firn (Landais, 2004).

One prerequisite for applying Eq. 1.57 is the availability of accurate values for the thermal diffusion constants. This is the case since the thermal diffusion constants were precisely measured by Grachev and Severinghaus (2003b,a). In the laboratory, they experimentally determined the values of thermal diffusion constants of \(N_2\) and \(Ar\) for temperatures spanning temperature gradients measured in the firn (\(-60\) to \(-10^\circ\)c). For nitrogen (\(^{15}N/^{14}N\)) in atmospheric air:

\[
\alpha_N \cdot 1000 = 8.656 - \frac{1232}{T_K},
\]  

(1.58)

and for Argon (\(^{40}Ar/^{36}Ar\)) in atmospheric air:

\[
\alpha_{\text{Ar}} \cdot 1000 = 26.08 - \frac{3952}{T_K},
\]  

(1.59)

where \(T_K\) is the mean effective temperature defined as \(T_K = T_1 \cdot T_2/(T_1 - T_2) \cdot \ln(T_1/T_2)\), where \(T_1\) is the warmest temperature of the gradient and \(T_2\) the coldest.

### 1.4.1.3 Bubble close-off fractionation

Among the firn processes, bubble closure at the firn-ice transition is the least understood (e.g. Mitchell et al., 2015). It is however critical to understand its mechanism to correct for fractionation that occurs during air entrapment at the firn to ice transition, and correctly interpret ice core records of past atmosphere. Bubble close-off fractionation is for instance believed to play an important role in past \(\delta O_2/N_2\) variations. Indeed, variations in the orbital scale of past atmospheric \(O_2\) mixing ratio (\(\delta O_2/N_2\)) trapped in ice cores correlate strongly with local insolation changes (Bender, 2002; Kawamura et al., 2007; Suwa and Bender, 2008; Landais et al., 2012), and a suggested mechanism to explain this link is that changes in local summer insolation affect physical properties of the snow at the surface, properties which are maintained at the firn to ice transition and influence bubble close-off fractionation, hence \(\delta O_2/N_2\) (Bender, 2002). In this section we describe the processes of bubble closure and air entrapment.
1.4.1.3.1 Size dependent fractionation

A systematic elemental fractionation occurs within the lock-in-zone (Fig. 1.16), with small collision diameter gas molecules (Ne, \(O_2\), Ar) being preferentially excluded from the occluding bubbles during bubble close off, hence accumulating in the open firn pores (Severinghaus and Battle, 2006). Bubble closure occurs gradually and is strongly dependent on density (Schwander et al., 1993). Under the overlying pressure of the successive precipitation, closed bubbles are pressurized, which increases the gas partial pressure gradient between the bubbles and the open porosity. As a result, permeation occurs through the ice lattice, provided that the collision diameter

Figure 1.19 – (a) Original figure 4 from Severinghaus and Battle (2006). Firn \(\delta O_2/N_2\) (gravitationally corrected) profile taken in 2001 at South Pole. By increasing the accumulation rate, the LIZ \(\delta O_2/N_2\) enrichment obtained from the authors’ permeation-related fractionation model becomes weaker. Indeed, with a higher accumulation rate, there is less time for the gas to escape, as the ice (and the advected air) moves faster in the LIZ, causing less enrichment in the LIZ. (b) Original figure 8 from Severinghaus and Battle (2006) Firn \(\delta O_2/N_2\) (gravitationally corrected) profile taken in 1996 at Siple Dome. \(\delta O_2/N_2\) was gravitationally corrected to isolate the close-off fractionation. These 2 figures show that the magnitude of \(\delta O_2/N_2\) enrichment in the lock-in-depth caused by bubble close-off fractionation varies from site to site. The higher permeation of \(O_2\), 3 times higher than \(N_2\), causes a \(\delta O_2/N_2\) enrichment in the lock-in-zone, confirming Ikeda-Fukazawa et al.’s prediction on selective permeability. Besides, one can see that the \(\delta O_2/N_2\) enrichment is strongest in the LIZ, where gradual occlusion of bubble occurs. Finally, the gradient observed at the top of the lock-in-depth, in the diffusive column of the firn (on gravitationally corrected data) reveals an upward diffusive flux across the lock-in depth (Severinghaus and Battle, 2006; Buizert, 2011): the \(O_2\) loss to the atmosphere is balanced by a corresponding \(O_2\) loss in bubble air, and provides thus a mean to estimate the isotope fractionation due to close-off fractionation.
of the molecules (c.f. 3.1) does not exceed 3.6 Å (Ikeda-Fukazawa et al., 2005), leading to an enrichment in O₂, Ar, and other small species such as He or Ne within the lock-in-zone (e.g. Huber et al., 2006a; Severinghaus and Battle, 2006). The existence of a size-dependent fractionation process is corroborated by the fact that large molecules like N₂, Kr or Xe are not escaping (or at a similar very low rate) from recently closed bubbles into open pores (e.g. Severinghaus and Battle, 2006; Battle et al., 2011). For instance, according to Ikeda-Fukazawa et al. (2005), the permeation rate of O₂ through the ice crystals is three times higher than the one of N₂ and has a value of $1.3 \cdot 10^{-20} \text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at $-25^\circ\text{C}$ (Severinghaus and Battle, 2006).

Not only the magnitude of $\delta O_2/N_2$ depletion varies from site to site, but also the slopes of Ar/N₂ vs O₂ /N₂ and Ne/N₂ vs O₂ /N₂, ratios vary, probably due to a strong temperature dependence of the breaking of hydrogen bonds (Ikeda-Fukazawa et al., 2005; Battle et al., 2011). Large diameter molecules (but under 3.6 Å) like O₂ and Ar, in contrast with Ne (2.820 Å), are especially sensitive to temperature. (Severinghaus and Battle, 2006; Battle et al., 2011). Table 1.6 indicates the ratio of enrichment of various species vs. $\delta O_2/N_2$ within the lock-in-zone of 3 polar sites characterized by different mean annual temperature. The colder temperature at South Pole relative to WAIS-D ($-51$ vs. $-31 ^\circ\text{C}$) probably explains the higher ratio of enrichment $R_{Ne}^{OE}$ (with a lower temperature, O₂ loss is reduced) and the slightly lower $R_{Ar}^{OE}$ (larger in diameter, hence more dependent to the temperature-dependent mechanism, Ar loss is more reduced than O₂ loss at $-51 ^\circ\text{C}$). This is also consistent with the relatively large slope of $R_{Ar}^{OE}$ at Siple Dome, but more measurements of Ar and Ne isotopes in the lock-in-zone are needed to confirm this hypothesis.

1.4.1.3.2 Mass-dependent fractionation

Recently, (Battle et al., 2011) found a mass-dependent enrichment of $\delta ^{18}O$ within the lock-in-zone, in contradiction with a purely size-dependent permeation process.
They suggest that for gases with a collision diameter lower than 3.6 Å, permeation can occur through the ice lattice by breaking of hydrogen bonds (O₂ and Ar) (Ikeda-Fukazawa et al., 2004), but also via interstitial hopping, a velocity-dependent hence mass-dependent process, as suggested by Ikeda-Fukazawa et al. (2004) for Ne. Battle et al. (2011) suggest therefore that the depletion observed in δ¹⁸O is due to permeation of O₂ through these two gas loss mechanisms.

1.4.1.3.3 Depleted δO₂/N₂ in ice core samples

This enrichment at the firn-ice transition is associated with a depletion in air bubbles entrapped in ice cores. Air in ice core bubbles is typically half as depleted in Ar/N₂ as in O₂/N₂ relative to atmospheric values (e.g. Battle et al., 1996; Sowers et al., 1992), and its O₂/N₂ ratio is typically around −4 to −10 % in well-preserved ice cores (Bender et al., 1995; Landais et al., 2010). It should be here emphasized that similar gas loss mechanisms as the one occurring at the firn-ice transition also cause size- and mass-dependent fractionation during coring and after coring (Sect. 4.6.4). Compelling evidences come from measurements of gases in ice cores (Ikeda-Fukazawa et al., 2005; Suwa and Bender, 2008; Bereiter et al., 2009; Vinther et al., 2009), showing in particular depleted δO₂/N₂ values (e.g. Bender et al., 1995; Suwa and Bender, 2008; Severinghaus et al., 2009; Landais et al., 2010). This can for instance result from long storage of ice in freezers at −25°C (Sect. 4.6.4). Consequently, it is not possible to isolate the effects of air entrapment and bubble closure from coring and post-coring effects on the composition of gases trapped in ice core samples. Section 4.6.3.3 details the results of firn air sampling studies aiming at obtaining more direct information on fractionation during bubble close off, so as to precisely correct the composition of ancient air trapped in ice core bubbles from this effect.

1.4.1.3.4 What factors influence close-off fractionation?

The permeation of gases through the ice lattice at close-off depth can be seen as the combination of two gas-loss processes, permeation via breaking of hydrogen bonds, causing size-dependent fractionation, and permeation via interstitial hoping, causing mass-dependent fractionation. Large diameter molecules (but less than 3.6 Å) like Ar or O₂ permeate primarily through the first mechanism, which is strongly temperature-dependent as it is the hydrogen-bond breaking mechanism which limits the rate of diffusion, whereas small diameter molecules like Ne favor permeation via the second mechanism, only slightly affected by temperature.

The magnitude of the fractionation during bubble close-off is ultimately determined by the amount of gas loss across the lock-in depth (Buizert, pers. comm., 2016) (and not by the magnitude of the enrichment in the LIZ). For instance, if most of the fugitive O₂ were to escape from the LIZ to the diffusive zone (across the lock-in-depth) and then to the atmosphere, one would expect a relative small enrichment in the LIZ but a large depletion in the ice core samples. In Figure 1.19, the gravitationally cor-
rected $\delta O_2/N_2$ gradient observed in the diffusive zone reveals a diffusive flux from the deep firn to the atmosphere, which can be used to assess the average $\delta O_2/N_2$ depletion in ice core samples.

Accumulation rate also play an important role on the magnitude of close-off fractionation as it controls the amount of time an ice layer spends in the LIZ (air is advected with ice in the LIZ): in a site with a high accumulation rate, there is less time for the air to escape, hence a lower enrichment with depth in the LIZ (Fig. 1.19a), and a less depleted $\delta O_2/N_2$ in ice core bubbles.

Layering, that is cm-scale variations in density is an ubiquitous process in the firn whose origin is debated (refer to Mitchell et al., 2015 and references therein). It causes close-off fractionation to vary with depth, as revealed by high-resolution density of the LIZ together with $CH_4$ mixing ratio and total air content measurements of the LIZ closed porosity to WAIS (Mitchell et al., 2015). An important implication for studies of trapped gases in ice cores (in particular for species with a short lifetime) is that the mean age of of gas samples from adjacent layers can vary by several years. For instance, quasi annual-scale variations observed in a continuous $CH_4$ record from a neem ice core (NEEM-2011-S1) are not of atmospheric origin but result from the stochastic nature of bubble close-off (Mitchell et al., 2015; Rhodes et al., 2013). This layering can also cause a scattering of $\delta O_2/N_2$ values in ice core bubbles.

Shallow and deep bubble close-off cause a highly contrasted $\delta O_2/N_2$ signature (Buizert, pers. comm., 2016), with a higher total air content when shallow trapping occurs (Mitchell et al., 2015). Bubbles/layers that close early/shallow in the LIZ are depleted in $O_2$ as $O_2$ escapes across the lock-in-depth, while bubbles/layers that close late/deep are enriched in $O_2$ as the $O_2$ permeate leaking out from occluding bubbles accumulates in the open porosity over time, and ultimately gets occluded in bubbles.

### 1.4.2 Fractionation due to clathrate hydrates

This process does not occur in the firn but deeper in the ice-sheet, but it can also be considered as a natural fractionating process. Fractionation due to clathrate hydrates is caused by the fact that $O_2$ is more easily dissolved in ice as gas hydrate than $N_2$. In the transition zone of each ice core, extending over several hundred meters, for instance between 1000 m and 1700 m in GISP2 and between 800 m and 1000 m in Vostok (Suwa and Bender, 2008), highly positive values are observed. Because the dissociation pressure of $O_2$ (and Ar) is lower, it forms clathrate hydrates at a shallower depth than $N_2$. There is thus more $N_2$ in the bubble air than $O_2$ within the transition zone, where both gas and solid phases coexist. After recovery of the ice, $N_2$ in bubble air is preferentially lost relative to $O_2$, because molecules in clathrate hydrates resist better post-coring fractionation (Suwa and Bender, 2008). Besides, gases exert a

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11In the LIZ, the total porosity, the volume fraction not occupied by ice, is divided into open and closed porosity. Open pores can exchange with the atmosphere. Total porosity decreases with depth due to firn compaction, until all the air is occluded in bubbles.
huge pressure on the ice, which becomes fractured during ice core recovery, and cause many fractures in the ice core samples (Kobashi et al., 2008; Bender et al., 1995).

1.5 Organization of the thesis

The work presented in this thesis focuses on the past evolution of stable isotopes of atmospheric oxygen. To unravel the climatic information they carry, the ancient atmospheric O$_2$ entrapped in polar ice core bubbles needs to be extracted, dried, purified, collected, measured and corrected. A new method of oxygen separation based on membrane technology was developed for the purpose of separating oxygen from all other air constituents such as N$_2$ and Ar, but proved not to be applicable for $^{17}\Delta_{atm}$ measurements (Chapter 2).

As an alternative, an analytical setup based on the classical method described in Barkan and Luz (2003) was build up from scratch. The developed setup and its associated analytical procedures (both for $\delta^{18}O_{atm}$ and $^{17}\Delta_{atm}$ measurements) are described in Chapter 3.

IRMS measurements of $\delta^{18}O_{atm}$ from air bubbles occluded in ice cores are the focus of Chapter 4. The chapter describes the automation of a sequence of up to ten ice core sample measurements with a Delta V mass spectrometer. It also focuses on the corrections applied to the raw data to retrieve the true climatic signal. The latter is indeed altered by processes in the firn, during coring and storage, and in the analytical setup. Finally, the ability of the analytical system to reproduce ice core $\delta^{18}O_{atm}$ measurements is assessed in this chapter based on 21 neem late Holocene ice core samples.

$\delta^{18}O_{atm}$ is a complex climatic proxy, involving global ice volume, the biosphere and the hydrosphere. Much work has already been devoted to orbital and millennial variation of $\delta^{18}O_{atm}$ (e.g. Landais et al., 2010; Severinghaus et al., 2009). Such a climatic proxy is indeed of great interest, as it is strongly influenced by low latitude climatic processes, and can therefore provide valuable information on the tropics, a region of the world which still lacks of climatic reconstructions and whose role is widely debated in the context of millennial-scale climate variations (e.g. reviews of Clement and Peterson, 2008; Seager and Battisti, 2007). Because of its global character, $\delta^{18}O_{atm}$ should provide added value compared to the different local records of hydrological cycle variations in different continental and marine archives. However, until now, no quantitative, robust interpretation of past variations in $\delta^{18}O_{atm}$ has been established, which limits the use of $\delta^{18}O_{atm}$ as a quantitative indicator for past biospheric production or variations of the hydrological cycle. The aim of the modeling study presented in Chapter 5 is thus to provide a quantitative interpretation for the systematic increase observed in $\delta^{18}O_{atm}$ over HSs. To reach this objective, we propose a global approach incorporating outputs from a water-isotope enabled general circulation model and focus on the millennial variability of the last glacial period. Following Hoffmann et al. (2004), we combine climatic parameters (temperature and humidity), isotopic com-
position of meteoric water, vegetation distribution and productivity simulated by different models with monthly mean temporal resolution. This work has been published in Climate of the Past in 2015 under the title *Quantifying molecular oxygen isotope variations during a Heinrich stadial* (Reutenauer et al., 2015) and is reproduced in Chapter 5.


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2 Science at risk: a new method of oxygen separation

2.1 INTRODUCTION

The INTRAMIF project was aiming at high-risk research. Accordingly, the primary goal of my PhD project was to develop a new method of $O_2$ separation to measure the triple isotope composition of atmospheric $O_2$ back to 800 kyr trapped in ice cores from Antarctica. Due to the small signal of $^{17} \Delta_{\text{atm}}$ anomaly ($\simeq 40$ permeg from glacial to interglacial), the proposed measurements on ice cores are extremely challenging on both the extraction and measurement side. To reach the targeted precision (10 permeg), a quantitative separation of $O_2$ from other atmospheric constituents is crucial. To determine isotopic ratios of oxygen at high accuracy and precision, the sample must be introduced as pure $O_2$ into the ms (noted ms hereafter) (Sarma et al., 2003). However, with common chromatographic techniques, (i) a carrier gas (usually He, which is very expensive) is needed to transfer the sample through the GC and (ii) triple oxygen isotopic ratios are determined in a mixture of gases ($O_2$-Ar, or $O_2$-Ar-N2) by dual-inlet mass spectrometry. Corrections are applied to account for the resulting interferences, causing a loss of precision.

In order to obtain pure $O_2$, membrane technology is an interesting alternative to the common method, as $O_2$ isotopologues are measured in a pure substance, avoiding the need for chemical slope correction (Sect. 4). A large part of my PhD was therefore dedicated to the development of this new technique. Many steps were involved, from prospecting, defining, designing and testing the new method. Unfortunately, membrane sealing issues, coupled to variable isotope fractionation during $O_2$ permeation across the membrane lead to an “early” stopping of the project. This chapter is structured as follows. Section 2.2 introduces the new method of oxygen separation, section 2.3 describes the experimental setups, Sect. 2.4 assesses the selectivity, permeability and isotope fractionation of the membrane, and discusses the application of such technology to ice core science.

2.2 PHYSICAL BASIS OF MEASUREMENTS

The new method described here for oxygen separation relies on membrane-based technology. There are many existing oxygen selective membranes, as a wide range of application require generation or removal of oxygen, including production of high purity oxygen for medical applications, aqua-culture and combustion processes, control of oxygen partial pressure in industrial environments, production of power and chemicals, and removal of oxygen from enclosures and gas streams (Badwal and Ciacchi, 2001). However, such applications usually do require very-high purity $O_2$, and research therefore focus on its permeation rate (e.g. Tablet, 2006; Wang et al., 2002)
rather than on its $O_2$ selectivity, whereas we would need the opposite characteristics for our application.

![Figure 2.1](image)

Figure 2.1 – Original figure from Badwal et al. (2003). Schematics of oxygen generation with pure ionic and mixed ionic/electronic conducting ceramic membranes. We are using the second type in this project.

**PROSPECTION**

Organic membranes were not considered during our prospection because they do not yield high purity oxygen. Indeed, transport in these membranes is based on molecular diffusion, and opportunity for higher oxygen selectivity is small as elemental gases like Ar have similar molecular sizes. We thus restricted our prospection to pure ionic and mixed ionic electronic conducting (noted MIEC hereafter) ceramic membranes, where permeation is based on ionic transport, enabling in theory higher $O_2$ selectivity.

There are two types of membranes based on solid electrolytes systems. The first one is based on pure or mainly oxygen-ion conducting transport. This consists in a solid electrolyte cell consisting of an ion-conducting electrolyte membrane coated with electrodes on both sides. The driving force for $O^{2-}$ migration is voltage or current driven, and the rate of the oxygen ionic flux is directly proportional to the current flowing through the device. The second type is a mixed ionic/electronic conducting ceramic membrane, with high oxygen ion and electronic conductivities. The electrons in the membrane combine with $O_2$ in the air to create negatively charged oxygen ions. No electrodes are required and driving force for oxygen ion transport is provided by the temperature and the differential partial pressure of oxygen (chemical potential gradient) across the membrane (Fig. 2.1).

The most promising (and available) membrane we found has been developed at the Fraunhofer-Institute for Interfacial Engineering and Biotechnology Inorganic Surfaces and Membranes (Germany). We therefore started a partnership (contact: Thomas
Schiestel and Marita Zipperle) and they provided us with a MIEC tubular perovskite membrane, characterized in theory by 100% selective $O_2$ permeation and no correlation between selectivity and permeability.

2.2.1 Characteristics

- The dimensions of the membranes may differ between each other but only in a range between 1.10 and 1.18 mm for the outer diameter and between 0.80 and 0.88 mm for the inner diameter, the wall thickness measuring usually between 140 and 150 μ. The membrane consists in a hollow fiber, because the tubular design is more robust than the flat shaped one. Besides, it allows a sealing far from the permeation area, hence in the "cold zone". A disk-shaped membrane would indeed force the sealing to be located in the hot zone, which makes it extremely challenging. Finally, such a design should offer higher thermal cycling capabilities, as it is also subjected to low thermal stresses during its use. Badwal et al. (2003). As sealing of the membrane, even at moderate temperature, quickly turned out to be a major issue (Sect. 2.4.2), we obtained membranes with one closed end from the Fraunhofer-Institute, so that only one side of the membrane would need to be sealed, at cold temperature.

- The ceramic membrane acts as a physical barrier to contaminants.

- The oxygen transport through the membrane is based on a diffusion process, strongly temperature-dependent. For solid state materials, such as this membrane, diffusion takes place at high temperatures. At room temperature, no $O_2$ permeation occurs. The permeation process starts at around 750°C, with optimal working conditions from 850 to 1000 °C. High-temperature is important in practice because most membranes exhibit poor oxygen ion mobility at low temperature. Permeation through the perovskite membrane is driven by the oxygen partial pressure gradient between both sides of the membrane (Sect. 2.2.2). The rate of $O_2$ flow is proportional to the ratio of partial pressure of $O_2$ on the inlet side (S1) to the oxygen partial pressure on the output side (S2).

- The composition of the membrane material is protected for secrecy reasons since the Fraunhofer-Institute has an industrial project partner involved in the project. What is published is the following composition: $BaCo_xFe_yZr_{1-x-y}O_{3-d}$ (noted BCFZO hereafter). Important to bear in mind is that the amount of oxygen in perovskites differs, as shown by the "d" in the formula, with the composition of the atmosphere and with temperature. It is thus challenging to quantify the amount of oxygen in the membrane.

2.2.2 Transport mechanisms

Transport mechanisms across perovskite membranes are briefly presented here, and the interested reader can find more details in e.g. Sunarso et al. (2008); Tablet (2006)
and ref. therein. Perovskite\(^1\)-type (ABO\(_3\)) ceramic membranes have a high ionic and electronic conductivity, thereby a high oxygen permeability compared to other mixed-conducting ceramic membranes (Tablet, 2006). To fulfill the electric neutrality criteria, the flux of O\(_2\) ions following the chemical potential gradient is charge compensated by a simultaneous flux of electrons in the opposite direction (Fig. 2.1). As shown in Fig. 2.2, O\(_2\) transport across the membrane occurs in three steps (Sunarso et al., 2008; Tablet, 2006):

- At the surface exchange reaction on interface I (high O\(_2\) partial pressure side). At the membrane surface, O\(_2\) molecules adsorb and are reduced (gain in electron) to their ionic form.

- simultaneous counter diffusion of O\(_2\) ions and electrons through the bulk of the membrane, driven by the O\(_2\) partial pressure.

- reversed surface exchange on Interface II (low O\(_2\) partial pressure side). O\(_2\) ions recombine to form O\(_2\) molecules.

Figure 2.2b reveals the presence of O\(_2\) vacancies and electron holes in the membrane. They maintain local charge neutrality and may control the permeation rate, as the slowest moving species determine the net O\(_2\) flux across the membrane. Indeed, the O\(_2\) flux across the membrane mainly depends on (i) the diffusive rate in the bulk of the membrane of O\(_2\) anions (O\(_2^–\)) and oxygen vacancies (V\(_{O}^{**}\)) and/or the simultaneous

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\(^1\)Perovskite is the most abundant (\(\approx 75\%\)) solid phase of the lower mantle of the Earth and is called after Count Lev Aleksevich von Perovski. It was first found in the Ural in 1839. The general structure of the perovskite mineral is ABX\(_3\) where A (generally an alkali earth metal or a transition metal) and B (generally a transition metal or a rare earth metal) are cations and X oxygen anions (Tablet, 2006).
counter flux of electrons ($e^-$) and electron holes ($h^\circ$) and (ii) the surface exchange at Interface I and II, which depends on several factors such as adsorption, dissociation, surface diffusion, charge transfer and incorporation in the surface layer (Tablet, 2006; Sunarso et al., 2008).

2.3 Experimental setup

In this section, we present the two experimental setups developed to assess $O_2$ isotope fractionation occurring during $O_2$ permeation. The reader is invited to refer to Chapter 4 for an introduction to the basics of mass spectrometry.

2.3.1 Setup A

The experimental setup presented in Fig. 2.3, called Setup A hereafter, was developed to estimate the permeation rate of the hollow perovskite fiber, and to assess the stability of the isotope composition of the permeated $O_2$ . While a constant supply of $O_2$ was provided to the feed side of the membrane, the permeated $O_2$ in the lumen was quickly flushed using He as carrier gas. The membrane was inserted in a 1/4” quartz tube heated to 700°C. The main advantage of this setup was to avoid sealing issues. Indeed, the permeating area of the membrane was isolated from lab air by a flow of atmospheric air or pure $O_2$ (working standards) introduced in the feed side of the membrane through a capillary\textsuperscript{2}. Within the membrane (lumen), a He capillary inserted to the end was used as carrier gas to flush the permeated $O_2$ in order to keep a low $O_2$ partial pressure. This also ensured a pressure above atmospheric pressure, hence isolating permeated $O_2$ from lab air. Finally, in an attempt to measure $O_2$ permeating from areas where conditions are isothermal, the inlet of the capillary (sniffing point) connecting the lumen of the membrane to the ms (via a vici 6-port valves and an open split) was located just before the hot zone (Fig. 2.3). Note that the coating of the capillaries inserted in the heated area was burned off prior introduction in the membrane unit to avoid contamination of the membrane surface.

\textsuperscript{2}Note that this capillary also enables a stable high pressure in the feed side. When lab air was exposed to the membrane (without capillary), large fluctuations in permeation occurred.
Initially, measurements of $O_2$ isotope ratios were done in the Continuous Flow (CF) mode of the MS (Delta V and Delta V Advantage, ThermoFisher). Sample (permeated $O_2$) and standard (pure $O_2$) were introduced to the ion source of the MS through two capillaries connected to the needle valve of the MS. There were caveats associated with this method. Indeed, He flowing from the standard line’s open split was diluting the sample (already diluted in He, see Fig. 2.3) to such an extent\(^3\) that size of sample and standards differed widely during the analysis (linearity, refer to Chapter 4), causing an important loss in precision. To improve the quality of the measurements, a pneumatically actuated 6-port valve\(^4\) (Valco, USA) was added to the setup, and measurements

\(^3\)in CF mode, the use of open splits as in Fig. 2.3 induces the use of a carrier gas which is constantly flowing to the ion source of the MS. Reference gas pulses are generated by moving the standard capillary upstream and downstream from the sniffing point (inlet of the capillary connected to the ion source).

\(^4\)a 4-port valve would have worked perfectly too.
performed in Dual Inlet (di) mode.

In di mode, the changeover valve (COV) enables the fast and repeated comparison of ion currents and ion current ratios, which minimizes instrumental effects (Werner and Brand 2001). The COV diverts the sample to waste while the standard is introduced to the source and inversely. Therefore, in the final experimental setup, the COV is replaced by an automated six-port valve (into four-position), in the configuration shown in Fig. 2.3. To "trick" the Isodat software of the MS in order to measure in di mode without using the COV valve, the Isodat function controlling the COV is modified so that the program controls the 6-port valve instead during the data acquisition.

$N_2$ (m/z 28) signal was measured with a magnetic scan to check for a possible contamination of the sample. Background values of m/z 28 with He only flowing to the ion source were about 3 mV. With pure $O_2$ and atmospheric $O_2$ introduced in the feed side of the membrane, they reached 10 and 30 mV, respectively, relative to a $O_2$ signal typically above 20 V (on the same cup). In Sect. 2.4.1, the $O_2/N_2$ separation factor is quantified more precisely.

2.3.2 Setup B

A schematic of the membrane separation unit is described in Fig. 2.4. Unlike setup A, this setup, designed to separate $O_2$ from other atmospheric constituents in gases trapped in ice cores, requires to seal the membrane under vacuum (Sect. 2.4.2), as the lumen of the membrane is evacuated to cryogenically and quantitatively collect the permeated $O_2$. As can be seen, the seal of the membrane is outside the heated area, which is critical as high temperature has proven to be extremely difficult, even for applications where high-purity $O_2$ is not required, and explains in part why tubular membranes are preferred over disk membranes (e.g. Badwal and Ciacchi, 2001; Sunarso et al., 2008). Obviously, the recovery will be limited by the decreasing $O_2$ pressure gradient across the membrane, due to a decrease of partial pressure of $O_2$ in the feeding side with permeation of $O_2$, but the influence of the collection efficiency could not be tested as sealing issues quickly arise (Sect. 2.4.2). We present here the components of setup B.

Given the high operating temperature of the perovskite membrane, we chose a fused silica tube (melting point: 1700°C) to be inserted in our custom-made tubular furnace. The quartz tube was closed on one end and narrowed to $\frac{1}{2}''$ on the other by a glassblower (Pantmann Glassware, Denmark). The low thermal conductivity of quartz material allowed us to seal the quartz tube to a $\frac{1}{2}''$ welded stainless steel (noted SST hereafter) microvolume cross (Swagelok, USA) with a $\frac{1}{2}''$ Ultra-Torr nut and associated O-ring (70 durometer fluorocarbon FKM, wetted with a thin film of silicone vacuum grease), whose maximum temperature does not exceed 204°C.

Furnaces are commercially available, but are rather expensive. The custom-made...
oven provides similar performances regarding maximum temperature, temperature stability, or width of the hot zone, where conditions are isothermal. The furnace consists in a 25 cm long quartz tube coated with nichrome (Nickel-Chromium, OMEGA, UK) wires⁵ held in position with thermal paste. Voltage is adjusted with a Variac to control the temperature, monitored with a K-type thermocouple. The oven major requirements were (i) to reach at least 800°C and (ii) to provide an area with isothermal conditions (Fig 2.5). Indeed, given the lack of knowledge on $O_2$ isotopic fractionation through the perovskite membrane, the parameters controlling the permeability of the membrane need to be closely monitored. As $O_2$ partial pressure gradient and temperature are the driving force for $O_2$ transport across the membrane, ensuring isothermal conditions where permeation occurs is essential. The temperature profile of the oven at different temperature can be seen in Fig. 2.5. An area of 5 cm presents homogenous temperatures, and is referred as the "hot zone". To define the length of the hot zone, a K-thermocouple, instead of the membrane, is inserted across the microvolume cross and into the quartz tube, so as to mimic the conditions of the experiment as closely as possible.

The micro-volume SST 1/4” cross (Swagelok) across which the membrane passes minimizes dead volumes on the feed side of the membrane. On Fig. 2.4, one can see that one end of the cross is used to introduce the sample, another to evacuate the feed side of the membrane, the third end connects the cross to the separation unit thanks to a 1/2” SST welded tube fitting, and the fourth end consists in a 1/8” SST welded tube fitting, connecting the permeate side (lumen) of the membrane either to the collection

---

⁵same principle as e.g. a bread toaster
Figure 2.5 – Temperature profiles of the oven made out of a nichrome wire and a quartz. It can reach the optimal operating temperature of the membrane (850 °C), and has a homogenous hot zone of around 5 cm, 7 to 12 cm from the oven inlet.

manifold or directly to the MS (not shown on the setup is another cross offering the possibility to evacuate the lumen of the membrane). The membrane is sealed with Ultra-Torr (Accu-Glass Products, USA) to the 1/8” SST welded tube.

2.4 Characterization of the membrane

In this section we evaluate the selectivity, the sealing, the permeability and the isotope fractionation of the perovskite membrane.

2.4.1 Selectivity

Atmospheric air samples permeating across the membrane at operating temperature were collected in a 65 ml glass flask previously evacuated using setup B. The samples were then expanded into the bellows of the DI unit and a magnetic mass scan was performed (Fig. 2.6). Height and peak area are measured with both the peak detection tool from Isodat software from a Delta V Plus MS (please refer to Chapter 4 for an introduction to mass spectrometry) and results are checked with an independent software. The high value of the $O_2/N_2$ ratio confirms the very high $O_2$ selectivity of the membrane, indicative of successive sealing and gas-tightness of the separation unit at the time of measurements. However, gas-tightness could not be maintained over period of times sufficiently long to reliably measure $^{17}\Delta$ (Sect. 2.4.2).

2.4.2 Sealing

Sealing of a tubular perovskite membrane is not trivial, as underlined by several studies (e.g. Li et al., 1999; Zhu et al., 2009; Sunarso et al., 2008), in particular at high temperature. In this case, the sealant must be flexible and gas-tight, have a thermal coefficient that corresponds to the one of the membrane and the supporting material, withstand thermal shock, and do not react with the surface of the membrane (Zhu et al., 2009). Even if the tubular geometry of the membrane requires minimal sealing
Figure 2.6 – Values of the scans and estimation of the $O_2/N_2$ separation factor based on the magnetic scans displayed in (b). (b) The selectivity of the membrane based on magnetic scans. Note the different scales. (a) 850°C: full scan after exposition of the membrane to atmosphere. b Zoom of a on m/z 28, 32, 33 and 34. c 25°C: absence of oxygen permeation when membrane exposed to atmosphere. d Background mass spectrum.

compared to a flat-shaped membrane (Badwal et al., 2003), and does not require a high-temperature sealing, we did not find a satisfactory solution to seal the membrane in this thesis. It needs to be underlined here that except for Zhu et al.’s study, production of very high-purity $O_2$ is not required for most of the applications described in literature, as the main industrial targets are the production of $O_2$-enriched mixture of gases. In other words, a successful sealing in these studies was likely to be a failure for the purpose of measuring air in ice cores. For instance, Wang et al. (2006) use silicon rubber O-rings to cold-seal the very same tubular BCFZO membrane, but this option does not provide the required gas tightness when applied here. In the same vein, fitting

\[^6\]Often, $O_2$ permeation rates are calculated assuming leakage of $O_2$ through pores or cracks by Knudsen diffusion, where $O_2$ and $N_2$ fluxes are related by $J_{O_2}/J_{N_2} = \sqrt{32/28} = 4.02$. They therefore calculate the $O_2$ flux as $J_{O_2} = (C_{O_2} - C_{N_2}/4.02) \cdot F/S$, where $C$ denotes concentration, $F$ the measured total flow rate and $S$ the effective permeation area of the membrane.
the membrane with silver plated ferrules or teflon ferrules (Valco, USA) would break
the membrane. Besides, applied sealing techniques in some of these studies required
elaborated procedures that could not be performed at CIC. As an illustration, Li et al.
(1999) developed a ceramic binder, containing extra-fine alumina and some of the
prepared perovskite type oxide. Consequently, we crushed in powder a broken mem-
brane, mixed it with Ultra-Torr sealant, but without success. Other sealants are tested
in the literature, including Pyrex glass rings, precious metal rings, ceramic binders, or
even Cu(OH)₂ binder in combination with phosphoric acid (see Li et al., 1999, and ref.
therein). Tablet (2006) applies a gold coating on the surface of the membrane⁷. How-
ever, gas-tightness is a problem with Au paste. Usually, the seal needs to be reworked
a few times to reach a gas-tight sealing because the paste looses a lot of volume dur-
ing the annealing step and the shrinkage is very high (Zipperle, 2010, pers. comm.).
In Zhu et al.’s study, a quartz cap is fixed to the membrane with a ceramic sealant
(HT767A, Huitian Adhesive Enterprise Co. LTD. China), which can solidify at room
temperature and remains hard at high temperatures. The ceramic sealant also holds
the melted Ag (silver) used as a sealant. This high-temperature sealing technique was
not tested, as it required to melt Ag, but inspired our most successful method, using
Ultra-Torr (very fine epoxy resin with Magnesium Silicate Hydrate (talc)) as sealant.
As shown in Sect. 2.4.1, this technique provides excellent results, but the sealant would
quickly degrade over time. It is not likely that the leak is caused by a mismatch of ther-
mal expansion coefficients of the Ultra-Torr paste and the perovskite membrane, as
this part of the membrane does not undergo important thermal stress. Adding new
layers of Ultra-Torr paste did not help.

To our view, the rough surface and tiny pores of the membranes are the main issues
when it comes to sealing a membrane in the cold zone. The sealing material must be
able to fill these pores, and without overcoming this problem, such a method of O₂
separation for ice core measurements is not feasible.

2.4.3 PERMEATION

The permeation rate (J₀₂) of perovskite membranes has been exhaustively studied for
various conditions (e.g. Wang et al., 2002; Tablet, 2006). However, the O₂ pressure
gradient across the membrane was much higher (in the 1 to 10 bar range) and sweep
gases were used on both sides of the membrane with high flows, the purpose being to
maximize J₀₂. For the purpose of measuring ice core samples, conditions are different:
the gradient of O₂ partial pressure is much more reduced, and vacuum conditions are
required*. As in other studies, we observed a fast increase of the permeation rate with
increasing temperature (before reaching a plateau) and increasing O₂ partial pressure
gradient. To calculate the O₂ permeation rate, we use setup A (Fig. 2.3). The modified

⁷ sealing with Au is typically done when high-temperature sealing is required, but it should also
work at cold temperatures

*Note that the setup used to estimate the permeation rate differs from the one built to separate O₂
from other gases trapped in ice cores, by the use of a career gas in the permeate side of the hollow fiber
in the first case, while vacuum is maintained in the second case.

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sniffing permeated $O_2$ capillary had an inner diameter of 0.1 mm.

**Calculations**

Calculating the permeation rate ($J_{O_2}$) requires a few assumptions:

- $J_{O_2}$ is based on the permeation rate of the most abundant $O_2$ isotopologue, $^{16}O_2$, neglecting the two heavier isotopologues.

- Permeation across the membrane is assumed to only occur in the hot zone of the oven, where conditions are isothermal. To ensure that permeation only occurs through the "hot zone", Tablet (2006) coated the ends of the membrane with Au paste. A dense Au film was obtained after sintering at 950 °C. As this method of high-temperature sealing could not be applied at CIC, we avoided to measure $O_2$ permeating from areas where conditions are not isothermal by ensuring that the sniffing point (inlet of the capillary that connects the lumen of the membrane to the sample open split of the ms) is located just before the hot zone (Fig. 2.3).

- the $O_2$-He mixture of the ion source is well mixed and the Helium signal in the ion source is constant throughout experiments.

$J_{O_2}$ can be calculated from the measured permeated $^{16}O_2$ signal (beam voltage $V^{32}$ of m/z 32) given by Isodat. The beam voltage of one block ($V_{b}^{32}$) is taken as the average of 8 cycles $V_{c}^{32}$ (cycle defined as in Fig. 2.3). The ion current $I^{32}$ (A) can be deduced from $V^{32}$ (V) and the resistance of the cup where m/z 32 is collected (here $R_{cup} = 1 \cdot 10^9 \Omega$) ($U = RI$):

$$I^{32} = \frac{V_{b}^{32}}{R_{cup}}.$$

(2.1)

Mol of $O_2$ ions per second ($n_{ions}^{32}$) can then be deduced, knowing Avogadro number $N_A = 6.02214179 \cdot 10^{23} \text{mol}^{-1}$, and the elementary charge ($e = 1.602176487 \cdot 10^{-19} \text{C (or A} \cdot \text{s})$):

$$n_{ions}^{32} = \frac{I^{32}}{e \cdot N_A}.$$

(2.2)

Ionization efficiencies of $O_2$ ($\zeta_{O_2}$, in molecules ιons$^{-1}$) and He ($\zeta_{He}$) are required to deduce the amount of $O_2$ ($n_{ms}^{32}$) and He molecules ($n_{ms}^{4}$) reaching the ion source every second (the permeated $O_2$ is carried to the source with He, introduced in the lumen of the membrane (Fig 2.3). Ionization efficiency represents the number of molecules needed to form an ion. The Diagnosis Absolute Sensitivity tool of Isodat software (ThermoFisher) enables us to calculate the molecules to ions ratio: a defined microvolume (0.145 cm$^{-3}$) located between the bellows of the ms (Refer to Chapter 4) and the inlet capillary to the ion source is filled with pure $O_2$, adjusting the signal around 8 V. Based on this defined volume, it is possible to estimate the ion current as a function of the gas consumption over a defined time period. Integrating the ion current over this time period provides the number of ions, while the number of molecules is calculated from the $O_2$ signal drop using the ideal gas law (Delta V manual, ThermoFisher). Helium ionization efficiency (11037 molecules ion$^{-1}$) is a factor of 5 lower
than \( O_2 \) ionization efficiency (2033 molecules ion\(^{-1}\)) for the Delta V Plus used in this experiment. It follows that:

\[
n_{ms}^{32} = n_{ions}^{32} \cdot \zeta_{O_2}.
\]  

(2.3)

He has a different ionization efficiency. The \( O_2 \) concentration in the source \((C_{O_2})\) can be expressed as:

\[
C_{O_2} = \frac{n_{ms}^{32}}{n_{ions}^{32} \cdot \zeta_{He}},
\]  

(2.4)

where the term \( n_{ions}^{4} \cdot \zeta_{He} \) is assumed constant over the experiment (He, m/z 4) signal \((V^4)\) is measured once at the start of the measurements on the same cup (collector) as m/z 32. Assuming a well mixed gas mixture (He and permeated \( O_2 \)) in the lumen of the membrane, we can assume that the fraction of the gas mixture sniffed by the ms capillary and to the ion source (Fig 2.3) has the same \( O_2 \) to He ratio as the gas mixture in the lumen of the membrane. As the flow rate of He \( F_{He} \) in the lumen is known \((49 \text{ cm}^3 \cdot \text{min}^{-1})\), the flux of \( O_2 \) molecules \( F_{O_2} \) permeating (in mol \cdot s\(^{-1}\) or cm\(^3\) \cdot s\(^{-1}\) according to the ideal gas law) through the membrane can be estimated as:

\[
F_{O_2} = C_{O_2} \cdot \frac{F_{He}}{60},
\]  

(2.5)

The effective permeation area \( S \) \((\text{cm}^2)\) of the membrane is calculated using the logarithmic mean diameter of the hollow membrane because the inner surface is smaller than the outer one:

\[
S = \frac{\pi L (d_o - d_i)}{\ln(d_o/d_i)},
\]  

(2.6)

where \( d_o \) and \( d_i \) stand for the outer (0.1 cm) and inner (0.08 cm) diameter of the membrane, and \( L \) represents the length of the permeating area of the membrane, taken as the distance between the membrane closed end and the snifing ms capillary (3 cm). Finally, by dividing Eq. 2.5 by Eq. 2.6, the permeation of \( O_2 \) \( J_{O_2} \) \((\text{cm}^3 \cdot \text{cm}^{-2} \cdot \text{s}^{-1})\) across the membrane can be calculated:

\[
J_{O_2} = \frac{F_{O_2}}{S}.
\]  

(2.7)

Fig. 2.7 summarizes results from the permeation experiment.

We observe a higher \( J_{O_2} \) variability with atmospheric air than with pure \( O_2 \), related to the lower \( O_2 \) partial pressure in air. The permeation rates found in these experiments are similar to those found in other experiments, though much less stable. Wang et al. (2002) reports for example values between 0.5 and 3.5 cm\(^3\) / cm\(^{-2}\)/min\(^{-1}\) with increasing temperature and \( O_2 \) partial pressure gradient. The most striking figure is the important variability of the permeation. It may relate to variations of \( O_2 \) partial pressure in the feed side of the membrane, or to small temperature fluctuations (variations of \( \pm 3^\circ \text{C} \) were observed in the hot zone). Alternatively, these large fluctuations may be due to changes in the location of the He and/or snifing (permeated \( O_2 \)) capillaries. However, the fact that the permeation oscillates around its mean before getting stable may also point to a equilibration time required for \( J_{O_2} \) to stabilize. This experiment would need to be reproduced in more stable conditions, so as to understand
Figure 2.7 – Permeation rate of the membrane over 60 runs at \( \cong 700^\circ\text{C} \). The permeation rate first describes large oscillations before reducing its variance around a mean value. The membrane was fed with pure oxygen for the first 30 runs, then with atmospheric air. With pure \( O_2 \), the permeation rate varied from 2.75 and 3.55 \( \text{ml} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \) with an average value of 3.03 \( \text{ml} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \). With air, from run 31 to run 60, values oscillated between 0.48 and 2.90 \( \text{ml} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \), with an average value calculated as 1.79 \( \text{ml} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \).

If the variability observed in \( J_{O_2} \) is inherent to the membrane or arises from the experiment. However, the collection of discrete samples of permeated \( O_2 \) using setup B revealed excessive isotope fractionation during \( O_2 \) permeation, which sounded the death knell of the membrane-based method for \( O_2 \) separation (Sect. 2.4.4).

2.4.4 Isotope Fractionation

A Rayleigh-type fractionation experiment in closed system was performed with the perovskite membrane to extract the three-isotope exponent \( \gamma \) from the experimental data. During the experiment, 7.2 cc of pure \( O_2 \) standards were introduced in the feed (sample) side of the membrane (setup B, Fig. 2.4) and were permeating through the membrane at operating temperature (850 °C). They were collected in a 65 ml glass flask after different permeation time (1 min to a 2 h). Collection of the sample was not quantitative as the samples (the permeated \( O_2 \)) were collected by expansion under vacuum \(^9\). Only collection time was allowed to vary. Typically, \( \cong 60 \% \) of the sample was collected.

\( \gamma \) can be derived from the best fit of a \( \delta^{17}O \) vs. \( \delta^{18}O \) plots in experiments where only \( O_2 \) consumption (here permeation) takes place in a closed system, as explained in Sect. 1.2.5.1.1. The results, obtained with \( \delta^{1} \) measurements, reveal that \( O_2 \) isotopes undergo mass-dependent fractionation when permeating through the membrane, with a slope \( \lambda = 0.528 \), at the high end of expected \( \theta \) values that lie between 0.5010 and 0.5305 for kinetic and equilibrium (high temperature) isotope fractionations (Matsumisa et al., 1978; Young et al., 2002; Kaiser et al., 2004). Indeed, the maximum value

\(^{9}\)the He cryocooler was not available at the time of these experiments
of $\theta$, corresponding to equilibrium fractionation at high temperature, is 0.5305 (Matsuhisa et al., 1978; Kaiser, 2008).

The non quantitative collection of the samples questions however the assumption of Rayleigh fractionation. Indeed, given the high $O_2$ permeation rate across the membrane, permeation occurs quickly, and pressures on the feed side and the permeate side of the membrane are balanced after after less than a minute. This was verified by calculating back the pressures in both sides of the membrane based on the volume and pressure of the introducing and collecting flasks after collection. With the absence of $O_2$ pressure gradient across the membrane, exchange of $O_2$ between the two sides of the membrane may occur, which implies that Rayleigh fractionation conditions are not respected. Increasing collection time causes $\delta^{18}O$ depletion. This may be caused (i) by temperature gradients within the membrane separation unit, or (ii) by an increasing amount of $O_2$ segregated in the perovskite membrane.

- Important temperature gradients exist between the collection flask (room temperature, around 25 °C) and the membrane unit (850 °C), which can cause unmixing of gaseous mixtures Grachev and Severinghaus (2003). A rough estimation can be done: given that $2/3$ of the sample is collected after permeation, and assuming a sensitivity of $\delta^{18}O$ to thermal diffusion of $0.03 \%/K$ in air, the potential fractionation is $\frac{0.03}{2} \times 800 = 8\%$, which is in the range of the observed enrichment. However, heavy $O_2$ isotopologues should migrate towards the cold end, and thus cause an enrichment of the measured mixture (and a depletion in the hot zone of the membrane) with increasing collecting time, while we observe the opposite pattern. Actually, on the feed side on the membrane,
Figure 2.9 – Loss of $O_2$ in the membrane separation unit in function of the collection time during the "Rayleigh" experiment. Note that the membrane was extensively flushed with a pure standard mixture before the beginning of the experiments. A new standard was introduced for each collection time, after evacuation of both sides of the membrane. On the right axis the proportion of $O_2$ in the membrane is indicated. For reason that we do not understand, the loss of $O_2$ after a collection of 5 min is almost as important as after 2 h, and may be related to an operator error.

Thermal diffusion causes a gradual $\delta^{18}O$ depletion in the hot zone relative to the introducing flask, which implies that $O_2$ permeating is depleted. In contrast, on the lumen side, permeated $O_2$ is artifactually depleted in $\delta^{18}O$ in the hot zone, but more enriched in the collection flask. It is therefore difficult to estimate the net effect of thermal diffusion, especially because we lack information on the $O_2$ exchange between the two reservoirs when there is no $O_2$ gradient across the membrane.

- Another explanation for the $\delta^{18}O_{atm}$ depletion with increasing collecting time is related to the perovskite membrane. It contains $O_2$, as indicated in the formula $(O_3-d)$, and the $O_2$ content of the membrane is adjusted by shifting the temperature and/or partial pressure (Sunarso et al., 2008). However, Yin and Lin (2007) shows that while the $O_2$ sorption kinetics are fast, desorption kinetics are complex and depend in part on the temperature and the sorbent structure. Our experiment seems to indicate a loss of $O_2$ with respect to collection time. Indeed, as shown in Fig. 2.9, assuming that all the $O_2$ is recovered from the membrane after 1 min of collection, 7 % are lost after a collection of 2 h, which corresponds to 0.5 ml for a 7.2 ml $O_2$ sample.

Such results demonstrate the need to repeat the experiment in conditions ensuring Rayleigh fractionation, which calls for a quantitative collection (Fig. 2.10) of the sample to confirm or not the segregation of $O_2$ in the membrane. Is it due to the absence of $O_2$ pressure gradients across the membrane at the end of the collection? Or is it due to thermal diffusion? The three-isotope plot displayed in Fig. 2.10 reveals excursions
of $\delta^{18}O$ and $\delta^{17}O$ values of pure $O_2$ permeated across the membrane. Similar experiments (in terms of temperature conditions, sample size or collection time) completed other days reveal similar excursions (not shown), with $\gamma$ oscillating between 0.49 and 0.54, which represents the full range of expected mass-dependent fractionation. Results underline the variable isotope fractionation occurring during $O_2$ permeation, which precludes high-precision isotope measurements as long as the origin of the variability has not been found.

The stability of the membrane was also assessed in a CF mode to circumvent the sealing issue and create conditions where one reservoir is infinite, so as to define directly the intrinsic fractionation from a three isotope plot (Young et al., 2014). In the setup, there was indeed no change in the isotope composition or the flow rate of either pure $O_2$ or air, flowing through a capillary to the sample (feed) side of the perovskite membrane. However, the experiment was too unstable to obtain reliable data. For instance, $\lambda$ has a value of 0.414 with pure $O_2$, and 0.601 with air, well beyond the predicted mass-dependent relationship.

2.5 Conclusion and perspectives

In this section we showed:

1. The high permeability of the membrane to $O_2$ is confirmed, ranging from 0.5 to 3.5 $ml \cdot cm^{-2} \cdot s^{-1}$.

2. The 100 % selectivity to $O_2$ was verified.

3. Variable mass-dependent fractionation is observed, even in the case of intense flushing before the measurements, probably because $O_2$ is not quantitatively released by the membrane during operation.
4. Based on the few experiments performed, fractionation of the membrane cannot be determined. Such unpredictable behavior precludes measurement of $^{17} \Delta_{atm}$.

5. Membrane's gas-tightness cannot be achieved.

To be applied to ice core science, the membrane requires a leak-tight sealing. Provided that an adequate sealant is found, the membrane can be used in applications where removal of $O_2$ is required, taking profit of its 100% selectivity to $O_2$. Additionally, pure $O_2$ standards can be produced in large amounts from atmospheric $O_2$ given the large permeability of the membrane.


Wang, H., Cong, Y., and Yang, W. (2002). Oxygen permeation study in a tubular ba0.5sr0.5co0.8fe0.2o3-d oxygen permeable membrane. *Journal of Membrane Science*, 210(2):259 – 271.


3 Building an extraction and collection line for oxygen isotopes

3.1 Introduction

In this chapter we present the experimental system developed at CIC to extract gases occluded in ice core bubbles and collect either pure \( O_2 \) for \( ^{17}\Delta \) measurements, or an \( O_2 -N_2 -Ar \) mixture for \( \delta^{18}O_{atm} \) measurements, together with \( \delta O_2/N_2 \) ratio, \( \delta^{15}N \) and \( \delta^{40}Ar \). \( \delta^{18}O \) measurements from the NEEM (North Eemian Drilling Project, Greenland) and RICE ice cores have been successfully performed on this experimental setup (Grzymala-Lubanski, 2015), with an acceptable precision (\( \sigma = 0.028\% \) with error propagation, see Chap. 4). In contrast, ice core \( ^{17}\Delta \) measurements have not started at the time of writing this thesis as the accuracy and precision they require has not been reached.

The first section of this chapter presents the analytical requirements of the analytical system (Sect. 3.2). The second section presents an overview of the system based on Barkan and Luz (2003) (Sect. 3.3). A third section describes the building and implementation of the extraction, purification and collection units of the experimental setup (Sect. 3.4). Sect. 3.5 focuses on the gas chromatograph \( O_2/N_2 \) separation unit. The fifth section describes the automation of the system and informs about the electrical characteristics of the setup (Sect. 3.6). Finally, Sect. 3.7 focuses on the development of the experimental protocols to measure stable oxygen isotopes (\( \delta^{18}O \) or \( ^{17}\Delta \)). The measurement sequence developed for IRMS measurements is described in Chapter 4.

3.2 Analytical Requirements

To measure the triple isotope composition of atmospheric oxygen, the fundamental requirement of an analytical system resides in its ability to preserve and measure variations as small as 10 permeg (0.01 %), corresponding to millennial-scale variations observed in \( ^{17}\Delta_{atm} \). In order to meet this requirement, the experimental procedure should respect the following criteria for:

1. Identical Treatment

   The gas sample introduced in the MS must be representative of the air extracted from the ice core. In other terms, the fractionation involved by extraction, separation, purification, collection and introduction of the sample in the IRMS must be accounted for. It is however almost impossible to prevent fractionation to occur in a system as there may be adsorption processes, temperature fluctuations, different equilibration times, incomplete transfer, etc. We therefore try to follow the principle of Identical Treatment (Werner and Brand, 2001) of the sample and the standard as closely as possible. Instead of preventing fraction-
ation to occur, which is not realistic nor feasible, the η principle requires to process samples and standards (reference material) in an identical manner, so that the setup-related alterations of the sample gas are canceled out by the standard ones.

2. Isobaric interference
Ionized molecules with the same mass/charge ratio must be avoided in the source of the ms to prevent isobaric interferences. Therefore, for $^{17}\Delta_{\text{atm}}$ measurements, O$_2$ needs to be separated from N$_2$, as these species react during ionization to form mass fragments, for instance $^{14}$N$^{18}$O$^+$ with a mass/charge ratio of 32 (like $^{16}$O$^{16}$O$^+$). Besides, $\delta^{18}$O and $\delta^{17}$O depend on the N$_2$/O$_2$ ratio of the sample gas relative to the working reference gas (Barkan and Luz, 2003), causing further corrections and loss of precision. As precision of $\delta^{18}$O$_{\text{atm}}$ measurements is not as critical, $\delta^{18}$O$_{\text{atm}}$ can be measured in air and corrections applied for N$_2$ interference.

3. Flow regime
The dimensions of the analytical setup must ensure a viscous flow regime. For instance, introduction of the standard in the system may lead to fractionation due to changes in physical principles of gas flow. Indeed, from a high pressure source to the vacuum area, 3 flow regimes appear with decreasing pressure: viscous flow, Knudsen flow and molecular flow 3.1. In Knudsen and molecular flow regime, diffusion of isotopocules with different masses causes fractionation of the gas species and their isotopes (Schmitt, 2006; Honig, 1945; Halsted and Nier, 1950). For instance, Knudsen diffusion causes fractionation that scales with the square root of the mass ratio while ordinary molecular diffusion scales as the proportional mass difference (Severinghaus and Battle, 2006). Viscous flow is required to avoid fractionation during transfer of the analyzed gases, as implemented for instance in a ms, where standard and sample are introduced with a narrow-bore capillary (0.1 mm ID) at pressures ensuring viscous flow conditions.

4. Precision
The analytical error of the procedure should not exceed 10 permeg, which correspond to the variation in $^{17}\Delta_{\text{atm}}$ associated with e.g. DO 19 (Landais et al., 2007). A precision an order of magnitude higher ($\approx$ 1 permeg) would be advantageous, but remains beyond the current analytical capabilities of IRMS measurements (5-10 per meg).

3.3 Overview of the system

3.3.1 General idea

This experimental setup is primarily built for automated $^{17}\Delta$ measurements. It requires a very high precision that only DI IRMS measurements can provide hitherto.
Figure 3.1 – Flow regimes and volumetric flow rate STP (log scale) according to pressure (log scale) and diameter of the pipe. The volumetric flow rates are calculated using Poiseuille’s law, thereby assuming laminar flow. The x-axis represents pressure drop along the pipe. Lines describe flow rates with different diameters (from 0.05 to 1/4”) corresponding to the characteristic dimensions of our setup. Except for the narrow bore capillary (0.05 mm id) which has a length of 2 m, calculations are done with tube length set to 20 cm. This graph shows for instance that viscous flow regime is only achieved with a pressure higher than 10 mbar in the narrow bore capillary.

Therefore we did not consider to develop a continuous extraction system as described for e.g. in Huber and Leuenberger (2004); Huber et al. (2003), but built an offline system. The ”^{17}O line” is nonetheless versatile. Indeed, separation of oxygen and nitrogen is not needed for $\delta^{18}O$ measurements. In this case, the oxygen separation unit, consisting of 2 focusing traps and a chromatographic column, is bypassed, as it is possible to measure $\delta^{18}O$ with a reasonable precision and accuracy within a $O_2$ -$N_2$ mixture and correct for $N_2$ interference.

The experimental setup described on this chapter is based on the system developed by Barkan and Luz (2003) in Jerusalem and relies on chromatographic technique for oxygen separation. Indeed, as explained in Chapter 2, after almost two years of prospection, development and testing of the perovskite membrane, this new method of oxygen separation was proven unadapted for $^{17}\Delta$ measurements. Still, the design, building, automation and calibration of the system took several months, regardless of the time needed to adjust our measurement protocols to a different ms. Among changes to improve the system or adapt it to the working space and environment, a
major modification in the design of the analytical setup relates to the sample collection unit. Indeed, to reduce operation costs, we cryogenically collect the samples with a Helium cryocooler instead of freezing the samples at 4 K in a sst tube lowered into a tank of liquid helium. The system was also thought to maximize sample throughput. It allows in theory the successive collection of 10 samples a day. However, 2 or more rods are in practice dedicated to standard measurements, to respect the principle of identical treatment (noted IT hereafter), by which samples and standards (reference material) are processed in an identical manner (Werner and Brand, 2001).

3.3.2 General layout of the experimental setup

The "17O line" allows measurements of δ18O in air or 17Δ in a O2 /Ar mixture. The off-line system is schematically described in Fig. 3.2. It can be divided into 2 main sections:

- A section common to δ18O and 17Δ measurements operated under vacuum (see Sect. 3.4). As mentioned earlier, δ18O can be precisely measured in a N2 -O2 -Ar mixture, while 17Δ measurements require O2 to be separated from N2. This section includes:
  1. a vacuum system (cf. box in fig 3.2)
  2. a standard introduction unit. Standard is introduced using a mass flow controller (MFC) or an aliquot equipped with two manual valves (SS-4H, SWAGELOK)
  3. an extraction unit
  4. a purification unit including a water trap (T1) and a CO2 trap (T2)
  5. a collection unit, called "LynnOax", consisting of ten sst rods

- A separation unit which allows the separation between an O2 -Ar mixture and N2, constantly flushed with high-purity He used as carrier gas. For δ18O measurements, this section is bypassed with a 1/8" sst tubing connecting valves L2 and L7. This section includes:
  1. a Gas Chromatography column
  2. two focusing traps: a Full Air trap (T3) to focus the N2 -O2 -Ar mixture before introduction to the GC and a O2 trap (T4)
  3. a He line providing the carrier gas needed for gas chromatography separation
  4. a Thermal Conductivity Detector (TCD, Vici, USA) to control the elution time of O2 and N2.

Quality check Stable temperature and pressure conditions are critical for quality measurements.
Two pressure gauges PG1 and PG2 (Pirani, Edwards) monitor the pressure in the system. PG1 is located between the extraction and purification section and PG2 between the separation and collection section. They are both located before a valve controlling the access to the pumping system. Typical measured vacuum background pressures are typically under range, with $P_{ur} < 10^{-3}$ Pa. All 4 traps, the extraction and GC units and a section of the line are equipped with K-thermocouples to monitor the temperature. Cooling elements (extraction unit, GC) and heating ropes (T2, T3, T4, GC, line) are connected to in-house PID controllers to ensure stability of temperature conditions (see details in section 3.4 and 3.5).

Almost all inner surfaces of the experimental line are made out of sst and are connected together either with Viton O-rings or swagelok connections. A few wetted surfaces, typically the stem tips of some valves are however made in polytetrafluoroethylene (PTFE, commonly called Teflon).

### 3.4 Extraction, purification and collection units

#### 3.4.1 Vacuum system

Vacuum background pressures are typically $< 10^{-5}$ mbar as measured on the two Pirani gauges (lower limit of detection: $< 2 \cdot 10^{-5}$ mbar). High vacuum ($< 10^{-5}$ mbar) is provided by a turbomolecular pumping station (HiCube, Pfeiffer, Germany) backed by a oil-free diaphragm pump integrated in the pumping station. This rough pump cannot be used to provide low vacuum ($> 0.1$ mbar) as the turbo pump would need to be switched off and on depending on the pressure in the system. Therefore, a rotary vane pump (EDM2, Edwards, USA) is connected to the vacuum line and is used whenever important amount of gases need to be rapidly removed from the analytical line. Evacuation takes place through 1/4” or larger sst tubes. The pumping system is connected to the main analytical line (where the sample is processed) through the 2 valves P1 and P2. This allows pumping upstream and downstream of the separation unit.

#### 3.4.2 Standard introduction unit

##### 3.4.2.1 Respecting the principle of identical treatment

Werner and Brand (2001) pointed out the importance of respecting the IT principle for accurate isotope analysis. Not only the sample and the standard should go through the same steps during the collecting and measuring steps, but the standard also needs to closely resemble the samples to be measured against, with an isotopic ratio close to the one of the samples. In addition, it should be in a stable form, homogeneous, easy and safe to handle and transport. For ice core analysis, real ice with $\approx 10$ % of air of known composition would be the perfect standard. As such a standard has not

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1^This rough pump is also used for evacuation of the vacuum casing of the cryocooler.
The setup is semi-automated and consists of an extraction, purification, separation, and collection section. It is based on Barkan and Luz (2003) for triple isotope oxygen collection built during this PhD thesis.

**Figure 3.2** – Schematic representation of the analytical system for triple isotope oxygen collection built during this PhD thesis.
been produced hitherto, the next best reference strategy consists in introducing an air standard on top of bubble-free ice (noted bfi hereafter), i.e ice that contains no air at all. At CIC, we produce bfi by degassing milli-Q (ultrapure) water under vacuum through a water trap while heating and stirring it. The evacuated vessel is then closed and brought to a $-15^\circ C$ cold room. The vessel is wrapped into a heated blanket (heating wire wrapped around a copper sheet) to maintain a temperature of $4^\circ C$. Then the water is slowly frozen from the bottom up at a rate of $\approx 10 cm \cdot day^{-1}$ to ensure that dissolved gases can diffuse faster than the ice grows. To avoid supercooled water to form, some tapwater is added for the ice crystals to have a site to nucleate. It however turned out that the bfi we tested for standard measurements still contained too much air, despite the absence of visible bubbles, which lead to unreliable results when standard air (neem air) was introduced over bfi, and we describe in section 3.7 the strategy used to overcome this issue.

### 3.4.2.2 Gas standards

Reference materials consist of natural minerals or compounds with desired isotopic composition, chemical purity, stability and homogeneity (Gonfiantini et al., 1995). They are the primary reference materials (noted PRMs hereafter) against which raw data are expressed and enable inter-laboratory comparisons. PRMs are certified by the IAEA or NIST for different isotopes and do not have associated uncertainties. For instance, IAEA defines by consensus the origin of the $\delta$ scale such as the Vienna Standard Mean Ocean Water (VSMOW, with the NIST material code RM 8535a), thus with $\delta^{18}O_{\text{VSMOW}} = 0\%e$ and $\delta^{17}O_{\text{VSMOW}} = 0\%e$. As a matter of fact, VSMOW was a calibration standard that has become de facto the PRM to express hydrogen and oxygen water stable isotope variations in replacement of the PRM SMOW (Craig, 1961), which was never physically available (Gonfiantini et al., 1995). Note that VSMOW2 has recently become the new PRM to replace VSMOW, exhausted. Contrary to VSMOW, VSMOW2 has a combined standard uncertainty associated to $\delta^2H$ and $\delta^{18}O$ reference values (IAEA, 2009).

Dried atmospheric oxygen is the PRM for molecular oxygen isotopic ratio ($^{18}O / ^{16}O$, $^{17}O / ^{16}O$). $\delta^{18}O$ and $\delta^{17}O$ values are hence defined as $0\%e$. Its abundant availability and spatial homogeneity (due to the long residence time of oxygen (>1200 yrs) relative to the inter-hemispheric mixing time in the atmosphere (1 yr)) are the main advantageous characteristics of this PRM.

The PRMs are often valuable materials of finite quantity that may not always be in an appropriate chemical form for simple isotope standardization or that are not sufficient to fix the scale expansion/contraction of the analytical methods employed (Berhanu, 2013). The calibration materials, or secondary reference materials, are carefully calibrated versus the PRMs, and the calibration values are internationally agreed and adopted (Gonfiantini et al., 1995). These calibration standards have been developed along the years to fill these gaps and their $\delta$ values and associated uncertainties
Another important distinction lays between primary and calibration standards on one hand, and working, or in-house standards, on the other hand. Primary or calibration standards are generally too rare to be used on a daily basis. Instead, working standards are calibrated against the formers. In the case of atmospheric \(O_2\), abundance is not an issue though. According to Carter and Barwick (2011), in-house standards must be homogeneous, easy and safe to store, handle and transport, stable during storage, abundant and easily replaceable and non hygroscopic.

**NEEM AIR**

A working standard thus needs to closely resemble the samples to be measured against, with an isotopic ratio close to the one of the samples. It should be in a stable form, homogeneous, easy and safe to handle and transport. An atmospheric air tank was sampled in the year 2008 at a clean-air site of the Neem camp in northwest Greenland (Sperlich et al., 2013). For stable oxygen isotopes measurements, this dried atmospheric air from Neem is used as a PRM standard but also as a working standard, owing to its abundance. It indeed respects all required criteria in terms of origin: Neem is a remote source far from polluted areas, and its elemental \((N_2, O_2, Ar)\) and isotopic composition is close to the one of the measured sample, given its long-term stability owing to the long residence time of \(O_2\) in the atmosphere.

**INTERMEDIATE STANDARD**

To respect the principle of identical treatment as closely as possible, the working standard is treated as a sample, going through all the steps that the latter experiences. Collected samples and standards are then introduced in the sample bellow of the MS. They are then measured against an intermediate standard introduced in the standard bellow of the DI system. This intermediate standard is the same as the working standard for \(\delta^{18}O_{\text{atm}}\) measurements (Neem air), and an \(O_2\)-Ar mixture (or pure \(O_2\) when oxygen separation was achieved with the perovskite membrane) for \(17\Delta_{\text{atm}}\) measurements, so as to closely match the elemental and isotopic composition of the gas mixture introduced in the IRMS. It should be mentioned that this intermediate standard is only used as a transition step to relate the sample to the working standard (see Sect. 4.5.5), and it is therefore not necessary to know its isotopic composition.

### 3.4.2.3 Gas standard introduction unit

The full air working standard Neem_S1 is stored in a 3 l Silco can (Restek, USA) to \(\approx 2.5 \text{ bar}\). It is filled from the high pressure tank Neem_C1. To check if fractionation occurs during the transfer, Neem_S1 is measured against Neem_C1 after filling\(^2\). If the oxygen stable isotopic ratios are identical between Neem_S1 and Neem_C1 within the uncertainty of measurements performed, the standard transfer is validated, and the Silco can is connected to the reference inlet of the experimental system (attached measurements are performed in DI mode, Neem_S1 being introduced to the sample bellow, and Neem_C1 to the standard bellow).
to valve M2 in Fig. 3.2) and the line located between the Silco can valve and valve M2 is purged. Between measurements, the line upstream the MFC is conditioned by filling it with Neem_S1 standard.

Pure O₂ working standards are stored in a high pressure cylinder and permanently hooked up to the main line via valve M3 (Fig. 3.2). It should be mentioned that all high pressure cylinders are equipped with high purity regulators (Y13-C444A, single stage, stainless steel with Kel-F and Teflon seals, Airgas, USA).

In our setup, the standard is introduced in the glass flask under vacuum via a mass flow controller (MFC) set to 2 ml·min⁻¹. At this flowrate, no mass-dependent elemental or isotopic fractionation should occur as viscous flow conditions prevail, inlet pressure (the pressure upstream the cryocooler) being higher than 2 bar. Knudsen or molecular diffusion would only be an issue at inlet pressures 4 orders of magnitude lower (Fig. 3.1). The line upstream the MFC is flushed 3 times prior each standard introduction. As the flow through the MFC is low, a high flow pathway (including valves M6 and M7) is used to evacuate the line upstream the MFC after flushing (Fig. 3.2). More details are given on Section 3.7.

3.4.3 Extraction Unit

Three main techniques exist for extracting gases from ice cores, all undertaken under vacuum. Melt-extraction is the oldest and most common technique, and have been used for gases such as O₂, N₂, Ar and CH₄. In contrast, gas species like CO₂ require dry extraction techniques (needle-crusher³, ball mill, ice mill, cheese-grater) due to their high solubility (see Table 3.1) in water caused by oxidation of organic acids or carbonate (CO³⁻) dissolution (Leuenberger et al., 2002) in acidic ice, i.e. the hydration of CO₂ to form carbonic acid (H₂CO₃). A third technique is based on sublimation of ice to prevent chemical reactions between extracted gases and water, but this limits the sample throughput as the extraction process is much slower. A major difference between the 3 techniques relates to the extraction efficiency. The dry extraction does not allow 100 % of the sample to be collected, but fractionation can be avoided by careful conditioning of the extraction unit (Leuenberger et al., 2002). With melt-extraction or sublimation techniques, a close to 100 % extraction-efficiency theoretically prevents isotope fractionation as all the air is extracted.

Melt-extraction is straightforward and was thus the first technique applied to extract fossil air occluded in ice core bubbles. It is still successfully used for δ¹⁸O atm measurements (e.g. Capron et al., 2010). Several melt extraction methods have been developed, from simple melting, vigorous stirring of the meltwater, to melting with subsequent refreezing of the sample (melt-refreeze technique). Sometimes, the sample is refrozen 3 times from the bottom to force the dissolved air above the water body. The different methods of melt extraction all follow a similar goal, maximizing

³At CIC, CO₂ is extracted thanks to a indium sealed needle-crusher unit.
Figure 3.3 – The design of the extraction flask was chosen to minimize the volume of the extraction flask while keeping an easy access for ice samples. A bottom-rounded glass vessel was chosen to favor a higher exchange surface between the melt water and the headspace.

extraction efficiency. Indeed, a quantitative transfer implies no fractionation during the extraction process. Depending on the considered gas specie, a substantial fraction of the extracted gas dissolves in the melted water, and reducing this dissolved fraction explains most of the aforementioned developments in the melt extraction technique. The solubility of a gas specie is controlled by the temperature (T) of the water body and by the partial pressure of the gas specie over the water body. For instance, about twice as much oxygen ($14.6 \text{mg} \cdot \text{L}^{-1}$) dissolves at $0^\circ\text{C}$ than at $20^\circ\text{C}$ ($7.6 \text{mg} \cdot \text{L}^{-1}$) (Emsley, 2011). We varied several parameters to determine the optimal gas extraction conditions depending on the focus of the measurements ($\delta^{18}\text{O}$ only or the three $\text{O}_2$ stable isotopes). Refer to the protocol section 3.7 for details.

Twelve identical glass vessels (Fig. 3.3) were made in the glassblowing workshop of IMAU, (Institute for Marine and Atmospheric Research, Utrecht, The Netherlands, contact: Wim Nieuwenhuis). The extraction vessel consists in a bottom-rounded 210 cm$^3$ borosilicate glass vessel. A Teflon centering ring (NW 50) with Viton O-ring and a clamp made out of high temperature plastic seals the bottom and upper part of the glass flask on its wider diameter (50 mm). The ice sample fits on the bottom part of the glass vessel. The upper part ends with a 6 mm glass tube, connected to the collection setup with a Swagelok 1/4” Ultratorr fitting with Viton O-ring. Note that these unions are nickel-plated to prevent corrosion as they are often in contact with water. The Ultra-Torr fittings are attached to a 1/4” pneumatically actuated bellow-sealed valve (SS-4BK-1C, swg), operated under Labview through dynamic link function libraries (noted dll hereafter) of cheap (compared to Labview acquisition cards) but very functional control boards (PC-control, UK) (see Sect. 3.6).
Table 3.1 – Properties of main atmospheric gases. In general, the lower the boiling point, the higher the partial pressure of the considered gas at any given temperature. Solubility decreases with increasing temperature: the solubility of a gas at 0°C is thus close to its maximal value.

<table>
<thead>
<tr>
<th>Gas</th>
<th>molar mass g·mol⁻¹</th>
<th>concentration in air % (by vol)</th>
<th>melting point °C</th>
<th>boiling point °C</th>
<th>solubility at 0°C vol/vol (STP)</th>
<th>molecular size* 10⁻¹⁰m</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>31.999</td>
<td>20.946</td>
<td>-218.79 (54.36 K)</td>
<td>-182.96 (90.19 K)</td>
<td>0.0489</td>
<td>3.467</td>
</tr>
<tr>
<td>N₂</td>
<td>28.013</td>
<td>78.084</td>
<td>-210.00 (63.15 K)</td>
<td>-195.80 (77.35 K)</td>
<td>0.02348</td>
<td>3.798</td>
</tr>
<tr>
<td>Ar</td>
<td>39.948</td>
<td>0.924</td>
<td>-189.37 (83.78 K)</td>
<td>-185.85 (87.30 K)</td>
<td>0.0537</td>
<td>3.542</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.01</td>
<td>0.04</td>
<td>-56.57 (216.58 K)</td>
<td>-78.45 (194.70 K)</td>
<td>1.7163</td>
<td>3.941</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.043</td>
<td>0.00018</td>
<td>-182.46 (90.69 K)</td>
<td>-161.48 (111.67 K)</td>
<td>0.054</td>
<td>3.758</td>
</tr>
</tbody>
</table>

*aSeveringhaus and Battle, 2006

A sst vessel, built by the CIC workshop, is filled either with cold ethanol or warm water. Ten extraction flasks can be simultaneously immersed in the vessel. The design allows its double wall evacuation thanks to a low vacuum (LV) rotary vane pump (Edwards, EDM2) to reduce heat exchange with the environment. 50 l of pre-cooled ethanol in a −25°C freezer are required to keep the samples frozen during overhead evacuation of the extraction flasks. Unfortunately, the available immersion cooler chiller (neslab CC-100 coldfinger) did not have the cooling capacity sufficient to keep such a mass of ethanol within the optimal temperature range (−22°C to −24°C). Additionally, the thermal gradient in the ethanol bath was too important between the 10 extraction flasks despite vigorous stirring. Finally, we were unable to prevent leakage to occur when many extraction flasks were simultaneously connected to the collection system. Resolving this issue remains critical to achieve a full automation of the collection system, as it requires some of the extraction vessels to remain sealed for a few hours.

We thus opted for a one-by-one sample extraction system. During evacuation the bottom part of the extraction vessel is submerged in an ethanol dewar. Ethanol is kept between −22°C and −24°C with a temperature controlled neslab coldfinger. Within this temperature range, sublimation causes a water vapor flow to effectively remove any gases adsorbed onto the ice surface during the evacuation process (Severinghaus et al., 2003). Meanwhile, such a low temperature prevents the sublimation rate from being too high to cause substantial loss of the sample. Additionally, the sweep out of the extraction vessel becomes more efficient.

Temperature is measured with a K-thermocouple and regulated by a proportional-integral-derivative (noted PID hereafter) controller (CN7500, OMEGA), which switches on and of the neslab coldfinger. We chose a 4°C temperature range to minimize the on-off cycles undergone by the chiller while ensuring a reasonable sublimation rate (Fig. 3.4). Since the density of ethanol decreases monotonically with temperature, unlike water, vertical thermal gradient within the dewar can easily form.
3.4 Saturated vapor pressure (in Pa) above water ($e_w$) and ice ($e_i$) (log scale) vs temperature (in K), using Murphy and Koop (2005) formula for $e_i$ and World Meteorological Organization No. 49, Technical Regulations, Basic Documents No. 2, Volume I, General Meteorological Standards and Recommended Practices, Appendix A formula for $e_w$. Note that the red curve extending below 273 K represents saturated vapor pressure over supercooled water, slightly higher than $e_i$. The stacked windows zoom on temperature ranges relevant for $O_2$ extraction and cryotrapping of $H_2O$.

(lower right panel) During the extraction process, saturated vapour pressure above the ice sample reaches up to 1 mbar at $-20^\circ C$, creating a sublimation flux that helps cleaning of the ice sample surface and pumpdown time (Section 3.4.3). $e_i$ is also used as a thermometer as its value is exclusively dependent on the temperature of the ice body above which it is measured. The temperature of the ice sample is thus more accurately estimated with $e_i$ than with a thermocouple measuring the temperature of the ethanol bath, separated from the ice sample by a glass vessel.

(upper left panel) Water vapour is trapped in a sst cylinder kept at a temperature ranging from $-85^\circ C$ to $-110^\circ C$. At these temperatures, sublimation provides a few hundredths of Pa to the total pressure measured in the line.

At the bottom of the dewar, a waterproof fan (Trevor Popp recovered it from an antic experimental setup at CIC) prevents ethanol stratification.

3.4.4 Water trap

Water vapour is trapped in a sst cylinder (trap T1 in Fig. 3.2) kept at a temperature ranging from $-85^\circ C$ to $-110^\circ C$. The coolant consists of ethanol cooled down
to $-110^\circ C$ with $LN_2$. When it gets close to its melting point ($-114^\circ C$), ethanol turns to slush. The increased viscosity of ethanol at low temperatures combined with higher density further inhibits mixing in the dewar, which results in a thermal gradient along the water trap. Temperature is therefore measured with 2 K thermocouples at the bottom and the top of the ethanol-filled dewar, and manual stirring is performed when the temperature gradient exceeds 5 to $10^\circ C$.

Some water still remains in the extraction line even after the water trap, since the freeze out occurs at around $-90^\circ C$ at which temperature $e_i$ is $0.00969 \text{ Pa} \left(10^{-4} \text{ mbar}\right)$ using equation (7) $^4$ of Murphy and Koop (2005) (Fig. 3.4).

The design of the water trap strongly evolved during the course of the PhD thesis. The initial water trap was a 1/4" tube filled with glass beads but the capacity was too low. A similar problem arose with the second water trap, similar to the current one but with a smaller height. The trap consisted of a one closed-end ssT cylinder (40 mm ID) sealed with a blank flange (DN 40 ISO-KF, Pfeiffer vacuum, Germany) drilled all the way through and connected to a 1/2" ssT tubing ending 2 cm above the bottom of the ssT cylinder. The cylinder and the blank flange were sealed with a compression O-ring. The trap had a too low volume to allow more than one ice sample to be processed before clogging, because of water freezing within the inner 1/2" tube. The lower limits of the 2 SingleGauge Pirani Transmitter PG1 and PG2, located after the water trap, were quickly reached ($< 5 \cdot 10^{-5} \text{ mbar}$), the frozen water acting as a seal between the extraction unit and the remaining part of the system. The third water trap was similar in shape as the first one, but 7 cm longer to increase its volume, hence its capacity to collect water. However, it would either get clogged, a plug of ice forming at the end of the ssT 1/2" inner tubing, or on the contrary too much water vapor would escape the water trap, when slightly lowering the ethanol level in the dewar. This resulted in high water levels in the collected samples.

To prevent water vapour from escaping the water trap, we filled the latter with glass beads (Ø 2 mm). By increasing the distance the gas had to travel in the water trap, the probability of freezing the water vapour should increase. However the water trap would quickly clogged by a layer of frozen water right on top of the beads, suggesting that instead of capacity, it was rather (i) the rate of water vapour transferred at a time through the water trap that was too large, and (ii) the inlet (1/2" ssT tubing) temperature of the water trap that was too low, freezing water vapour before it would reach the glass beads. To solve these issues, two changes were implemented:

- **Water flow.**
  The 1/4” ssT tubing connecting the extraction unit to the water trap was reduced to 1/16”. It aimed at reducing the amount of water vapour reaching the water trap at a time, hence lowering the probability that a ring of frozen water would form immediately at the water trap inlet. It turned out that it significantly

\[ 4 \ln(e_i) = 9.550426 - 5723.265/T + 3.53068 \cdot \ln(T) - 0.00728332 \cdot T \text{ Pa, with T in Kelvin and } e_i \text{ in Pa.} \]

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$^4$ \( \ln(e_i) = 9.550426 - 5723.265/T + 3.53068 \cdot \ln(T) - 0.00728332 \cdot T \text{ Pa, with T in Kelvin and } e_i \text{ in Pa.} \)
reduced the transfer time of the sample too, the flow of water vapour through a 1/16” line acting efficiently as a carrier gas for the released fossil air (Severinghaus et al., 2003). This can be explained by the reduced ratio between free-mean path of a molecule and the cross-section diameter of the tube (Knudsen number), which implies an increasing number of collisions between air constituents and water vapour molecules. Additionally, this change minimized the risk of gas occlusion under the freezing water vapor that can occur when a large amount of water is transferred to the water trap (Headly and Severinghaus, 2007).

Figure 3.5 – (black curve) Oxygen vapor pressure curve from Air Liquid (http://encyclopedia.airliquide.com/images_encyclopedie/VaporPressureGraph/Oxygen_Vapor_Pressure.GIF). The critical point is indicated by a black spot on the liquid-vapor equilibrium curve. (red line) Boiling temperature of $O_2$ at atmospheric pressure. (blue line) Melting temperature of $O_2$ at atmospheric pressure. (dashed black line) Liquid Nitrogen ($LN_2$) temperature. At 77 K, $O_2$ would be liquid at atmospheric pressure. (yellow line) To ensure that $O_2$ remains in its gaseous phase at $LN_2$ temperature, the total pressure of the sample in the system must be kept below 0.2 atmosphere. This condition is largely met as the system has a volume of a few hundreds of $cm^3$, 2 orders of magnitude higher than the volume of any air sample (up to 4 $cm^3$).
Temperature.
The line connecting the extraction unit to the water trap was heated with a rope heater (FGR-060, Omegalux, UK) to the set temperature of 50°C, regulated by a PID controller (CN7500, Omegalux, UK). It ensured that freezing of the water vapour would not occur immediately after entering the water trap.

3.4.5 CO₂ TRAP

CO₂ needs to be excluded from the extracted air mixture:

- As for $^{17}\Delta$ measurements, the $O_2$ - Ar mixture needs to be separated from $N_2$ to obtain precise measurements. Indeed, measuring a pure gas avoids pressure effect and isobaric interferences in the ms. Besides, this separation step requires to remove $CO_2$, as the material in the gas chromatography (GC) column used for $N_2$ - $O_2$ separation tends to trap $CO_2$ (Section 3.5).

- As for $\delta^{18}O_{atm}$ measurements in air, the presence of $CO_2$ in the ms can lead to isobaric interference with $N_2$ isotopes. Indeed, formation of $^{13}C^{16}O$ may affect the measurements of $\delta^{15}N$, measured on m/z 29. As for $O_2$ measurements, $^{14}N^{18}O$ can be created in the ion source and is isobaric with $^{16}O_2$, but the error introduced is very small as $^{16}O_2$ is abundant.

Just after the water trap, the trap T2 (Fig. 3.2) is set to LN₂ temperature and freezes out $CO_2$. Indeed, with a boiling point at $-78.45^\circ$C STP, $CO_2$ freezes out at LN₂ temperature⁵, even at the low pressure of the operating system (a few tens of mbar). $N_2$ and Ar, with a boiling point close to the one of $O_2$ (Table 3.1), remain also in their gas phase at the system pressure (Fig. 3.5).

Besides its primary function, the $CO_2$ trap acts as a secondary trap in case water vapour remains in the system after the water trap. We are aware that gases may adsorb on ice at LN₂ temperature. However, at $-100^\circ$C (temperature of the water trap), water vapour pressure only amounts to $\simeq 10^{-2}$ Pa (Fig. 3.4). Hence adsorption of the fossil gases on ice should be avoided given the extremely low water content.

3.4.6 COLLECTION UNIT

3.4.6.1 Closed cycle He cooler

Motivations

The reasons we decided to use a closed cycle refrigerator are manyfold⁶:

- Short sample tubes can be used (Kawamura, pers. comm, 2010).

⁵$N_2O$ is also trapped at this temperature, as it has nearly identical physical properties

⁶We did not consider to trap $O_2$ with molecular sieve at LN₂ temperature as Barkan and Luz (2003) showed that the adsorption process is not complete, and found out that measured $\delta^{18}O$ and $\delta^{17}O$ are lower than true values. The same holds true for the $O_2/Ar$ ratio.
• It is more convenient than liquid helium as the only need is electricity. The reservoir of He within the compressor has not been refilled since its installation in 2010.

• It is safer as a helium cryocooler does not require handling of liquid helium.

• Cost of the product is reimbursed only after a few years of use, as no liquid He is required. Obviously, it varies according to the costs of electricity and liquid Helium, and recent years have shown how pricy the latter has gone.

3.4.6.1.2 Design

The cryogenic cold head (CH-204SFF) and water-cooled He compressor (HC-4E) were purchased at Sumitomo (SHI Cryogenics, Japan) together with the He gas lines for \( \approx 8000 \) euros. The CH204SFF cold head is a two-stage cryogenic refrigerator that operates on the Gifford-McMahon refrigeration cycle. The cold head uses helium gas (99.995% purity) from a He compressor to produce the cold temperatures. Electricity to power the cold head’s valve motor is supplied from the compressor by the cold head cable (Sumitomo manual). We exchanged closely with a cryogenic engineering company called AS Scientific (contact Colin Hillier) who have long experience with manufacturing systems specifically designed for a particular purpose. The design of the cryocooler needed to meet the following criteria:

• Trapping temperature: 12 K. Such a temperature is a good trade-off between performance and price. Cooling 10 tubes at 4 K is possible but requires huge power. A 12 K refrigerator is powerful enough for trapping gases like \( O_2 \), and a lot less expensive. The performance of the refrigerator is determined by the power of cooling unit, the size of cooling chamber and the amount of heat intrusion from outside (radiation, conduction), and thus require specific design and dimensions (Fig. 3.6).

• Minimal volume for the collection tubes. The length of 1/4" tubes must be as short as possible, because the amount of \( O_2 \) trapped is further expanded into the 40 ml bellow of the ms. However, the longer the tubes, the less heat conducted from outside to the second stage cold station (see Sect. 3.4.6.1.4).

• Heat load. Dimension and volume of the tubes of the collection manifold control the heat transferred by conduction to the cryocooler (see Sect. 3.4.6.1.4). Furthermore, the mass of copper needs to be minimized to reduce cool down times. While the specified cooling time of the cold head to 20 K is 40 min, it takes 50 minutes more to reach 10-12 K.

• Cleanness. All 10 tubes were assembled in a copper block and vacuum brazed to ensure that the inside of the tube is kept clean.

• Mobility. A few cryocoolers allow the removal of a single sample tube while the cryocooler is still operating. This makes it significantly more functional (and
Figure 3.6 – (a) Vacuum casing in which the collection manifold (LynnOax) is cooled to 12 K. Vacuum flanges and clamps are used to connect LynnOax to the cryocooler. The vacuum shroud can be evacuated with a rough pump to $10^{-3}$ mbar. Also shown are the gas lines connecting the cold head to the water-cooled He compressor. (b) Similar as in (a) without the vacuum casing. A copper shield conducts cold from the first stage heat station (77 K) to the rods of the collection manifold. The polished copper (emissivity $\varepsilon = 0.03$) also acts as a radiation shield, which reduces radiation loss to the second stage cold station.

expensive) but is actually not necessary for our experiment. Indeed, mass spectrometry measurements require stable conditions, which are more likely to be respected if samples are measured within a short period of time. As extraction and collection of samples is time-consuming, it is preferable to first collect the samples offline and measure them together. On the first design, the copper block would be flanged to the 2nd stage cold station of the cooler. However, this option was discarded as it would prevent an easy removal of the collection manifold from the cryocooler. Rather, thermal grease is used to ensure a good thermal contact between the copper surround block of the collection manifold and the copper cup connected to the second stage cold station (Fig. 3.7a). Note that the pressure difference created during evacuation of the vacuum casing after LynnOax is inserted in the cryocooler helps connecting the 2 copper blocks.
Figure 3.7 – (a) The copper cup connected to the second stage cold station (12 K) is reached by removing the copper shield flanged to the first stage cold station. The silicon diode temperature sensor and the cartridge heater attached to the copper cup are shown. Note however that they are not wired, the figure being taken after both cease to function due to mechanical stress. (b) Zoom on the second stage cold station where the damage caused on the leads can be seen. The failure occurred during the removal of the collection manifold by rotating it. Being still too cold, the solid thermal grease forced the copper cup, screwed to the cold station, to rotate together with the collection manifold. This lead to the breakage of the leads of the cartridge heater and silicon diode temperature sensor as they are wrapped around the the copper cup on which LynnOax’s copper block is incrustd. The silicon diode leads could be soldered again but the cartridge heater needed replacement. It is thus very important to wait for the thermal grease to soften by allowing more warming time - and not to use an excessive amount. (c) Top-view on the vacuum flange through which LynnOax is inserted into the vacuum casing of the cryocooler. Also shown are the copper shield and copper cup.

- Thermal stability. The copper surround block (Fig. 3.8a) needs to have high purity to give thermal stability to the stainless tubes. To ensure homogeneous thermal distribution, each ssT tube needs to be surrounded by copper to avoid contact between them, which however increases the copper block’s mass, thus increasing the time needed to reach 12 K.

- Faster heating of the collection manifold to room temperature is achieved thanks to an internal cartridge heater fitted into the copper cup of the cryocooler (Fig. 3.7). Refer to Sect. 3.7.2.2 for details.
3.4.6.1.3 Instrumentation collar

The instrumentation collar includes thermometry devices, an electrical feedthrough and two KF25 evacuation ports. A rough pump is attached to one port via a manual on-off valve (red handle on Fig. 3.6). The pressure is monitored with a pressure gauge attached to the second KF25 port. This port is also used to vent the vacuum casing of the cryocooler. The thermometry is wired to the second stage heat station through an electrical feedthrough (Fig. 3.8b). It consists in a silicon diode temperature sensor (DT-470-CU-12A, Lakeshore) and cartridge heater (40V, 40 W). The silicon diode temperature sensor follows the Curve 10 standard temperature response curve, describing the relation between temperature and voltage output of the silicon diode when excited by a current source.

3.4.6.1.4 Heat load

The final design of the cryocooler is the following: the sample holder is mounted to the second-stage heat station and a radiant heat shield mounts to the first stage heat station (Fig. 3.6). According to the specifications provided by Sumitomo, the first stage heat station provides 13.5 W at 77 K and the second stage cold station provides 7 W at 12 K (50 Hz). It is essential that the heat intake to the second stage heat station is significantly lower than the cooling capacity of the cold head. Excluding gas load, heat load is essentially due to conduction of heat within the 10 sample tubes walls and infrared radiation from the vacuum shroud. Rapid calculations show that heat transfer from outside (298 K) to the first stage heat station (77 K) amounts at max to $\approx 10$ W, of which 5 W arise from radiation and $\approx 3.5$ W from conduction. The heat transfer from the first stage (77 K) to the second stage heat station (12 K) is reduced to 0.44 W by conduction of heat along the 304 SST tubes. Indeed, radiation can be neglected given the very low emissivity of the polished copper radiation shield. In conclusion, the heat transfer does not challenge the cooling capacity of the cryocooler, as observed during experiments.

3.4.6.1.5 Installation setup

The cryocooler (cold head and vacuum casing in which the collection manifold is inserted) can’t be moved, and is therefore located close to the experimental line, so that the collection manifold can be connected with a 1/4” 30 cm long flexible SST tube (SS-FM4TA4TA4-12H, SWAGELOK). Two manual bellow-sealed valves (SS-4H, SWAGELOK) command the access to the main line and the collection manifold (3.8b). Gas lines filled with He connect the cold head to the He compressor. To operate, the latter needs to be cooled by a constant flow of water, which is currently provided by the cold water circuit of the building in which the experiment is located\(^7\).

\(^7\)This improvement is essential, as In the previous setup, an air-cooled water chiller (LC3500, ICS Cool Energy Ltd, UK) provided the cold water required for the He compressor to operate. The main drawback was caused by the fact that the operation of the air-cooled water-chiller would function only
Figure 3.8 – (a) Profile view of the collection manifold (LynnOax). Visible are the 10 sample rods vacuum brazed to a copper block at their closed end. The copper block enables a good transfer of cold from the second stage heat station to the sample rods. An O-ring fitted in the groove of a copper block ensures a leak tight connection when LynnOax is attached to the vacuum casing of the cryocooler. (b) Top-view of LynnOax. A manual 1/4” valve (SS-4H, SWAGELOK) controls the access to the sst ring of the collection manifold. Pneumatically actuated normally-closed 1/4” diaphragm valves are attached to the sample tubes with vcr silver-plated gaskets.

3.4.7 Collection manifold

The collection manifold can be seen on Fig. 3.8. The ten sst tubes vacuum brazed to the copper blocks were provided by AS Scientific. Bending of the tubes, connection to pneumatically actuated diaphragm valves (6LVV-DPVR4-P-C, SWAGELOK), design and building of the distributing 1/4” sst ring and welding took place at the CIC workshop (thanks to the great skills of Carsten). A manual bellow-sealed valve (SS-4H, SWAGELOK) seals the collection manifold from ambient air.

In general, 1/4” tubes (\( ID = 5.3 \text{ mm} \)) are used but their length and volume differ widely in previous studies. When collection is achieved with liquid He, sample tubes can vary from 0.70 m (\( V = 15 \text{ ml} \)) (Severinghaus et al., 2003) to 1.5 m (\( V = 33 \text{ ml} \)) (Mani et al., 2008), for 4 ml of air and 2 ml of \( N_2 \)-Ar, resp. This length is required to expose a maximum of fresh surfaces to improve sample collection. With a He cy-
cle cooler, tubes can be much shorter (Kawamura, 2010, pers. comm). For instance, Kawamura et al. (2003) use 35 cm long tubes, i.e. a inner volume of 6 ml, to collect 30 ml of air. In sharp contrast, for O₂ -Ar samples (0.75 ml after N₂ separation), Barkan and Luz (2003) opted for 95 cm long 1/4” sample tubes (20 ml) to ensure a gas pressure lower than 50 mbar after warming to room temperature, observing that above 100 mbar, a significant amount of gas remains adsorbed on the walls after warming from liquid He temperatures when introduced to the inlet of the IRMS.

The sample tubes used in our experiment are 42 cm long, 1/4” in diameter (ID=5.3 mm). This corresponds to a volume of ~9 ml, planned to collect samples varying from 0.8 ml to 4 ml. This means that a pressure up to 500 mbar can build up in the sample tube at room temperature. By varying the size of the standards from 4 to 0.4 ml, we did not observe systematic differences in O₂ isotope ratios after conditioning of the rods, suggesting that the effect seen by Barkan and Luz (2003) does not occur on our analytical system. It should be mentioned that ice samples dedicated for ¹⁷Δ atm measurements build up a total pressure of maximum 100 mbar after warming from 12 K, hence in the acceptable range according to Barkan and Luz (2003).

### 3.5 O₂ /Ar - N₂ SEPARATION UNIT

We rely on the classical gas chromatography method to separate O₂ and Ar from N₂ (Barkan and Luz, 2003). However, we use a different GC column to separate N₂ from the O₂ -Ar mixture, and we direct the carrier gas flow thanks to a combination of a 4-port and 6-port Valco valve (Fig. 3.2) rather than 4 three-way valves to minimize dead-volumes in the system.

#### 3.5.1 Helium lines

High purity He (≥ 99.999%, 50 l cylinder, Air Liquid, Denmark), additionally purified by a getter (Gas Purifier, VICI, Valco Instruments Co. Inc, USA), is permanently provided to the O₂ /Ar - N₂ separation unit. The total He consumption of the system amounts to ~34 cc.min⁻¹ in operation, and 5.7 cc.min⁻¹ at rest. Similar to the analytical system, all lines are made out of sst. He flow is regulated with a pressure controller and 2 upstream-referenced flow controllers (Bronkhorst) to provide ~28 cc.min⁻¹ to the GC column and ~6 cc.min⁻¹ to the reference side of the TCD (see Fig. 3.2).

#### 3.5.2 Focusing traps

##### 3.5.2.1 full air trap T₃

Prior introduction to the GC column, the O₂ -Ar-N₂ mixture is focused on a molecular sieve trap. The full air trap T₃ consists of a ~40 cm 1/4” sst U-tube filled with molecular sieve (5A, 30-40 mesh size) over 10 cm, i.e. 1.25 g of trapping material.
Figure 3.9 – focusing traps prior and after introduction to the GC column. Not to scale. After removal of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), the remaining extracted gases, mainly \( \text{N}_2 \), \( \text{O}_2 \) and \( \text{Ar} \) are focused in the trap T3 at LN temperature. The gas mixture is released by heating the trap to room temperature.

The trap is similar to the trap developed by Barkan and Luz (2003), consisting in a SST U-tube, 0.45 m x 1/4” o.d., filled to one-third of its height with molecular sieves (5 Å, 100-140 mesh). Two quartz wool’s plugs (\( \approx \) 2 cm) hold the trap into place (Fig. 3.9). A rope heater (FGR100, 240 V, 500 W, 10 ft, Omegalux, UK) enables a fast heating to room temperature. The heating starts as soon as the LN dewar is removed, as the dewar hits a push for "on" electrical switch which enables supply of current to the rope heater (Fig. 3.9). The heating procedure is temperature controlled with a PID controller tuned to avoid temperature overshooting. It takes 30 s to reach a stable temperature after warming the trap. The molecular sieve trap is regenerated after each serie of measurements by heating it to 200°C and flushing the traps with a stream of He.
3.5.2.2 \( \text{O}_2 - \text{Ar} \) trap T4

trap T4 is identical to trap T3, in terms of design, dimensions and amount of trapping material, but is used to focus an \( \text{O}_2 - \text{Ar} \) mixture (instead of dry air) at the GC outlet.

3.5.3 Gas Chromatograph unit

3.5.3.1 GC column

The packed chromatographic column (88014-800, Restek, USA) used to separate the \( \text{O}_2 - \text{Ar} \) mixture from \( \text{N}_2 \) consists of 10 feet (\( \simeq 3.1 \) m) of a 2 mm ID (1/8” OD) stainless steel tubing\(^8\), packed with molecular sieve material (5A, 80-100 mesh size), synthetic forms of zeolite packing. We selected a packed rather than a capillary GC column because it enables a baseline separation between \( \text{N}_2 \) and \( \text{O}_2 \) at positive temperatures with a relatively short length (3 m in our case). For comparison, Barkan and Luz (2003) also used a packed GC column with fine 5 Å molecular sieves (45-60 mesh), but much shorter (20 cm · 2 mm ID), requiring the GC column to be cooled to \(-85^\circ\)C to operate, which we find not practical. Note that to separate \( \text{O}_2 \) and \( \text{Ar} \), a much longer column would be needed.

The basis of the separation process relies on molecular size and shape difference of analyzed gases. We selected 5A (pore size: 5 Å) instead of 13X (pore size: 10 Å) packing as the 5A packing provides greater retention, which improves the separation of \( \text{O}_2 - \text{Ar} \) and \( \text{N}_2 \). The retention time represents the time for a compound to travel through the GC column (here defined as the time between the sample's release from trap T3 and its detection on the TCD.). Retention time is controlled by the stationary phase (molecular sieve material), the flow rate of the carrier gas (He in our case), the dimensions (length and ID) and the temperature of the GC column. The GC column's ID is constrained by the balance between separation efficiency (narrow peak) and sample capacity.

At normal temperatures, \( \text{CO}_2 \) is permanently adsorbed in molecular sieve material, and can lead to loss of \( \text{O}_2 - \text{N}_2 \) resolution. Similarly, \( \text{H}_2\text{O} \) may be trapped in the GC column and affect the retention time of the analyzed gases. Fortunately, the process is reversible, and the GC column can be reconditioned by baking it to 200°C for several hours. To avoid GC column contamination, as mentioned earlier in this chapter, trapping of water and \( \text{CO}_2 \) occurs prior to the sample introduction in the GC column in our experiment.

3.5.3.2 GC box

The temperature of the GC column needs to be closely controlled, as it determines

\(^8\)at the beginning of the experiments, we used a shorter (1 m) GC column, but we replaced it due to a too low resolution between \( \text{O}_2 - \text{Ar} \) and \( \text{N}_2 \).
3.5.3.2.1 Peltier unit

The GC column is cooled with a thermo-electric cooler, also known as peltier element. A peltier element\(^\text{10}\) typically consists of several thermocouples in series mounted between two thermally conductive plates. When a voltage is applied to a thermocouple, it causes a temperature difference between the 2 junctions. This is called the Peltier effect, inverse of the Seebeck effect (basis for thermocouple thermometers).

In our setup, the peltier unit consists of the peltier element itself, a massive heat sink blown by a fan (24 V, 0.35 A) to improve the dissipation of heat, and an insulated sst box (built at the CIC workshop) sitting on the cold anodised aluminium plate of the peltier element (Fig. 3.10). An advanced programmable PID temperature controller (PR-59 Series, Supercool, Sweden) enables a precise temperature control of the GC box by comparing the temperature measured by a platinum resistance temperature (PT1000) with the targeted temperature (\(\simeq 0^\circ\text{C}\)) and regulating the power applied to the peltier element (maximum load: 240 W, 30 V, 8A).

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\(^{10}\)The main advantage of a peltier element is its ability to cool below ambient temperature. However, peltier element's efficiency drops off as the input power rises, often consuming more power than they transport (hence the need of a massive heatsink).
3.5.3.2.2 \( \text{LN}_2 \) pump

Besides the peltier unit, a \( \text{LN}_2 \) pump provides additional cooling to the GC box (Fig. 3.10). This \( \text{LN}_2 \) pump significantly reduces the time needed to cool the GC box. It was added while the former GC column was still in use for 3 main reasons.

- To improve cooling efficiency of the peltier unit. Indeed, the cold plate is very sensitive to change of air temperature. Once exposed to warm and moist lab air, it takes a long time to cool the GC box down. By lowering the air temperature within the GC box, the targeted temperature is reached quickly.

- To reach negative temperatures that the peltier element could not reach alone. Indeed, condensation of water vapour trapped in the insulated GC box releases latent heat during cooling, which increases significantly the time needed to reach negative temperature. It takes up to 1 h for the temperature of the GC box to reach below 0\(^\circ\)C.

- To homogenize the temperature within the GC box. The GC column sits on the cold plate, but its geometry and the heavy heating tape (FGH052-060, 240V, 310W, Omegalux, UK) wrapped around (for baking purposes) reduces the flow of heat energy by conduction from the GC column to the the cold plate. A fan located within the GC box ensures that the vaporized LN cools homogeneously the GC box.

The pumping device consists of a LN dewar, a resistance (10 \( \Omega \)), a funnel, a power supply (Lascar, PSU130, 0-30 V, 1 A), a PID controller (CN7500, Omegalux, UK) and a plastic tubing (ID 6 mm). The resistance is attached to a funnel immersed in a LN dewar (see Fig. 3.11). When a current (6 V, 3.6 W) flows through the resistance, electrical energy is converted into heat energy. The temperature measured by a K-thermocouple sitting on the GC column is compared with the set-point temperature (0\(^\circ\)C). A PID controller allows an electric current to flow through the heating element.
to trigger the LN$_2$ pump until the set-point temperature is reached: a stream of LN droplets is then automatically carried in their gas phase from the LN dewar to the GC box.

**Leidenfrost principle**

Heat dissipated by the 10 $\Omega$ resistance creates a high temperature gradient between the resistance and LN. If the temperature difference exceeds 100°C (Leidenfrost point), LN droplets are hold up by an insulated layer of N$_2$ vapor forming at the hot surface. As thermal conductivity of vapor is low, heat transfer from the resistance's surface to LN droplets is greatly reduced, which enables LN droplets to remain liquid and be carried in their own vapour cushion (Linke et al., 2006; Schmitt, 2006) through a plastic tubing to the GC box. This physical phenomenon is called the Leidenfrost principle.

### 3.5.3.3 Separation validation

#### 3.5.3.3.1 Thermal Conductivity Detector

A thermal conductivity detector (TCD, Vici, USA) measures the difference in thermal conductivity between the sample flow eluting from the GC column and the reference flow. Changes in conductivity are measured only by the change in current required to keep the filament at a constant temperature. The sample flow consists in a mixture of air and carrier gas (He), while only carrier gas flows through the reference channel. The measured difference is proportional to a voltage and a typical output signal is shown in Fig. 3.12. The two gas streams are switched over the filament at a rate of 5 times per second.

**Configuration**

The TCD filament can be permanently damaged if gas flow through the detector cell is interrupted while the filament is operating. As shown in Fig 3.2, the total sample flow out of the TCD amounts to 7.4 cc.min$^{-1}$, of which 5.7 cc.min$^{-1}$ originate directly from the reference flow. Such a configuration efficiently discards this possible source of damage.

#### 3.5.3.3.2 Chromatograms

Fig. 3.12 presents chromatogram showing retention time of O$_2$ (and Ar), and N$_2$. Temperature of the GC column is set to 0°C. Carrier gas is He, with a flow rate of $\approx$28 mL.min$^{-1}$. After release of the sample from the full air trap (T3) to the GC column, O$_2$ elutes after 345 s and ends at 580 s, and N$_2$ elution starts after 825 s. With 4 min between the end of O$_2$ elution and the start of N$_2$ elution, there is enough time for O$_2$ to divert the N$_2$ flow towards the TCD (Fig. 3.12) and out to waste while O$_2$ is being trapped in T4 (refer to section 3.7).

**Baseline**

The baseline variability is mainly due to the communication between the TCD and the computer. At best, the TCD output signal ranges from 0 to 10 V. As the analog
Figure 3.12 – (a) Chromatogram as it appears on the Labview Visual Interface (VI) developed during this thesis. The first peak represents O$_2$ and elutes from 5 min 45 s to 9 min 40 s and the second peak represents N$_2$ eluting at 13 min 45 s. The green curve represents the difference in thermal conductivities between the gases flowing in the sample channel (black line) and the reference channel (red line), fed by He alone. The output signals (mV) are provided by the TCD every 0.2 s and show elution time for O$_2$ and N$_2$ through the GC column used in our setup. (b) Fig. 2 from Barkan and Luz (2003), original caption: chromatogram showing separation of N$_2$ from O$_2$-Ar mixture. He flow rate is $\approx 25$ mL $\cdot$ min$^{-1}$. In their system, 13 minutes separate O$_2$ and N$_2$ elution.

input of the electronic board ("Wasp", PC-control Ltd, UK) used to transmit the signal to Labview doesn’t accept values higher than 2.0 V, we chose to use the 0-1 V output signal of the TCD. As a result, only 128 steps are available to represent the TCD output signal's variations (see Section 3.6), with $\Delta$V between 2 steps reaching $\approx 7.8$ mV. In Fig 3.12, the apparent high variability of the baseline actually translates a $\pm 1$ step variation, caused by the chip card precision. The baseline has typically a standard deviation $\sigma < 5$ mV.

The recording chart of the TCD signal remains systematically blocked for a short while at 500 mV, which is clearly seen in Fig. 3.12. All the TCD measurements show a similar pattern, and suggest an artifact most likely due to an electronic deficiency in the transmission of the TCD output signal to Labview through the WASP electronic card.

The very high precision needed for $^{17}\Delta$ measurements requires N$_2$ to be removed despite its interest$^{11}$. In our setup, the TCD is essential for setting up the GC system, choosing the optimal temperature and carrier gas flow to obtain a excellent separation between O$_2$ and N$_2$. During the collection of a sample, the TCD informs on the elution time of N$_2$, but no O$_2$ peak can be detected. Indeed, to avoid a possible contamination/loss of the sample, the possibly-leaky TCD is not included in the high purity line. The O$_2$/N$_2$ mixing ratio of a sample can not thus be retrieved from the TCD in

$^{11}$Isotopic composition of N$_2$ ($\delta^{15}N$) is used for thermal fractionation corrections (Sect. 1.4.1.2) and picks up rapid temperature changes in Greenland that can be linked to other gas archives like $\delta^{18}O_{atm}$, CO$_2$ or CH$_4$ on a common gas time scale.
our configuration. The TCD also helps us to monitor the stability of the GC unit. A valve switch, a flow variation, or a slight temperature change in the path (GC column or the traps T3 and T4) of the carrier gas indeed modifies the thermal conductivity of the sample flow measured in the detector cell.

3.6 AUTOMATION

This setup was built with the ultimate objective of fully automating the system so that samples and standards can be collected in an identical manner and without the need of an operator. A few steps are missing to complete this goal, from the replacement of a few manual valves by pneumatically-actuated valves, to the implementation and testing of the automated procedure from extraction to collection.

The experimental setup is therefore semi-automated currently, in the sense that it can be remotely controlled under Labview environment (Fig. 3.14), at the exception of (i) a few valves that only need to be opened at the start of the measurements (valves M1, M4, M5 in Fig. 3.2, and (ii) essentially the manual valve that commands the access to the turbo molecular pump12.

Instead of relying on acquisition cards from Labview, device/computer communication is achieved with electronic board from PC-control. They are connected to a USB port of the computer and considered as human interface device, making it easy to install. Dynamic linked libraries containing all the available functions are used to control the board with Labview. The real advantage of this library is that it gives the possibility to combine several boards of different types and build a custom and flexible control system, which is needed for the experimental setup.

Details on the control system of the experimental setup run with Labview can be seen in figures 3.13. The 11 pneumatically actuated valves of the extraction unit (E1 to E11 on Fig. 3.2) are controlled via 11 high voltage capable DC switching outputs of a ”Mini-Bee” type board (supplied with 24V DC power supply (PSU130, 30 V, 30 W, Lascar)), that supply/interrupt a current flow to the solenoid valves (24 V, 30 mA DC) enabling/interrupting the flow of compressed air to the pneumatic valves. Another ”Mini-Bee” board is connected in a similar way to control the 10 valves of the collection manifold (R1 to R10) and R11 (for evacuation of the standard introduction unit). It should be mentioned that the connection is slightly modified as the valves of the collection manifold need to be controlled both by Labview (when collecting the samples) and the MS (when releasing the sample):

1. The switching outputs of the ”Mini-Bee” board are soldered to a female 24 pins D-sub socket.

2. The MS provides 24 V DC external switching outputs (controlled with Isodat,

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12 at pressures higher than 0.1-1 mbar, the primary pump is preferably used to avoid any damage to the turbo pump.
The MS software) that one can physically access at the back of the MS with D-sub cables (24 pins). 2 D-sub cables are connected to the MS sockets JO520 and JO521. These cables are cut and the relevant leads are soldered to the pins of a female D-sub adapter in the same pin configuration as in (1).

3. The leads of the solenoid valves controlling the yield of compressed air are soldered to the pins of a male D-sub adapter with the pin configuration matching (1) and (2).

This design enables a simple switching between the two setups. The block valve (consisting of the 12 solenoid valves) is moved together with LynnOax and it only requires to connect it either to the female D-sub socket attached to the MS or to the Mini-Bee board.

A Digi-Bee card is used to control the remaining valves of the experimental line, including the 4 and 6-port position Valco valves V1 and V2.

Labview communicates with the two pressure gauges PG1 and PG2 (Pirani, Edwards) thanks to a RS232 serial port.

As seen in Sect. 3.5.3.2, the 0-1 V output signal of the TCD is transmitted to an analog input of a "Wasp" electronic board ("Wasp", PC-control Ltd, UK). This analog input is converted to a digital output which is transmitted to Labview using DLLs.

The silicon diode temperature sensor is connected in the same way as the TCD to an analog input of the "Wasp" board to communicate with Labview via DLLs.

\(13\) 2 different D-sub cables are needed to control 12 valves (the 10 of the collection manifold and 2 for the standard introduction) as only 8 pins per MS socket provide 24 V DC.
Figure 3.14 – The $O_2$ line is controlled with Labview. The figures displays the manual interface used to control the opening/closing of the MFC and the pneumatically-actuated valves and cylinders of the system. The upper left part displays the status of the different electronic boards. A value of 0 corresponds to no error. The large green dot on the right controls the opening of the MFC. Note that in another screen are constantly monitored the TCD signal, the temperature of the cryocooler (e.g. Fig 3.15) and the pressure measured at PG1 and PG2.
3.7 **Procedure for extraction and collection of $O_2$ isotopologues**

This section describes the two methods used to collect stable oxygen isotopes from trapped gases in ice cores, with the aim of measuring $\delta^{18}O_{atm}$ only, or $^{17}\Delta_{atm}$, hence the three isotopes of $O_2$. Extraction, purification and collection are similar for both methods, the only difference relating to the separation unit (Sect. 3.7.6). Indeed, when measuring $\delta^{18}O_{atm}$, this step is bypassed as it can be measured in air. However, when it comes to $^{17}\Delta_{atm}$ measurements, the very high precision needed requires to separate $N_2$ from the $O_2$/Ar mixture. This section therefore describes the method applied for $^{17}\Delta_{atm}$ measurements, as it covers all the steps of the procedure. The full procedure excluding extraction takes $\approx 45$ min, similar to the procedure of Barkan and Luz (2003). Note that except the Sect. 3.7.6 on the GC unit, all other sections also apply to $\delta^{18}O_{atm}$ measurements.

3.7.1 **Ice core samples**

3.7.1.1 **Ice core storage**

Ice samples are usually stored in a cold chamber at a maximal temperature of $-25^\circ$C. The $\delta O_2/N_2$ of air trapped in ice core samples is known to decrease with storage time because the $O_2$ molecule preferentially leaks through the ice lattice (Kawamura, 2000). Craig et al. (1988) and Severinghaus and Battle (2006) found that small atoms Ar, Ne and $O_2$ were leaking out, contrary to Kr, Xe and $N_2$, suggesting a size-dependent fractionation during leakage from overpressured air bubbles. This gas loss process appears temperature dependent, as samples stored at lower temperatures ($-50^\circ$C) experience less gas loss (Ikeda-Fukazawa et al., 2005), similar to gas-loss fractionation observed in the LIZ (Sect. 1.4.1.3). It is therefore crucial to keep the storage temperature as low as possible to preserve the air entrapped in ice core bubbles. Consequently, our ice samples dedicated to $^{17}\Delta$ measurements, not measured yet, are stored below $-50^\circ$C to minimize gas loss. Details on gas loss fractionation during storage can be found in Sect 4.6.4.

3.7.1.2 **Ice sample preparation**

Ice samples typically weight 40 g after cutting. Dimensions of the piece are $\approx 2.5 \cdot 2.5 \cdot 7.5$ cm, with the long axis oriented parallel to the ice core so as to average over several annual layers (Severinghaus et al., 2003). With 10% of fossil air, this sample size yields around 4 cc of gas, hence 0.8 cc of $O_2$. This amount of $O_2$ is reduced during expansion of the sample from the sst rod of the collection manifold to the bellows of the ms, but the loss of gas caused by expansion of the sample to the ms bellow is minimized by setting the bellow to its maximum volume ($\approx 40$ cc). In the case of $\delta^{18}O$ ($^{17}\Delta$) measurements, this sample size corresponds to $\approx 40$ mbar (8 mbar) in the bellow in full expansion, i.e. $\approx 1.6$ cc (0.3 cc) STP. The bellow is then compressed to reach a range of pressure that ensures viscous flow conditions throughout the full measurement cycle.
The outer layer (1 to 3 mm) of the sample is cut with a bandsaw in a cold chamber at \(-15^\circ\text{C}\), adjacent to the storage chamber at \(-25^\circ\text{C}\). This minimizes risks of drilling fluid contamination for deep ice cores and fractionation due to gas loss processes by exposing fresh surface. The sample is then cleaned with a synthetic bristle brush and smoothed with a scalpel to remove surface cracks and irregularities. Care is taken to minimize glove contact with the ice sample as handling may weaken the ice (by warming it on the surface before it has annealed) and create fractures causing mass-dependent fractionation (Bender et al., 1995; Bender, 2002; Severinghaus et al., 2009). After cutting and cleaning, the ice sample is put in an pre-cooled \((-25^\circ\text{C})\) extraction flask (Sect. 3.4.3). This step is usually performed in the morning just before the start of the measurements.

### 3.7.2 Pre-operation

#### 3.7.2.1 Conditioning of the analytical line

The extraction line and the 10 rods of the collection manifold are filled with a pure \(O_2\) standard to 300 mbar (\(^{17}\Delta\) measurements) or with Neem_S1 standard (for \(\delta^{18}O\) measurements) when not in operation. This step was added to the procedure because of the systematic poor accuracy observed at the start of a measurement period, and a gradual improvement with successive collections.

Before each use, molecular sieve traps T3 and T4, as well as the GC column (after removal of insulating material that would melt at this temperature) are heated to 200°C for some hours while flushed with the carrier gas (He). This baking step ensures that no water remains within the molecular sieve and enables its regeneration. After the baking step, the He flow is maintained until the start of the measurements to condition the separation unit. In addition, following Barkan and Luz (2003), traps T3, T4 and GC column are baked at 200°C while pumping whenever the molecular sieves are in contact with ambient air.

#### 3.7.2.2 Collection unit

In general, the day prior to measurements, LynnOax is inserted to the cryocooler. A vacuum flange and O-ring mounted on a centering ring are used to connect LynnOax to the vacuum casing of the cryocooler. 4 small clamps fitted with screws ensure a leak-tight connection. Thermal grease (Apiezon N-grease) is added on the copper block of the collection manifold to ensure a good thermal contact with the cryocooler cold station. Without grease, the lowest temperature reached by the cryocooler exceeds 15 K, thus reducing its trapping power. However, too large amount of grease bends LynnOax to the cold station, and make it very difficult to disconnect the collection manifold from the cryocooler after warming to room temperature.
Figure 3.15 – (a) Cooling of LynnOax as recorded on the Labview interface. (b) The operating temperature of the cryocooler is \( \approx 12 \) K. (c) LynnOax heating. Note the transition in the heating process (shown by the black arrow) when cartridge heater \((40 \text{ V}, 40 \text{ W})\) is switched on. Note that the DT-470-CU-12A silicon diode temperature sensor (Lakeshore cryotronics, USA) sensitivity \((S = \frac{dV}{dt})\) is much larger in the 10-25 K temperature range, which explains the sudden decrease in the variability of the signal in this temperature range. The larger variability during warming is due to interferences caused by the operation of the internal cartridge heater.

Once the collection manifold is attached to the cryocooler, LynnOax is connected with a 1/4” VCR meshed gasket to the main line. One hour before the start of the measurements, all sample tubes are evacuated from the standard mixture simultaneously through P2.

It is critical to ensure a good vacuum within the vacuum casing before starting the He cryocooler primarily for safety reasons. Indeed, at 12 K, \(N_2\) and \(O_2\) would freeze in the vacuum casing, then build up an enormous pressure and probably a burst while heating the unit. The volume of the gas phase of \(O_2\), for instance, is \(\approx 840\) times more important than the volume of the solid phase.

Once the pressure in the vacuum casing reads below \(4 \cdot 10^{-2}\) mbar on the pressure gauge PG3, the vacuum shroud is isolated, and a rapid leak check is performed. If no rise in pressure is observed, the He compressor is switched on and cooling of the cold head starts. It takes 90 minutes for the cryocooler to reach 12 K, temperature at which the samples are cryotrapped (Fig. 3.15a). When 12 K is reached, the pressure in the vacuum casing is typically in the \(2.9 \cdot 10^{-4} - 4.5 \cdot 10^{-4}\) mbar range. This is due to the fact that the remaining \(O_2\) and \(N_2\) after vacuum casing evacuation freeze at these temperatures. While the cryocooler always reaches its minimum temperature in 90 min, the latter may vary depending on the initial vacuum pressure within the vacuum casing or, most frequently, on the quality of the thermal contact between the second stage cold station and the collection manifold. The optimal thermal contact is observed when only a thin and smooth layer of grease is added on the copper block. The grease indeed becomes solid at low temperatures, and rough surfaces then probably reduce the area of the copper block in physical contact with the cold station.
3.7.2.3 Extraction unit

While the cryocooler is cooling to 12 K, the extraction dewar filled with ethanol is cooled down to $-24^\circ$C thanks to the PID controlled NESLAB coldfinger. To fasten the cooling process, ethanol is stored beforehand in a cold room at $-15^\circ$C. Temperature is homogenized thanks to a fan located at the bottom of the dewar\(^\text{14}\). The temperature of the cold bath is allowed to vary between $-22^\circ$C and $-24^\circ$C to limit the on-off cycles undergone by the coldfinger. In practice, the temperature of the cold bath vary by less than $2^\circ$C for each sample.

3.7.2.4 Separation unit

This pre-operating step is only necessary for $^{17}\Delta_{\text{atm}}$ measurements, as $\delta^{18}O_{\text{atm}}$ measurements do not require separation of $O_2$ from $N_2$. The GC column is cooled down to $0^\circ$C with the Peltier element and droplets of LN carried in their vapor cushion (see Sect. 3.5.3.2.2) 2 h before the start of the first gas separation to let time for the temperature to stabilize. Traps T3 and T4 are kept in room temperature. The 2 Valco valves V1 and V2 are set to "load" mode, and the carrier gas flows through the GC column at $\approx 28$ ml·min$^{-1}$ out to waste. Typical flow rates can be found on Fig. 3.2.

3.7.2.5 Initial configuration

The initial configuration can be seen in details in Fig. 3.16. Water trap T1 is cooled to $-100^\circ$C with a slush of ethanol and liquid $N_2$. It should be mentioned that the water trap is disconnected from the system after a day of measurement, and dried overnight in an oven set to $150^\circ$C. The $CO_2$ trap T2 is immersed in a LN dewar ($-196^\circ$C) using a double actuated pneumatic cylinder (CD85N20–250B, SMC, Denmark). The entire system, including traps T1, T2, T3 and T4 and the collection manifold, is evacuated through P1 and P2. Once the pressure in the system reaches $5 \cdot 10^{-5}$mbar on PG1 and PG2, a static leak-check is performed and validated if no rise in pressure is observed for 2 min after closing P1 and P2.

3.7.3 Considerations on working standard introduction

Whenever trapped gases in ice cores are collected in LynnOax, two rods are dedicated to working standards collection. Both samples (Sa) and working standards are then measured against an intermediate standard by IRMS as described in Sect. 4.5.5. Working standards are also use for system characterization, stability assessment and daily calibration. Section 3.4.2.3 describes the purging and flushing steps before introducing the standards in the extraction flask. To respect the IT principle and mimic the steps experienced by the ice core sample in the analytical setup, the standard is introduced at a flow rate of 2 ml·min$^{-1}$ above BFI after overhead evacuation. The in-\(^\text{14}\)Note that the fan needs to be switched on simultaneously with the coldfinger. Indeed, the viscosity of ethanol at low temperature prevents the fan from starting below $-20^\circ$C.
Figure 3.16 – Step: initial configuration. Valves E11, L2 to L7, M1, M4 and M5 are opened, enabling evacuation of traps T1, T2, T3 and T4 and the collection manifold, is evacuated through P1 and P2 until the pressure in the system reaches the limit of detection of the pressure gauges (P < 5 · 10⁻³ Pa).

Introduction is performed as follows: the gas standard is allowed to flow through the MFC out to waste (valve R11 opened and L1 closed) for 2 min (more if the flow rate is not stable). Access to pump is then closed and valve L1 opened for standard introduction. After a variable amount of time, depending on the desired standard size (e.g. 2 min for 4 ml), valve L1 is closed.

Different procedures have been tested to assess the fractionation caused by the gas standard introduction, from (1) direct collection in LynnOax after standard introduction, to (2) expansion in the extraction vessel over BFI, via (3) expansion in the glass flask without ice and (4) change in the flow-rate of standard introduction. Introduction (1) and (3) at different flow-rates (4) gave satisfactory results, but it turned out that standard measurements with introduction over BFI (2) were not reliable, possibly due to the presence of dissolved air in the blank ice, as observed by Bock et al. (2010). Sperlich et al. (2013) showed that the presence of dissolved gases in BFI (a different batch produced at CIC too) affected CH₄ measurements (in CF mode) during the melting process of BFI. In contrast, the stability of consecutive extraction of standard gas above melted BFI showed that BFI was fully degassed. A simple test of this effect in our setup would be to collect and measure successive Neem_S1 standards injected first over frozen BFI, then over the same melted BFI, and should be performed in the future to closely follow the IT principle.
Instead of relating the isotope composition of ice core samples to the working standard Neem_S1 over bfi because of the aforementioned considerations, Grzymala-Lubanski (2015) chose to reference the samples to Neem_C1 standard (introduced in the standard bellow of the DI system), measuring neem Holocene ice core samples from the same depth to control the accuracy of the rice measurements. Such a "choice" (which was forced by the large $\delta^{18}O$ variability of the standards introduced over bfi), came with pros and cons. On one hand, as pointed out by Schmitt (2006), the best, but utopic standard hitherto, would be artificial ice with \( \leq 10\% \) air inclusions of known composition formed in the same way as air bubbles form during ice formation. One could thus argue that this procedure would respect even more closely the IT principle than the standard introduction over bfi, as the process of air entrapment within the ice would be similar for both sample and neem quality standards. On the other hand, this choice obviously meant that besides the uncertainties in the true value of the standard itself, fractionation processes associated with transport in firn, bubble close-off, ice core recovery and ice core storage are modifying $O_2$ isotope ratios and need to be corrected for, causing a loss in precision and accuracy.

3.7.4 Sample overhead evacuation

Figure 3.17 – Step: sample overhead evacuation. Valves L2 and P2 are closed once vacuum in the system is established, monitored by PG1 and PG2. Valve E1 is opened to enable sample overhead evacuation.

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Just before the start of the measurements, the pre-flanged glass flask containing the ice sample is brought from the cold room to the lab freezer, both at $-25^\circ$C. As soon as the system evacuation is completed, the 6 mm glass tube of the flask is connected
to the 1/4” nickel plated UltraTorr fitting attached to valve E1 of the extraction line with a Viton O-ring. The glass flask is then immediately immersed in the pre-cooled ethanol dewar (3.7.2.3), whose temperature is stabilized to \(-23 \pm 1^\circ\text{C}\) by the PID controlled neslab coldfinger. The temperature of the extraction bath must be stable as it controls the sublimation rate of the ice sample (Fig. 3.4). Indeed, at this temperature, saturated vapour pressure above the ice sample, \(e_i\), reaches up to 1 mbar, creating a sublimation flux that helps cleaning of the ice sample surface and improves pump-down time during sample overhead evacuation (Sect. 3.4.4).

Figure 3.17 describes the system configuration during sample overhead evacuation. Once vacuum is reached in the system in its initial configuration (Fig. 3.16), the separation unit and collection unit are isolated and sample overhead evacuation starts through the cold water and \(\text{CO}_2\) trap (through P1).

### 3.7.5 Ice core sample extraction

Overhead evacuation is complete when the pressure read on PG1, located after the water trap, where all water vapor should removed from the gas stream, reduces to \(5 \cdot 10^{-5}\) mbar. Then the glass flask is isolated, and the cold ethanol dewar is replaced by a warm bath heated to 40°C. The warmer the warm bath, the higher the flux of water vapor, and the more efficient the gas extraction. Note however than a too high flux of water may clog the water trap or cause fractionation in the water trap due to occlusion of gases within the frozen ice (Sect. 3.4.4). Moreover, less dissolved \(\text{O}_2\), \(\text{N}_2\) and Ar should remain in the water as solubility of these gases decreases with increasing temperature (at least in this 280-320 K temperature range), thereby improving extraction efficiency.

Regarding \(\delta^{18}\text{O}\) measurements, the next step of the analytical procedure is described in Sect. 3.7.7. Indeed, the separation unit is bypassed by connecting valves L2 to L7, as the dry and \(\text{CO}_2\) free \(\text{O}_2\)-\(\text{N}_2\)-Ar gas mixture is directly cryotrapped in the sample rod of the collection manifold.

### 3.7.6 \(\text{O}_2\)-Ar / \(\text{N}_2\) separation

#### 3.7.6.1 Focusing the sample in full air trap T3

Once the extraction vessel is immersed in the water bath, molecular sieve trap T3 is isolated from the main line by closing valves L3 and L4. Trap T3 is then immersed in a LN dewar. Note that the LN level in the dewar is carefully check to ensure similar conditions for all the samples. Then, after checking that pressure read in PG1 is under-range, extraction valve E1 and valve L2 are opened to start transfer of the sample to trap T3. At this temperature, molecular sieve acts as a cryo-pump that drives the pressure gradient from the extraction vessel to trap T3. The trapping process takes \(\pm8\) min and trapping is considered complete when pressure read on PG1 reaches 3...
Figure 3.18 – Step: focusing the sample in the molecular sieve full air trap T3. After sample overhead evacuation is completed (PG1 needs to reach under-range values), valve E1 is closed and the cold ethanol bath is replaced by a warm water bath at 40°C. Then trap T3 is immersed into LN by lifting the LN dewar using a pneumatic cylinder after isolating the trap by closing L3 and L4 (note that L2 is already closed). Evacuation of the transfer line is stopped by closing P1, and the sample is transferred to trap T3 while melting by opening E1 and L2. Meanwhile, trap T4 and collection unit are evacuated through P2 to ensure vacuum conditions in the rest of the system.

3.7.6.2 Switching sequence from load to injection mode

After trapping is complete, residual air is evacuated through P1. Then valves L2 and L7 are closed to isolate the separation unit and valve L3 and L4 are opened. At this time, He flows through the GC column at \(\geq 28 \text{ ml·min}^{-1}\) out to waste while T3 (at LN temperature) and T4 (at room temperature) are under vacuum. The next step consists in switching successively (as fast as possible) Valco valves V2 and V1. Figure 3.19 describes the effect of switching V1 before V2 and inversely.

**V1 then V2** By switching V1 first, He from the GC column is simultaneously sucked into the outlet of T3 and the inlet of T4, both traps being under vacuum (Fig. 3.19B1). With this switching sequence, the carrier gas flows directly from V2 out to waste. As soon as V2 is switched to injection mode (Figure 3.19C), the carrier gas is directed towards T3 inlet. With this switching sequence, the carrier gas needs to fill T3 and T4 before the reverse flow established into the waste line is stopped. At a rate of 28 ml·min\(^{-1}\),
it takes a bit less than 1 min to fill both T3 and T4 traps (\(\sim 12.5 \text{ cm}^3\) volume each accounting for the volume of the valve), time during which ambient air could potentially contaminate the line.

By switching V2 first (Fig. 3.19B2), the He flow is directed through the GC column, T3 then T4. Instead of creating a reverse flow of He towards T3 outlet (other switching sequence), trap T3 starts immediately to be filled with He from its inlet. This enables a faster stabilization of the carrier gas flow. Once V2 is switched to injection mode, the path of the carrier gas goes from GC column-T3-T4 to T3-GC column-T4 and out to waste. Similar to the other sequence, a reverse flow in the waste line occurs as long as the carrier gas has not reached trap T4. The change in the flow is confirmed by the decrease of the He flow in the sample channel of the TCD. Indeed, the TCD configuration ensures that a flow of 5.7 ml·min\(^{-1}\) of He from the reference channel outlet feeds permanently the sample side of the TCD, in addition to a flow of 1.7 ml·min\(^{-1}\) from the separation unit (Fig. 3.2). After switching, the sample flow rate decreases by 1.7 ml·min\(^{-1}\), from 7.4 to 5.7 ml·min\(^{-1}\), strongly suggesting that no more He flows through the capillary connecting the separation unit to the sample channel of the TCD. The following paragraph describes how to overcome this issue.

To summarize, we selected the B2 switching sequence because it prevents a reverse flow of He from the GC column to T3, enabling a faster carrier gas flow stabilization. However, both switching sequences B1 and B2 (from load of the sample into T3 to
Figure 3.20 – Step: Separation of $N_2$ from the $O_2$-Ar mixture. Trap T3 is warmed to room temperature while T4 is cooled down to LN temperature. As a result, the gas mixture desorbed from the molecular sieve is injected into the GC column, where separation takes place. The $O_2$-Ar mixture is then adsorbed in trap T4.

its injection in the GC column) have the common caveat of causing a reverse flow into the waste line (a flow meter located at the outlet of the waste line sees the flow rate drop to 0 ml·min$^{-1}$) and thereby contaminating the system with ambient air, as already noted by Barkan and Luz (2003). Therefore it is critical for the waste line to have a large volume (>50 cm$^3$) to ensure that only He would be sucked into T4 by its outlet after switching the Valco valves. By precaution, valve L6 is closed immediately before switching V2 and V1 to injection mode, so that no gas can enter into trap T4 from its outlet. Besides, the reverse flow in the waste line is also reduced as there is not a 12.5 cm$^3$ evacuated volume to fill anymore. The valve is reopened after ≈ 2 min, once the He pressure within the trap exceeds the pressure in the waste line. It then takes a couple of minutes until the flow of carrier gas stabilizes to its equilibrium value. At this point, injection of the sample into the GC column can start.

3.7.6.3 Desorption (T3), separation (GC) and adsorption (T4)

The dry air mixture adsorbed into the molecular sieve trap is desorbed by heating T3 to room temperature. Warming of the trap is automatically controlled thanks to a push-for "on" switch closed mechanically during removal of the LN dewar from trap T3 (see Fig. 3.9 for details). Meanwhile, trap T4 is cooled to $-196^\circ$C by immersing the latter in a LN dewar. When T3 reaches room temperature, the gas mixture is injected together with the carrier gas in the GC column. After elution, the $O_2$-Ar mixture is
trapped in trap T4 (Fig. 3.20). Once O₂-Ar elution is complete, Valco valves V1 and V2 are switched back to load mode to divert the N₂ flow out to waste (Fig. 3.21).

As described in Sect. 3.5.3.3.2, the O₂-Ar mixture elutes after 345 s and ends at 580 s, while N₂ elution starts after 825 s. With 4 min between the end of O₂ elution and the start of N₂ elution, there is enough time to divert the N₂ flow towards the TCD and out to waste while O₂ is still being adsorbed in trap T4. Valves V1 and V2 are switched once the elution mid-term point is reached so that the N₂ stream is diverted from the GC column out to waste. The success of the separation process can be rapidly assessed with the TCD signal. Indeed, if the switch were to occur too early, the tail of the O₂-Ar peak would be detected by the TCD; if it were to occur too late, no N₂ peak would be recorded. The chromatogram shown in Fig. 3.12 represents a typical successful O₂-Ar separation from N₂.

### 3.7.7 Sample collection

#### 3.7.7.1 $\delta^{18}O$

The trapping time is consistent between collections rods and days of measurements.
Typically, for a dry air sample of \( \geq 4 \text{cm}^3 \), it takes 10 min to reach a pressure (as read on PG2) of \( 10^{-2} \) mbar (efficiency of sample collection: 99.9%) and 15 min to reach \( 2 \cdot 10^{-3} \) mbar (99.99%).

**ICE SAMPLES**

The fossil air samples dedicated to \( \delta^{18}O \) measurements are collected in a sample rod of the collection manifold while melting the sample. During transfer the pressure in the main line reaches an equilibrium of about 3 to 5 mbar between the gas released from the melting ice and the pumping power of the rod. Collection lasts until the pressure gauges PG1 and PG2 show \( \geq 1\% \) of the equilibrium pressure value, in order to collect up to 99% of the extracted sample gas.

**COLLECTION TIME**

A potential source of error, resulting from sample fractionation, can be caused by an incomplete collection of the sample in the collection tube. To investigate this the working standard freezing time was increased to collect up to 99.999% of the extracted air (collection stopped when the pressure in the system is below \( 5 \cdot 10^{-4} \) mbar), which did not modify the measured \( \delta^{18}O \) values. This suggests that there were no fractionation effect caused by an incomplete collection.

### 3.7.7.2

Before the transfer of the \( O_2 \)-Ar mixture to the sample rod of the collection manifold, residual He in T4 trap is pumped away while maintaining T4 at LN temperature. The access to pump (P2) is then closed, while L7 and one of the valve of the collection rod (R1 to R10) are opened. Meanwhile, T4 is warmed to room temperature (30 s) to release the sample. The pressure read on PG2 immediately after sample release typically lies the 5-8 mbar range then decreases until a threshold pressure is reached around 0.3 mbar after \( \geq 5 \) min. The role of water vapor was quickly discarded as it would have frozen at these temperatures. Besides, no water vapor is present in this part of the system, as it is located after the \( \text{H}_2\text{O} \) trap. To understand what causes this threshold pressure, 2 different experiments were performed. First, two collection rods were used to collect a sample. The pressure in the system in this configuration was similar, suggesting that the high pressure was not due to a lack of pumping power of the cryocooler. This was further confirmed by a blank experiment, where the same threshold pressure was observed at the end of the collection. Based on these tests, we concluded that the pressure plateau is probably due to residual He in the trap T4 and transferring line, which is not trapped at 12 K.

### 3.7.8 Warming the collection manifold to room temperature

Once collection of samples and standards is completed, the He cryocooler is switched off. Then, with the help of the internal heater (40W, 40 V), the collection manifold is warmed to 25 °C. Once room temperature is reached according to the temperature sensor of the cryocooler, a delay of 30 min is observed before venting the vacuum casing. Indeed, the cartridge heater is inserted within the copper cup on which the
temperature sensor is attached. Thereby, transfer of heat to the temperature sensor (and the copper block of the collection manifold) is efficient given the high thermal conductivity of copper, but the temperature of the vacuum casing itself is still much lower, vacuum acting as an insulator and only allowing weak radiative heat transfer from the cartridge heater.

If the vacuum casing is vented too early, massive condensation of water vapor occurs on the wall of the vacuum casing. As a matter of fact, even after the 30 min delay, water vapor condensation occurs on the walls, but to a lesser extent.

In summary, the collection manifold can be disconnected from the cold head of the cryocooler after \( \approx 2 \) h. This may seem long, but note that a more efficient heating of the cryocooler would not shorten the period of time needed between the end of the collection and the start of \textit{IRMS} measurements, as a couple of hours are usually required for sample rod homogenization in the sample tube after warming. Note however that this step can vary from 40 min (Barkan and Luz, 2003; Landais et al., 2012) to a full night\(^{15}\) (Kawamura et al., 2003).

As mentioned above, the silicon diode sensor attached to the copper cup of the cold station is not representative of the temperature of the vacuum casing. Therefore we monitor its pressure for additional control. We observe systematic patterns during the heating (cooling) procedure, for instance a sudden rise (drop) of pressure occurring when \( N_2 \) and \( O_2 \) trapped in the vacuum shroud reach their gas phase. From this time on only, the warming procedure could be fastened by venting the vacuum casing with dry \( N_2 \), or dry air, thereby allowing efficient heat transfer by conduction.

### 3.7.9 LynnOax Transfer to the Mass Spectrometer

LynnOax is transferred to the \textit{ms} and attached to the the sample bellow of the \textit{di} system with the usual UltraTorr fitting with Viton O-ring. From this point, the measuring sequence is fully automated and described in Chapter 4.

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\(^{15}\)the sample consists of 300 g of ice, vs 40 g in Landais et al., 2012’s study.
Bibliography


4 Mass spectrometry

4.1 INTRODUCTION

The $\delta^{18}O_{\text{atm}}$, $\delta O_2/N_2$, and $\delta^{15}N$ of twenty-one shallow neem ice core samples from the same depth (331±1 m) were extracted with the experimental line presented in Chap. 3 by Grzymala-Lubanski (2015), used as quality control standards for rice (Roosevelt Island Climate Evolution) ice core samples (Sect. 4.5.5). They were subsequently measured by IRMS. The neem shallow samples provide valuable information on the stability of the system and its ability to reproduce ice core measurements. In this chapter, we thus take benefit of the neem ice core measurements to assess the performance of the analytical system, which includes the extraction line and mass spectrometry measurements. We also show that neem samples were affected by gas loss processes, as inferred from $\delta^{18}O_{\text{atm}}$, $\delta O_2/N_2$ and $\delta^{15}N$ variations of the 21 replicates. After corrections for gravitational (Sect. 4.6.3.1), thermal (Sect. 4.6.3.2) and gas loss (Sect. 4.6.3.3) fractionation, the precision of ice core measurements with the analytical system is estimated as $\sigma = 0.021\%$ with error propagation ($\sigma = 0.008\%$ without).

This chapter introduces the principle of IRMS in Sect. 4.2, with a focus on the DI mode (Sect. 4.4). Section 4.5 focuses on the development of the protocol and the automation of IRMS measurements, while Sect. 4.6 details data post-processing, i.e. the sequence of corrections applied to the measured $\delta$ values. Finally, Sect. 4.6.7 assesses the quality of the analytical system based on 21 late Holocene neem ice core samples from the same depth.

4.1.1 LASER SPECTROMETERS VS MASS SPECTROMETERS

Ideally, ice core gases analysis should take place in the field, in the science trench just where the ice core is drilled, thereby avoiding possible contamination, partial melting and/or gas loss during ice core transport and storage. This is happening nowadays with laser spectroscopy techniques1, allowing for instance high-resolution online measurements of greenhouse gases mixing ratios (Chappellaz et al., 2013) and water isotopic ratios (e.g. Gkinis, 2011) from ice cores in a field-based setting, with the analyzed gas stream originating directly from a continuously melting rod. However this technique cannot be applied to molecular $O_2$ isotopic measurements, as the $O_2$ molecule does not absorb in the near-infrared region.

Instead, measurements of $O_2$ isotopes described in this thesis are made with a Delta V Plus Advantage (ThermoFisher) IRMS. IRMS usually enables two operating modes,

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1The operating principle is described briefly: vibrational or rotational motions of all molecules with three or more atoms, thus including $CO_2$, $CH_4$, $N_2O$ or $H_2O$ isotopocouples, induce a net change in the dipole moment of the molecule, allowing absorption of IR energy at wavelengths that correspond to the transition energy between two quantum mechanical energy states, called absorption lines (Balslev-Clausen, 2011). The absorption spectrum at these long wavelengths is unique for each isotopocouple as the energy states depend on the masses, configurations and binding energy of the atoms in the molecule. Isotopologues of a same molecule can thus be distinguished based on their mass differences.
and continuous flow. In CF mode, the IRMS is alternatively fed by a stream of standard or sample gas, with the help of a carrier gas and an open split. This offers a higher temporal resolution but lower precision compared to measurements of discrete samples in DI mode, as the sample is measured several times against the standard to achieve a very high precision.

4.2 Mass spectrometry basics

The MS enables the separation of isotopologues according to their mass, and consists essentially of three parts: an ion source, a mass analyser and a detector (Fig. 4.1). The sample and reference gases are introduced in the sample and standard below, resp., of the MS. Thanks to the changeover valve, sample and standard gases are alternatively introduced into the ion source of the MS or diverted to waste through a capillary, ensuring stable flow conditions. Gas molecules are ionized in the ionization chamber by an electron beam produced by a heated tungsten filament. The ionized molecules (charge \( q \)) are then focused with focusing plates and accelerated to several kV by a voltage difference (\( V \), in volts). The kinetic energy of a charged particle can be expressed as the product of \( Vq \) such as:

\[
\frac{1}{2}mv^2 = Vq, \tag{4.1}
\]

where \( v \) is the velocity of the charged isotopologue. The ionized molecules are then deflected by a magnetic field according to their mass to charge ratio (noted m/z hereafter) and their velocity. Indeed, the radius of curvature \( r \) of the charged particle's trajectory can be expressed as follows:

\[
r = \sqrt{\frac{2mV}{qB^2}}, \tag{4.2}
\]

where \( B \) (gauss) is the magnetic field. Equation 4.2 shows that a heavier isotopologue will move along a curved trajectory having a longer radius than a lighter one. It also shows that increasing the high voltage and/or decreasing the magnetic field leads to a higher \( r \), i.e. a weaker deflection. In a MS, it is possible to control both \( V \) and \( B \), which thereby enables a large selection of masses to be measured. However, during a set of measurements, \( V \) and \( B \) are kept constant and stored in the gas configuration corresponding to the gas to be measured, e.g. \( O_2 \), \( N_2 \), or \( CO_2 \) isotopologues. The detector consists in an array of Faraday cups located along the focal place of the MS to allow a simultaneous collection of isotopologues, e.g. m/z 32, 33 and 34 for \( O_2 \). The ions hitting the Faraday cup are neutralized by electrons flowing from ground to the cup. This flow of electron generate a current, which is first amplified then attenuated in an amplifier. It is the attenuation of the amplified current, controlled by a resistance, which gets converted into pulses in a voltage-to-frequency converter. The pulses are counted over a preset integration time, the result of which is collected by a processor and sent to the software of the MS, Isodat, as a signal in Volt, used to calculate isotope ratios. The amplifiers collecting the rare ionized isotopologues (e.g. m/z 33 or 34 for \( O_2 \)) are equipped with low resistances while high resistances are used for the abundant isotopologues so as to match natural isotopic abundances (Sect. 4.3).
4.3 Delta V Advantage Isotope Ratio Mass Spectrometer

During the first years of this PhD thesis, oxygen isotope ratios were measured on a Delta V Plus (Thermo Fisher) IRMS, equipped with 7 Faraday cups enabling the measurement of atmospheric air (masses over charge (m/z) 28, 29, 32, 33, 34, 36 and 40), $N_2$ (m/z 28, 29 and 30) or CO$_2$ (m/z 44, 45 and 46). This 7-cups configuration was advantageous as this enabled simultaneous collection of O$_2$ isotopologues together with $^{14}$N$^{14}$N, $^{15}$N$^{14}$N and $^{40}$Ar, which are needed for correcting the measured O$_2$ isotope ratios (see Sect. 4.6).

After a couple of years, we decided to exclusively dedicate the Delta V Plus to CO$_2$ measurements, and another IRMS, a Delta V Advantage (Thermo Fisher) to O$_2$ measurements. This IRMS, originally dedicated for $H_2O$ measurements, needed maintenance:

- the DI system was contaminated with oil that had been introduced through the pumping system, probably after a power outage. Indeed, if the MS is not vented before shutdown, oil from the rough pump can be sucked in the DI system, driven by the high vacuum in the DI line. The whole pumping system, the DI block valves and tubings were consequently unmounted and ultrasonic cleaning of sst parts was applied to remove grease and oil traces.

- the O-rings of half of the block valves that control the DI system, including the
change-over valve, had become stiff. As a result, cracks in the O-ring caused massive internal leakage within the d1 system, as the compressed air pressure was too low to properly close the pneumatically-actuated valves of the IRMS, which are normally open. Besides, a few gold ring and gold gaskets of the block valves had to be replaced too, as they were causing external leakage.

The Delta V Advantage is equipped with 5 Faraday cups. In this collector configuration (universal triple collector + HD), 2 cups (1 and 5) are dedicated to m/z 2 and 3, that is the two stable isotopes of molecular hydrogen, (¹H) and deuterium (²H¹H). Their large relative difference in mass to charge ratio requires these 2 cups to be distant from each other. As a result, they can only be used for hydrogen isotope measurements. Depending on the selected gas configuration, the 3 remaining cups can simultaneously collect:

- N₂ isotopologues, ¹⁴N¹⁴N⁺ (m/z 28) and ¹⁵N¹⁴N⁺ (m/z 29) or CO isotopologues, ¹²C¹⁶O⁺ (m/z 28), ¹³C¹⁶O⁺ (m/z 29) and ¹²C¹⁸O⁺ (m/z 30).
- CO₂ isotopologues, ¹²C¹⁶O¹⁶O⁺ (m/z 44), ¹³C¹⁶O¹⁶O⁺ and ¹²C¹⁷O¹⁶O⁺ (m/z 45), ¹²C¹⁸O¹⁶O⁺ (m/z 46).
- O₂ isotopologues, ¹⁶O¹⁶O⁺ (m/z 32), ¹⁷O¹⁶O⁺ (m/z 33), ¹⁶O¹⁸O⁺ (m/z 34).

The main drawback of this collector configuration, compared to the one of the Delta V Plus, is caused by its inability to measure simultaneously O₂, N₂ and Ar. They can nonetheless be measured separately by "peak jumping", where the magnetic field is modified while the high voltage is kept constant. However, this procedure lengthens the sequence of measurements and imposes more data processing. Besides, the ionization efficiency of the Delta V Advantage is lower (1200-1500 molecules·ions⁻¹) than the Delta V Plus (800-1100 molecules·ions⁻¹), which translates into a lower sensitivity.

The ionized molecule hitting a Faraday cup transmits an electric charge that is then amplified in order to balance the abundance of the isotopes collected in the different cups. Because of a too small amplification of the electric signal associated with O₂ isotopologues, especially ¹⁷O¹⁶O⁺ (m/z 33), resistors were replaced. Following this change, resistors of 10⁸Ω, 10¹²Ω and 3 · 10¹¹Ω are associated with the Faraday cups tuned to collect m/z 32, m/z 33 and m/z 34 in the O₂ gas configuration, respectively.

4.4 Dual Inlet System

The d1 system of a IRMS is an ultra-clean device consisting of SST tubes, capillaries, connectors, gauges, and valves, of all metal design, with wetted surfaces being either from SST (body and membranes) or gold (gaskets, seals). Stable isotope measurements in d1 mode are performed by often and quickly comparing the ion current ratio of a sample with the one of a standard and by reporting the relative deviation to the

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²here we do not distinguish between charged isotopomers such as ¹⁷O¹⁶O⁺ and ¹⁶O¹⁷O⁺
standard in the usual delta notation. IRMS are indeed designed to compare ion current ratios rather than absolute ion currents in order to achieve a very high precision Brand1996. The core of the δ1 system consists in the changeover valve and the variable volume of the sample and standard reservoirs (Werner and Brand, 2001). Together, they allow an identical treatment of the sample and the standard during the analysis, in line with the IT principle.

The changeover valve enables an uninterrupted flow of sample and standard gas by alternatively diverting the flow to the ion source of the IRMS or to the waste line, both maintained under very high vacuum (2 to 6·10⁻⁸ mbar). This fast switching, repeated several times, between the sample and the standard (a cycle) during a measurement run cancels out instrumental effects like temperature drifts or fluctuations of sensitivity over time (McKinney et al., 1950; Werner and Brand, 2001), and thereby enables high-precision measurements.

The transfer of gas from the variable volume to the changeover valve occurs through 2 thin capillaries (≥1.5 m, 0.1 mm ID). A pressure higher than 15 mbar at the capillary inlet, obtained by adjusting the variable volumes of the sample and standard reservoirs, ensures viscous flow conditions. Such conditions are critical to avoid isotopic fractionation in the reservoir during the gas transfer to the ion source of the IRMS. Ensuring viscous flow thus imposes a minimal sample size as the amount of air (or pure O₂) in the δ1 bellows (after full compression) must be sufficient to reach 15 mbar even at the end of the measurement cycle. With these variable volumes, the standard and sample ion beams (corresponding to the most abundant isotopologue, e.g. ¹⁶O¹⁶O for O₂) can be precisely balanced, thereby minimizing the loss of precision due to the "linearity" of the ms. However, the sample and standard major ion beams usually get unbalanced with time, requiring correction (Sect. 4.6.1).

4.4.0.1 Sensitivity versus linearity

Adjusting the source parameters and focusing the beam is performed every time the ion source is opened, usually after a filament replacement. There are two optimal settings, one favoring the linearity, the other the sensitivity of the IRMS. Linearity focusing requires a high extraction voltage in order to efficiently extract the ions out of the ionization housing. This leads to less collisions between molecules and ions in the ion source and to a higher isotope ratio linearity. Usually, linearity is favored in CF mode, where large differences in sample and standard beam voltages can occur. On the other hand, sensitivity is favored in δ1 mode. Indeed, linearity corrections are minimized (but still exist) in this mode, as sample and standard voltages are balanced by adjusting the pressure of the variable volumes before the measurements. Sensitivity focusing requires a low extraction voltage to maximize the time spent by the ions

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³As a rule of thumb, the mean free path of a gas molecule should not exceed 1/10th of the capillary dimensions to be in viscous flow conditions

⁴Linearity can be seen as the dependence of the delta value to the intensity of the signal.

⁵a batch of THERMOFISHER filaments proved to be faulty
in the ionization housing. This setting aims at optimizing ionization efficiency. For our measurements performed in DI mode, we chose however to favor linearity over sensitivity to minimize corrections caused by pressure imbalance. Besides, linearity settings also reduce the chemical slope corrections (Sect. 4.6.2), as already observed by Severinghaus et al. (2003).

4.5 Measurements

This section focuses on the protocol associated with measurements of $\delta^{18}O$ and $^{17}\Delta$ in DI mode. It includes the minor changes made on the MS to improve precision (Sect. 4.5.2), a typical ice core measurement sequence, as well as the automated procedures developed under ISL (language from the IRMS software Isodat) to measure the collected samples (Sect. 4.5.3).

4.5.1 Dual Inlet measurements: cycle, block and run

The ionized molecules hitting a Faraday cup transmit an ion current signal (nA) that is then amplified in order to balance the natural abundance of the isotopes collected in the different cups (see Sect. 4.4). To the ion current signal corresponds a voltage between 0 and 50 V (with a Delta V Advantage MS). In the following $V_{sa}$ and $V_{std}$ represent the sample and standard beam voltage, resp., on mass (m/z) m.

The electronic noise on each Faraday cup is measured once before a period of measurements and kept constant over this period. This is a tiny contribution, denoted $B^m$ for background of the Faraday cup collecting mass m/z m.

In DI mode, the $\delta^{18}O$ value of a cycle is calculated by Isodat in the following way:

$$\delta^{18}O = \frac{\delta^{18}O_a + \delta^{18}O_b}{2}, \quad (4.3)$$

where

$$\delta^{18}O_a = \frac{(V_{34\text{sa}1} - B^{34})/(V_{32\text{sa}1} - B^{32})}{(V_{34\text{std}1} - B^{34})/(V_{32\text{std}1} - B^{32}) - 1}, \quad (4.4)$$

$$\delta^{18}O_b = \frac{(V_{34\text{sa}1} - B^{34})/(V_{32\text{sa}1} - B^{32})}{(V_{34\text{std}2} - B^{34})/(V_{32\text{std}2} - B^{32}) - 1}, \quad (4.5)$$

The two standard measurements of a cycle (std1 and std2 for cycle 1, then std2 and std3 for cycle 2, etc) are averaged to normalize for instrument drift (Severinghaus et al., 2003).

A measurement cycle consists in 3 steps: simultaneously integrating $V_{34\text{std}1}$ and $V_{32\text{std}1}$ for 16 s, then $V_{34\text{sa}1}$ and $V_{32\text{sa}1}$, and finally $V_{34\text{std}2}$ and $V_{32\text{std}2}$. An idle time of 16 s enables the flow to stabilize after every switch between the sample and the standard. The cycle sequence is repeated 16 times, defining a block. Idle time, integration time and number of cycles are chosen based on zero-enrichment tests to optimize measurement precision.

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The $\delta^{18}O$ value of a block represents the average of 16 cycle $\delta^{18}O$ values, excluding outliers, i.e. cycle $\delta^{18}O$ values that don't lie within two $\sigma$ of the mean block value (Dixon outlier test performed by Isodat). This block $\delta^{18}O$ value corresponds to the evaluated data of Isodat.

The $\delta^{18}O$ value of a run is defined as the average of 3 blocks, that is 48 cycles (or less if there are outliers). The standard deviation of the 3 $\delta^{18}O$ block values defines the precision of the run.

4.5.2 Changes on the mass spectrometer

A few changes were done on the IRMS in order to better monitor the vacuum in the DI system and as an attempt to improve the precision of the measurements:

- The pressure gauge (noted PG hereafter) of the DI system is installed by default in the fore vacuum pumping line, which means that pressure in the DI system can only be monitored while pumping with the rough pump. In order to monitor the pressure in the line at any time, the pressure gauge location has been modified. It lies therefore just before the block valve controlling the access to the high vacuum or low vacuum line. The real advantage of this modification arises from the possibility to use a pressure threshold instead of a time threshold to control the quality of the vacuum in the automated measurement sequence. It would be advantageous to replace the PG (limit of detection at $10^{-3}$ mbar) with a more sensitive one to be able to detect very small leaks as the pressure in the DI line is usually well below $10^{-3}$ (as high vacuum is provided by a turbomolecular pump).

- In the original configuration, the two bellows of the DI system are connected together with a $1/4”$ sst line. This line is also connected to the low and high vacuum pumps of the DI system. As a consequence, every time the DI system sees atmosphere (e.g. when connecting a device to the sample inlet), moist lab air containing trace gases is evacuated through this line. Besides, with the aforementioned modification, a potential contamination may occur through the pressure gauge. To avoid using this potentially “dirty” line when transferring standards from the right (standard) inlet of the MS to the left bellow (e.g. for zero-enrichment tests), a "clean" $1/4”$ sst line has been installed which connects the sample cross to the standard cross of the DI system. This clean line is kept closed when lab air is introduced in the DI line and is only used to transfer standard gas from one side to the other.

- As suggested by Severinghaus et al. (2003), we wrapped the bellows, block valves and DI lines with insulating material to limit the effect of short term temperature fluctuations and minimize thermal fractionation during the transfer of the sample from LynnOax collection rod to the sample bellow of the IRMS.
4.5.3 Automation of irms measurements

The principle of identical treatment (IT principle) by which samples and reference materials (RMs) are processed in an identical manner calls for an automated measuring sequence of $O_2$ isotopologues, which reduces operator-related errors (but not programming ones). Mass spectrometry measurements are performed with the software Isodat, and the script developed to control the automated sequence is thus written with the programming language from Isodat (isl).

4.5.3.1 Sequence and method

Fig. 4.2 represents an example of sequence of ice core measurements run automatically. The sequence starts with 2 zero-enrichment runs. These runs do not only estimate the internal precision and stability of the ms, but also condition the DI lines of the ms with standard gas (Neem_C1 for $\delta^{18}O_{atm}$ measurements). Besides, this allows the samples collected in LynnOax multiport to have a sufficient time to equilibrate after warming from 12 K. The zero-enrichment tests at the end of the sequence (usually 2 runs but 1 row is missing in Fig. 4.2) are not systematically performed, but can be useful to check whether a drift of the isotopic composition of the standard occurred during the ice core sample measurements.

$O_2$ isotope ratios (1 run of 3 blocks) and $N_2$ isotope ratio (1 block) of samples collected in rod 3, 2, 1, 7, 8, 9, 10 are successively measured in this sequence, resulting in 28 sample blocks. To each block (or row) correspond one method file, defined in the rightmost column of the sequence. In Fig. 4.2, two methods files are used throughout the whole sequence. One (LynnOax_automated_d18O2N2.met) dedicated to $O_2$ isotopologues (and $\delta^{18}O_2/N_2$ via "peak jumping"), the other (LynnOax_automated_d29N2.met) to $N_2$ isotopologues. Cycle numbers, idle and integration times are defined in the method file, as well as the standard parameters (like its delta-value w.r.t. the isotope scale of reference, see Sect. 3.4.2.2) and settings for the pressure adjustment (called PA hereafter), background and peak center procedures (Sect. 4.5.3.2). Besides, an isl script is attached to each method.

The flow diagram presented in Fig. 4.3 describes the successive actions performed before, during and after a block of $O_2$ isotope ratio measurements. The different columns of the sequence (Fig. 4.2) represent parameters that the operator must set for each measuring block before the start of the automated sequence as they are interpreted by the isl script. Depending on their values, different actions are performed during the block, as described in Sect. 4.5.3.2.

---

6The number of rods measured and their order may differ according to the experiments. A few rods were permanently discarded, because of internal leakage occurring probably through the pneumatic valves to the ring of LynnOax
Figure 4.2 – An example of sequence dedicated to $\delta^{18}O$ measurements of ice core samples overnight. The sample measurements are bracketed by 2 runs of 3 blocks of zero-enrichment tests. For each measuring block (row), columns of the sequence provide parameters required by the isl script (Fig. 4.3). Refer to text for details.

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<td>Zero enrichment</td>
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<td>Zero enrichment</td>
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<td>Zero enrichment</td>
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<td>Zero enrichment</td>
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<td>Zero enrichment</td>
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<td>Zero enrichment</td>
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<td></td>
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</tr>
</tbody>
</table>
4.5.3.2 Protocol for $\delta^{18}O_{atm}$ IRMS measurements

Once the samples have been collected to the collection manifold (LynnOax) and allowed to warm, LynnOax is hooked up to the sample inlet of the ms, and the standard line (Neem_C1) is purged 3 times. Then, the "O2_gaslab" gas configuration is set to ensure that high voltage, magnetic field, focus and cup settings allow measurements of $O_2$ isotope ratios.

Peak centering is either determined once before the start of the sequence and "passed" to the $O_2$ gas configuration, or determined before each block, as in Fig. 4.2. The latter option can be very time-consuming. However, zero-enrichment tests showed that performing a peak center only at the start of a run (i.e. 1 peak center every 3 blocks) leads to a loss of accuracy, as the peak center determined at the start of the run is not preserved at the end of the first block, but replaced by the peak center defined in the $O_2$ gas configuration for the 2 next ones. We therefore usually choose to perform a peak center for each block in the case where only a few samples have to be measured. Finally, the background value (Sect. 4.5.1) is measured once before a set of measurements.

From this point, an isl script (refer to Annex i for the main script and to Annex ii for the developed isl functions) schematically described in Fig. 4.3 allows a complete automation of standard and sample introductions, pressure adjustment, oxygen ratio measurements, mass monitoring and peak jumping (called PJ hereafter) procedure to measure m/z 28 and m/z 32 so as to obtain $\delta O_2/N_2$ value.

The script described in Fig. 4.3 is run for every blocks of the automated sequence, at the exception of the block dedicated to $N_2$ isotope ratios. It allows the measurement of $\delta^{18}O_1$ and $\delta O_2/N_2$ by peak jumping for successive samples. The action of the script can be divided in 3 main parts: (1) sample and standard introduction, (2) pressure adjustment procedure, and (3) measurements (Fig: 4.3).

4.5.3.2.1 Sample and standard introductions

Regarding the sample and standard introduction in the di bellows, the requirements of the program are to (i) introduce (or not) a standard in the right bellow (RB) and check whether the standard pressure in the RB is high enough to ensure viscous flow conditions (>5000 mV with Neem_C1 as standard) throughout the considered block; and (ii) introduce or not a standard or a sample to the left bellow at the start of a block:

- A standard is introduced to the RB if the flag state "Evacuate Std" in Fig. 4.2 is checked in the considered block (row). If no standard needs to be introduced, the pressure of the RB is still measured and a new standard is reintroduced if

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7peak centering is the action of varying the accelerating high voltage of the ion source to center the peak at the center of the narrowest Faraday cup, collecting m/z 33 in the "O2_gaslab" gas configuration. The optimal value of the high voltage is then used for the block, only.

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Figure 4.3 – Schematic representation of the automated IRMS measurements program written with ISL scripts. The script was written to enable overnight measurements of up to 10 air/O₂ samples and is used for every block (a row in the sequence described in Fig. 4.2) of the automated sequence (except for δ¹⁵N measurements). White boxes represent boolean conditions, where a green (black) arrow means that the condition is (not) met. The colored boxes represent actions. Note that a few actions, performed or not, lead to the same step (green and black arrow lead to the same box). For instance, the PA procedure will always follow peak centering and background steps.
Table 4.1 – Definitions of abbreviations used in Figure 4.3. Note that the threshold pressure and beam voltages can be found in the isl script in Annex A

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name</th>
</tr>
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<tbody>
<tr>
<td>SA</td>
<td>sample</td>
</tr>
<tr>
<td>STD</td>
<td>standard</td>
</tr>
<tr>
<td>DI</td>
<td>Dual Inlet</td>
</tr>
<tr>
<td>LynnOax SA</td>
<td>SA in a rod of the collection manifold</td>
</tr>
<tr>
<td>PA</td>
<td>pressure adjustment</td>
</tr>
<tr>
<td>LB</td>
<td>left bellow (SA is always introduced in LB in our setup)</td>
</tr>
<tr>
<td>RB</td>
<td>right bellow (STD is always introduced in RB in our setup)</td>
</tr>
<tr>
<td>@RB</td>
<td>towards, or in RB</td>
</tr>
<tr>
<td>@LB</td>
<td>towards, or in LB</td>
</tr>
<tr>
<td>@RB100%</td>
<td>towards, or in RB expanded to 100 %</td>
</tr>
<tr>
<td>@LB100%</td>
<td>towards, or in LB expanded to 100 %</td>
</tr>
<tr>
<td>@LB0%</td>
<td>towards, or in LB compressed to 0 %</td>
</tr>
<tr>
<td>$P_{\text{STD}}$</td>
<td>pressure of STD in RB</td>
</tr>
<tr>
<td>$P_{\text{SA}}$</td>
<td>pressure of SA in LB</td>
</tr>
<tr>
<td>$P_{\text{visc}}$</td>
<td>minimal pressure ensuring viscous flow conditions for the coming block</td>
</tr>
<tr>
<td>$P_{\text{sat}}$</td>
<td>maximal pressure above which $V_{32}^{\text{sa}}$ is saturated (&gt; 50 volts)</td>
</tr>
<tr>
<td>$P_{\text{PA}}$</td>
<td>pressure in LB at 0 % corresponding to $V_{32}^{\text{pa}}$</td>
</tr>
<tr>
<td>$V_{32}^{\text{sa}}$</td>
<td>beam voltage associated with m/z 32</td>
</tr>
<tr>
<td>$V_{32}^{\text{visc}}$</td>
<td>minimal beam voltage value to ensure viscous flow conditions</td>
</tr>
<tr>
<td>$V_{32}^{\text{PA}}$</td>
<td>beam voltage value at which both LB and RB are adjusted (manual PA)</td>
</tr>
<tr>
<td>COV</td>
<td>ChangeOver valve</td>
</tr>
</tbody>
</table>

Viscous flow conditions are not met.

- If the flag state "Evacuate Sa" is checked, column "Lynn Oax Inlet" is used by the isl script to distinguish between a zero-enrichment test or a sample block. Neem_C1 standard is introduced from the right inlet of the ms to the LB in the first case, whereas a sample collected in LynnOax is introduced from the left inlet of the ms to the LB in the second case. It should be mentioned that LynnOax needs to be physically connected to the ms for the sample transfer to happen, which avoids possible contamination of the di line with ambient air. If "Evacuate Sa" is not checked, a new sample or standard is not reloaded.

- In case the sample contains too much air, the sample is expanded to the cross of the ms until the pressure of the LB at 100 % ensures no saturation in the $O_2$ beam voltages.

4.5.3.2.2 Pressure adjustment

Depending on the sample beam voltage $V_{32}^{\text{sa}}$, either a manual pressure adjustment (PA) is performed at 10 V or at the sample beam voltage level. Manual PA is favored but in case of a too high $V_{32}^{\text{sa}}$ in the fully expanded LB or a too low pressure in the fully compressed LB, the program changes of PA mode and performs a PA at the sample beam voltage $V_{32}^{\text{sa}}$. If too low, the standard beam voltage $V_{32}^{\text{std}}$ is set to a value that ensures viscous flow conditions by compressing the RB. Then the sample pressure is set above the standard pressure (in case it was not the case) by compressing the LB by 10

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*Note that the columns "Sample Intro" and "Standard Intro" in Fig. 4.2 inform from which ms inlet samples and standard are introduced, but are not used by the isl script.
% steps. This pre-PA procedure was added to ensure that $V_{32}^{sa}$ could be adjusted to $V_{32}^{sa}$ by compressing the RB. Typically, the amount of sample gas is lower than the amount of standard gas at the beginning of the 10 sample measurements, which leads to a higher rate of pressure decrease on the sample side, but this ratio gets inverted with time. To correct for this beam voltages difference, a pressure imbalance correction is applied (Sect. 4.6.1).

4.5.3.2.3 $O_2$ isotope ratio measurements

We’ve seen in Sect. 4.5.1 that 16 cycles per block were optimal for $O_2$ isotope ratio measurements. Therefore, one run of three blocks of 16 cycles is performed for each sample (and each zero-enrichment test) with the "O2_gaslab" configuration to measure $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios. The $\delta^{18}O$ of a run represents the average of 3 $\delta^{18}O$ ($\delta^{17}O$) blocks, and the precision of the run is defined by the standard deviation of 3 $\delta^{18}O$ ($\delta^{17}O$) block values. This step corresponds to the box "Acquisition start" in Fig. 4.3.

4.5.3.2.4 Measuring $\delta O_2/N_2$ by peak jumping

The collector configuration of the ms (Sect. 4.3) does not enable a simultaneous collection of m/z 28 and m/z 32, necessary to calculate $\delta O_2/N_2$:

$$\delta O_2/N_2 = \left( \frac{V_{32}^{sa} - B_{32}}{V_{28}^{sa} - B_{28}} \right) \left( \frac{V_{32}^{std} - B_{32}}{V_{28}^{std} - B_{28}} \right) - 1,$$

(4.6)

where $V_{28}$ is the beam voltage on m/z 28 (14$^N14^N$). Note that $B_{28}$ and $B_{32}$ have identical values, as both m/z 28 and m/z 32 are measured on the same cup (see below). Instead, $\delta O_2/N_2$ is measured by peak jumping (called PJ hereafter) at the end of the third block of a sample run. PJ is done in the same gas configuration as $O_2$ ("O2_gaslab") by jumping forth and back the magnetic field $B$ between the $O_2$ and $N_2$ peaks.

PJ is performed only if "MagnetScan" is checked in the sequence displayed in Fig. 4.2. For this procedure, we adapted a script (refer to Annex A) that was developed by Severinghaus et al. (2003) to improve the PJ precision of $^{84}Kr/^{36}Ar$ measurements\(^9\). The gain in precision is mostly linked to a faster PJ procedure, which minimizes instrumental drift and saves time by avoiding a reset of the magnet between each measurement (Severinghaus et al., 2003). Note that $\delta O_2/Ar$ can not be measured easily in our automated sequence because of the impossibility to switch between high and low amplification with isl (probaly related to an issue with the Isodat version used), as detailed in Sect. 4.6.5.

As the amount of sample and standard gas generally differs, their beam voltages are characterized by a different decrease rates. As the peak jumping procedure requires

\(^9\)The script from Severinghaus et al. (2003) is based itself on the Interfering Masses program from Isodat (accessible from the method file), corresponding to the box "MonitorM" in Fig. 4.3. This program is called during a block if "Magnet" is checked in the sequence (Fig. 4.2)
to reset the magnet after each peak jump to account for hysteresis effect, and as integration and idle times are set to 16 s, sample and standard voltage beams can be too unbalanced to obtain reliable $\delta O_2/N_2$ values. $O_2$ and $N_2$ sample and standard beam voltages are therefore measured 6 times and the individual decrease rate for each beam voltages except $V_{32}^{sa}$ is obtained by fitting their measured beam voltages with a linear function over time (Fig. 4.4). The individual decrease rates are used to interpolate all beam voltages to the times where $V_{32}^{sa}$ was measured:

$$V_n^i(T_{32}^{sa}) = V_n^i(T_{32}^i) + \Delta \cdot (T_{32}^{sa} - T_{32}^i),$$

(4.7)

where $\Delta V$ is the decrease rate, $T$ the time of measurement, $n$ stands either for sample or standard and $i$ for 28 or 32. Voltage beams were measured 6 times instead of 3 to ensure a good fit (in case of outliers). A Python script was developed by Grzymala-Lubanski (2015) to automate the calculation of $\delta O_2/N_2$ value from the exported text file produced by the peak jumping isl program (Severinghaus et al., 2003) and can be found in the Annex B.

Figure 4.4 – Original figure from Grzymala-Lubanski (2015). Quality of the linear regression (in a limited range, the exponential decrease of the beam voltages can be considered to be linear) for $V_{32}^{sa}$ (top) and $V_{32}^{std}$ (bottom).
The IRMS stability was checked with zero-enrichment experiments. These tests were performed daily during ice core measurements periods, and after a change in the focus settings of the ms, mostly caused by a filament replacement. These tests consist in expanding the same standard gas (neem air for $\delta^{18}O$ measurements, $O_2$ - Ar mixture for $^{17}A$ measurements\(^{19}\)) in both sample and standard bellows. The standard is transferred from a 50 l cylinder to a 1/4” sst aliquot located between 2 pneumatically-actuated bellow valves (controlled under Isodat). The pressure of the standard line is adjusted so that the standard size is in the range of the measured samples. A zero-enrichment test reflects any fractionation of sample or reference occurring during transfer to the source, informs about the conditioning of the $\text{di}$ line and assesses any leaks in the inlet system during a measurement sequence. As mentioned earlier, zero-enrichment tests are performed before and after a sequence of sample measurements to ensure that the IRMS is stable, at least over a sequence of measurements. Over the time period of neem measurements, results for Neem_C1 ($\delta^{18}O = 0.001 \pm 0.005$, $\delta^{15}N = 0.0005 \pm 0.008$) are identical within the uncertainty associated with the measurements.

Zero-test enrichments can be slightly modified over time, with a change of filament or focus settings, and typically show anomalous values if the $\text{di}$ system and ion source has not been conditioned to air or $O_2$ (depending on the measurements), as observed by Bender et al. (1994c)\(^{11}\).

4.5.5 Referencing to the isotope scales

As mentioned in Sect. 3.4.2.2, the isotope ratios of ice core samples are referenced against present-day atmospheric air, as it is commonly done when measuring molecular $O_2$ (e.g. Barkan and Luz, 2003; Severinghaus et al., 2009). An atmospheric air tank was sampled in the year 2008 at a clean-air site of the neem camp in northwest Greenland (Sperlich et al., 2013) and is referred to as Neem_C1 air. We use it as a working standard (Neem_S1) but also as a reference material (PRM) as it is available in large amount and the isotopic composition of $\delta^{18}O$, $\delta^{15}N$ and $\deltaO_2/N_2$ was stable in the last 50 years.

In order to fulfill the IT-principle, and gain in precision, both the sample and the

\(^{16}\)we use an $O_2$ - Ar mixture when $O_2$ is separated with the GC method, as the sample still contains Ar. In contrast, both $N_2$ and Ar were separated from $O_2$ with the perovskite membrane, that was hence measured against a pure $O_2$ mixture in the standard bellow.

\(^{11}\)Bender et al. (1994c) also observed that reversing capillaries was not affecting the value of zero-enrichment tests. We observed similar results. However, balancing sample and standard flows in the ion source capillaries proved to be difficult, because a differential drift in ion beam voltages between the sample and the standard was systematically observed in the day following crimping adjustment. Non-balanced beam voltages lead to a larger pressure imbalance over a block of measurements despite an identical amount, which requires corrections (Sect. 4.6.1).
working standard against which the sample is measured must be introduced in theory through the sample side of the IRMS. This means that the isotopic content of the intermediate standard in the standard bellow does not need to be known with precision. However, it needs to be of similar nature, and in the isotopic range of the sample and working standard to be measured (Werner and Brand, 2001). Unfortunately, as mentioned in Sect. 3.7.3, introduction of the working standard Neem_S1 over BF1 caused isotope fractionation of $O_2$. The rice ice core samples measured by Grzymala-Lubanski (2015) were thus referenced against the intermediate standard Neem_C1 (which is also the PRM for $O_2$ measurements and has a $\delta^{18}O$ and $\Delta^{17}A$ value of 0 \%e by definition) introduced in the standard (right) bellow of the MS. To assess the stability of the extraction line, 21 late Holocene Neem ice core samples were run together with the rice ice core samples and displayed a remarkable stability around $-0.05 \pm 0.03$ %e (Sect. 4.6.7) after usual corrections (Sect. 4.6). Such results, from ice core samples that were collected in different rods and at different days, give us confidence that the conditions of the analytical system are similar at least during a sequence of ice core measurements. Summarizing, we are aware that referencing ice core samples against the intermediate standard NEEM_C1 does not fully respect the IT principle, and introduction of Neem_S1 above BF1 should be implemented in the future to fulfill this condition. However, the stability of the measured $\delta^{18}O_{atm}$ of 21 Neem shallow ice core samples from the same depth, that can thus be considered as replicates, underline the ability of the system to reproduce measurements of gas trapped in ice core bubbles. Concretely, this means that the measured rice $\delta^{18}O_{atm}$ values may be offset relative to the true value on the $O_2_{atm}$ isotopic scale, but their relative variations are real and not the result of random artifactual fractionation during the experiment.

4.6 Corrections

This section describes data post-processing for $\delta^{18}O$. Several corrections need to be applied to the raw delta values calculated by Isodat. There are 4 main sources of error that need to be accounted for:

1. biases associated with mass spectrometry measurements: internal stability of the MS, pressure imbalance, chemical slope. These biases depend on the settings of the IRMS ion source, and vary with time.

2. biases associated with the experimental setup, which can be reduced by referencing the samples against a standard that was treated the same way.

3. processes occurring in the firn, associated with the transition of snow to ice: gravitative settling, thermal diffusion, and ordinary diffusion.

4. processes associated with the drilling, retrieval and storage of the ice core samples: coring and post coring processes

These corrections significantly improve the precision of the measurements. The standard deviation of 21 ice samples from the same sampling site (Neem) and depth
(337 m) improves from 0.09 % to 0.03 % after data post-processing. The corrections are presented in the same way as they are done, that is (1) pressure imbalance correction, (2) chemical slope correction, (3) corrections associated with molecular diffusion processes in the firn and (4) gas loss corrections.

4.6.1 PRESSURE IMBALANCE

A difference of pressure between the sample and standard bellows slightly affects the measured δ18O values, requiring a small correction.

Avoiding differences in pressure in the bellows would be ideal. With a similar amount on both sides, the decreasing pressure with measurement time would indeed be similar in both bellows, implying a similar gas flow decrease through the transfer capillaries, and therefore balanced beam voltages throughout the run. However, as the amount of gas always slightly differ from one ice core sample to another (many causes can be invoked: various dimensions of the cleaned samples after chiseling off their external layers, various total air content, small changes in the fossil air extraction and collection efficiencies, etc), ensuring an (almost) identical amount in both sample and standard bellows would require to first measure the amount of sample gas introduced in the bellow, and then adjust the volume of the standard bellow so that the amount of expanded standard gas matches the amount of expanded sample gas, as recommended by e.g. Bender et al. (1994a) for O2/N2 analysis.

Actually, as δ18O is measured in a mixture of gases (N2 - O2 - Ar), with grossly 4 times more N2 than O2, an identical amount in both bellows is not sufficient to ensure balanced O2 beam voltages throughout the run if the O2 mixing ratio differs between the sample and standard gas mixtures. Indeed, when measuring O2 isotope ratios, the Isodat function “press adjust” (PA) balances the major O2 beam voltages (m/z 32), hence the O2 partial pressure, just before the start of the measurement sequence.
Figure 4.5 – (a) Voltage difference between a sample and a standard ($\Delta V = V_{sa} - V_{std}$) for m/z 32, 33 and 34 over a typical automated sequence of 3 blocks of 16 cycles each (the 4th block, including cycles 49 to 64, is corresponds to a zero-enrichment test). The pressure in the sample bellow is first increased to obtain a difference of $\leq 1000$ mV between the 2 bellows during the first block, and the opposite is done during the third block. Sample and standard pressures are balanced over the second block. (b) Pressure imbalance determination (Feb. 2014) using a pure O$_2$ working standard (Tank_1b). Black diamonds correspond to the $\delta^{18}$O values of 48 individual cycles and their associated $\Delta V = V_{sa} - V_{std}$. Red squares correspond to the mean $\delta^{18}$O values of the 3 blocks versus $\Delta V$. The slope of the linear regression line represents the sensitivity of $\delta^{18}$O to pressure imbalance in $\%_0 \cdot mV^{-1}$. (c) Similar as in (b) (July 2015) but with an atmospheric air working standard (Neem_C1). The PI sensitivity is an order of magnitude higher in air than in pure O$_2$, and the PI slopes are of opposite sign. Values of the PI slope during rice and neem ice core measurements can be found in Table 4.2. It should be mentioned that the ion source had to be opened between the 2 experiments, so the source parameters and focus settings are slightly different between (a) and (b).

But it is the total pressure in the bellow that controls the flow of gas through the transfer capillary, not the O$_2$ partial pressure. As a result, even with an identical amount of gas, the sample and standard beam voltages will become unbalanced over time, the bellow with the lower O$_2$ partial pressure being more compressed after the PA procedure, that is with a higher total pressure at the start of the measurements and consequently losing more gas per unit of time.

In our fully automated D$_1$ measurement sequence, the standard bellow is not refilled after each sample introduction, but only when it reaches a threshold pressure under
which isotope ratios can’t be precisely measured, as viscous flow conditions are not met. Refilling the bellow with a new standard after each sample introduction would be too time-consuming. Besides, as explained in this section, introducing a similar amount in both bellows does not ensure balanced beam voltages throughout the run. Finally, we favor a manual "PressAdjust" (cf Sect. 4.5.3), by which both sample \((V_{sa}^{32})\) and standard \((V_{std}^{32})\) major \(\text{O}_2\) beam voltages are balanced to a preset value \((\simeq 7000 \text{ mV on m/z 32})\) after each block, so that measurements are performed in similar conditions.

Typically, the amount of sample gas is lower than the amount of standard gas after a standard refill, which leads to a higher rate of pressure decrease on the sample side, but this ratio gets inverted with time. As shown by Grzymala-Lubanski (2015) for ice core measurements, during a block of 16 cycles, the sample and standard beam voltages can differ by up to 200 mV despite being balanced at start.

To correct for this pressure imbalance, a run of 3 blocks of 16 cycles is included at the start of the measuring sequence (Fig. 4.5a) and is run every week of measurements. An aliquot of the standard gas Neem_C1 is successively introduced in both bellows from the standard inlet of the IRMS. The first (third) block is run with the sample (standard) major \(\text{O}_2\) beam voltage unbalanced by \(\simeq 5\) to 10 \%, and the second block with both beam voltages balanced, as in a zero-enrichment test. A typical chart used to determine the sensitivity of \(\delta^{18}\)O to pressure imbalance is shown in figure 4.5b. The slope of the linear regression line represents the sensitivity of \(\delta^{18}\)O to pressure imbalance \(\text{im} \% \cdot \text{mV}^{-1}\). This correction thus assumes a linear relationship between \(\Delta \delta\) (the PI-related \(\delta\) deviation from its true value) and \(\Delta V\) (pressure imbalance expressed as the beam voltage difference between sample and standard) (Severinghaus et al., 2003), as observed by e.g. Bender et al. (1994b).

Table 4.2 demonstrates the stability of the PI slope, determined in an air mixture, Neem_C1, over the 4 weeks of rice core measurements (Grzymala-Lubanski, 2015), with a typical value of \(5 \cdot 10^{-4} \% \cdot \text{mV}^{-1}\). A difference of 200 mV thus causes a shift of 0.1 \% in the measured value.

Once the PI slope is determined, the raw \(\delta^{18}\)O value calculated by Isodat can be corrected. We choose to correct every cycle rather than the mean block value, obtaining a better precision with this method:

\[
\delta_{\text{PI corrected}} = \delta_{\text{measured}} - \text{PI slope} \cdot \Delta V,
\]

where \(\delta_{\text{measured}}\) corresponds to the cycle \(\delta\) values as calculated by Isodat, and \(\Delta V = V_{sa} - V_{std}\), with \(V_{sa}\) and \(V_{std}\) representing the sample and standard beam voltage of the most abundant isotope of the measured gas (e.g. m/z 28 for \(\text{N}_2\), m/z 32 for \(\text{O}_2\) ), resp. Please keep in mind that a beam voltage corresponds to the amplified ion current signal produced by hitting of ionized molecules in the Faraday cup.

Typical corrections of \(\simeq 0.03\)–0.07 \% are applied to \(\delta^{18}\)O values, which are in the high range of other studies measuring \(\text{O}_2\) isotopes in fossil air. For instance, Capron...
Table 4.2 – Pressure Imbalance slope during the 4 weeks of rice core measurements. Gas standard: Neem_C1. Original Table 5.1 from Grzymala-Lubanski (2015)

<table>
<thead>
<tr>
<th>PI slope (%/·mV−1)</th>
<th>$R^2$ of linear regression</th>
<th>week number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000498</td>
<td>0.982</td>
<td>1</td>
</tr>
<tr>
<td>0.000556</td>
<td>0.999</td>
<td>2</td>
</tr>
<tr>
<td>0.000536</td>
<td>0.958</td>
<td>2</td>
</tr>
<tr>
<td>0.000559</td>
<td>0.997</td>
<td>2</td>
</tr>
</tbody>
</table>

(2010) corrects $\delta^{18}O$ for PI imbalance by $\approx 0.02$ to $0.03\%$. The PI correction on cycle $\delta^{18}O$ is useful as the standard deviation of the PI corrected block $\delta^{18}O$ is reduced.

4.6.2 CHEMICAL SLOPE

A better precision is achieved when measuring isotope ratios in a pure substance\(^\text{12}\). This gain in precision is due to the fact that in a mixture of gases, the variations of elemental ratios have an influence on the measure of the isotopic ratios of a single element: $\delta O_2/N_2$ influences $\delta^{18}O$ and $\delta^{15}N$ measurements, $\delta^{15}N_2/Ar$ affects $\delta^{40}Ar$ (Severinghaus et al., 2001, 2003; Landais et al., 2003; Capron, 2010). Different causes have been invoked, like molecules-ions interactions in the source that affect the relative ionization efficiencies of light and heavy isotopologues, hypothesis which is supported by the fact that the chemical slope is reduced when source parameters are tuned to optimize linearity. Indeed, linearity settings are likely to reduce ion-molecule interactions in the ion source as the ions are quickly extracted (Sect. 4.4.0.1). However, the process is not really well understood and varies between mss. We apply an empirical correction to account for these interfering masses as done by Severinghaus et al. (2003). We assume this correction to be linear in the range of our measurements. This chemical slope correction for $\delta^{18}O$ is done before a set of measurements by adding increasing amounts of high-purity $N_2$ in aliquots of standard gas (here Neem_C1), and measuring it against the standard gas alone. A mass flow controller is used to introduce increasing amounts of $N_2$ to the standard gas line.

The figure 4.6a presents the chemical slope characterization performed by Grzymala-Lubanski (2015) on the Delta V Advantage. The quality of the fit is not excellent, and its intersection with the y-axis ($\delta^{18}O (0, 0) = -0.053 \pm 0.021\%$) does not lie within the measurement uncertainty of a zero-enrichment test (while it should in theory, as it corresponds to the measurements of the standard gas versus itself). The uncertainty associated with the chemical slope can be due to large pressure imbalance observed

\(^{12}\text{This gain in precision is the main motivation to separate } N_2 \text{ from } O_2 \text{ for } ^{17}\Delta \text{ measurements, requiring a very high precision (\approx 10 permeg) to gain climatic information from the small signal (\approx 40 permeg between glacial and interglacial).}\)
Figure 4.6 – Original figure from Grzymala-Lubanski (2015) (a) Empirical determination of the chemical slope characterization performed by Grzymala-Lubanski (2015) on the Delta V Advantage. Increasing amounts of pure $N_2$ were progressively added to the standard gas (Neem_C1) and measured against itself, as in a zero-enrichment test. Resulting $\delta^{18}O$ values are plotted against $\delta O_2/N_2$ values. The red line represents the linear fit corresponding to the chemical slope. $p_0$ gives the intercept of the linear regression with the y-axis and its associated error, while $p_1$ stands for the slope of the linear fit and its associated error (b) Chemical slope when forced through (0,0). $p_0$ stands for the slope of the fit. A $\chi^2$ test is used to evaluate the goodness of the fit for both plots. $\chi^2$ is the squared difference between the measured $\delta$ values and their theoretical predictions given by the fit weighted by the expected errors of measurements (Barlow, 1989), set to the standard deviation of a zero enrichment test.

$$\chi^2 = \sum \frac{(y_i - f(x_i))^2}{\sigma_i^2} = \sum \left( \frac{\delta_i^{\text{measured}} - \delta_i^{\text{theoretical}}}{\text{expected error}} \right)^2$$ (4.9)

The closer $\chi^2$ divided by the number of degrees of freedom is closed to 1, the better the fit matches the measurements.
for samples highly enriched in $N_2$ (up to $\delta V = 400 mV$, Grzymala-Lubanski, 2015), so that the PI corrections applied on $\delta^{18}O$ became significant. The large imbalance arises from the fact that Neem_C1 (atmospheric air) already contains $\approx 80 \% N_2$. Indeed, to obtain 90 % $N_2$ in the final gas mixture, the size of the standard had to be doubled (2 ml of $N_2$ added to 2 ml of Neem_C1). It should also be reminded that the $\delta O_2/N_2$ ratio cannot be measured simultaneously (because of the Universal Triple collector configuration of the IRMS, Sect. 4.3), which requires further data treatment and possible loss of precision. Based on the aforementioned considerations, the fit is forced to $(0,0)$ (Fig. 4.6b). The quality of the fit is reduced, but the slope is only slightly affected. Indeed, with a $\delta O_2/N_2$ of $-10 \%$, taking a different slope does not affect $\delta^{18}O$ by more than $0.003 \%$, which is lower than the internal precision of the ms (Sect. 4.5.4).

More measurements will be needed in the future to determine more precisely the chemical slope, especially in the range $\delta O_2/N_2 \in [-30 \%, 0 \%]$, where most of our measurements lie. This is important as the uncertainty of the fit affects the final $\delta^{18}O$ values. The chemical slope correction is applied to $\delta^{18}O_{PI\ corrected}$ in the following way:

$$\delta^{18}O_{CS\ corrected} = \delta^{18}O_{PI\ corrected} + \text{chemical slope} \cdot \delta O_2/N_2,$$

where $\delta O_2/N_2$ is measured by peak jumping (Sect. 4.5.3.2.4). Despite the uncertainty associated with the chemical slope, the correction makes sense, as demonstrated by the pooled standard deviation of the 21 neem ice core samples from the same sampling depth (337 m), which reduces from $0.077 \%$ ($\delta^{18}O_{PI\ corrected}$) to $0.068 \%$ after chemical slope correction ($\delta^{18}O_{CS\ corrected}$).

4.6.3 Corrections due to diffusive processes in the firn

The firn alters the elemental and isotopic composition of the air bubbles trapped in ice cores (Sect. 1.4.1). It is therefore required to apply corrections to retrieve the true atmospheric signal.

4.6.3.1 Gravitational fractionation

To separate the firn and atmospheric fractionation processes, the influence of gravitational fractionation in the firn is removed from corrected $\delta^{18}O$ of $O_2$ using the $\delta^{15}N$ measurements. In Sec. 1.4.1.1, we describe how gravitational fractionation scales with $\Delta m$. Following Bender et al. (1994c), Sowers and Bender (1995), Severinghaus et al. (2009), $\delta^{18}O$ is corrected in the following way:

$$\delta_{gravcorr} = \delta_{CS\ corrected} - \Delta m \cdot \delta^{15}N,$$

where the mass difference $\Delta m = 2$ for $\delta^{18}O$ and $\Delta m = 4$ for $\delta O_2/N_2$. This correction assumes that $\delta^{15}N$ enrichment is only of gravitational origin (Fig. 4.9), which is a fair assumption here as explained in the next section. Note that fractionation processes that scale with the absolute mass difference $\Delta m$, that can occur for instance during the experiment, will be also removed by this correction (Sect. 4.6.6).
4.6.3.2 Thermal fractionation

Difference in $O_2$ and $N_2$ coefficients of thermal diffusion leads to a thermal fractionation 1.6 times larger for $\delta^{18}O$ than for $\delta^{15}N$ (Severinghaus et al., 2001). However, in general, correction for thermal fractionation can be neglected. Indeed, large and rapid temperature changes (Sect. 1.4.1.2) are necessary to affect isotope ratios. In East Antarctica, firnification and temperature changes are too slow to create large transient temperature gradients in the firn (Goujon et al., 2003). Furthermore, the thermal equilibration evolves as the square of the firn thickness, which is only 40-60 m in Antarctic coastal zones (Paterson, 1994; van den Broeke, 2008), where the Rice ice core measured by Grzymala-Lubanski (2015) originates. As a consequence, no correction for thermal fractionation is applied to Rice ice core samples in Grzymala-Lubanski (2015).

In contrast, large millennial scale temperature changes (DO events) occurred during the last glacial period in Greenland. Resulting temperature gradients in the firn are much larger than in Antarctica, and modify substantially the isotopic composition of the bubbles (Landais et al., 2010). As explained in Sect. 1.4.1.2, the effect on $\delta^{18}O$ can be corrected for by combining $\delta^{15}N$ and $^{40}Ar$ measurements. The Neem (and Eurocore, drilled at Summit drilling station) ice core measurements presented in this thesis are dated from the late Holocene, where temperature variations were low. Indeed, reconstructed surface temperature histories (from 2000 to 0 yrs A.D.) based on borehole temperature measurements performed at GRIP (Greenland, 72.4°N, 37.4°W) do not vary by more than $\pm 1^\circ$C (Dahl-Jensen et al., 1998). It is thus reasonable to assume that the effect of thermal fractionation can be neglected. As a consequence, no correction for thermal fractionation is applied to Neem and Eurocore standards.

4.6.3.3 Bubble close-off fractionation

While gravitational and thermal fractionation are mass-dependent diffusive processes occurring in the gas phase, bubble close-off fractionation combines size-dependent and mass-dependent diffusive process occurring in the ice matrix (Sect 1.4.1.3). As mentioned in Sect. 1.4.1.3 and developed in Sect. 4.6.4, artifactual gas loss from the ice can also occur during coring and storage, making difficult to estimate solely the effect of bubble close-off fractionation on $\delta O_2/N_2$ and $\delta^{18}O_{atm}$. We present here the alternative strategies adopted to quantify the effect of bubble close-off fractionation on the elemental and isotopic composition of gases trapped in ice core bubbles, with a focus on $\delta O_2/N_2$, required to correct $\delta^{18}O_{atm}$.

One could imagine that pumping firn air directly in the LIZ would help estimate bubble close-off fractionation. As shown in Fig. 1.19, a gradual $\delta O_2/N_2$ enrichment with depth occurs in the lock-in-zone. However, the observed $\delta O_2/N_2$ enrichment in the LIZ found by firn air studies (e.g. Severinghaus and Battle, 2006) is due to the fact that the sampling of deep firn air is incomplete, accessing only the open porosity,
but not macropores or the closed porosity (Severinghaus, pers. comm., 2016). Hence the observed enriched $\delta O_2/N_2$ is not representative of the average $\delta O_2/N_2$ in ice core bubbles. At the close-off-depth, the very limited open porosity actually even precludes the extraction of firn air samples (Battle et al., 2011). In the following, we detail the cause of $\delta O_2/N_2$ enrichment in the LIZ.

Large differences in $\delta O_2/N_2$ are observed between summer and winter layers, the former being consistently less depleted than the latter\textsuperscript{13}. Summer layers are less depleted because bubbles in summer layers close later/deeper than bubbles in winter layers:

1. $O_2$ permeating 3 times faster than $N_2$ through the ice lattice, the permeate, that is the air expelled from closing bubbles) is highly enriched in $O_2$ (with a $\delta O_2/N_2$ of $\simeq 2000\%$) and accumulates in the high open porosity of the summer layers.

2. As explained in Sect. 1.4.1.3.4 for layering, the $O_2$ enriched air cannot escape to the atmosphere from the open pores of the deep summer layers of the LIZ, because of the formation of quasi impermeable horizontal layers in the LIZ (e.g. denser winter layers, whose open porosity is low, as bubbles are already mostly closed off), and ultimately gets trapped in bubbles.

It follows that the pumping of air from the LIZ is mostly originating from the $\delta O_2/N_2$ enriched open pores of the summer layers, which explains, as aforementioned, the observed gradual enrichment in $\delta O_2/N_2$ (Severinghaus, pers. comm., 2016). It should be underlined that the difference in $\delta O_2/N_2$ of summer and winter layers probably explain a large part of the scattering of $\delta O_2/N_2$ values observed in replicate ice core samples. This also explain why the long axis of the samples need to be orientated parallel to the ice core so as to average over several (depending on the accumulation rate) seasonal layers.

We’ve seen in Sect. 1.4.1.3.4 that close-off fractionation is ultimately depending on the amount of gas-loss across the lock-in-depth. A method to estimate the average $\delta O_2/N_2$ depletion solely due to bubble close-off in ice core samples consists in estimating the upward $O_2$ loss flux to the atmosphere from the observed $O_2/N_2$ gradient in the diffusive zone, above the lock-in-depth, applying Fick’s second Law\textsuperscript{14}, and assuming steady state after correcting for anthropogenic atmospheric $O_2$ change (Severinghaus and Battle, 2006). At NEEM, this method only requires precise $\delta O_2/N_2$ firn air measurements, as $D$ at NEEM is well-known (Buizert et al., 2012). This method was applied at Siple Dome and South Pole by Severinghaus and Battle (2006). They estimated that the upward flux of $O_2$ accross the LIZ should leave the air bubbles in ice depleted with an average $\delta O_2/N_2$ of $\simeq -2\%$. However, $\delta O_2/N_2$ from South Pole ice core samples was consistently depleted by $\simeq -8\%$ (Severinghaus, pers. comm.,\textsuperscript{13})

\textsuperscript{13}a careful study of this was done at Siple Dome, where it was possible to visually identify the summer layers in shallow mature ice (90 m depth, vs. a close-off around 60 m) (Severinghaus, pers. comm., 2016)

\textsuperscript{14}$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial z^2}$, where $c$ stands for gas concentration, $t$ stands for time, $D$ is diffusivity and $z$ is depth.
This difference between the two $\delta O_2/N_2$ values evidences artifactual gas loss caused by coring and post coring processes, as detailed in Sect. 4.6.4.

### 4.6.4 Coring and post-corning gas loss fractionation

This section focuses on the two processes altering the elemental and isotope composition of ice core samples during ice core recovery and storage. Observations indeed show that artifactual gas loss can be divided into two categories, which may be difficult to distinguish: gas loss associated with size-dependent fractionation and gas loss associated with mass-dependent fractionation, similar to the one observed for close-off fractionation (Sect. 1.4.1.3). This section also describes the different correction strategies, which widely differ between studies, applied to samples affected by gas loss fractionation. It finally focuses on the NEEM late Holocene ice core samples measured by Grzymala-Lubanski (2015) on the analytical line built during this thesis and present the empirical correction applied to $\delta O_2/N_2$ and $\delta^{18}O_{atm}$ for gas loss fractionation.

#### 4.6.4.1 Size-dependent fractionation

Similar to the gas-loss mechanism during the bubble close-off, size-dependent diffusion from overpressured air bubbles through the ice lattice takes place during storage. Suwa and Bender (2008) remeasured $\delta O_2/N_2$ of well preserved deep GISP2 samples after 12 years of storage at $-35^\circ$C. Figure 4.7 presents the evolution of $\delta O_2/N_2$ for 7 samples with a similar depth. A constant depletion of 7.3‰ is observed, suggesting that the loss of $O_2$ is correlated with the storage duration, as already observed by Ikeda-Fukazawa et al. (2005). $\delta^{18}O$ remains almost unaffected in this study, with a $\delta^{18}O$ depletion by $0.021 \pm 0.074$‰ during storage. The fact that the isotope composition of molecular $O_2$ remains unaffected while elemental $O_2/N_2$ ratio gets depleted calls against a mass dependent fractionation process.

Ikeda-Fukazawa et al. (2005) explains that no mass-dependent fractionation occurs because it is not the velocity of the molecules but the rate of gas diffusion through the ice lattice that is controlled by the rate of hydrogen-bond-breaking (cf. Sect. 1.4.1.3). This view is supported by the fact that gas loss is strongly dependent on temperature (Kawamura et al., 2007; Ikeda-Fukazawa et al., 2005). These observations are in agreement with the hypothesis of Bender et al. (1995), who proposed that gas loss during and after coring is caused by a process fractionating elements in a size-dependent way (depending on the molecular diameter) rather than in a mass-dependent way (depending on the diffusivity). Severinghaus et al. (2009) suggests that the absence of mass-dependent fractionation can be explained by the absence of cracks, due to the low stress associated with annealing of the ice core over a long time during storage, in spite of gas constantly leaking out of overpressured bubbles in ice.

Available observations suggest that size-dependent fractionation also occurs in...
highly-fractured ice. Fractures can be caused by drilling an ice core without pressure-compensating the borehole with drilling fluid. As described in Sect. 1.4.1.3, small gas molecules like $O_2$ and Ar diffuse much faster than $N_2$ through the ice lattice, causing loss of $O_2$ and Ar in roughly equal proportions (Severinghaus et al., 2009). No isotope fractionation should occur through this process as isotopologues have an identical molecular diameter. However, replicate pairs of ice core samples affected by artificial gas loss present a characteristic signature in which Ar is half as much depleted as $O_2$ (Bender et al., 1995; Severinghaus et al., 2009), while one would expect a similar depletion of $O_2$ and Ar with size-dependent fractionation only. This discrepancy arises from the fact that mass-dependent fractionation also occurs during coring and post-coring (Sect. 4.6.4.2).

### 4.6.4.2 Mass-dependent fractionation

In contrast with observations presented in the previous section, fractionation of Ar isotopes has been evidenced on samples stored at $-20^\circ C$ for more than 5 years by Severinghaus et al. (2003), Grachev (2004) and Kobashi et al. (2008), in apparent contradiction with above-mentioned results. Several studies revealed that a loss of $O_2$ ($\delta O_2/N_2$ depletion) is associated with an increase in $\delta^{18}O$ during ice core storage. In her thesis, Landais (2004) also found a $\delta^{18}O$ enrichment associated with an increasing loss of $O_2$ from the inner core to the periphery of a NorthGRIP sample drilled in 1992. Bender et al. (1995) found that samples with highly anomalous $O_2/N_2$ ratios with respect to modern air were enriched in $\delta^{18}O$ by 0.1-0.2 °. Similarly, GRIP ice core samples remeasured after 6 years of storage were affected by a preferential loss of $O_2$ on the order of 3 %, associated with an increase of $\delta^{18}O$. The depletion of $\delta O_2/N_2$ and fractionation of $\delta^{18}O$ were shown to correlate linearly by measuring replicate samples (Landais et al., 2003). Several other studies revealed a similar constant slope of $0.01%_o \cdot %_o^{-1}$ between $\delta O_2/N_2$ variations and $\delta^{18}O$ variations for Antarctic
ice cores - Vostok (Suwa and Bender, 2008), EDC (Dreyfus et al., 2007), Siple Dome (Severinghaus et al., 2009).

Artifactual gas loss associated with mass-dependent fractionation is often associated with poorly-preserved or highly-fractured ice core samples and is called "core-cracking fractionation" (Bender, 2002; Severinghaus et al., 2009). Cracking can occur during handling, as non annealed ice can weaken if warmed on the surface (Bender et al., 1995; Bender, 2002; Severinghaus et al., 2009), or during ice core recovery, caused by high stresses in the ice after depressurization as the ice is brought to surface pressures. Fractures in the ice are often created during recovery of ice belonging to the gas-clathrate transition zone. Indeed, in this "brittle" zone, long of several hundred meters, gases in ice cores transform their state from gas to solid (clathrate) owing to the overlying pressure which increases with depth (Shoji and Langway, 1982). The air entrapped in the ice coexists in both states, gas and solid (clathrate). During ice recovery, the important pressure exerted by the gas fraction on the surrounding ice leads to many fractures in the ice sample. Kobashi et al. (2008) propose that the presence of cracks in the ice leads to gas loss by viscous flow, molecular or Knudsen diffusion, the two latter causing mass-dependent fractionation.

Summarizing, gas-loss processes involve a mix of size- and mass-dependent fractionation that can be caused by bubble close-off, coring and post-coring processes. It is therefore difficult to distinguish between these mechanisms.

4.6.5 Gas-loss corrections applied to neem ice core samples

In this section we first present the strategies employed in literature for gas-loss corrections (Sect. 4.6.5.1), then present the strategy adopted for the neem ice core samples (Sect. 4.6.5.2).

4.6.5.1 Existing gas-loss correction strategies

We've seen that gas-loss fractionation can occur (i) through two different mechanisms described in the previous sections. Both size and mass-dependent mechanisms are caused by gas leaking out of overpressured bubbles in ice (Severinghaus et al., 2009), and (ii) are not limited to post coring (sample handling, transport and storage), but also fractionate gases during bubble close-off or ice core retrieval\(^{15}\). It follows that applying a specific gas loss correction for each of these steps is hardly possible, and prior work circumvent this issue by applying a empirical correction accounting for all gas-loss processes.

As mentioned earlier, fossil air in fractured ice core samples that suffered gas loss typically present an elemental composition half as depleted in Ar as in \(\delta O_2/N_2\) and \(^{40}Ar\) (Bender

\(^{15}\)here we do not consider gas loss fractionation associated with the bubble-clathrate transition zone, as measured neem samples were coming from much shallower depths.
et al., 1995; Severinghaus et al., 2009). Severinghaus et al. (2009) suggest that this typical gas loss signature results from the combination of diffusion in the ice lattice (size-dependent fractionation) then through cracks (mass-dependent fractionation). Indeed, the apparent slope of 0.5 between \( \delta\text{Ar}/\delta^{15}\text{N} \) and \( \delta\text{O}_2/\text{N}_2 \) can be obtained by combining a size-dependent fractionation mechanism, in which \( \text{O}_2 \) and \( \text{Ar} \) are affected in similar proportions (slope of 1), and a mass-dependent process, where \( \text{Ar} \) is 3 times as much enriched as \( \text{O}_2 \) relative to \( \text{N}_2 \), owing to the relative mass difference (Fig. 4.8). If this assumption holds true, it is then possible to separate the size-dependent from the mass-dependent process by combining \( \delta\text{Ar}/\delta^{15}\text{N} \) and \( \delta\text{O}_2/\text{N}_2 \) measurements. Adopting this logic, Severinghaus et al. (2009) correct Siple Dome \( \delta^{18}\text{O} \) in the following way:

\[
\delta^{18}\text{O}_{\text{atm}} = \delta^{18}\text{O}_{\text{gravcorr}} + 0.0136 \cdot \left( \delta\text{O}_2/\text{N}_2^{\text{gravcorr}} + 2.1\%_0 \right) - 0.0130 \cdot \delta\text{Ar}/\text{N}_2^{\text{gravcorr}}
\]  

(4.12)

Note the typical slope of \( \approx 0.01 \) between \( \delta^{18}\text{O} \) and \( \delta\text{O}_2/\text{N}_2 \) associated with gas-loss processes, as well as the 2.1 \( \%_0 \) value which is an adjustable parameter tuned to force the mean of the last 1000 yrs of \( \delta^{18}\text{O}_{\text{atm}} \) to 0 \( \%_0 \).

\( \delta\text{O}_2/\text{N}_2 \) only Various empirical corrections based solely on \( \delta\text{O}_2/\text{N}_2 \) for artefactual gas loss are described in literature. (Landais et al., 2003) applied a correction to measured GRIP \( \delta^{18}\text{O}_{\text{atm}} \) depending on the time of storage, as observed by Ikeda-Fukazawa et al. (2005): in their study, given the rough dependence of \( \delta\text{O}_2/\text{N}_2 \) and \( \delta^{18}\text{O} \) (\( R^2 = 0.6 \)), the \( \delta^{18}\text{O}_{\text{atm}} \) correction consisted of discarding samples with an \( \text{O}_2 \) loss higher than 5 \( \%_0 \) and decreasing valid \( \delta^{18}\text{O}_{\text{atm}} \) by 0.07 \( \%_0 \) based on the storage effect (over 14 yrs) observed in \( \delta^{18}\text{O}_{\text{atm}} \) of 6 duplicate Vostok ice core samples.

Temperature of storage is crit-
ic to minimize gas-loss: $\delta O_2/N_2$ of EDC ice core samples stored at $-50^\circ$C were associated with a standard deviation of 0.32‰ while EDC samples stored at $-25^\circ$C had a standard deviation of 10‰ (Landais et al., 2012). Consequently, they only corrections were only applied to samples stored at $-25^\circ$C.

### 4.6.5.2 Gas-loss correction applied to NEEM ice core samples

The gas-loss correction applied to NEEM ice core samples’ $\delta^{18}O_{atm}$ is adapted from the correction applied by (Landais et al., 2010) for NGRIP ice core samples. They found the typical slope of 0.01‰ · °C$^{-1}$ between $\delta O_2/N_2$ variations and $\delta^{18}O_{atm}$ variations (4.6.4.2), and corrected $\delta^{18}O_{atm}$ for this effect. As NGRIP ice core samples measured immediately after the recovery of the ice core had a mean $\delta O_2/N_2$ value of $-10$‰ relative to atmospheric air (Landais et al., 2010). The authors concluded that a natural process (i.e. not occurring during shipping, storage or handling of the ice core) had depleted the elemental composition of the ice bubble air and needed to be corrected for. $\delta O_2/N_2$ was thus corrected for gas-loss fractionation during close-off by adding 10‰ to the measured $\delta O_2/N_2$ values. However, the assumption that no artifactual gas loss occurred may be incorrect, because of core-cracking fractionation: an ice core undergoes enormous stress while being brought to the surface (Sect. 4.6.4.2). Small cracks open up during depressurization and may later re-heal, giving the appearance of a well-preserved ice sample without cracks at the surface. This has been shown by shining certain wavelengths of light at the core, which cause drilling fluid trapped in re-healed cracks to fluoresce (Severinghaus, pers. comm., 2016). However, not accounting for core-cracking fractionation does not affect the quality of the $\delta^{18}O_{atm}$ corrections, because natural and artifactual gas loss cause similar fractionation of the trapped gases in ice. In other words, it is not necessary to know the relative contribution of bubble close-off, coring and post-coring processes to the total gas loss fractionation as a general empirical correction is applied correct for these effects without distinguishing between them.

Our mass spectrometry procedure (Sect. 4.5) developed to measure $\delta^{18}O_{atm}$ did not include $\delta^{40}Ar$ measurements, in spite of its potential to correct $\delta^{18}O_{atm}$ from thermal fractionation and to distinguish between mass-dependent and size-dependent gas-loss processes (e.g. Severinghaus et al., 2009). The resistors attached to the Universal triple collector of the Delta V plus ms were such that m/z 40 was saturated in the most sensitive Faraday cup (devoted usually to m/z 33) in the "O2_gaslab" configuration. Switching off high amplification proved to be impossible to program with ISL scripts in an automated sequence, requiring a change of configuration to obtain a measurable m/z 40 ion voltage. Grzymala-Lubanski (2015) did the choice to significantly reduce measurement time at the expense of $\delta^{40}Ar$ measurements. As $^{40}Ar$ was not measured, the correction for NEEM ice core samples presented here is solely based on $\delta O_2/N_2$.

$\delta O_2/N_2$ was measured with an improved peak jumping procedure, based on Sever-
Figure 4.9 – neem δ¹⁸O atm or neem δ¹⁵N versus δO₂/N₂. Both neem δ¹⁸O atm and δO₂/N₂ ice core samples are gravitationally corrected based on δ¹⁵N. Text in blue (green) gives the slope and intercept of the regression line and its associated R². Intercepts of the linear fit only reflect the choice of the O₂/N₂ standard. Note that δ¹⁵N is insensitive to gas-loss fractionation in our experiments, which confirms that δ¹⁵N can be used with confidence to correct δ¹⁸O atm for gravitational fractionation. The enriched δ¹⁵N results probably from pressure-gradient driven fractionation during the experiment (scaling with the absolute mass-difference as gravitational fractionation), as δ¹⁸O atm from the same sample is identical to other neem replicates after gravitational correction (Sect. 4.6.6).

inghaus et al. (2003), as described in Sect. 4.5.3.2.4, as the collector configuration of the IRMS did not enable the simultaneous measurements of masses m/z 32 (O₂) and 28 (N₂). The mean corrected δO₂/N₂ value of the 21 well preserved neem Holocene ice core samples is −3.9 ± 4.4‰. When plotting δ¹⁸O against δO₂/N₂ of the 21 neem late Holocene ice core samples, we find a slope of 0.0129‰ · δO₂/N₂ of the 21 neem late Holocene ice core samples, we find a slope of 0.0129‰ · δO₂/N₂ variations and δ¹⁸O variations (Fig. 4.9), similar to the one found in other studies, and therefore correct δ¹⁸O measurements from gas loss through the following equation:

\[
δ¹⁸O_{atm} = δ¹⁸O_{gravcorr} + 0.0129 \cdot (δO₂/N₂_{gravcorr} + 4.2),
\]

where 4.2 is a adjustable parameter used to force the mean δ¹⁸O of the 21 late Holocene neem ice core samples to 0‰. Here we follow the approach from Severinghaus et al. (2009), who applied such a correction to δO₂/N₂ to account for a poorly understood O₂ consumption process occurring during the experiment, which could be caused by oxidative reactions with SST surface. We also indicate in Table 4.3 δ¹⁸O_gaslosscorrected.
which is defined as follows:

\[
\delta^{18}O_{\text{gas loss corrected}} = \delta^{18}O_{\text{CScorrected}} + 0.0129 \cdot (\delta O_2/N_2\text{gravcorr}),
\]  

(4.14)

4.6.6 Correction synthesis

This section summarizes the data processing of neem \(\delta^{18}O_{\text{atm}}\) and details how error propagation is evaluated. The uncertainty of the fully-corrected data is estimated with error propagation.

4.6.6.1 Ensemble of corrections applied to neem \(\delta O_2/N_2\)

We present in Fig. 4.10 the results of gas-isotopic analyses of neem ice core samples. Precise values of \(\delta^{18}O_{\text{atm}}, \delta^{15}N\) and \(\delta O_2/N_2\) at different stages of the correction process, together with their average and standard deviation can be found in Table 4.3.

Figure 4.10 – Synthesis of all the corrections applied to Late Holocene neem ice samples. The loss of precision of individual ice core samples from the pressure-imbalanced corrected data (\(\delta^{18}O_{\text{PI corrected}}\)) to the fully corrected data (\(\delta^{18}O_{\text{atm}}\)), resulting from error propagation as described in Sect. 4.6.6.2, is illustrated by the increase of the error bars. In parallel, the pooled standard deviation of the 21 neem ice core \(\delta^{18}O_{\text{atm}}\) decreases from 0.077 to 0.028 \(\%_o\), validating the applied corrections (refer to Table 4.3 for precise values). Note that \(\delta^{18}O_{\text{atm}}\) is not forced to 0 \(\%_o\) by adding a constant offset to \(\delta O_2/N_2\) values.

Pressure-gradient fractionation during evacuation of the frozen ice sample sitting in the extraction flask may be responsible for \(\delta^{15}N\) and \(\delta^{18}O_{\text{atm}}\) enrichment observed in neem ice core sample number 3 (measurement from 26/08/2015, with \(\delta^{15}N=0.395 \%_o\)) (Severinghaus et al., 2009; Kobashi et al., 2008). Indeed, the presence of micro-

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cracks, from which lighter isotopes would preferentially escape during evacuation, could explain an isotopic enrichment. Alternatively, an internal leak from the collecting rod through the valve of the collection manifold after collection of the sample may also cause an isotopic enrichment. Pressure-gradient fractionation scales as the absolute mass difference, which would enrich $\delta^{18}O_{atm}$ twice as much as $\delta^{15}N$. As revealed in Fig. 4.10, $\delta^{18}O_{gasloss corrected}$ of the anomalous neem sample is enriched by 0.28‰ compared to the mean $\delta^{18}O_{gasloss corrected}$ value, roughly twice as much as the enrichment observed in $\delta^{15}N$. Besides, once corrected for gravitational fractionation, which is a particular case of pressure-gradient fractionation, where the pressure gradient results from hydrostatic equilibrium (Severinghaus and Battle, 2006), $\delta^{18}O_{atm}$ of the anomalous neem ice core sample is identical to the mean $\delta^{18}O_{atm}$ within the uncertainty associated with the experiment.

4.6.6.2 Estimation of uncertainty

Assuming that errors are statistically independent, the error propagation formula for $f(x, y, z)$ reduces to:

$$\sigma \cdot f = \sqrt{\left(\frac{\partial f}{\partial x} \sigma_x\right)^2 + \left(\frac{\partial f}{\partial y} \sigma_y\right)^2 + \left(\frac{\partial f}{\partial z} \sigma_z\right)^2}$$ (4.15)

Simple expressions can be employed (Barlow, 1989) to propagate the uncertainty to the sequence of corrections applied to $\delta^{18}O_{atm}$:

$$f = aA \rightarrow \sigma_f^2 = a^2 \cdot \sigma_A^2$$ (4.16a)

$$f = A + B \rightarrow \sigma_f^2 = \sigma_A^2 + \sigma_B^2$$ (4.16b)

$$f = AB \rightarrow \sigma_f^2 = B^2 \cdot \sigma_A^2 + A^2 \sigma_B^2$$ (4.16c)

Applied to $\delta^{18}O_{atm}$ correction procedure, the total uncertainty of a block of $\delta^{18}O_{atm}$ measurements is calculated as follows\(^\text{16}\) using equations 4.16. First:

$$\sigma^2_{\delta^{18}O_{corrected}} = \sigma^2_{\delta^{18}O_{uncorrected}} + \delta^2 \frac{O_2}{N_2} \cdot \sigma_{\text{chemical slope}} + (\text{chemical slope})^2 \cdot \sigma^2 \frac{O_2}{N_2}$$ (4.17)

And:

$$\sigma^2_{\delta^{18}O_{gasloss corrected}} = \sigma^2_{\delta^{18}O_{O_{corrected}}} + 0.0129 \cdot \sigma^2 \frac{O_2}{N_2}$$ (4.18)

Besides:

$$\sigma^2_{\delta^{18}O_{atm}} = \sigma^2_{\delta^{18}O_{gasloss corrected}} + 2 \cdot \sigma^2 \delta^{15}N.$$ (4.19)

Inserting Eq. 4.18 into Eq. 4.19:

$$\sigma^2_{\delta^{18}O_{atm}} = \sigma^2_{\delta^{18}O_{uncorrected}} + 0.0129 \cdot \sigma^2 \frac{O_2}{N_2} + 2 \cdot \sigma^2 \delta^{15}N.$$ (4.20)

\(^{16}\)Note that the gravitational fractionation correction applied to $\delta O_2/N_2$ was neglected given that $\delta O_2/N_2$ uncertainty is 20 times higher than $\delta^{15}N$ uncertainty.
Table 4.3 – Summary of δ\(^{18}\)O\(_{atm}\) measurements of neem Late Holocene ice core samples and applied corrections. Note that neem ice core sample number 3 (measurement from 26/08/2015), in red in the table, is considered as an outlier due to its anomalously enriched δ\(^{15}\)N (0.395 \(\%\)) and is therefore not included in average and standard deviation calculations.

<table>
<thead>
<tr>
<th>Date</th>
<th>Depth</th>
<th>Rod #</th>
<th>(\delta^{18})O(_{atm})corrected</th>
<th>(\delta^{18})N</th>
<th>(\delta^{15})O/(\delta^{18})N(_{2})</th>
<th>(\delta^{18})O(_{calculated})corrected</th>
<th>(\delta^{18})O(_{gravcorr})corrected</th>
<th>(\delta^{18})O(_{atm}) (not forced(^a))</th>
<th>(\delta^{18})O(_{atm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>26/08/2015</td>
<td>337</td>
<td>1</td>
<td>0.443 ± 0.006</td>
<td>0.228 ± 0.01</td>
<td>-0.11 ± 0.1</td>
<td>0.443</td>
<td>0.043</td>
<td>0.013</td>
<td>-0.0233</td>
</tr>
<tr>
<td>26/08/2015</td>
<td>337</td>
<td>2</td>
<td>0.425 ± 0.005</td>
<td>0.234 ± 0.009</td>
<td>-2.38 ± 0.28</td>
<td>0.414</td>
<td>0.371</td>
<td>-0.054</td>
<td>-0.0068</td>
</tr>
<tr>
<td>26/08/2015</td>
<td>337</td>
<td>3</td>
<td>0.709 ± 0.007</td>
<td>0.395 ± 0.009</td>
<td>0.54 ± 0.2</td>
<td>0.711</td>
<td>0.698</td>
<td>-0.079</td>
<td>-0.0924</td>
</tr>
<tr>
<td>26/08/2015</td>
<td>337</td>
<td>7</td>
<td>0.357 ± 0.003</td>
<td>0.219 ± 0.014</td>
<td>2.1 ± 0.17</td>
<td>0.366</td>
<td>0.382</td>
<td>-0.072</td>
<td>-0.0562</td>
</tr>
<tr>
<td>28/08/2015</td>
<td>337</td>
<td>1</td>
<td>0.441 ± 0.002</td>
<td>0.201 ± 0.011</td>
<td>-5.32 ± 0.26</td>
<td>0.417</td>
<td>0.338</td>
<td>0.015</td>
<td>-0.0064</td>
</tr>
<tr>
<td>28/08/2015</td>
<td>337</td>
<td>2</td>
<td>0.418 ± 0.007</td>
<td>0.214 ± 0.008</td>
<td>-2.97 ± 0.2</td>
<td>0.405</td>
<td>0.356</td>
<td>-0.023</td>
<td>-0.0072</td>
</tr>
<tr>
<td>28/08/2015</td>
<td>337</td>
<td>3</td>
<td>0.519 ± 0.004</td>
<td>0.256 ± 0.007</td>
<td>-3.98 ± 0.17</td>
<td>0.501</td>
<td>0.436</td>
<td>-0.011</td>
<td>-0.0075</td>
</tr>
<tr>
<td>28/08/2015</td>
<td>337</td>
<td>7</td>
<td>0.311 ± 0.006</td>
<td>0.213 ± 0.012</td>
<td>4.46 ± 0.19</td>
<td>0.351</td>
<td>0.398</td>
<td>-0.075</td>
<td>-0.0285</td>
</tr>
<tr>
<td>31/08/2015</td>
<td>337</td>
<td>1</td>
<td>0.564 ± 0.006</td>
<td>0.225 ± 0.007</td>
<td>-5.93 ± 0.16</td>
<td>0.537</td>
<td>0.449</td>
<td>0.087</td>
<td>-0.0011</td>
</tr>
<tr>
<td>31/08/2015</td>
<td>337</td>
<td>2</td>
<td>0.556 ± 0.006</td>
<td>0.227 ± 0.001</td>
<td>-10.2 ± 0.25</td>
<td>0.51</td>
<td>0.367</td>
<td>0.056</td>
<td>-0.0873</td>
</tr>
<tr>
<td>31/08/2015</td>
<td>337</td>
<td>3</td>
<td>0.505 ± 0.012</td>
<td>0.299 ± 0.008</td>
<td>-1.52 ± 0.25</td>
<td>0.498</td>
<td>0.465</td>
<td>-0.02</td>
<td>-0.0031</td>
</tr>
<tr>
<td>31/08/2015</td>
<td>337</td>
<td>7</td>
<td>0.41 ± 0.01</td>
<td>0.214 ± 0.001</td>
<td>-1.98 ± 0.2</td>
<td>0.401</td>
<td>0.365</td>
<td>-0.023</td>
<td>-0.0059</td>
</tr>
<tr>
<td>31/08/2015</td>
<td>337</td>
<td>8</td>
<td>0.485 ± 0.004</td>
<td>0.186 ± 0.008</td>
<td>-7.93 ± 0.4</td>
<td>0.449</td>
<td>0.337</td>
<td>0.077</td>
<td>-0.0049</td>
</tr>
<tr>
<td>02/09/2015</td>
<td>337</td>
<td>1</td>
<td>0.529 ± 0.002</td>
<td>0.232 ± 0.008</td>
<td>-8.91 ± 0.16</td>
<td>0.489</td>
<td>0.363</td>
<td>0.063</td>
<td>-0.0029</td>
</tr>
<tr>
<td>02/09/2015</td>
<td>337</td>
<td>2</td>
<td>0.43 ± 0.003</td>
<td>0.22 ± 0.006</td>
<td>-1.64 ± 0.4</td>
<td>0.423</td>
<td>0.390</td>
<td>-0.017</td>
<td>-0.0045</td>
</tr>
<tr>
<td>02/09/2015</td>
<td>337</td>
<td>3</td>
<td>0.559 ± 0.005</td>
<td>0.278 ± 0.009</td>
<td>-4.71 ± 0.12</td>
<td>0.538</td>
<td>0.463</td>
<td>-0.018</td>
<td>-0.0031</td>
</tr>
<tr>
<td>02/09/2015</td>
<td>337</td>
<td>7</td>
<td>0.6 ± 0.006</td>
<td>0.236 ± 0.012</td>
<td>-11.09 ± 0.37</td>
<td>0.55</td>
<td>0.395</td>
<td>0.084</td>
<td>-0.0071</td>
</tr>
<tr>
<td>02/09/2015</td>
<td>337</td>
<td>8</td>
<td>0.58 ± 0.007</td>
<td>0.21 ± 0.007</td>
<td>-9.36 ± 0.25</td>
<td>0.516</td>
<td>0.384</td>
<td>0.096</td>
<td>-0.0036</td>
</tr>
<tr>
<td>10/09/2015</td>
<td>337</td>
<td>7</td>
<td>0.486 ± 0.009</td>
<td>0.232 ± 0.011</td>
<td>-4.5 ± 0.37</td>
<td>0.506</td>
<td>0.436</td>
<td>0.042</td>
<td>-0.0080</td>
</tr>
<tr>
<td>10/09/2015</td>
<td>337</td>
<td>8</td>
<td>0.39 ± 0.002</td>
<td>0.223 ± 0.012</td>
<td>1.98 ± 0.17</td>
<td>0.381</td>
<td>0.395</td>
<td>-0.005</td>
<td>-0.0010</td>
</tr>
<tr>
<td>14/09/2015</td>
<td>337</td>
<td>na</td>
<td>0.555 ± 0.005</td>
<td>0.234 ± 0.005</td>
<td>-8.73 ± 0.21</td>
<td>0.594</td>
<td>0.469</td>
<td>0.126</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

Mean  
Std dev 1σ  

\(^a\)No gas loss correction applied (Fig. 4.10).  
\(^b\)No constant offset is added to the gravitationally corrected \(\delta\)O\(_2/\delta\)N\(_2\) so as to force the mean of the 21 \(\delta\)O\(_{atm}\) neem samples to be 0 \(\%\).  
\(^c\)Calculated excluding the outlier \(\delta^{15}\)N value in red in the table (Fig. 4.11). Mean is 2.234 \(\%\).  
\(^d\)\(\sigma = 0.042\)\(\%\) when the outlier \(\delta^{15}\)N value (Fig. 4.11) is not excluded (red value).
Finally, inserting Eq. 4.17 into Eq. 4.20 provides the uncertainty associated with corrected $\delta^{18}O_{atm}$:

$$\sigma^2_{\delta^{18}O_{atm}} = \sigma^2_{\delta^{18}O_{corrected}} + \frac{\sigma_{\text{chemical slope}}}{N_2} + (\text{chemical slope})^2 \cdot 0.0129 \cdot \frac{\sigma^2_{\delta^{18}O}}{N_2} + 2 \cdot \sigma^2_{\delta^{15}N}.$$  (4.21)

### 4.6.7 Reproducibility of $\delta^{18}O_{atm}$ ice core measurements

The external precision of the setup associated with $\delta^{18}O_{atm}$ ice core measurements is assessed with the 21 late Holocene neem ice core samples measured over the 3 weeks during which rice ice core measurements were performed by Grzymala-Lubanski (2015). Indeed, the usual procedure, where standard gas (Neem_S1) is injected on top of bfi, resulted in a depletion and a large scatter of measured $\delta^{18}O$ and $\delta^{15}N$ values, which is probably due to the presence of dissolved gases in bfi, even in the absence of visible inclusion, in line with the description of Bock et al. (2010). Using shallow ice core samples as quality control standard allows us to take into account potential fractionation of neem in our analytical system. They are also used to check the stability of the experimental set-up and estimate the uncertainty associated with ice core sample measurements.

As pointed out by Severinghaus et al. (2003), it is reasonable to expect that samples cut from around the same depth of an ice core should have the same true isotope composition. It is especially true for molecular $O_2$, whose signal is quasi constant over the Holocene. Here these 21 neem ice core samples, measured at different days, collected in different rods, are associated after corrections with a standard deviation of 0.028‰ for $\delta^{18}O$ and 0.021‰ for $\delta^{15}N$ after excluding one outlier (Fig. 4.11).

Neem $\delta^{15}N$ measurements are depleted by $\simeq 0.11\%_o$ compared to the published measurements. Indeed, the mean 5 neem Holocene samples from the depths 396-416 m and ages 1846-1957 yr b2k, measured at LSCE, have a mean $\delta^{15}N$ value of 0.34 ± 0.02 ‰ (NEEM members, 2013), while the mean $\delta^{15}N$ of neem ice core samples measured by Grzymala-Lubanski (2015) is enriched by 0.23 ± 0.021 ‰. This offset might be due to an undetected artifact during the experiment. Atmospheric air leaking-in, maybe associated with the sealing of the air samples in the extraction flasks, would cause a $\delta^{15}N$ depletion of the sample, which should also be observed in $\delta^{18}O_{atm}$, but this is not clear from neem ice core measurements. As the background of water (m/z 18) was consistently low, and no anomalous increase in sample amount was observed while measuring the samples, this hypothesis is not favored. The offset could express the isotopic signature of the analytical setup, as neem ice core samples are referenced again Neem_C1 introduced in the standard bellow of the ms (Sect. 4.5.5).

### 4.7 Conclusions and perspectives

In this chapter we described mass spectrometry measurements in di mode of atmospheric $O_2$ and $N_2$ isotope ratios:
Figure 4.11 – $\delta^{18}O$ or $\delta^{15}N$ obtained from the Late Holocene neem ice samples. Both neem $\delta^{18}O$ and $\delta O_2/N_2$ are gravitationally corrected using $\delta^{15}N$. Text in blue (green) gives the average (represented by the line of the same color) and standard deviation (represented by the dashed lines) associated with $\delta^{18}O$ ($\delta^{15}N$) after routine (pressure imbalance, chemical slope, gravitational fractionation) and gas loss corrections.

- We developed a custom-based script to fully automate high-precision DI ice core sample measurements of $\delta^{18}O$, $\delta^{17}O$, $\delta^{15}N$ and $\delta O_2/N_2$, including samples (collected in a collection manifold connected to the sample inlet of the MS (Chapter 3)) and standard introduction, adjusted pressure adjustment and peak-jumping procedures. The peak-jumping procedure for $\delta O_2/N_2$ measurements is based on the script developed by Severinghaus et al. (2003) for Kr/Ar measurements.

- We made minor changes and major maintenance on the MS to minimize artifactual fractionation during DI measurements.

- The measured 21 NEEM ice core samples from the same depth display large variations in their $\delta O_2/N_2$ and $\delta^{18}O$ ratio, not representative of a true atmospheric change as they should carry the same signal. The scatter underlines the occurrence of gas loss processes causing varying $O_2$ isotope ratios, with a dependence of $\delta^{18}O_{atm}$ on $\delta O_2/N_2$ ($0.0129 \%_e \cdot \%_{e^{-1}}$) similar to the one described in literature. Improvements for the future should include $\delta Ar/N_2$ measurements to evaluate, in combination with $\delta O_2/N_2$, the relative contribution of mass-dependent and size-dependent fractionation components to gas loss processes. Besides, the neem science trench, where the ice cores were stored, was significantly too warm during the first years of the ice core drilling campaign, likely to have caused a fair amount of gas loss in ice core samples stored on the field.

- Pressure-gradient fractionation during extraction flask evacuation may be responsible for $\delta^{15}N$ and $\delta^{18}O_{atm}$ enrichment observed in the outlier NEEM ice
core sample, due to the presence of microcracks. Once corrected for gravitational fractionation, the anomalous neem ice core sample is identical to the mean \( \delta^{18}O_{\text{atm}} \) within the uncertainty associated with the experiment.

- Based on 21 neem ice core samples from the same depth, collected over a time period of 3 weeks over different rods, we proved the ability of the analytical system (including extraction line and mass spectrometry) to reproduce ice core sample measurements of corrected \( \delta^{18}O_{\text{atm}} \) and \( \delta^{15}N \) with an external precision of 0.028 \( \%_0 \) and 0.021 \( \%_0 \), respectively.

- Using the peak jumping procedure of Severinghaus et al. (2003), \( \delta O_2/N_2 \) is measured with a precision ranging from 0.1 to 0.4 \( \%_0 \) for an individual ice core sample. The 21 neem samples exhibit the expected large scatter (pm 4.40) caused by a varying amount of mass-dependent and size-dependent fractionation during gas loss processes.

- Based on zero-enrichment tests, the internal precision of \( \delta \) measurements of \( \delta^{18}O \) and \( \delta^{15}N \) is 0.008 \( \%_0 \) (1 \( \sigma \)) and 0.005 \( \%_0 \) (1 \( \sigma \)). As seen in Table 4.3, individual ice core sample measurements have a similar precision. This level of precision is similar to the one found in other studies.

- We detail the data-processing method, its associated uncertainty and the strategy employed to correct for non-climatic effects, including effects of sample and standard beam voltage imbalance on the measured \( \delta^{18}O_{\text{atm}} \) ratio (pressure imbalance), of variations of the \( O_2/N_2 \) ratio on \( \delta^{18}O_{\text{atm}} \) (chemical slope), of gravitational fractionation, and of gas loss processes associated with bubble close-off and air entrapment, coring and post-coring processes.

The work presented in this chapter can be further developed by:

- Referencing the ice core samples to the working standard Neem_S1 introduced over BFI so as to fully respect the IT principle and enable confident comparison with other \( \delta^{18}O_{\text{atm}} \) records measured in other laboratories. Such standard measurements involving BFI were not reproducible hitherto, and may arise from the fact that Neem_S1 was introduced before melting the BFI. To circumvent this problem, the adopted strategy in this thesis is to reference the sample against Neem_C1 introduced in the right bellow of the MS, and to check the reproducibility and accuracy of the measurements by measuring real ice core samples with known \( \delta^{18}O_{\text{atm}} \) and unknown \( \delta^{19}O_{\text{atm}} \) isotope ratios.

- The setup is built for three-oxygen isotope measurements, but the precision required for ice core \( \Delta^{atm} \) measurement is three times better than the precision which is also the PRM for atmospheric \( O_2 \) measurements

\[ \text{we know what the true atmospheric signal should be for a given period of time as it is the same in all ice cores owing to the long lifetime of } O_2 \text{ in the atmosphere relative to the inter-hemispheric mixing time.} \]

\[ \text{we know that the signal preserved in ice cores is different than the true atmospheric signal} \]
obtained in this thesis for $\delta^{18}O_{atm}$ measurements in ice cores. To obtain such a precision, reproducible measurements of standard gas introduced over BFI are required, as well as a complete automation of the extraction line to respect an identical extraction/collection procedure for each ice core sample and enhance precision.


Kobashi, T., Severinghaus, J. P., and Kawamura, K. (2008). Argon and nitrogen isotopes of trapped air in the {GISP2} ice core during the holocene epoch (o$\overline{1}$1,500

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5 Quantifying molecular oxygen isotope variations during a Heinrich stadial

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5.1 Abstract

δ18O of atmospheric oxygen (δ18Oatm) undergoes millennial-scale variations during the last glacial period, and systematically increases during Heinrich stadials (HSs). Changes in δ18Oatm combine variations in biospheric and water cycle processes. The identification of the main driver of the millennial variability in δ18Oatm is thus not straightforward. Here, we quantify the response of δ18Oatm to such millennial events using a freshwater hosing simulation performed under glacial boundary conditions. Our global approach takes into account the latest estimates of isotope fractionation factor for respiratory and photosynthetic processes and make use of atmospheric water isotope and vegetation changes. Our modeling approach allows to reproduce the main observed features of a HS in terms of climatic conditions, vegetation distribution and δ18O of precipitation. We use it to decipher the relative importance of the different processes behind the observed changes in δ18Oatm. The results highlight the dominant role of hydrology on δ18Oatm and confirm that δ18Oatm can be seen as a global integrator of hydrological changes over vegetated areas.

5.2 Introduction

Oxygen is one of the most abundant species in atmospheric air. As oxygen is produced by photosynthesis and consumed by respiration, a record of oxygen concentration in the past should help us to constrain these two major biospheric fluxes on Earth and potentially provide information on their link with the carbon cycle.
Changes in the O$_2$ / N$_2$ ratio can be measured in air trapped in ice cores back to 800 kyr (Bender, 2002; Kawamura et al., 2007; Landais et al., 2012; Bazin et al., 2014). Unfortunately the O$_2$ / N$_2$ ratio in ice cores does not provide a direct information on the true atmospheric variations because it is affected by permeation through the ice lattice during bubble formation at pore close-off, roughly 100 m below the ice sheet surface, and by gas loss during ice core storage. These effects have less impact on the isotopic composition of oxygen. These isotopic compositions have thus been explored as possible constraints on biospheric productivity (Luz et al., 1999).

When dealing with isotopes, it is standard to use the isotope ratio, $R$, defined as the fraction of the abundance of the rare isotope over the dominant one in a substance. Since changes in isotope ratios through natural processes are very small, they are expressed in relation to a standard (recent air and Vienna Standard Mean Ocean Water (VSMOW) being used for O$_2$ and H$_2$O, respectively) using the $\delta$ notation,

$$\delta^{18}O = \frac{^{18}R_{\text{sample}}}{^{18}R_{\text{standard}}} - 1.$$  

$\delta^{18}O$ and $\delta^{17}O$ of atmospheric oxygen have been measured for the period of the past 800 kyr with a mean resolution of about 1500 years (e.g., Landais et al., 2010, and references therein; Blunier et al., 2012). As shown by Bender et al. (1994), $\delta^{18}O$ of atmospheric oxygen, noted $\delta^{18}O_{\text{atm}}$ hereafter, cannot easily be related to biospheric productivity through photosynthesis and respiration fluxes. $\delta^{18}O_{\text{atm}}$ variations actually reflect for a large part the isotopic composition of the meteoric water. The latter is transmitted to the plant through its roots and stems to the leaves, where photosynthesis produces oxygen with an isotopic composition close to the isotopic composition in leaf water. Respiration modifies the isotopic composition of atmospheric oxygen in a complex way. While the processes consuming oxygen enrich atmospheric oxygen through a preferential consumption of the lightest molecules, individual biological pathways are associated with a wide range of oxygen fractionations (Helman et al., 2005).

Based on fractionation factors available at the time, Bender et al. (1994) established that the relative proportion of oceanic vs. terrestrial biospheric productivities together with the difference in isotope fractionation over land and ocean were driving the $\delta^{18}O_{\text{atm}}$ budget. Several studies have built on this idea and interpret the $\delta^{18}O_{\text{atm}}$ variations mainly as variations in the oceanic vs. terrestrial biospheric productivities (Hoffmann et al., 2004; Ciais et al., 2012). However, recent measurements have revealed that, overall, fractionation associated with oceanic productivity is very similar to its terrestrial counterpart (Hendricks et al., 2004; Eisenstadt et al., 2010), questioning the interpretation of $\delta^{18}O_{\text{atm}}$ as an indicator of the relative proportion of oceanic vs. terrestrial biosphere productivity (Luz and Barkan, 2011).

Despite the complex interpretation of $\delta^{18}O_{\text{atm}}$, several robust features have already been observed that highlight the potential of these measurements. At the orbital scale, $\delta^{18}O_{\text{atm}}$ is showing clear variations at a 23 kyr periodicity (Dreyfus et al., 2007).
Figure 5.1 – Greenland stadials and Heinrich stadials during the last glacial period. Red numbers indicate GSs and black labels HSs. (a) Black line: NGRIP δ¹⁸O, %e, on the GICC05 timescale back to 60 ka b2k. (b) Red line: Siple Dome atmospheric δ¹⁸O (Severinghaus et al., 2009) on GICC05 timescale. Red dots denote intervals in the core where deep air convection or cracked firn layer may have thermally fractionated these samples, as shown by anomalous δ¹⁵N in Figs. S1 and S8 of Severinghaus et al. (2009). The transfer of Siple Dome atmospheric δ¹⁸O on the GICC05 chronology is achieved by using the Siple Dome gas age scale compatible with the GICC05 chronology (Guillevic, 2013), based on match points between Siple Dome methane variations (Brook et al., 2005; Ahn et al., 2012; depth point) and NEEM methane variations (Chappellaz et al., 2013; GICC05 gas age point). A linear interpolation is then performed between match points to calculate the Siple Dome gas age. Green line: NEEM atmospheric δ¹⁸O, %e (±0.03 %e; Guillevic et al., 2014). Colored areas: GSs. Grey: GS with no major Heinrich event. Orange: HS1, HS2, HS3, HS4, HS5 and end of HS6 – GSs with a major Heinrich event. Black error bars indicate HS onset and end uncertainty (2σ), based on the Rasmussen et al. (2013) maximum counting error (MCE). Top (right to left): black and white horizontal bar indicate Marine Isotope Stage 1 to 4.

This strong link with precession is probably related to the variations in the hydrological cycle at low latitudes (Bender et al., 1994). Indeed, variations related to the monsoon regime strongly imprint the isotopic composition of meteoric water as observed in speleothem records (e.g., Wang et al., 2008). They are easily transmitted to the isotopic composition of atmospheric oxygen because the major part of the biospheric productivity, and hence photosynthesis, is occurring in the tropics and subtropics.

At the millennial scale, it has recently been shown that δ¹⁸O atm is responding to the abrupt climate changes of the last glacial period (Landais et al., 2007a; Severinghaus et al., 2009). Millennial-scale climate variability is perhaps best known from the
Greenland ice cores, where it is manifested in the stable water isotopes of ice. During the last glacial period, these cores show 25 Dansgaard–Oeschger (DO) events (NGRIP members, 2004). A DO event typically exhibits a sawtooth pattern: (i) a cold phase (Greenland stadial, noted GS hereafter) lasting from centuries to millennia, followed by a warm phase (Greenland interstadial, GI) starting with (ii) a rapid transition (a few decades) with an amplitude of up to $16 \pm 2.5\, ^\circ C$ (Landais et al., 2004; Huber et al., 2006; Kindler et al., 2014), and ending with (iii) a gradual cooling before an abrupt decrease towards cold, stadial values.

During the last decade, mechanisms of glacial abrupt events have been investigated using coupled ocean–atmosphere models of varying complexity (e.g., Kageyama et al., 2010, 2013; Stouffer et al., 2006). Recent hypotheses often invoke internal variability (Kleppin et al., 2015; Dokken et al., 2013), involving sea ice–atmosphere interactions (e.g., Li et al., 2005, 2010), through ice–albedo feedback and the impact of sea ice cover on regional temperatures by preventing heat exchange between the ocean and atmosphere. There remains robust evidence from multiple lines of paleoceanographic information and modeling that millennial-scale variability is linked to changes in the Atlantic meridional overturning circulation (AMOC) intensity (e.g., McManus et al., 1998), potentially initiated by large freshwater input in the North Atlantic (e.g., Broecker et al., 1990). The presence of ice rafted debris (IRD; Ruddiman, 1977; Heinrich, 1988) in marine sediments from the North Atlantic region during the largest GS document episodes of massive iceberg discharge in the North Atlantic (Heinrich events) mainly from the Laurentide (H2, H4, H5) and Fennoscandian (H3, H6) ice sheets (Grousset et al., 1993; Guillevic et al., 2014 and references therein). Even though IRD is present in each GS (Elliot et al., 2002), not all GSs contain a Heinrich event. Heinrich stadials (noted HSs hereafter) are GSs associated with a Heinrich event (Barker et al., 2009; Sanchez Goni and Harrison, 2010).

Several aspects of the observed patterns during DO events can be captured through the response of the Earth system to imposed freshwater perturbations in the North Atlantic (Liu et al., 2009; Otto-Bliesner and Brady, 2010; Kageyama et al., 2010; Roche et al., 2010), mimicking Heinrich events. Depending on the background state of the climate (glacial or interglacial, orbital context) and the AMOC, as well as on the magnitude of the freshwater forcing, these models produce a complete shutdown of the AMOC (HS-like state) or a reduction of the strength of the AMOC (GS-like state; e.g., Menviel et al., 2014). The injection of freshwater produces in all models a significant cooling of the North Atlantic region. The amplitude of the associated temperature change is probably affected by the simulated change in sea ice extent and feedbacks between sea ice and temperature that vary in the different models (Kageyama et al., 2013). These hosing experiments also produce an interhemispheric see-saw temperature pattern, associated with a southward shift of the Intertropical Convergence Zone (ITCZ) (e.g., Dahl et al., 2005; Broccoli et al., 2006; Krebs and Timmermann, 2007; Swingedouw et al., 2009; Cvijanovic and Chiang, 2013). Abrupt climate variation associated with the Greenland signal is found down to low latitudes in numerous ter-
restrial and marine archives (e.g., Clement and Peterson, 2008). Its climatic impact is recorded in large parts of the North Atlantic region, both in marine cores (e.g., Bond et al., 1993; Broecker, 2000) and in speleothems (Fleitmann et al., 2009). Concomitant methane excursions and variations in the isotopic composition of the calcite of speleothems in eastern Asia (e.g., Wang et al., 2001; Cheng et al., 2012) strongly support the fact that these DO events are associated with major reorganization of the tropical water cycle and hence monsoon intensity through a shift in the ITCZ and its terrestrial equivalent, the tropical rain belt (Chappellaz et al., 2013; Wang et al., 2008; Pausata et al., 2011).

For this period of millennial-scale variability, high-resolution measurements of $\delta^{18}O_{atm}$ have been obtained in Greenland and Antarctic ice cores (e.g., Guillevic et al., 2014; Landais et al., 2007a, 2010; Severinghaus et al., 2009). In Fig. 5.1 we present a synthesis of $\delta^{18}O_{atm}$ evolution from the Siple Dome ice core over HSs displayed on Greenland Ice Core Chronology 2005 (GICC05) timescale, using definitions of Rasmussen et al. (2013) of the onset of GS. The $\delta^{18}O_{atm}$ records show a systematic increase in a few thousand years following the onset of a HS (Fig. 5.2) by around 0.13‰, from $+0.08$‰ (HS1) to $+0.18$‰ (HS5). The difference in the slope inflection at the onset of HS4 and HS5, more pronounced that for HS1, HS2 and HS3, may be due to the long-term trend observed in $\delta^{18}O_{atm}$. Indeed, from 35 to 15 kyr, $\delta^{18}O_{atm}$ exhibits a constant increase, consistent with the build-up of polar ice sheet, and hence enrichment of ocean water in $^{18}O$, but remains relatively stable over MIS3 (Fig. 5.1).

Because of its global character, $\delta^{18}O_{atm}$ should provide added value compared to the different local records of hydrological cycle variations in different continental and marine archives. However, until now, no quantitative, robust interpretation of past variations in $\delta^{18}O_{atm}$ has been established, which limits the use of $\delta^{18}O_{atm}$ as a quantitative indicator for past biospheric production or variations in the hydrological cycle. The aim of this

![Figure 5.2 – Evolution of Siple Dome atmospheric oxygen $\delta^{18}O$ (Severinghaus et al., 2009) during Heinrich stadials on the GICC05 timescale.](image)
modeling study is thus to provide a quantitative interpretation for the systematic increase in $\delta^{18}O_{\text{atm}}$ over HSs. To reach this objective, we propose a global approach incorporating outputs from a general circulation model implemented with water isotopes and focus on the millennial variability in the last glacial period. We follow a modeling approach already developed by Hoffmann et al. (2004). We combine climatic parameters (temperature and humidity), isotopic composition of meteoric water, vegetation distribution and productivity simulated by different models with monthly mean temporal resolution.

In the following section, we describe the general method used to simulate a global $\delta^{18}O_{\text{atm}}$ signal. Section 5.4.1 is dedicated to model validation and Section 5.4.2 proposes to quantify the different contributions (hydrology, vegetation, climatic conditions) to the $\delta^{18}O_{\text{atm}}$ signal over a HS equivalent.

5.3 Method

According to Landais et al. (2007a, 2010) and Severinghaus et al. (2009), the millennial variations in $\delta^{18}O_{\text{atm}}$ during the last glacial period are driven by shifts in the tropical rain belt modifying the relative humidity distribution and the isotopic composition of meteoric water consumed by terrestrial biosphere. The isotopic content of atmospheric oxygen is controlled by numerous processes, so we must consider (i) the worldwide meteoric water isotopic composition, from which ground water is derived; (ii) the worldwide temperature and humidity, from which evaporative enrichment of leaf water $\delta^{18}O$ is calculated; (iii) the worldwide vegetation cover and gross primary productivity, defining the photosynthetically and respiratory active areas that contribute to $\delta^{18}O_{\text{atm}}$; and (iv) respiratory processes.

5.3.1 Oxygen isotopes mass balance model

Oxygen is exchanged with the terrestrial and marine biospheres as well as with the stratosphere. Assuming a steady state, $\delta^{18}O_{\text{atm}}$ can thus be expressed as follows:

$$
\delta^{18}O_{\text{atm}} = \frac{(F_{\text{terr}} \cdot \delta^{18}O_{\text{terr}} + F_{\text{mar}} \cdot \delta^{18}O_{\text{mar}})}{(F_{\text{terr}} + F_{\text{mar}})} - 18\epsilon_{\text{strat}},
$$

(5.2)

where $18\epsilon_{\text{strat}}$ represents the stratospheric isotope fractionation caused by photochemical reaction in the stratosphere involving $O_2$, $O_3$ and $CO_2$. $F_{\text{terr}}$ and $F_{\text{mar}}$ denote $O_2$ fluxes of gross terrestrial and oceanic productivity, respectively. $\delta^{18}O_{\text{terr}}$ and $\delta^{18}O_{\text{mar}}$ are the isotopic composition arising from the terrestrial and oceanic realms, respectively. $18\epsilon_{\text{strat}}$ is a small term, 0.4% compared to $\approx 23.8\%$ for $\delta^{18}O_{\text{atm}}$ with reference to V-SMOW (Luz et al., 2014) and is not assumed to change significantly over a HS because $CO_2$ level remains relatively stable. We assume a constant $CO_2$ level between the LGM and HS in our study. Ahn and Brook’s (2014) study shows that variations over HSs are small (increase of less than 20 ppm). Effect of isotopic exchange between $CO_2$ and $O_2$ in the stratosphere on $\delta^{18}O_{\text{atm}}$ is expected to be proportional to $CO_2$ mixing ratio. Following the calculation of Bender et al. (1994), which estimates a $\delta^{18}O_{\text{atm}}$
depletion of 0.4% for a CO₂ concentration of 353 ppm, we can estimate that a 20 ppm increase between the LGM and HS can modify δ¹⁸Oₐtm by −0.023%. The sign of this change is actually opposite to the sign of the observed δ¹⁸Oₐtm signal. We focus mainly on the millennial-scale variations in the terrestrial contribution to δ¹⁸Oₐtm signal, i.e., F₆₅terr · δ¹⁸O₆₅terr/(F₆₅terr + F₆₅mar).

We do not consider the marine influence, in this first approach, for the following reasons. First, our aim is to test the hypothesis of Landais et al. (2007b) and Severinghaus et al. (2009) that δ¹⁸Oₐtm millennial-scale variations are largely driven by changes in the low-latitude hydrological cycle through changes in the δ¹⁸O of precipitation. Second, Hendricks et al. (2004) and Luz and Barkan (2011) have shown that the difference between δ¹⁸Oterr and δ¹⁸Omar is not significant. Finally, the spatial and temporal variations in water δ¹⁸O and respiration pathways in the ocean are expected to be relatively small compared to the variations on land, which renders their integration for δ¹⁸Oₐtm modeling less crucial, as illustrated in the study of Hoffmann et al. (2004).

5.3.2 Calculation of δ¹⁸O₆₅terr

The major source of atmospheric oxygen from the terrestrial biosphere is the oxygen produced during photosynthesis. The fractionation associated with photosynthesis is small (Guy et al., 1993; Eisenstadt et al., 2010). The oxygen produced by this process thus has almost the same isotopic composition as the leaf water. Consumption of oxygen is also associated with biosphere productivity through different pathways (dark respiration, photorespiration, Mehler reaction). δ¹⁸O₆₅terr, thus results from isotope fractionation associated with photosynthesis and oxygen uptake. Following Bender et al. (1994), Blunier et al. (2002), Hoffmann et al. (2004), and Landais et al. (2007b), we assume a steady state, where photosynthesis equals respiration. δ¹⁸O₆₅terr calculates as

\[
δ¹⁸O₆₅terr = \frac{δ¹⁸O₆₅lw + 1}{18α_{resp}} - 1,
\]

where δ¹⁸O₆₅lw is the global production-weighted average isotopic composition of leaf water and 18αresp is the global apparent respiratory isotope fractionation factor associated with global oxygen uptake, i.e., oxygen consumption weighted average of fractionation factors associated with specific respiratory pathways.

5.3.3 Photosynthetic oxygen

As classically done, we estimate the value of δ¹⁸O of leaf water, hereafter δ¹⁸O₆₅lw, based on the Craig and Gordon (1965) equation (C&G) of evaporation applied to leaf transpiration (Dongmann, 1974; Flanagan et al., 1991b). It is thus calculated in the following way:

\[
δ¹⁸O₆₅lw = h \cdot (δ¹⁸O₆₅cap + 18ε_{eq}) + (1 - h) \cdot (δ¹⁸O₆₅gw + 18ε_{eq} + 18ε_{kin}),
\]

where h is the relative humidity at the site of photosynthesis, 18εeq is the temperature-dependent liquid–vapor equilibrium isotope effect (Majoube, 1971), 18εkin is the ki-
netic isotope effect occurring when humidity is below saturation, $\delta^{18}O_{gw}$ is the isotopic composition of soil water and $\delta^{18}O_{vap}$ is the water vapor $\delta^{18}O$ near the surface. $^{18}\varepsilon_{\text{kin}}$ is deduced from the ratio of the diffusion coefficient associated with $H_2^{16}O$ ($D$) and $H_2^{18}O$ ($D^*$). Several values for the ratio $D/D^*$ can be found in the literature (Merlivat, 1978; Cappa et al., 2003; Luz et al., 2009), varying from 1.028 to 1.032. For leaf water evaporation, many studies have reported lower enrichment in $\delta^{18}O_{lw}$ than that predicted by Eq. (5.4a) with $^{18}\varepsilon_{\text{kin}} = D/D^* - 1$ as classically assumed (e.g., Allison et al., 1985; Bariac et al., 1989; Walker et al., 1989; Walker and Brunel, 1990; Yakir et al., 1990; Flanagan et al., 1991a, 1993, 1994). Farquhar et al. (1989) suggested that $^{18}\varepsilon_{\text{kin}}$ depends on the importance of either stomatal or boundary layer resistances. In moist conditions, stomata resistance is low and boundary layer resistance high, leading $^{18}\varepsilon_{\text{kin}}$ to values as low as 19%o when using the Merlivat (1978) value for $D/D^*$. In this study, we have imposed a mean value for $^{18}\varepsilon_{\text{kin}}$ of 20%o because higher values led to too high a global value for $\delta^{18}O_{atm}$.

The calculation of $\delta^{18}O_{lw}$ using Eq. (5.4a) requires spatial and temporal variations in temperature and relative humidity as well as the variations in the isotopic composition of water vapor and meteoric water, from which $\delta^{18}O_{gw}$ will be deduced (Sect. 5.3.3.2). These variables are obtained from outputs of modeling experiments.

5.3.3.1 Simulated climatic variations over an abrupt cooling

Temperature and relative humidity variations over a HS are inferred from simulations with the atmosphere–ocean general circulation model (AOGCM) IPSL_CM4 (Marti et al., 2010) with a horizontal resolution for the atmosphere grid of 3.75 ° × 2.5 ° (latitude × longitude) and with a 19 vertical layer atmosphere. To model the $\delta^{18}O_{atm}$ variations over a HS, we have used a glacial simulation perturbed by a freshwater hosing experiment. We will compare in the following the outputs of two simulations: one for the Last Glacial Maximum (LGM_ctrl) and one for the Heinrich stadial (HS_exp).

The LGM_ctrl boundary conditions are as follows (see Kageyama et al., 2009, for a detailed presentation of the climate setup): orbital parameters for 21 ky BP, $CO_2$, $CH_4$ and $N_2O$ levels set to 185 ppm, 350 and 200 ppb, respectively (Minnin et al., 2001; Dällenbach et al., 2000; Flückiger et al., 1999), ICE-5G ice sheet reconstruction and land–sea mask (Peltier, 2004).

The first experiment is an equilibrated glacial run (LGM_ctrl) used as a reference run (see LGMb in Kageyama et al., 2009). The second experiment (HS_exp) is a water hosing experiment, where an additional freshwater flux of 0.15 Sv (1Sv = 10^6 m^3 s^-1) is imposed instantaneously in the Atlantic north of 40°N and the Arctic (see LGMc in Kageyama et al., 2009) from year 150 for 400 years. The input of freshwater in HS_exp, mimicking a Heinrich event, leads to an AMOC collapse in 250 years (see Fig. 1 in Kageyama et al., 2009). We selected this HS_exp experiment since the most efficient way to simulate the climate state during an Heinrich event with a model is to add
freshwater in the high latitudes of the Atlantic ocean, even though results from recent studies (Marcott et al., 2011; Guillevic et al., 2014; Rhodes et al., 2015; Alvarez-Solas et al., 2013) suggest that this does not satisfactorily explain the observed sequences of events (freshwater discharges from ice sheets might not be the initial trigger of Heinrich events) and especially the decoupling between Greenland and low latitudes. We therefore center our study on the mean state of two contrasted periods rather than investigate the dynamics of the transition from the LGM to HS. It also explains why we only focus on HSSs and not DO events.

The climate response to the AMOC collapse in the HS_exp is of global extent and qualitatively agrees with paleoarchive reconstructions for the North Atlantic cooling, southwards Atlantic ITCZ migration and weakening of Indian and African monsoons (Kageyama et al., 2009, 2013). However, the model does not simulate an Antarctic warming or weakened East Asian monsoon (Kageyama et al., 2009). In the following we used the monthly averaged spatial fields of temperature (Tm) and humidity calculated on the first layer of the atmosphere grid. From these data we followed the Lloyd and Farquhar (1994) approach to link leaf temperature during photosynthesis, Tp, to Tm, through Tp = 1.05 · (Tm + 2.5). An additional 2.5°C is added to Tm to account for the daytime increase in air temperature at the time of photosynthesis. The 5 % increase allows for net canopy to air heat fluxes (Farquhar and Lloyd, 1993). The relative humidity from the first layer is not modified (Farquhar et al., 2007).
5.3.3.2 Modeling of $\delta^{18}O$ of meteoric water and groundwater

For our estimate, we also need the distribution of the oxygen isotopic composition of meteoric water. We extract it from the isotopic version of the atmospheric general circulation model developed at the Laboratoire de Météorologie Dynamique (LMDZ4; Risi et al., 2010). LMDZ is the atmospheric component of the IPSL-CM4 model used above. The physical package is described in detail by Hourdin et al. (2006). It includes in particular the Emanuel convective parameterization (Emanuel, 1991; Grandpeix et al., 2004) coupled to the Bony and Emanuel (2001) cloud scheme. Each grid cell is divided into four subsurfaces: ocean, land, ice sheet and sea ice (Risi et al., 2010).

The monthly sea surface temperature and sea ice fields obtained from the two aforementioned experiments at equilibrium (LGM_ctrl and HS_exp) have been used as surface boundary conditions for the isotopic simulations. Monthly mean outputs of the IPSL-CM4 are imposed to the LMDZ4 model, so there is no coupling between ocean and atmosphere, and nonlinear submonthly scale processes are thus not taken into account here. This choice should not alter our results. Indeed, LeGrande and Schmidt (2008) analyze changes in water isotopes following the 8.2 ka event’s meltwater pulse (meltwater $\delta^{18}O: -30 \%$) in a fully coupled AOGCM (Goddard Institute for Space Studies Model E-R) and show that the effect of the freshwater impulse on $\delta^{18}O$ of precipitation, noted $\delta^{18}O_p$ hereafter, can be neglected because the signal is very short-lived, only a few decades, before the climatic component dominates. Furthermore, the main changes are constrained to the northern North Atlantic and its surrounding regions (Fig. 6 of LeGrande and Schmidt, 2008). Those regions only have a limited contribution to the $\delta^{18}O_{atm}$ signal, as most of the terrestrial photosynthesis occurs in the tropics. Figure 7 of LeGrande and Schmidt (2008) shows that two decades after a meltwater pulse, the ensemble mean (five simulations) anomaly of $\delta^{18}O_p$ calculates to $-0.01 \%$, confirming the small impact of $\delta^{18}O$ depleted meltwater.

Figure 5.3 shows the mean annual $\delta^{18}O_p$, simulated for the LGM_ctrl and the HS_exp experiments. The $\delta^{18}O_p$ distribution for the LGM_ctrl experiment has already been confronted to observations of water isotopes in vapor and precipitation (Risi et al., 2010) and seasonal patterns are well captured. For validation purposes, $\delta^{18}O_p$ changes from the LGM to HS are compared with changes in (i) calcite $\delta^{18}O$ in speleothems, noted $\delta^{18}O_c$ hereafter, and in (ii) ice $\delta^{18}O$ in Greenland ice cores over Heinrich events (Sect. 5.4.1.2; see Fig. 5.4a for $\delta^{18}O_p$ anomaly).

Finally Eq. (5.4a) also requires an estimate of $\delta^{18}O_{gw}$. Groundwater pumped through the plant’s roots represents a mixture of stored water and incoming precipitation water (McGuire et al., 2002). Indeed, during spring/summer, when maximal productivity occurs, the groundwater is composed of significant amounts of fall/winter precipitation. In order to take the mixing into account we use amount-weighted annual-mean $\delta^{18}O$ of precipitation. This approach has been shown to be realistic in a field experiment in Kenya (Wang et al., 2012) and has been implemented in a global coupled climate model of intermediate complexity (Caley et al., 2014). When implementing
Figure 5.4 – (a) Model–data comparison of $\delta^{18}O$ precipitation anomaly during HS compared to the LGM. Data represent speleothem’s calcite $\delta^{18}O$ from various locations (see Table 5.3 for details). (b) Comparison of reconstructed HS precipitation anomaly $\Delta \delta^{18}O$ from selected proxies shown in (a) and simulated $\Delta \delta^{18}O_p$ anomaly ($R = 0.89$, $n = 13$). Note that the correlation is done with point XIII corrected, as we assume a bias in the model. Refer to Table 5.3 for details on reconstructed precipitation. Points falling on the line depict the same anomaly in the reconstruction and the simulation. Note that Timta and Dongge (Wang et al., 2005) Cave $\delta^{18}O_c$ values were estimated from the Younger Dryas excursion, sometimes called Ho and characterized by a large freshwater input in the North Atlantic (Pausata et al., 2011).

this, we neglect the fractionation effects that can significantly affect the soil water isotopic composition, especially in dry regions (Kanner et al., 2014).

5.3.4 Oxygen uptake in respiratory processes

5.3.4.1 Global oxygen production

The geographical distribution of respiratory $O_2$ fluxes (noted GPP$_{O_2}$ hereafter from the hypothesis of equilibrium between oxygen production and consumption) is computed from the vegetation cover and gross primary productivity (GPP) distribution provided by the ORCHIDEE model, which simulates the vegetation distribution of 10 natural plant functional types (PFTs) and bare soil (Krinner et al., 2005). ORCHIDEE is the land surface component of the IPSL-CM4 model. It is used here with the same spatial resolution as the aforementioned models (latitude × longitude 3.75° × 2.5°) and is run in offline mode, forced by the high-frequency outputs from IPSL-CM4 for the two experiments LGM_ctrl and HS_exp. The prescribed forcing has a 6 h time step temporal resolution, and thus takes into account daily variability and diurnal cycle simulated by the IPSL model (Woillez, 2012). Each grid cell simulates the vegetation cover by splitting the cell into fractions of 10 PFTs (see Table 5.1 for names) and provides GPP fluxes (gCm$^{-2}$yr$^{-1}$) for each PFT. Validation of the vegetation cover can be found in Woillez et al. (2011) for LGM_ctrl and Woillez et al. (2013) for HS_exp over western Europe. Here we extend this work and compare the LGM
Table 5.1 - Plant functional types (PFT) in ORCHIDEE, abbreviation used and mega-biome assignment in this study.

<table>
<thead>
<tr>
<th>PFT</th>
<th>Abbreviation</th>
<th>Mega-biome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare soil</td>
<td>Bare soil</td>
<td>Bare soil</td>
</tr>
<tr>
<td>Tropical broadleaf evergreen trees</td>
<td>TrBE</td>
<td>Tropical trees</td>
</tr>
<tr>
<td>Tropical broadleaf rainforest trees</td>
<td>TrBR</td>
<td>Tropical trees</td>
</tr>
<tr>
<td>Temperate needleleaf evergreen trees</td>
<td>TempNE</td>
<td>Temperate trees</td>
</tr>
<tr>
<td>Temperate broadleaf evergreen trees</td>
<td>TempBE</td>
<td>Temperate trees</td>
</tr>
<tr>
<td>Temperate broadleaf summergreen trees</td>
<td>TempBS</td>
<td>Temperate trees</td>
</tr>
<tr>
<td>Boreal needleleaf evergreen trees</td>
<td>BoNE</td>
<td>Boreal trees</td>
</tr>
<tr>
<td>Boreal broadleaf summergreen trees</td>
<td>BoBS</td>
<td>Boreal trees</td>
</tr>
<tr>
<td>Boreal needleleaf summergreen trees</td>
<td>BoNS</td>
<td>Boreal trees</td>
</tr>
<tr>
<td>C3 grass</td>
<td>C3 grass</td>
<td>C3 grass</td>
</tr>
<tr>
<td>C4 grass</td>
<td>C4 grass</td>
<td>C4 grass</td>
</tr>
</tbody>
</table>

and HS simulation with worldwide vegetation reconstructions selected from marine (coastal) and terrestrial paleoarchives with high temporal resolution (Sect. 5.4.1.3).

In this study, following Hoffmann et al. (2004), we calculate the terrestrial biosphere’s $O_2$ fluxes in three steps. First, the outputs from ORCHIDEE provide the GPP expressed in $gCm^{-2}yr^{-1}$ for each of the 10 PFTs on each model grid point. Second, simulated carbon molar fluxes for each PFT are converted to oxygen molar fluxes, based on the biochemical model of photosynthesis from Farquhar et al. (1980). The model accounts for the fraction of photorespiration and the photosynthetic quotient (PQ) – measured by Keeling (1988) and Severinghaus (1995) as ≈ 1.1. Third, $GPP_{O_2}$ for each PFT is expressed in terms of dark respiration (mitochondrial), Mehler respiration and photorespiration, each of these respiratory uptake processes being associated with a specific fractionation (refer to Table 5.2 for values):

\[
GPP_{O_2} = GPP_{O_2,\text{Mehler}} + GPP_{O_2,\text{dark}} + GPP_{O_2,\text{photo}} = \frac{GPP \cdot PQ \cdot (1 + f_{\text{photo}})}{1 - f_{\text{Mehler}}},
\]

(5.4a)

with

\[
GPP_{O_2,\text{Mehler}} = f_{\text{Mehler}} \cdot GPP_{O_2},
\]

(5.4b)

\[
GPP_{O_2,\text{dark}} = (1 - f_{\text{Mehler}}) \cdot PQ \cdot GPP,
\]

(5.4c)

\[
GPP_{O_2,\text{photo}} = (1 - f_{\text{Mehler}}) \cdot (GPP_{O_2} - PQ \cdot GPP)
\]

(5.4d)

\[
GPP_{O_2,\text{photo}} = (1 - f_{\text{Mehler}}) \cdot PQ \cdot GPP \cdot f_{\text{photo}},
\]

where $f_{\text{Mehler}}$ denotes the fraction of Mehler reaction, and accounts for 10% of the total respiration (Badger et al., 2000) and $f_{\text{photo}}$ represents the fraction of photorespiration.
5.3.4.2 Photorespiration

All types of C3 plants photorespire, but in different proportions. In contrast, C4 plants do not photorespire, because of a CO$_2$ concentration mechanism allowing them to operate at high chloroplast CO$_2$ partial pressures and thereby inhibit the oxygenation reaction during photosynthesis (Von Caemmerer, 2000). The proportion of photorespiration is calculated from the proportion of C$_4$ vs. C$_3$ plants, temperature and CO$_2$ level (assumed constant in our study) as depicted in the biochemical model of photosynthesis from Farquhar et al. (1980) and already done in the studies of Hoffmann et al. (2004) and Landais et al. (2007a). Increasing photorespiration modifies $\delta^{18}O_{\text{terr}}$, as photorespiration is associated with a high discrimination and in turn affects $\delta^{18}O_{\text{terr}}$. Details on equations used in our offline model for $\delta^{18}O_{\text{terr}}$ calculation can be found in Hoffmann et al. (2004).

5.3.4.3 Soil respiration

We have assigned fractionation factors for each soil using the soil type discrimination proposed by Angert et al. (2003). For this, we relate the Angert soil types to the type of vegetation cover over the considered soil in the ORCHIDEE model. As an example, we have assigned tropical soils (fractionation coefficient of $-10.1\%$) to soil covered by dominant the PFT tropical broadleaf evergreen trees and the PFT tropical broadleaf raingreen trees. Tropical soils ($-10.1\%$) discriminate significantly less than temperate ($-17.8\%$) or boreal soils ($-22.4\%$) following Angert et al. (2003). The global respiratory isotope fractionation for the control run calculates as $-15.895\%$, much weaker than the common value ($-18\%$) used for terrestrial ecosystems. As soil respiration only occurs where vegetation exists, a shift of the latter modifies the spatial distribution of soils where dark respiration takes place. In our model, the change in vegetation cover from the LGM to HS leads to a very slight weakening of soil respiration isotope fractionation using fractionation values of Angert et al. (2003). We present in Sect. 5.4.2.2 a sensitivity test to assess the magnitude of the uncertainty in soil respiration isotope fractionation that is introduced by not taking into account the effect of soil aeration, i.e. the weakening of respired O$_2$ back-diffusion in waterlogged soils.

5.3.4.4 Global terrestrial fractionation factor

Uptake of oxygen by respiration discriminates against heavy isotopes, leaving the substrate oxygen, atmospheric O$_2$, enriched in $^{18}O$. Each of the oxygen uptake processes is affected by a specific, spatially and temporally constant fractionation (Table 5.2) and the global terrestrial isotope fractionation factor $^{18}\alpha_{\text{resp}}$ is expressed as follows:

$$^{18}\alpha_{\text{resp}} = ^{18}\alpha_{\text{photo}} \cdot f_{\text{photo}} + ^{18}\alpha_{\text{Mehler}} \cdot f_{\text{Mehler}} + ^{18}\alpha_{\text{dark_soil}} \cdot f_{\text{dark_soil}} + ^{18}\alpha_{\text{dark_leaves}} \cdot f_{\text{dark_leaves}},$$

(5.5)

The latest estimations of $^{18}\alpha_{\text{Mehler}}$, $^{18}\alpha_{\text{photo}}$ and $^{18}\alpha_{\text{dark_leaves}}$ can be found in Table 5.2. A significant proportion of terrestrial respiration (30 to 40\%) occurs below the sur-
face (Raich and Potter, 1995) with varying fractionation values. Respiration below 
surface ($^{18}$\text{\textalpha}_{\text{dark\_soil}}$) thereby needs to be considered for the different types of soils (bo-
real, temperate, tropical), as each soil type is associated with a specific fractionation 
factor because of different diffusion pathways (Angert et al., 2003). The Mehler frac-
tion, $f_{\text{Mehler}}$, represents 10 % of global respiration (Badger et al., 2000) and $f_{\text{photo}}$ is 
calculated from the outputs of the ORCHIDEE and IPSL-CM4 models. The dark res-
piration fraction is composed of leaf (38 %) and soil (62 %) respiration, following 
Landais et al. (2007b).

5.4 Results

5.4.1 Simulation of regional climate, vegetation and isotopic pattern during a HS

We propose here a model–data comparison on a regional scale to evaluate the model 
performances, as the climatic and water cycle responses during a HS are not spa-
tially homogeneous. Climatic outputs of the HS experiments are already discussed 
in Kageyama et al. (2009) and Woillez et al. (2013). In the following we thus mainly 
discuss the simulated change in relative humidity (Sect. 5.4.1.1) since the latter has 
an important influence on the $\delta^{18}$O$_{\text{lw}}$ and hence $\delta^{18}$O$_{\text{terr}}$. Then, we further compare 
the modeled change in $\delta^{18}$O of precipitation over a HS with changes in speleothems 
calcite $\delta^{18}$O (Sect. 5.4.1.2) and modeled fraction of vegetation with vegetation recon-
structions (Sect. 5.4.1.3).

5.4.1.1 Simulated humidity validation

According to climate reconstructions, during HS, wet periods in northeastern Brazil 
are synchronous with periods of weak East Asian summer monsoons (Wang et al., 
2001) and with cold periods in Greenland (Grootes and Stuiver, 1997) and Europe 
(Genty et al., 2003). Reorganization in tropical rainfall patterns leads to wetter condi-
tions in southwestern North America (Asmerom et al., 2010) and southern South 
America (Kanner et al., 2012), and to dryer conditions in the Australian–Indonesian 
monsoon region (Mohtadi et al., 2011), wide parts of Asia (Wang et al., 2008), northern 
South America (Peterson and Haug, 2006), Mediterranean region (Fleitmann 
et al., 2009), and equatorial western Africa (e.g., Weldeab, 2012).

During HS, the model simulates similar humidity patterns as reconstructed ones, 
with dryer conditions over Europe, the Mediterranean region, northern and equa-
torial Africa, southern and eastern Asia, Middle East, India, southern Australia and 
parts of Indonesia. In South America, a region of particular interest, where major sim-
ulated changes in vegetation and oxygen production occur, the model captures well 
the observed contrast with increased moisture in northeastern Brazil, and drying in 
northern South America and Central America.
These rapid comparisons show that there is a good general agreement between modeled changes in humidity over an HS and climatic reconstructions over the different regions.

5.4.1.2 Simulated amount-weighted $\delta^{18}O_p$ validation

5.4.1.2.1 Tropics

Comparisons of modeled hosing-driven amount-weighted $\Delta\delta^{18}O_p$ anomalies with reconstructed $\Delta\delta^{18}O$ of speleothem’s calcite during HSs are presented in Table 5.3 and Fig. 5.4. Thirteen Heinrich $\Delta\delta^{18}O_p$ proxy reconstructions arise from Lewis et al. (2010) ($n = 11$) and Pausata et al. (2011) ($n = 4$). They are located in the eastern Mediterranean, and in the regions of the South American monsoon, East Asian monsoon, Indian summer monsoon, North American monsoon and the Australian–Indonesian monsoon. Those regions represent the most productive ones and therefore carry a substantial part of the $\delta^{18}O_{terr}$ signal. Although reconstructed $\Delta\delta^{18}O_p$ anomalies from Lewis et al. (2010) and Pausata et al. (2011) studies were estimated differently, they are consistent and common reconstructed $\Delta\delta^{18}O_p$ estimates (for Hulu and Songjia Cave) are similar in both studies (Table 5.3, this study; method section of Pausata et al., 2011).

The dominant hydrological controls on reconstructed $\delta^{18}O_p$ are site-specific and are
Table 5.3 – Comparison of isotopic proxy records (speleothem’s calcite δ¹⁸O) with annual average modeled amount-weighted δ¹⁸O_p. Note that anomalies from Pausata et al. (2011) are calculated from H1 and YD, while anomalies from Lewis et al. (2010) arise from all identifiable δ¹⁸O_c excursions.

<table>
<thead>
<tr>
<th>Core</th>
<th>ID</th>
<th>Region</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Data ∆δ¹⁸O</th>
<th>Model ∆δ¹⁸O</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hulu Cave</td>
<td>XI</td>
<td>China</td>
<td>32.5</td>
<td>119.2</td>
<td>1.4</td>
<td>1.1</td>
<td>Pausata et al. (2011); Lewis et al. (2010)</td>
</tr>
<tr>
<td>Songjia Cave</td>
<td>XII</td>
<td>China</td>
<td>32.3</td>
<td>107.2</td>
<td>1.4</td>
<td>1.1</td>
<td>Pausata et al. (2011); Lewis et al. (2010)</td>
</tr>
<tr>
<td>Dongge Cave</td>
<td>IX</td>
<td>China</td>
<td>35.3</td>
<td>108.8</td>
<td>1.0</td>
<td>0.8</td>
<td>Pausata et al. (2011)</td>
</tr>
<tr>
<td>Timta Cave</td>
<td>XIII</td>
<td>India</td>
<td>29.8</td>
<td>80.0</td>
<td>−3.7</td>
<td>−3.7</td>
<td>Pausata et al. (2011)</td>
</tr>
<tr>
<td>Sanbao Cave</td>
<td>X</td>
<td>China</td>
<td>31.7</td>
<td>110.5</td>
<td>1.2</td>
<td>1.1</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Borneo Cave</td>
<td>VII</td>
<td>Indonesia</td>
<td>4.0</td>
<td>114.0</td>
<td>0.8</td>
<td>0.6</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Mooni Cave</td>
<td>VIII</td>
<td>Yemen</td>
<td>12.5</td>
<td>54.3</td>
<td>0.9</td>
<td>0.6</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Soreq Cave</td>
<td>VI</td>
<td>Israel</td>
<td>31.5</td>
<td>35.0</td>
<td>0.5</td>
<td>0.5</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Rio Grande do Norte</td>
<td>II</td>
<td>northeastern Brazil</td>
<td>−5.7</td>
<td>−37.7</td>
<td>−1.6</td>
<td>−0.1</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Santana Cave</td>
<td>V</td>
<td>southern Brazil</td>
<td>−24.5</td>
<td>−48.7</td>
<td>−0.8</td>
<td>−0.9</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Botuvera Cave</td>
<td>IV</td>
<td>southern Brazil</td>
<td>−27.2</td>
<td>−49.2</td>
<td>−1.1</td>
<td>−1.1</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Cave of the Bells</td>
<td>III</td>
<td>North America</td>
<td>31.7</td>
<td>−110.8</td>
<td>−0.8</td>
<td>0.8</td>
<td>Lewis et al. (2010)</td>
</tr>
<tr>
<td>Poleva Cave</td>
<td>I</td>
<td>Europe</td>
<td>44.7</td>
<td>21.8</td>
<td>−2</td>
<td>−1.0</td>
<td>Lewis et al. (2010)</td>
</tr>
</tbody>
</table>

described by Lewis et al. (2010). Figure 5.4 demonstrates the ability of the AOGCM LMDZ-iso to reproduce the observed ∆δ¹⁸O_p spatial pattern for most of the sites, particularly in regions strongly affected by ITCZ (and its land extension) variations and hence by changes in the water cycle, regardless of the processes at play. There are two regions where the model does not properly reproduce the observed signal over HS. The first one occurs in the Indian summer monsoon domain (Timta Cave). Model and observation would reconcile two grid cells south of Timta Cave, as it is located just at the transition between a positive and negative simulated δ¹⁸O_p anomaly. This disagreement can be due to a model bias. The IPSL model indeed does not simulate the monsoon signal at the right place, with an Indian monsoon located too far south even for modern climate (Marti et al., 2010). In the LGM simulation also, the IPSL model predicts that it mostly takes place over the ocean (−0.5 to −2 mm · day⁻¹ is only simulated over the ocean; see Fig. 9 (lower panel) of Kageyama et al., 2009), while there is evidence for a monsoonal signal over land. In northern India, i.e., the Timta Cave site, the model does not simulate any significant rainfall change between the two periods. A more intense weakening of the Indian monsoon over land in the HS run, and hence less rainfall, would have helped in reconciling the model and data at Timta Cave, since δ¹⁸O_p would have been enriched through the amount effect. Pausata et al. (2011) recently suggested that change in rainfall amount associated with Indian monsoon rather than in southeastern Asia explains changes observed in calcite δ¹⁸O in Chinese stalagmites (in southeastern Asia). As in Pausata et al. (2011), a freshwater impulse was applied to the control simulation with LGM background climate. Rainfall amount drops in eastern Asia and northwestern India, mostly over the ocean, but increases in southeastern India, as shown in Fig. 5.3d. Values of −0.17 and −0.13mm · day⁻¹ are simulated at Hulu and Songjia Cave during HS, respectively. The enrichment in δ¹⁸O_p observed in Chinese caves is reproduced by the model, but the latter fails to capture the enrichment in Timta Cave. Overall, δ¹⁸O_p is enriched over the whole of India (with an abrupt change south of Timta Cave) and southern Asia. The possible role of the Indian monsoon in the oxygen isotopic enrichment of Chinese stalagmites is limited in our simulation, probably because the monsoonal signal is lo-
icated too far south in the IPSL model. The increase in $\delta^{18}O$ over southeastern Asia is consistent with local amount effect.

Another mismatch occurs in the North American monsoon domain (Cave of the Bells), where the observed $\Delta \delta^{18}O_p$ ($-0.8\%$) and the modeled $\Delta \delta^{18}O_p$ ($0.9\%$) are of opposite sign. The elevation of the site (1700 m a.s.l.) might explain the disagreement between model and data, in a region where the coarse model resolution does not allow for the role of orography to be properly represented. At Timta Cave and Cave of the Bells, our model fails to capture the calcite $\delta^{18}O$ anomaly recorded in speleothems. These two sites are located at high altitude and do not correspond to the regions where most of the oxygen is produced.

As shown in Table 5.3, the modeled increase in $\delta^{18}O_p$ quantitatively agrees with data $\delta^{18}O_c$ increase during HS in most of the compared sites (Fig. 5.4). In conclusion, the key features of HS precipitation inferred from speleothem’s $\delta^{18}O_c$, i.e., a low-latitude interhemispheric see-saw pattern (Cheng et al., 2012), are generally well captured by the LMDZ model.

5.4.1.2.2 High latitudes

In Greenland, HS can hardly be distinguished from the GS or from the mean LGM state. The only clear $\delta^{18}O_{ice}$ signal is observed from GI to GS (or HS) with an approximately $4\%$ decrease in central Greenland sites (GRIP, GISP2, NGRIP). The depletion simulated in Greenland, with a $1.6\%$ decrease at the GRIP site, by the model for a HS compared to a glacial background state does not compare well with available data. However, it is difficult to compare the $\delta^{18}O$ change simulated by a freshwater input (the most efficient way to model a Heinrich event, as mentioned in Sect. 5.3.3.1) and the $\delta^{18}O$ depletion between a GI and a GS. Indeed, there is more and more evidence that the $\delta^{18}O_p$ depletion at the end of a GI is not due to the same freshwater discharge than the one associated with a Heinrich event. It can well be due to a threshold in the extent in sea ice or an atmospheric heat transport. Therefore our choice of modeling approach may potentially explain some of the discrepancies observed in the low latitudes, but our approach is the best we can realize today.

5.4.1.3 Validation of simulated vegetation

In order to compare model and data easily, simulated PFTs are gathered into five mega-biomes (boreal, temperate and tropical trees, C3 and C4 grasses) as well as bare soil. We distinguish between C3 and C4 plants as their partitioning has a strong impact on photorespiration fraction. The simulated dominant vegetation fraction is shown for LGM_ctrl (Fig. 5.5) and HS_exp (Fig. 5.6), together with pollen-based reconstructed mega-biomes. Given its domination, we display bare soil fraction only if it covers more than 80 % of a grid cell.
<table>
<thead>
<tr>
<th>Core ID</th>
<th>Region</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Resolution (yr/sample)</th>
<th>Which HS?</th>
<th>Mega-biome distribution flora and dominant/subdominant biome</th>
<th>Agreement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kashiru Bog 1</td>
<td>equatorial Africa</td>
<td>−3.47</td>
<td>29.57</td>
<td>410</td>
<td>HS4</td>
<td>grassland and shrubland, savannah and xerophytic scrubland</td>
<td>tropical forest and open forest, woodland</td>
<td>good</td>
</tr>
<tr>
<td>Lake Tanganyika 2</td>
<td>equatorial Africa</td>
<td>−8.5</td>
<td>31.95</td>
<td>610</td>
<td>HS5</td>
<td>warm temperate mixed forest, savannah and xerophytic scrubland</td>
<td>temperate forest, grasses</td>
<td>fair</td>
</tr>
<tr>
<td>Lake Malawi 3</td>
<td>equatorial Africa</td>
<td>−9.33</td>
<td>33.75</td>
<td>550</td>
<td>HS5</td>
<td>warm temperate mixed forest, savannah and xerophytic scrubland</td>
<td>temperate forest, grasses</td>
<td>fair</td>
</tr>
<tr>
<td>Lake Malawi 4</td>
<td>equatorial Africa</td>
<td>−11.29</td>
<td>34.44</td>
<td>200</td>
<td>HS5</td>
<td>savannah and xerophytic scrubland, tropical forest</td>
<td>tropical forest, grasses</td>
<td>good</td>
</tr>
<tr>
<td>Bumomboko Mbo 5</td>
<td>equatorial Africa</td>
<td>−4.51</td>
<td>9.4</td>
<td>590</td>
<td>HS5</td>
<td>savannah and xerophytic scrubland, tropical forest</td>
<td>tropical forest, grasses</td>
<td>good</td>
</tr>
<tr>
<td>KS 84-063 6</td>
<td>equatorial Africa</td>
<td>−4.4</td>
<td>−4.18</td>
<td>450</td>
<td>HS5</td>
<td>tropical forest, warm temperate mixed forest</td>
<td>tropical forest, temperate forest</td>
<td>good</td>
</tr>
<tr>
<td>ODP 1078-C 7</td>
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<td>−11.91</td>
<td>15.4</td>
<td>140</td>
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<td>warm temperate mixed forest, temperate montane forest</td>
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<td>−43.42</td>
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</tr>
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<td>Colonia 10</td>
<td>South America</td>
<td>−23.87</td>
<td>−46.71</td>
<td>710</td>
<td>HS5</td>
<td>savannah and xerophytic scrubland, grassland and shrubland</td>
<td>temperate forest, grasses</td>
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</tr>
<tr>
<td>La Laguna, Bogota 11</td>
<td>South America</td>
<td>4.94</td>
<td>−74.03</td>
<td>670</td>
<td>HS5</td>
<td>savannah and xerophytic scrubland, grassland and shrubland</td>
<td>temperate forest, grasses</td>
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<td>−57.72</td>
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<td>112.08</td>
<td>370</td>
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<td>tropical forest, grasses</td>
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<td>Tyrendarra Swamp 20</td>
<td>Australia</td>
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<td>141.76</td>
<td>337</td>
<td>HS4</td>
<td>herbaceous and shrublands</td>
<td>tropical forest, grasses</td>
<td>bad</td>
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<td>Lake Surprise 21</td>
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<td>−38.06</td>
<td>141.92</td>
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<td>tropical forest and open forest, woodland</td>
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<td>Core ID Region</td>
<td>Lat/Long (yr/sample)</td>
<td>Which HS?</td>
<td>Model results</td>
<td>Flora biome(s)</td>
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<td>Ioannina 284</td>
<td>Europe 38.73 21.89 31</td>
<td>HS4</td>
<td>grassland and dry shrubland</td>
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<td>Europe 38.4 26.32 150</td>
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<td>good</td>
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<td>MD95-284</td>
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<td>bad (soil &gt; 90%)</td>
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<td>bad (soil &gt; 90%)</td>
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<td>Lake Nojiri 56</td>
<td>Japan 58.83 158.22 100</td>
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<td>Kamiyoshi Basin 58</td>
<td>Japan 53.1 135.59 500</td>
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<td>increase in cool conifer forest within temperate conifer forest, and deciduous broadleaf forest</td>
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<td>fair</td>
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<td>Tosahe Basin 59</td>
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<td>HS4</td>
<td>increase in cool conifer forest within temperate conifer forest, and deciduous broadleaf forest</td>
<td>temperate forest, boreal forest, temperate forest</td>
<td>fair</td>
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<td>Fargher Lake 40</td>
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<td>North America 45.91 −120.88 650</td>
<td>HS4</td>
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<td>Little Lake 44</td>
<td>North America 44.16 −132.58 260</td>
<td>HS4</td>
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<td>HS4</td>
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<td>temperate forest, boreal forest</td>
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<td>HS4</td>
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<td>Bear Lake 46</td>
<td>North America 41.95 −111.3 680</td>
<td>HS4</td>
<td>xerophytic shrubland</td>
<td>temperate forest, boreal forest</td>
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<td>Camel Lake 47</td>
<td>North America 50.16 −85.01 300</td>
<td>HS4</td>
<td>temperate forest within increase in southeastern pine forest</td>
<td>temperate forest, boreal forest</td>
<td>good</td>
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Note: Sampling resolutions of the MIS where vegetation changes occur. Mean sampling resolution is 393 years. Similar to Handiani et al. (2012) model results.
5.4.1.3.1 Global oxygen production

Present-day carbon and oxygen productions amount to 10.5 $Pmol C \cdot yr^{-1}$ and 17.95 $Pmol O_2 \cdot yr^{-1}$ (taking into account photorespiration) in the ORCHIDEE model, respectively. This is in line with other estimates, e.g., Angert et al. (2003) or Welp et al. (2011), estimating 8 to 13 $Pmol C \cdot yr^{-1}$ and 12.5 to 14.2 $Pmol O_2 \cdot yr^{-1}$, respectively. For the LGM and HS, land carbon production estimates from the ORCHIDEE model are rather low, 6.8 and 6.5 $Pmol C \cdot yr^{-1}$, which translates into 11.8 and 11.4 $Pmol O_2 \cdot yr^{-1}$ for the LGM and HS, respectively. This is up to a factor of 2 lower than model-based LGM estimates from Joos et al. (2004), Hoffmann et al. (2004) or Bender et al. (1994), ranging from 23 to 16.7 $Pmol O_2 \cdot yr^{-1}$.

The ORCHIDEE model is known to underestimate LGM productivity at both low latitudes (too low productivity in tropical forests, especially Amazonia) and high latitudes (too low productivity in the absence of permafrost modeling).

Photorespiration fraction (see Sect. 5.3.4.2) may also be invoked to explain part of the model–data discrepancy for the LGM and HS. Underestimation of photorespiration may arise from uncertainties related to the time of photosynthesis. In the real world, plants must reduce their CO$_2$ uptake under water stress, as stomata close to preclude water loss. This leads to a higher proportion of photorespiration, not necessarily considered during experiments performed under ideal hydric conditions, whose results are used in the classical Farquhar parameterization (Farquhar et al., 1980).

The classical scaling factor between carbon uptake and oxygen production (Keeling, 1988) of 1.07 used in our study may also have been underestimated. Indeed, plants can produce oxygen without involving carbon uptake during times of stress, which is not considered in experiments run under ideal conditions. The oxygen production calculated here from the ORCHIDEE model seems to be biased toward too low values for the LGM. The same bias is true for HS. Still, it should be noted that the $\delta^{18}O_{terr}$ calculations of our study and hence the final results do not depend on the absolute value of oxygen production at the LGM and HS.

5.4.1.3.2 LGM_ctrl vegetation

The main features of the glacial vegetation are correctly reproduced by the ORCHIDEE model, as briefly presented by Woillez et al. (2011): reduced fractions of tropical forest, particularly in Amazonia, and high grass fractions in Siberia, Alaska, and western North America. Main biases are an overestimation of the tree fractions over western Europe, eastern Eurasia and eastern North America, as well as an overestimation in bare soil fractions over India, southern Africa, Siberia and South America (Woillez et al., 2011), leading to an underestimation of the global carbon production, as mentioned in the previous section.
Figure 5.5 – (a) Model–data comparison of mega-biome distribution for LGM_ctrl based on dominant PFT type simulated by ORCHIDEE. For each grid cell, the fraction of bare soil, tropical forests, temperate forests, boreal forests, and C3 and C4 grasses is considered. The type covering the greatest cell fraction is the dominant type. Note that dominant bare soil fraction denotes more than 80 %. Circles denote LGM mega-biomes inferred from pollen and plant macrofossil records compiled by the BIOME6000 project. Refer to Table 5.4 to see how PFTs simulated by ORCHIDEE have been assigned to the mega-biomes mapped in this figure. (b) Detail of the averaged vegetation composition in grid cells occupied by a dominant mega-biome for LGM_ctrl.

The model simulates temperate trees in southeastern Asia (Vietnam, southern China, Cambodia), tropical trees and grasses over the western Pacific warm pool (Malaysia, Thailand, Indonesia) and over southern Africa, in agreement with BIOME6000 reconstructions (Prentice et al., 2000). The model underestimates temperate trees in Asia and overestimates bare soil in South Africa.

A more detailed comparison shows that the important (boreal) tree fraction over southwestern Europe differs from palynological reconstructions depicting an important grass fraction, but this bias mainly comes from the overestimation of Boreal broadleaf summergreen trees, which is a common feature in the version of ORCHIDEE used here, also found in present-day vegetation simulations. The bias might also be the sign that the LGM climate simulated by IPSL-CM4 over western Europe is too warm and wet (Woillez et al., 2011). In a few regions, ORCHIDEE correctly simulates the presence of forest, but the dominant type of tree disagrees with pollen reconstructions: tropical trees over Papua New Guinea and western Indonesia, while reconstructions reveal the presence of temperate trees over these regions. Simulated forests over southern Australia (a thin coastal band in the southeast) are composed of temperate and tropical trees, while reconstructions rather indicate the presence of a few tropical trees. The model simulates mixed vegetation composed of grasses, boreal and temperate trees in eastern North America, consistent with pollen data, but the spatial distribution is incorrect.
Figure 5.6 – (a) Model–data comparison of mega-biome distribution for HS_exp based on dominant PFT type simulated by ORCHIDEE. For each grid cell, the fraction of bare soil, tropical forests, temperate forests, boreal forests, and C3 and C4 grasses is considered. The type covering the greatest cell fraction is the dominant type. Note that dominant bare soil fraction denotes more than 80 %. Circles denote HS_exp mega-biomes inferred from pollen and plant macrofossil records compilation. Refer to Table 5.4 to see how PFTs simulated by ORCHIDEE and reconstructed vegetation have been assigned to the mega-biomes mapped in this figure. (b) Detail of the averaged vegetation composition in grid cells occupied by a dominant mega-biome for HS_exp.

It is important to keep in mind that model–data comparison of vegetation can only remain qualitative given the coarse resolution of the vegetation model, related to the model resolution of the climatic forcing fields. Furthermore, pollen records represent the surrounding vegetation distribution at different altitudes, while the ORCHIDEE model does not account for elevation changes within a grid cell (Woillez et al., 2013).

5.4.1.3.3 HS_exp vegetation

To validate the simulated HS vegetation, we compare the millennial-scale changes in selected high-resolution (< 800 years; mean resolution is 400 years) pollen records of 48 sites described for HS1-GS2 (n = 16) in South America and southern Africa (Hessler et al., 2010; Handiani et al., 2012), and for HS4–GS9 (n = 31) in Europe (Fletcher et al., 2010), North America (Jimenez-Moreno et al., 2010), Japan (Takahara et al., 2010) and Australasia (Harrison and Goni, 2010). Figure 5.7 displays the location of paleorecords discussed in this study. Table 5.4 summarizes the model–data comparison at a grid cell level and provides additional information revealed by palynological reconstructions. The sampling resolution for the analyzed period (MIS2 for HS1, MIS3 for HS4), the other biomes represented for a given site, and the potential occurrences of similar reconstructed vegetation changes over other HSs are presented.

The model–data comparison has been performed as follows: the two dominant re-
constructed biomes are compared with the two dominant simulated biomes over the grid cell covering the site where the proxy originates. Among the 48 sites with pollen reconstructions, 12 were discarded because of absence of vegetation on the considered grid cell. Among the remaining 36 terrestrial and coastal sites, 11 disagree (30 %) and 25 (70 %) display moderate to good agreement (Table 5.4). Good agreement \((n = 13)\) is obtained when reconstructed and simulated dominant biomes are alike, fair agreement \((n = 9)\) when a subdominant biome agrees with a dominant one, and moderate agreement \((n = 3)\) when subdominant biomes only are similar.

Simulated vegetation in regions associated with high oxygen productivity agrees well with pollen reconstruction. This is the case for South America, where a strong increase in tropical forest at the expense of bare soil is simulated in eastern Brazil, and in the West Pacific Warm Pool region, where tropical forest represents the dominant biome. The slight southward shift of the southern border of desert areas in equatorial Africa is also well captured by ORCHIDEE. In the Indian summer monsoon region, the simulated weakened monsoon (Kageyama et al., 2009) leads to the appearance of desert areas south and east of India, consistent with a dryer climate revealed by a core from the Indus region (Deplazes et al., 2014).

From this analysis it appears that sites showing a disagreement between model and data are coastal sites and/or have a very high bare soil fraction. Coastal sites do not necessarily only represent the vegetation in the coastal region, but they offer numerous records and allow high-resolution analysis thanks to their high sedimentation rate, so it is crucial to include them for millennial-scale analysis. Five (50 %) of the sites showing no agreement present a very high simulated bare soil fractions (> 90 %). Woillez et al. (2013) already pointed out the overestimation of the bare soil fractions by the ORCHIDEE model. We argue that this bias might partly explain the observed
discrepancy between model and data. Furthermore, the other sites showing a disagreement, over Europe and Australia, underestimate grass fraction. For Europe, the bias is already present in the LGM simulation and is probably partly due to the systematic overestimation of forest by ORCHIDEE in this region (Woillez et al., 2011). Given the scarcity of data offering a time resolution high enough to catch millennial-scale vegetation variability, further testing of the simulated vegetation remains challenging. In conclusion, HS_exp vegetation agrees reasonably well with available pollen-based vegetation reconstruction.

Finally, based on the reasonable agreement of the simulated changes in vegetation, humidity and precipitation with observations depicted in this section, we can rely on the validity of the model to simulate $\delta^{18}O_{\text{terr}}$ over a HS.

5.4.2 Global increase in $\delta^{18}O_{\text{terr}}$ during a HS

The model calculates $\delta^{18}O_{\text{terr}}$ for LGM_ctrl and HS_exp as 23.41 and 23.52‰, respectively (Table 5.2). This average $\delta^{18}O_{\text{terr}}$ value is coherent with the $\delta^{18}O_{\text{atm}}$ value of 23.8‰ with respect to V-SMOW and the finding that terrestrial and marine contribution to $\delta^{18}O_{\text{atm}}$ are similar (Luz et al., 2014). Moreover, the global increase in $\delta^{18}O_{\text{terr}}$ of 0.11‰ (Fig. 5.8) can quantitatively explain most of the 0.1 ‰ $\delta^{18}O_{\text{atm}}$ increase over HS (Severinghaus et al., 2009; Guillevic et al., 2014; Fig. 5.1). In the following, we use the different model outputs to decipher the main influences on $\delta^{18}O_{\text{terr}}$ and hence on $\delta^{18}O_{\text{atm}}$.

By construction (Eq. 5.3), $\delta^{18}O_{\text{terr}}$ is linearly dependent on both $\delta^{18}O_{\text{lw}}$ and $\varepsilon_{\text{resp}}$; we discuss these two effects below. Figure 5.8 (upper panel) details the different contributions to $\delta^{18}O_{\text{terr}}$ change over a HS and demonstrates the dominant role of $\delta^{18}O_{\text{lw}}$ (Sect. 5.4.2.1) compared to $\varepsilon_{\text{resp}}$ (Sect. 5.4.2.2). Indeed, the 0.11‰ increase in $\delta^{18}O_{\text{terr}}$ exclusively stems from $\delta^{18}O_{\text{lw}}$ increase (+0.14‰ over HS_exp), while respiratory fractionation leads to a negative anomaly (−0.03‰) over HS_exp. We explore in more details below the origin of the relative changes in $\varepsilon_{\text{resp}}$ and $\delta^{18}O_{\text{lw}}$ as calculated by our modeling approach. In particular, we look at the different regional contributions to the global $\varepsilon_{\text{resp}}$ and $\delta^{18}O_{\text{lw}}$ signals since low-latitude regions are associated with the largest GPP$_O_2$ (Fig. 5.9a for the whole latitudinal range and Fig. 5.10a for a closeup of the tropics) and hence have the strongest influence on the global $\delta^{18}O_{\text{terr}}$ signal (Fig. 5.9c).

5.4.2.1 Leaf water

We find global $\delta^{18}O_{\text{lw}}$ values of 5.16 and 5.30‰ for LGM_ctrl and HS_exp, respectively. The 0.14‰ difference is similar to the $\delta^{18}O$ increase observed in ice cores during HS (Fig. 5.2). The increase in $\delta^{18}O_{\text{lw}}$ is clearly visible in the low-latitude regions. It corresponds to an increase in $\delta^{18}O_p$ and a decrease in GPP$_O_2$ weighted relative humidity, both effects leading to a global $\delta^{18}O_{\text{lw}}$ increase (Fig. 5.9b).
Figure 5.8 – Evolution of the main simulated factors controlling atmospheric δ\textsuperscript{18}O. Note that all variables are oxygen-production-weighted, i.e., integrated over vegetated areas, if not stated with "non w.". (a) Left panel: HS_exp – LGM_ctrl anomalies of temperature and relative humidity. Right panel: (left to right) HS_exp – LGM_ctrl anomalies of seawater δ\textsuperscript{18}O, amount-weighted precipitation δ\textsuperscript{18}O, precipitation δ\textsuperscript{18}O (δ\textsuperscript{18}O\textsubscript{p}), water vapor δ\textsuperscript{18}O, leaf water δ\textsuperscript{18}O (δ\textsuperscript{18}O\textsubscript{lw}), respiratory isotope fractionation (−\textsuperscript{18}ε\textsubscript{resp}) and terrestrial contribution to atmospheric δ\textsuperscript{18}O (δ\textsuperscript{18}O\textsubscript{terr}). (b) LGM_ctrl values of same relevant factors as in (a) in δ\textsuperscript{18}O\textsubscript{terr} budget. Note that plotted respiratory isotope fractionation anomaly is inverted as respiration is an oxygen uptake process. Note also that the −\textsuperscript{18}ε\textsubscript{resp} anomaly totals 0.02 % when soil aeration influence on soil respiratory isotope fractionation is considered. δ\textsuperscript{18}O\textsubscript{lw} is controlled by δ\textsuperscript{18}O\textsubscript{p}, temperature and relative humidity as described by Eq. (5.4a). Combined with \textsuperscript{18}ε\textsubscript{resp} as described in Eq. (5.3), one obtains δ\textsuperscript{18}O\textsubscript{terr}.

Still, when looking at the whole latitudinal range, the GPP\textsubscript{O\textsubscript{2}} weighted relative humidity is not significantly different in HS and in LGM state. This is due to the decrease in relative humidity during HS in the extratropical regions (Fig. 5.9b). The net effect of relative humidity on δ\textsuperscript{18}O\textsubscript{bw} is thus zero. As a consequence, the main driver of δ\textsuperscript{18}O\textsubscript{bw} (and hence δ\textsuperscript{18}O\textsubscript{terr}) is the increase in GPP\textsubscript{O\textsubscript{2}}-weighted δ\textsuperscript{18}O\textsubscript{p} (Fig. 5.9b) by 0.18 % (Fig. 5.8). This increase is linked to the southward shift of the tropical belt occurring during HS, as suggested from the speleothem data compilation (see Sect. 5.4.1.2).

Figure 5.10 clearly shows how rainfall amount and δ\textsuperscript{18}O\textsubscript{p} are anticorrelated as expected on most of the intertropical band. During a HS, δ\textsuperscript{18}O\textsubscript{p} is enriched in the Northern Hemisphere down to 14°S. A particular pattern occurs between the Equator and 14°S, where oxygen production is most enhanced at HS, as precipitation is more abundant but also heavier in δ\textsuperscript{18}O\textsubscript{p}.
Figure 5.9 – (a) Zonal annual mean of gross primary productivity expressed in terms of carbon (GPP_C) and oxygen (GPP_O2) annual molar fluxes for LGM_ctrl and HS_exp, respectively. (b) Zonal annual-mean anomalies of δ18Olw, δ18Op and relative humidity (note its inverted x axis). (c) Zonal annual-mean anomalies for −18εresp, δ18Olw and δ18Oterr. Note that all variables of panels (b) and (c) are oxygen-production- (GPP_O2) weighted.

5.4.2.2 Respiration

Respiratory processes lead to a 0.03‰ decrease in δ18Oterr in HS_exp compared to δ18Oterr in LGM_ctrl (Fig. 5.8a). This variation is too small to challenge δ18Oterr enrichment caused by hydrological processes, but the sign of its anomaly raises questions. Here we explain the stability of 18εresp on millennial timescales by a compensatory effect taking place between the main respiratory pathways. We then carry out a simple sensitivity experiment to get a better understanding of the causes of 18εdark_soil negative anomaly during HS.

18εresp is classically separated into four contributions as given in Eq. (5.5): soil respiration, leaf respiration, photorespiration and Mehler reaction.
Soil respiration with associated fractionation factor $^{18}\alpha_{\text{dark, soil}}$ represents 63 % of dark respiration (Schlesinger and Andrews, 2000). It represents 39 % of global terrestrial respiration in our simulation, in agreement with estimates from Raich and Potter (1995) of 30 to 40 %. $^{18}\alpha_{\text{dark, soil}}$ is temperature-dependent (Angert et al., 2003), with higher fractionation associated with colder soils, causing a high zonal contrast. This temperature effect leads to a change in $^{18}\alpha_{\text{dark, soil}}$ by 0.19 h at HS, increasing $^{18}\epsilon_{\text{resp}}$ by 0.12 % and in turn depleting $^{18}O_{\text{terr}}$.

The photorespiration fraction, strongly discriminative against $^{18}O$ ($^{18}\alpha_{\text{photo}} = -21.4 \%$), represents 28.56 % of the global terrestrial oxygen uptake in LGM_ctrl. The proportion of photorespiration is mainly linked to the change in the C3 vs. C4 plant proportions and in temperature during photosynthesis (Von Caemmerer, 2000; Hoffmann et al., 2004). During HS_exp, photorespiration fraction increases by 1 % (29.52 %), driven by a slight decrease in C4 grass (1.3 %) and a slight photosynthesis temperature increase (0.3°C). As a result, change in photorespiration fraction and soil respiration lead $^{18}\epsilon_{\text{resp}}$ to decrease by 0.03 % in HS_exp, thus causing $^{18}O_{\text{terr}}$ enrichment.

Figure 5.10 – Intertropical profiles of (a) zonal annual mean of gross primary productivity expressed in terms of oxygen (GPP$_{O_2}$) annual molar fluxes for LGM_ctrl and HS_exp. (b) Zonal annual mean of oxygen-production-weighted $\delta^{18}O_p$ for LGM_ctrl and HS_exp. (c) Zonal annual mean of rainfall amount for LGM_ctrl and HS_exp.
In summary, in our model, a weaker $^{18}\alpha_{\text{dark_soil}}$ during HS cancels out the effect of increased photorespiration on $^{18}\epsilon_{\text{resp}}$. Note that this compensation between the two main respiratory processes explains not only the temporal stability of $^{18}\epsilon_{\text{resp}}$ but also its zonal stability. Indeed, in high latitudes, cold temperatures lead to a weak photorespiration but strong soil isotope fractionation. In low latitudes, despite a weak soil isotope fractionation, high temperatures and variable C4 fraction lead to a highly variable photorespiration.

The 0.19 % increase in $^{18}\alpha_{\text{dark_soil}}$ during HS needs to be considered carefully. Indeed, following the southward migration of the tropical rain belt during HS, tropical soils generally dry out during HSs, as inferred from the lower atmospheric nitrous oxide concentration and its isotopic composition during HS1 (Schilt et al., 2014). Well-aerated soils are associated with a strong discrimination (Angert et al., 2003). Well-aerated tropical soils of the Northern Hemisphere should thus lead to a stronger $^{18}\alpha_{\text{dark_soil}}$, owing to the greater area of the northern vs. southern tropics. We perform a sensitivity study to assess the effect of soil moisture content on $^{18}\alpha_{\text{dark_soil}}$ by allowing the latter to vary in the intertropical band according to the amount of precipitation simulated by the IPSL model, used as a proxy for soil aeration. Concretely, $^{18}\alpha_{\text{dark_soil}}$ is allowed to vary from its initial value (e.g., $-10.2$ % for tropical waterlogged soils) up to a factor of 2 ($-20.2$ % for well-aerated tropical soils). Note that not only tropical but also temperate soils are simulated in the 30°s–30°n latitudinal band, as the type of soil is related to the vegetation cover in our model (Sect. 5.3.4.3). 18$\alpha_{\text{dark_soil}}$ totals $-22.36$ % in the modified run, 6.12 % stronger than in the LGM control run ($-16.24$ %). $^{18}\delta_{\text{O_{terr}}}$ increases subsequently by 2.91 %. The picture is similar for HS_exp run, where $^{18}\alpha_{\text{dark_soil}}$ strengthens by 6.17 % from $-16.06$ to $-22.23$ %, leading $^{18}\delta_{\text{O_{terr}}}$ to increase by 2.96 % at HS.

While the absolute values of $^{18}\alpha_{\text{dark_soil}}$, $^{18}\epsilon_{\text{resp}}$ and $^{18}\delta_{\text{O_{terr}}}$ are significantly modified by accounting for tropical soil aeration, this does not modify the sign of $^{18}\alpha_{\text{dark_soil}}$ anomaly between the LGM and HS. However, its magnitude is slightly reduced by 0.05 %, which causes the $^{18}\epsilon_{\text{resp}}$ anomaly to vary from $-0.03$ to $+0.02$ %. As a result, $^{18}\delta_{\text{O_{terr}}}$ is enriched by 0.16 % during HS. This 0.05 % increase in $^{18}\delta_{\text{O_{terr}}}$ anomaly may give an estimate of the magnitude of the uncertainty associated with $^{18}\alpha_{\text{dark_soil}}$ when considering soil wetness. This sensitivity test does not fundamentally affect the conclusion of the present study, as the $^{18}\epsilon_{\text{resp}}$ anomaly, although becoming positive, remains very small ($+0.02$ %) but underlines the limitations of our approach. Why does a $^{18}\alpha_{\text{dark_soil}}$ negative anomaly persist when soil aeration is considered? First, in our sensitivity test, we use the amount of precipitation as an index for soil aeration. This approach may be too simple and could be improved by quantitatively relating the soil aeration to the model’s rainfall amount and land surface slope by using existing parameterizations employed in models that predict nitrous oxide production (e.g., LPX-Bern, which is a state-of-the-art bottom-up dynamic global vegetation and
land surface process model; Stocker et al., 2013). Second, soil respiration is closely linked to the vegetation cover in our model, as types of soil (boreal, temperate, tropical) and their associated fractionation factor are related to PFTs rather than land area (Sect. 5.3.4.3). Third, aboveground oxygen productivity controls the rate of soil respiration. As Southern Hemisphere tropics dominate over Northern Hemisphere tropics in terms of GPP_{O_2} for both LGM and HS runs, 18\alpha_{\text{dark, soil}} anomaly remains negative even when considering soil aeration. The distribution of vegetation simulated by ORCHIDEE, favoring Southern Hemisphere tropics, combined with the GPP_{O_2} weighting of soil respiration, explains why the drying-out of the Northern Hemisphere soils, albeit covering a greater land area, does not lead to a stronger 18\alpha_{\text{dark, soil}} during HS in our model.

5.5 Discussion

Our results suggest a strong control of tropical hydrology on \delta^{18}O_{\text{terr}} through changes in \delta^{18}O_p. It suggests that \delta^{18}O_{\text{atm}} is related to tropical hydrology and may be a good tracer for global monsoon signal. The aim of the following discussion is to evaluate these results by (i) providing some insights on \delta^{18}O_{\text{mar}} estimate and (ii) testing the robustness of our conclusion on the driver of \delta^{18}O_{\text{terr}} changes through three sensitivity experiments separating the different parameters (hydrology, climate and vegetation).

5.5.1 Estimate of \delta^{18}O_{\text{MAR}} over a Heinrich stadial

\delta^{18}O_{\text{mar}} has been recently estimated as 24.3 ± 2.0 \% for present day (Luz et al., 2014). In order to estimate \delta^{18}O_{\text{mar}} for the LGM and HS, we assumed that fractionation during oxygen uptake by marine biosphere remained constant between the LGM/HS and present day and used a mean ocean \delta^{18}O enriched by 1 \% at the LGM (Waelbroeck et al., 2002). This results in a value of \delta^{18}O_{\text{mar}} of 25.3 ± 2.0 \% for the LGM and HS. It is important to note that a rise in sea level during a HS would lead to a depleted mean ocean \delta^{18}O, as polar ice sheets accumulate ^{16}O, and can therefore not explain the increased \delta^{18}O_{\text{atm}} observed during stadials.

Because of the spatial limitation of paleorecords to provide a global picture of marine primary productivity, we have estimated the marine productivity for the LGM and HS using the Pelagic Interaction Scheme for Carbon and Ecosystem Studies (PISCES) model. The PISCES model is a biogeochemical model of the global ocean including a simple representation of marine ecosystem and forced offline by the AOGCM IPSL-CM4 (Aumont and Bopp, 2006; Mariotti et al., 2012). The model PISCES has already been compared under glacial conditions with observations (Mariotti et al., 2012; Tagliabue et al., 2009; Bopp et al., 2003) and reproduces roughly the paleoproductivity reconstruction of Kohfeld et al. (2005). Using the same forcings as for our simulations, Mariotti et al. (2012) simulate a global decrease in oceanic primary productivity of 16 \% during a Heinrich event, in agreement with independent modeling studies (Schmittner, 2005; Menviel et al., 2008; Schmittner and Galbraith, 2008) and more important
than the one in terrestrial GPP (3.5 %). Because $\delta^{18}O_{\text{mar}}$ is larger than $\delta^{18}O_{\text{terr}}$, this decrease in marine productivity would lead to a decrease in global $\delta^{18}O_{\text{atm}}$ during the HS, opposite to the observation. We simulated a change in the marine production to assess its impact on $\delta^{18}O_{\text{atm}}$ signal. With a change of 10 % in marine export, $\delta^{18}O_{\text{atm}}$ varies by 0.05 %. However this result needs to be treated with caution for two main reasons. (i) The fraction of land versus ocean production is strongly affecting $\delta^{18}O_{\text{atm}}$ if the isotope fractionation factors associated with the terrestrial and marine production are not similar. Pioneer studies on the Dole effect often invoked the marine-to-terrestrial production ratio to explain the observed variations. Though it is not the case in our model, recent studies suggest their magnitude to be very close, with $\delta^{18}O_{\text{mar}}$ 1.8 %0 higher than $\delta^{18}O_{\text{terr}}$. The change in $\delta^{18}O_{\text{atm}}$ is thus likely to be smaller in the real world. (ii) Recent studies (eg. Mariotti et al., 2012) rather suggest a decrease in marine export after a Heinrich event. This would lead to a decrease in $\delta^{18}O_{\text{atm}}$ signal that is in opposition to the observations as mentioned in Section 5.5.1. We conclude that marine productivity is not the driver for $\delta^{18}O_{\text{atm}}$ increase during HS.

5.5.2 Disentangling the influences of climate, hydrology and vegetation on $\delta^{18}O_{\text{atm}}$: sensitivity experiments.

In order to assess the robustness of our conclusion stating that the low-latitude hydrological cycle is the driver of $\delta^{18}O_{\text{atm}}$ changes, we have run three different experiments:

- In HSclim we test the impact of the climatic conditions. This simulation is similar to LGM-ctrl, except that the temperature and relative humidity from HS_exp are prescribed as boundary conditions.

- In HShydro we test the impact of the hydrological cycle. This simulation is similar to LGM-ctrl, except that $\delta^{18}O_{\text{p}}$ and $\delta^{18}O_{\text{vap}}$ from HS_exp are prescribed as boundary conditions.

- In HSveget we test the impact of the vegetation. This simulation is similar to LGM-ctrl, except that the vegetation production and distribution from HS_exp are prescribed as boundary conditions.

Figure 5.11 summarizes the results of the sensitivity analysis in terms of temperature, humidity, and oxygen isotopic composition of $\delta^{18}O_{\text{p}}$, $\delta^{18}O_{\text{lw}}$ and $\delta^{18}O_{\text{terr}}$. The sensitivity tests show that the implementation of one parameter from HS_exp (HSclim, HShydro and HSveget) leads to a simulated $\delta^{18}O_{\text{terr}}$ anomaly similar to or higher than in the full HS_exp.

In HSclim, $\delta^{18}O_{\text{terr}}$ enrichment is mostly caused by the 0.3 % decrease in relative humidity over the LGM vegetated areas after the AMOC collapse, since $\delta^{18}O_{\text{p}}$ and $\delta^{18}O_{\text{lw}}$ are not modified by definition. This global decrease in GPP_{$O_2$} -weighted relative humidity is not visible in the global HS_exp (Fig. 5.8) and hence does not explain the $\delta^{18}O_{\text{terr}}$ increase in HS_exp. In HSveget, the southward shift of HS_exp vegetation leads to a global GPP_{$O_2$} weighted relative humidity decrease by 0.5 %. As in
Figure 5.11 – Summary of sensitivity study experiments. HSfull uses the same settings as HS_exp, while HSclim, HShydro and HSveget experiments are identical to LGM_ctrl, except for meteoric water isotopic composition, climatic conditions, or vegetation production and distribution, respectively, originating from HS_exp. For each of the experiments, an annual-mean anomaly (experiment – LGM_ctrl) of oxygen-production-weighted temperature, relative humidity, $\delta^{18}O_p$, water vapor $\delta^{18}O$, $\delta^{18}O_{lw}$, $\epsilon_{\text{resp}}$ and $\delta^{18}O_{terr}$ is presented.

HSclim, this leads to a high $\delta^{18}O_{terr}$ positive anomaly. The effect of relative humidity on $\delta^{18}O_{terr}$ is minimized in HS_exp, as the southward shift in vegetation counterbalances the change in climatic conditions. This compensation explains why the final GPP$_{O_2}$ weighted relative humidity does not vary.

In HShydro, the $\delta^{18}O_p$ increase explains the whole $\delta^{18}O_{terr}$ increase. This increase in GPP$_{O_2}$-weighted $\delta^{18}O_p$ is similar in HShydro and HS_exp, which confirms that the $\delta^{18}O_{terr}$ simulated by the model in the full experiment HS_exp is arising from a change intrinsic to the hydrological cycle, only slightly affected by vegetation distribution.

In addition, note that a weakening of $\delta^{18}O_{lw}$ only occurs with HS vegetation (HS_exp, HSveget), regardless of the climatic conditions. Moreover, HSclim depicts a stronger $\delta^{18}O_{lw}$, caused by a higher temperature increase over HS, leading to an enhanced photorespiration fraction among C$_3$ plants. However, the temperature effect on $\delta^{18}O_{lw}$ remains minor.

The global impact of $\epsilon_{\text{resp}}$ is negligible in all experiments, with variations 1 order of magnitude lower than $\delta^{18}O_p$.

Finally, these tests confirm the strong control of hydrological processes on $\delta^{18}O_{terr}$.
and highlight the role of the vegetation distribution in defining $\delta^{18}O_p$ and climatic conditions recorded by $\delta^{18}O_{\text{terr}}$.

5.6 Conclusions and perspective

Our study first aimed at quantitatively testing the driving of $\delta^{18}O_{\text{atm}}$ by tropical hydrology as suggested by the strong correlation between local records of $\delta^{18}O_c$ and global record of $\delta^{18}O_{\text{atm}}$ on the millennial scale. For this we used a HS-type simulation under LGM background conditions with an oxygen isotope mass balance model using spatial and temporal fields of (i) temperature and relative humidity from the AOGCM IPSL-CM4, (ii) PFT distribution and GPP provided by the dynamic global vegetation model ORCHIDEE, (iii) oxygen isotope composition of water vapor and precipitation from the AOGCM LMDZ-iso, and (iv) the latest isotope fractionation factor measurements involved in respiratory and photosynthetic processes.

Validation of AOGCM outputs feeding the oxygen isotope mass balance model was performed through a model–data comparison of the main drivers of $\delta^{18}O_{\text{terr}}$: (i) simulated $\delta^{18}O_p$ was compared to speleothem's calcite $\delta^{18}O$ anomalies, and in most sites showed excellent agreement despite the complexity of the $\delta^{18}O_c$ signal; (ii) simulated HS humidity was compared to the reconstructed ones, broadly agreeing with paleo-data; and (iii) simulated vegetation was compared with palynological reconstructions for LGM and HS, and was qualitatively consistent.

The model simulates a terrestrial enrichment of $\delta^{18}O_{\text{terr}}$ of 0.11‰, which mostly arises from the $\delta^{18}O_p$ signal. On a global scale, respiration fractionation only plays a minor role in the anomaly observed during HS, and slightly decreases $\delta^{18}O_{\text{terr}}$ in our simulation, driven by a weaker isotope fractionation of soil respiration during HS that masks the effect of increased photorespiration. Accounting for the effect of soil aeration on $^{18}\alpha_{\text{dark_soil}}$ modifies the $^{18}\epsilon_{\text{resp}}$ anomaly by 0.05‰, a change too small to challenge $\delta^{18}O_p$ main control on $\delta^{18}O_{\text{terr}}$. However, the simplicity of our approach to model soil moisture content and the GPP $O_2$ weighting of $^{18}\alpha_{\text{dark_soil}}$ favoring Southern Hemisphere tropics are likely to explain this result. In order to precisely evaluate the uncertainty associated with $^{18}\epsilon_{\text{resp}}$, an improved parameterization of soil aeration will be needed. This limitation of the model must thus be kept in mind when considering the conclusion of this study.

The strong control of the low-latitude hydrological cycle on simulated $\delta^{18}O_{\text{atm}}$ on millennial timescales suggests that $\delta^{18}O_{\text{atm}}$ records, at first order, changes in monsoonal activity on millennial timescales, in agreement with $CH_4$ mixing ratio variations. Indeed, rapid $CH_4$ variations during the last glacial period are generally attributed to changes in the low-latitude water cycle (Baumgartner et al., 2014; Brook et al., 2000; Chappellaz et al., 1993) driven by latitudinal shifts of the ITCZ and the monsoon systems (e.g., Chiang, 2009). Such a signal can also be used for exploring the low-latitude hydrological cycle characteristic of Heinrich events. Indeed, the re-
cent study of Rhodes et al. (2015) suggests that observed $CH_4$ spikes in WAIS Divide ice core during the cold phases of HSs represent the hydrological signature of Heinrich events, through activation of Southern Hemisphere wetlands. The Guillevic et al. (2014) multi-ice-core proxies approach over GS9–HS4 also suggests a decoupling between changes in Greenland temperatures and low-latitude hydrology identified in both $CH_4$ and $\delta^{18}O_{atm}$, and demonstrates the need for high-resolution data with common precise chronology to explore submillennial variations.

$\delta^{18}O_{atm}$ is a valuable tool to assess the validity of Earth system model simulations, as it integrates a combination of hydrological, climatic and biological processes. Furthermore, $\delta^{18}O_{atm}$ is a global signal, which mostly arises from the tropics and integrates all vegetated areas. Therefore, the ability of a model to catch $\delta^{18}O_{atm}$ millennial-scale variations implies a correct spatial representation of an ensemble of processes. The comparison of Earth system model outputs with global proxies such as $\delta^{18}O_{atm}$, involving the main components of the climatic system, is crucial for gaining confidence in their ability to represent the real world. Our approach is mainly restricted to terrestrial contribution, but future modeling exercises should also include the oceanic $\delta^{18}O_{atm}$ signal.

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6 Conclusions and perspectives

This thesis addresses (i) the technical aspects of $O_2$ isotope ratio measurements from ice core samples, and (ii) our ability to model the observed variations of $\delta^{18}O_{atm}$ during a Heinrich Stadial. In the following we summarize our findings.

**Can the perovskite membrane be applied to ice core science?**

Improving the precision of $^{17}\Delta_{atm}$ measurements is a crucial requirement to further explore millennial scale variations and confirm the 10 permeg variation observed over DO 19 (Landais et al., 2007). Indeed, $^{17}\Delta_{atm}$ millennial scale variations hardly exceed the precision of the measurements (currently between 5 and 10 per meg). In line with this observation, Chapter 2 presented the development and testing of a new method of $O_2$ separation from other atmospheric constituents in order to measure a pure $O_2$, as isotope ratio determination in a gas mixture requires corrections and therefore decrease precision. It is based on a perovskite membrane ($BaCo_xFe_yZr_{1-x-y}O_{3-d}$), the transport mechanism of which is based on mixed-ionic-electronic technology: at high temperature (typically around 800 °C), permeation of $O_2$ across the membrane occurs in 3 steps, driven by the $O_2$ partial pressure gradient: reduction of $O_2$ molecules adsorbed at the surface with high $O_2$ partial pressure, counter diffusion of $O_2$ ions and electrons through the bulk of the membrane and oxidation of $O_2$ ions (loss of electron) desorbed at the surface with low $O_2$ partial pressure. The 100 % selectivity and high $O_2$ permeability of the membrane to $O_2$ was confirmed, ranging from 0.5 to 3.5 $ml \cdot cm^{-2} \cdot s^{-1}$. However, constant sealing issues, related to the rough and porous surface of the membrane, and variable mass-dependent fractionation, likely related to the fact that $O_2$ is not quantitatively released from the membrane, precludes high-precision $^{17}\Delta_{atm}$ measurements. The use of the hollow tube fiber in ice core sciences primarily requires a long-lasting gas-tight sealing. If this condition is met, the membrane can be used in applications where removal of $O_2$ is required, taking profit of its 100 % selectivity to $O_2$. Indeed, for such applications, the fractionation of the membrane caused by $O_2$ segregation is not relevant. Besides, a career gas can be used to create a low $O_2$ partial pressure in the permeate side, hence ensuring a fast and efficient $O_2$ permeation. Additionally, pure $O_2$ standards can be produced in large amounts from e.g. atmospheric $O_2$ given the large permeability of the membrane.

**Does the analytical system developed at CIC enable precise and accurate $\delta^{18}O_{atm}$ and $^{17}\Delta_{atm}$ measurements?**

Chapter 3 described the semi-automated, offline experimental setup to extract $O_2$ from air preserved in ice core bubbles. The developed extraction line is based on the conventional Barkan and Luz’s method, relying on GC separation of $O_2$ and $N_2$. Minor changes were made to the original method: a closed-He cryocooler is used to collect $O_2$ samples at 12 K instead of liquid He, and the gas flow to the GC column is
directed with Valco valves. The setup includes air extraction from ice, standard introduction and cryo-collection in a sample manifold. As for δ17Δatm measurements, an O2/Ar mixture is collected after separation from H2O, CO2 and N2. As for δ18Oatm, measured in a dried and CO2-free air mixture, the GC unit is bypassed as no N2 separation is required.

We gave an overview of the units and controls of the experimental setup and presented the developed routine associated with the extraction-purification-collection of δ18Oatm and 17Δatm. We showed that it is critical to condition the extraction line, the collection manifold and the lines of the DI system with standard gas prior a sequence of measurements to obtain a good reproducibility of ice core measurements.

Chapter 4 showed that successful IRMS measurements of δ18Oatm from ice core samples can be performed with the developed analytical setup at CIC. Using a wet-extraction method, δ18Oatm from 21 NEEM Late Holocene shallow ice core samples from the same depth was measured by Grzymala-Lubanski (2015) to control the stability of the analytical system during a rice ice core measurement campaign. These large samples (∼30 g) were collected offline and δ18Oatm, δO2/N2 and δ15N were measured in an O2/N2/Ar mixture by IRMS in DI mode. The complete automation of a DI measuring sequence of ten ice core samples using a custom-based isl script was described. The scatter observed in δ18Oatm and δO2/N2 of the replicate NEEM samples underlines the occurrence of gas loss fractionation processes, causing δ18Oatm to increase by ∼0.01‰ for 1‰ change in δO2/N2, as described in the literature.

We detailed the method of data-processing, its associated uncertainty and the strategy employed to correct δ18Oatm for non climatic effects, including effects of sample and standard beam voltage imbalance on the measured O2 ratio, dependence of δ18Oatm on the O2/N2 ratio (chemical slope), of gravitational settling in the firn, and of gas loss processes associated with bubble close-off, coring and post-coring processes.

Based on zero-enrichment tests, the internal precision of DI measurements of δ18O and δ15N is 0.008‰ (1 σ) and 0.005‰ (1 σ). A similar precision is reached with individual ice core sample measurements, in the range of what can be found in the literature. Based on the 21 NEEM samples, the ability of the analytical system to reproduce δ18Oatm and δO2/N2 ice core measurements is estimated as 0.028‰ (1 σ) and 0.021‰ (1 σ), respectively.

In contrast, the level of precision (<10 permeg) required for 17Δatm measurements is not reached in the current configuration of the experimental setup. Critical improvements are required, in particular the ability of the analytical system to reproduce measurements of standard gas introduced over BFI to fully respect the IT principle.

Improvement in the ice core reproducibility of the analytical setup can be achieved by:

- Melting BFI before standard introduction in order to avoid sample contamination by dissolved gases. As long as this step is not reproducible, the Identical Treatment principle cannot be respected, and precludes very high-precision δ18Oatm and especially 17Δatm measurements.
• A full automation of the extraction line in order to maintain similar conditions for each sample and avoid operator-related error, in particular in terms of timing (e.g. switching valves).

• A collector configuration of the ms enabling simultaneous collection of air isotopologues, i.e. m/z 28, 29, 32, 33, 34, 36 and 40. We are currently measuring $\delta O_2/N_2$ with a modified peak jumping procedure, obtaining a precision ranging from 0.1 to 0.4 $\%_\text{o}$ for an individual ice core sample. Simultaneous measurements of $O_2$, $N_2$ (and Ar) would enhance the overall precision of the measurements by avoiding corrections related to the time delay between the integration of ion currents m/z 28 and m/z 32.

What drives $\delta^{18}O_{\text{atm}}$ variations during Heinrich stadials?

Finally, chapter 5 explores the causes of $\delta^{18}O_{\text{atm}}$ millennial scale variations during the last glacial period, with a focus on Heinrich Stadials, where a systematic $\delta^{18}O_{\text{atm}}$ increase is recorded. We quantified the response of $\delta^{18}O_{\text{atm}}$ to such millennial events with an oxygen isotope mass balance model using spatial and temporal fields of (i) temperature and relative humidity from a freshwater hosing simulation performed under glacial boundary conditions with the AOGCM IPSL-CM4, (ii) PFT distribution and GPP provided by the dynamic global vegetation model ORCHIDEE, (iii) oxygen isotope composition of water vapor and precipitation from the AOGCM LMDZiso, and (iv) the latest isotope fractionation factor measurements involved in respiratory and photosynthetic processes. AOGCM outputs (precipitation, vegetation cover and humidity) were compared with paleodata for validation and show in general a good agreement. The model simulated a terrestrial enrichment of $\delta^{18}O_{\text{terr}}$ of 0.11 $\%_\text{o}$, which mostly arises from the $\delta^{18}O_p$ signal. On a global scale, respiration fractionation only plays a minor role in the anomaly observed during HS, and slightly decreases $\delta^{18}O_{\text{terr}}$ in our simulation, driven by a weaker isotope fractionation of soil respiration during HS that masks the effect of increased photorespiration. Our results confirmed the strong control of the low-latitude hydrological cycle on $\delta^{18}O_{\text{atm}}$ as suggested by the strong correlation between local records of $\delta^{18}O_c$ and global record of $\delta^{18}O_{\text{atm}}$ on the millennial scale.

The $O_2$ isotopic mass balance model could be improved by including:

• The dependence of $^{18}\epsilon_{\text{resp}}$ on soil aeration. Variations in the water content of soils modify the effective fractionation $^{18}\epsilon_{\text{resp}}$, because diffusion of $O_2$ in water is slower than diffusion in air. It causes a drop in concentration at the site of soil respiration, which translates into a weaker back flux to the atmosphere of the $\delta^{18}O$ -enriched residual $O_2$ after partial respiration. In order to precisely evaluate the uncertainty associated with $^{18}\epsilon_{\text{resp}}$, an improved parameterization of soil aeration is needed.

• A model of the marine component ($DE_{\text{mar}}$) of the Dole effect, as it has been suggested that changes of fractionations in the marine biosphere are more im-
portant than the land-sea control in regulating the magnitude of the Dole effect and its past variations.

Additionally, future research should focus on $^{17}\Delta_{atm}$ by:

- Quantifying the contribution of the processes controlling $^{17}\Delta_{atm}$ changes, using a similar modeling approach as for $^{18}\delta O_{atm}$. Subsequently, comparing the different sensitivities of $^{18}\delta O_{atm}$ and $^{17}\Delta_{atm}$ to these controlling processes should help constrain the causes of the observed $O_2$ isotope variations. This work is well advanced as the modeling of $^{17}\Delta_{atm}$ is already integrated in the $O_2$ mass balance model.

- Modeling the stratospheric photochemistry, following Young et al. (2014), to account for the numerous reactions that affect the magnitude of stratospheric $^{17}O$ depletion in $O_2$.

- Exploring the possibility to use carbonyl sulfide as a tracer of $CO_2$ uptake, and thereby obtain valuable information on ecosystem photosynthesis and on the time of photosynthesis. Such constraints would enable a more precise estimation of e.g. $^{18}\delta O_{lw}$ as humidity and temperature conditions could be better estimated if the time of photosynthesis is known.

- High-resolution $^{17}\Delta_{atm}$ measurements from ice core samples to characterize its past millennial time-scale variations. So far, only one study has combined high resolution $^{18}\delta O_{atm}$ and $^{17}\Delta_{atm}$ measurements (Landais et al., 2007 over DO 19).


A Isl scripts for automated $\delta^{18}O_{atm}$ measurements

1 Main script: lynnoax_automated_d18o2n2.isl

//
// =================================================================================
// ISODAT NT SCRIPT LANGUAGE (ISL): Dual Inlet Basic Script
// =================================================================================
//
// History list
//
// Author      changes Date           Reason
//
// hjs         created novembre 2005
// hjs         modified and extended for Jeff Severinghaus, Scripps December 2005
// hjs         modified, now universally applicable for any gas jumps April 2006
// okt/fth     Dec 2008 refinement for Bern university
// okt/fth     Sept 2009 adjusted for Bern university
// C. Reutenauer 18.10.2012 adjusted for CPH to be integrated to the main acquisition file
// L. Lubanski 07.08.2015 Argon 40 removed from the Peak jumping

//
// DEAR DELTA/MAT253 USER !!!

// Script for performing a dual inlet peak jump acquisition.
// replace default acquisition.isl with this script in dual inlet method.
// Start a jump measurement between two gases as dual inlet measurement using
// some parameters as defined in dual inlet method.
// The script writes results into a comma separated *.txt file (can be imported and subsequently evaluated in Excel).
// The default folder is: c:\jump_results. This folder must be created by the user !!!
// To change the folder name and path go to xxx
// Background is determined for each gas individually if checked in the sequence line
// Press adjust is done for the first gas to be measured when checked in the sequence line
// Parameters to be modified by user are at the end of the script.
// Please find more info at the bottom of the script.

external array g_nInties of number [10];
// external array g_n1Inties of number [10];
external array g_n1Inties of number [10];
external array g_n2Inties of number [10];
external array g_nBackgrounds of number [10];
external array g_sBgd of string [10]; //added
external number g_NumberOfCurrInties = 0;
external array g_ChannelArr of channel [10];
external array g_sLastIntiesStr of string [10]; //added
// external array g_sInties of string [10]; //added
external string g_sInties="";
external string g_resultstr="";
external string g_sOldGasConf="";
external string g_sFileName="";
external number g_n1Inties=0;
external number g_n2Inties=0;
external number g_nNumCycle=0;
external number g_nBackgroundDelay = 60; //must be defined here in the script. Method value ignored. Value in seconds.
external number g_nPressAdjustDelay = 10; //second

script DualInletPeakJumpAdjustLynnOax
{
  const number NUM_CHANNELS=10; // see above!
  const number KEEP_GC=0;    // gas configuration
  const number CHANGE_GC=1;
  const number NO_PC=0;       // peak center
  const number YES_PC=1;
  const number NO_BGD=0;      // background
  const number YES_BGD=1;
  const number NO_PA=0;       // press adjust
  const number YES_PA=1;
}
```c
#include "lib\math.isl"
#include "lib\stdisl.isl"
#include "lib\instrument.isl"
#include "lib\DualInlet_lib.isl"
#include "lib\LynnOax_lib_waterMS.isl"
#include "lib\InterferingMassLynnOax.isl"

function ConvertIntyStr (string sIntyStr)
{
    g_NumberOfCurrInties = 0;
    number nCnt = 0;
    string sSubStr;
    string sHlpStr;
    number nStrLen = _strlen (sIntyStr);
    number nPos = 0;

    if (nStrLen > 0)
    {
        nPos = _strstr (sIntyStr, ",");
        while ((nPos>=0) && (nCnt<10))
        {
            sSubStr = _strleft (sIntyStr, nPos);
            g_nCurrInties[nCnt] = _strtod (sSubStr);
            g_NumberOfCurrInties++;

            sHlpStr = _strright (sIntyStr, (nStrLen - nPos - 1));
            sIntyStr = sHlpStr;
            nStrLen = _strlen (sIntyStr);
            nPos = _strstr (sIntyStr, ",");

            nCnt++;
        }
    }

    if (nStrLen>0) && (nCnt<10))
    {
        g_nCurrInties[nCnt] = _strtod (sIntyStr);
        g_NumberOfCurrInties++;
    }

    //

    function AppendIntensities (string sIntyStr)
    {
        call ConvertIntyStr (sIntyStr);
    }
```
number nCnt = 0;
for (nCnt=0; nCnt<g_NumberOfCurrInties; nCnt++) {
    g_nInties[nCnt] = g_nInties[nCnt] + g_nCurrInties[nCnt];
}

function MyBackground(channel nChan, number nIntegrationTime) {
    string csResult="?";
    string csInfo="Background: ";
    number nBGDDelay = g_nBackgroundDelay * 1000;
    string sLastIntiesStr;
    string sTransition
    number nNumDigits = 3;
    number nChanIdx = 0; // added
    number nCnt = 0;
    number nMaxChan = NUM_CHANNELS;

    bool bBackground = _GetSequenceFlag("Background", TRUE);
    if (bBackground==TRUE) {
        _UserInfo("Start Background", 0, 1);
        call ChangeOverClose();
        _Delay(nBGDDelay);

        _ResetLastAcqInty();
        number nIntyEx = _GetIntensityEx(nChan, nIntegrationTime);
        // sLastIntiesStr = _GetLastAcqInty(nNumDigits);
        sLastIntiesStr = _strFromNumber(nIntyEx);
        call AppendIntensities(sLastIntiesStr);
        for (nCnt=0; nCnt<g_NumberOfCurrInties; nCnt++) {
            g_nBackgrounds[nCnt] = g_nInties[nCnt];
            g_nInties[nCnt] = 0;
        }
    }
}

function sci2str(number in): string // converts scientific format into string {
    number i;
    string out;
    for (i=0; in<1; i++)
    {
        in = in * 10;
    }
function Inty_Mass(channel chan, number mass): number
{
    number int_time = 10000;  // integration time default
    number inty;

    number Dac = 0;
    Dac = _SetMassViaDac(1, mass);
    _PeakCenter(1);
    _Delay(int_time); _Delay(int_time); // Delay(int_time); Delay(int_time);
    inty = _GetIntensityEx(chan, int_time);

    return inty;
}

function Jump2Mass(string GasConfigGasX, channel measchannel, number mass, string& csOld, bool ChangeGasConfig, bool DoPeakCenter): number
// jump to desired mass
{
    bool bPeakCenterOn = _GetSequenceFlag("Peak Center", FALSE);
    number Dac;
    number ActMass;
    number MassAcurr = 0.3;
    // magnet is switched only if mass difference is greater than MassAcurr
    // otherwise mass will be corrected by peakcenter
    if (ChangeGasConfig==TRUE)
    {
        _SetGasConfiguration(GasConfigGasX, csOld);
    }
    ActMass = _GetMass(measchannel);
    if (abs(mass-ActMass) > MassAcurr)
    {
        Dac = _SetMassViaDac(measchannel, mass);
    }
    if ((DoPeakCenter==TRUE) && (bPeakCenterOn==TRUE))
    {
        _UserInfo("Start Peak Center after jump to mass", 0, 1);
        number nResult = _PeakCenter(measchannel);
        if (nResult < 0)
        {
            _ScriptError("Peak Center failed <%0.0f>", ERROR_TYPE_SCR_SEQ, nResult);
        }

}  
}  
_Delay(Ms_PeakCenterPostDelay);  
}  
\return Dac;  
}  

// function Delay_Sec(number time)  
{  
number delay_msec=time*1000;  
_Delay(delay_msec);  
}  

// function ResetChannelArr()  
{  
number nChanIdx=0;  
for(nChanIdx=0; nChanIdx<NUM_CHANNELS; nChanIdx++ )  
{  
g_ChannelArr[nChanIdx]= -1;  
}  
}  

// function MeasureGas(string sGasConfName, string SampleName, number mass, channel nChan, number nIntegrationTime, number nSampleSide, bool ChangeGasConfig, bool DoPeakCenter, bool bDoBackground, bool bDoPressAdjust): number  
{  
number IntRepGas2 = 1; // how often is integration repeated with IntegrationTime, result is mean value (not to mix with cycle times)  

number nResult = 0;  
string sOld;  
string helpstr;  
string resultstr;  
//number nPreDelay = Dual_Inlet_Idle;  
number time_sec = 0;  
number nLen=0;  
number nPressAdjustDelay = g_nPressAdjustDelay * 1000;  

if (ChangeGasConfig)  
{  
nResult= call Jump2Mass(sGasConfName, nChan, mass , sOld, ChangeGasConfig, DoPeakCenter);  
}  

}
```c
nLen=_strlen ( g_sOldGasConf ) ;
if ( nLen == 0 )
{
    g_sOldGasConf = sOld ;
}

number nChanIdx=0;
string sLastIntiesStr ;
string sTransInties
for ( nChanIdx=0; nChanIdx<NUM_CHANNELS; nChanIdx++ ;)
{
    g_nInties[nChanIdx] =0 ;
g_nBackgrounds[nChanIdx] =0 ;
}

if ( bDoBackground )
{
    call MyBackground(nChan, nIntegrationTime) ;
}

if ( bDoPressAdjust )
{
    _Delay(nPressAdjustDelay) ;
call Pressureadjust() ;
}

call SwitchChangeOver(nSampleSide);
resultstr=_strFromNumber(g_nNumCycle) ;
helpstr=" ",
resultstr+= helpstr ;
time_sec=_ElapsedTime() / 1000 ;
helpstr=_strFromNumber(time_sec); resultstr+= helpstr ;
helpstr=" ",
resultstr+= helpstr ;
helpstr=SampleName; // " , Sample , " ;
resultstr+= helpstr ;
helpstr=" ",
resultstr+= helpstr ;
helpstr=sGasConfName ;
resultstr+= helpstr ;
helpstr=" ",
resultstr+= helpstr ;
helpstr=_strFromNumber(mass) ; resultstr+= helpstr ;
helpstr=" ",
resultstr+= helpstr ;
_Delay(Dual_Inlet_Idle);
number nDefault = (-1000);
number inty = 0;
number k = 0;
number nMaxChan = NUM_CHANNELS;
nChanIdx = 0;
for (nChanIdx = 0; nChanIdx < NUM_CHANNELS; nChanIdx++)
{
    g_nInties[nChanIdx] = 0;
} // removed
nDefault = (-999);

number nNumDigits = 3;
number ff = 15000;
for (k = 0; k < IntRepGas2; k++)
{
    _ResetLastAcqInty();
    _GetIntensityEx(nChan, nIntegrationTime);
    // sLastIntiesStr = _GetLastAcqInty(nNumDigits);
    number nIntyEx = _GetIntensityEx(nChan, nIntegrationTime);
    sLastIntiesStr = _strFromNumber(nIntyEx);
    call AppendIntensities(sLastIntiesStr);
}
for (nChanIdx = 0; nChanIdx < nMaxChan; nChanIdx++)
{
    if (g_ChannelArr[nChanIdx] < 0)
    {
        nMaxChan = nChanIdx;
    }
    else
    {
        g_nInties[nChanIdx] = g_nInties[nChanIdx] / IntRepGas2;
        g_nInties[nChanIdx] = g_nInties[nChanIdx] - g_nBackgrounds[nChanIdx];
        inty = g_nInties[nChanIdx];
        helpstr = _strFromNumber(inty);
        resultstr += helpstr;
        helpstr = ", ";
        resultstr += helpstr;
    }
}
helpstr = _strFromNumber(nIntegrationTime);
helpstr += " ", resultstr += helpstr;
_Write(g_sFileName, g_sSection, resultstr, "", line_end");
UserInfo(resultstr, 0, 0);
_Trace(resultstr, g_nNumCycle); g_resultstr = resultstr;
```csharp
return nResult;

function CleanUp()
{
}

function InitScript()
{
    OnBreak CleanUp;
}

main()
{
    bool DoPeakCenter=TRUE;

    string NameGas1="Default1";
    string GasConfigGas1="O2_gaslab"; // Default
    string NameGas2="Default2";
    string GasConfigGas2="O2_gaslab"; // Default
    channel cChannel=1; // Default
    number nIntegrationTime=16000; // Integration time default value
    Can be set individually for each gas below.

    string helpstr;
    string helpstr2;
    string infodefault="line,Sa_";
    string section="header";
    string userinfo;
    string filename_default;
    string filename=filename_default;
    string resultstr;
    string i_as_str;
    string csOld;
    number i;
    number j;
    number k;
    number line;
    number strpos;
    number nResult;
```
bool bOK;
number inty;
number nSampleSide=Dual_Inlet_Sample;
number nStandardSide=Dual_Inlet_Standard;
number nPreDelay=Dual_Inlet_Idle;
number time_sec;
number helpnumber;
bool ChangeGasConfig=TRUE;

string sGasName="";
number nMassSelect=0;
number nSaStartPressure;
number nStdStartPressure;

call InitScript();

if (_stricmp (GasConfigGas1, GasConfigGas2)==0)
{
  ChangeGasConfig=FALSE;
}

_Set("Dual Inlet System/Valve 15",1); // open valve 15
_Set("Dual Inlet System/Valve 25",1); // open valve 25

bool bEvacuateSa  = _GetSequenceFlag("Evacuate Sa",FALSE); // evacuate sample side
bool bEvacuateStd = _GetSequenceFlag("Evacuate Std",FALSE); // evacuate std side
bool bMonitorMass = _GetSequenceFlag("MonitorMass",FALSE);
bool bPressAdjustOn=_GetSequenceFlag("Pressadjust",FALSE); // <--- press adjust if checked in sequence
bool bPeakCenterOn=_GetSequenceFlag("Peak Center",FALSE);
bool bPILeft=_GetSequenceFlag("PLeft+",FALSE);
bool bPIRight=_GetSequenceFlag("PRight+",FALSE);

// added april 2013, used for correction, tuning, what needs to be monitored on the MS

g_sMeasType = _GetSequenceText("Measurement Type","none");
g_sStdInj = _GetSequenceText("Standard Injection","none");
g_sChecks = _GetSequenceText("Checks","none");
g_nAmountBellow = _GetSequenceNumber("AmountBellow",0.0);
g_nPercentBellow = _GetSequenceNumber("Preparation",1000);
g_sEquilTime = _GetSequenceText("Preparation","");
g_sPortName = _GetSequenceText("Lynn Oax Inlet", "none");
string sSampleIDstring = _strleft(g_sPortName, (_strlen("sample")))
;
// check if std signal is higher than 10mbar at full expansion
if (_strcmp(sSampleIDstring, "sample") == 0) // depending on the string on Lynn Oax Inlet sequence's column, switch from script
{
    if (bEvacuateSa == TRUE) // if box checked, means sample needs to be transferred
        {_UserInfo("Vacuuming Sample Side", 0, 1);
        if (bEvacuateStd == TRUE) { call StdTransferDIRIGHT(); } // if (_GetSequenceInfo(IS_FIRST_SAMPLE_RUNNING, FALSE)) { call StdTransferDIRIGHT(); }
        if (bEvacuateStd == FALSE) { call StdRefill(); }
    
g_sPortName = _GetSequenceText("Lynn Oax Inlet", "none"); // get column string from attached sequence
    channel chPA_channel = chPa; // _GetChannelForCup(PAcup);
    call SwitchChangeOver(Dual_Inlet_Standard); // switch changeover to std side
    call MpTransfer(); // call DiSwitchX(nside, nNo, bOpen, delay) first close valve 11 and open 15
                           // if port recognized, starts MpTransferMp
    call PeakCenter();
    // call GetIntPress_Introduction();
    if (bPressAdjustOn == TRUE)
        {
            nStdStartPressure = call GetIntPressStd_Introduction();
            nSaStartPressure = call GetIntPressSa_Introduction();
        }
    call Background();
    // call DiSetVolume(Dual_Inlet_Standard, 100); // to remove if PA manual!! as Sample is Master, Standard pressure in bellow has to be lower than sample pressure. Can be improved
    call Pressureadjust_LynnOaxd18O2N2();
    call GetVoltage_Pressure_diff(nSaStartPressure, nStdStartPressure);
    call Acquisition();
    call MonitorMass();
    // call MagnetScan();
    if (_GetSequenceInfo(IS_LAST_SAMPLE_RUNNING, TRUE))
        {
            call ChangeOverClose();
        }
}
else
{
    _UserInfo("Skip Sample Side Evacuation",0,1);
    call StdRefill();
    // call DiBellowAdjust_Increase(Dual_Inlet_Sample, nMaxContractionTries);
    call PeakCenter();
    if (bPressAdjustOn==TRUE)
    {
        nStdStartPressure = call GetIntPressStd_Introduction();
        nSaStartPressure = call GetIntPressSa_Introduction();
    }
    call Background();
call Pressureadjust_LynnOaxd18O2N2();
call GetVoltage_Pressure_diff(nSaStartPressure, nStdStartPressure);
call Acquisition();
call MonitorMass();
    // call MagnetScan();
    if (._GetSequenceInfo(IS_LAST_SAMPLE_RUNNING,TRUE))
    {
        call ChangeOverClose();
    }
else
{
if ( _strcmp( g_sPortName ,"none") ==0)
{
    if (bEvacuateSa==TRUE)
    {
        _UserInfo("Vacuuming Sample Side for Zero-enrichment test",0,1);
        g_sPortName=_GetSequenceText("Lynn Oax Inlet","none"); // get column string from attached sequence
        g_nSeqRowNumber = _GetSequenceNumber("Row",0);
        channel chPA_channel = chPa; //channel chPA_channel =
        _GetChannelForCup(PAcup);
        // call SwitchChangeOver(Dual_Inlet_Standard); // switch changeover to std side

        // if (g_nSeqRowNumber = 1) { call StdTransferDIRIGHT();}
        if (bEvacuateStd==TRUE) { call StdTransferDIRIGHT();} // if (_GetSequenceInfo(IS_FIRST_SAMPLE_RUNNING, FALSE)) { call StdTransferDIRIGHT();}
        if (bEvacuateStd==FALSE) { call StdRefill();}
        // call Flushing(); added in StdTransferDILEFT // FlushingCycles=3 flush std line 3 times by default
        call StdTransferDILEFT();
    }
}
call DiSwitchX(Dual_Inlet_Sample,2,0,DI_DEFAULT_VALVE_DELAY);
call DiSwitchX(Dual_Inlet_Sample,3,0,DI_DEFAULT_VALVE_DELAY);
call DiSwitchX(Dual_Inlet_Standard,2,0,DI_DEFAULT_VALVE_DELAY);
call CheckVacuum(Dual_Inlet_Standard,3,Press_read_waitin_time);
// close vac pumps, open specified valve and check vacuum

call PeakCenter();
    if (bPressAdjustOn==TRUE)
    {
        nStdStartPressure = call GetIntPressStd_Introduction();
        nSaStartPressure = call GetIntPressSa_Introduction();
    }
call Background();
call Pressureadjust_LynnOaxd18O2N2();
call GetVoltage_Pressure_diff(nSaStartPressure,nStdStartPressure);
call Acquisition();
call MonitorMass();
// call MagnetScan();
}
else
{
    _UserInfo("Skip Sample Side Evacuation",0,1);
call StdRefill();
    // call DiBellowAdjust_Increase(Dual_Inlet_Sample,nMaxContractionTries);
call PeakCenter();
    if (bPressAdjustOn==TRUE)
    {
        nStdStartPressure = call GetIntPressStd_Introduction();
        nSaStartPressure = call GetIntPressSa_Introduction();
    }
call Background();
call Pressureadjust_LynnOaxd18O2N2();
call GetVoltage_Pressure_diff(nSaStartPressure,nStdStartPressure);
call Acquisition();
call MonitorMass();
// call MagnetScan();
    
    if (_GetSequenceInfo(IS_LAST_SAMPLE_RUNNING,TRUE))
    { 
        call ChangeOverClose();
    }
}
// Start peak jumps

XIII
bool bMagnetScan = _GetSequenceFlag ("MagnetScan", FALSE);

if (bMagnetScan==TRUE)
{
    filename_default="C:\Thermo\Isodat NT\Global\User\Dual Inlet System\Results\ACQ_O2_Results\jump_results";
    // <= define your result folder here, make sure it exists !!
    filename_default="O2_N2_Ar"; // <= define your filename here
    filename_default+="__000.txt";
    filename=filename_default;

    // check for next free file
    _Write(filename, section, infodefault, "header");

    for (i=1;i<999;i++)
    {
        strpos=_strstr (filename, "__");
        strpos=strpos+2;
        helpstr=_strleft (filename, strpos);
        filename=helpstr;
        i_as_str="00";
        i_as_str+=_strFromNumber (i);
        helpstr=_strright (i_as_str, 7);
        helpstr=_strleft (helpstr, 3);
        filename+=helpstr;
        filename+=".txt";
        bOK=_ExistFile (filename);
        if (bOK==FALSE) { i =999; }
    }

    // helpstr = _GetDate();
    // helpstr2 = _GetTime();
    infodefault = "Date: ";
    // infodefault += helpstr;
    infodefault += " Time: ";
    // infodefault += helpstr2;
    _Write(filename, section, infodefault, "header");
    section="greetings_from_bremen";
    infodefault="line, time/sec, Std/Sa, Gas, Mass/Da, Inty/mV, Inty mV, Inty mV, Intytime/msec "; // time/sec is related to acquisition start after each integration.

    _Write(filename, section, infodefault, "info");

g_sFileName=filename;
g_sSection=section;

    helpstr = "Analysis started. Result file is ";
    helpstr += g_sFileName;
    _UserInfo (helpstr,0,1);

    // Acquisition starts here
call SwitchChangeOver(nStandardSide);
helpnumber=i*4;
_ResetTimer();

for (i=0;i<3;i++) // the measurement cycles start here
Dual_Inlet_Cycles
{
  g_nNumCycle = i+1;

  // Measurement sequence example: (IN CASE OF Kr/Ar, see
  // Severinghaus 2003, p. 333)
  // jump to 84
  // peak center
  // switch changeover to sample
  // idle 10 sec
  // integrate 16 sec
  // switch changeover to standard
  // idle 10 sec
  // integrate 16 sec
  // jump to 36
  // peak center
  // switch changeover to sample
  // idle 10 sec
  // integrate 8 sec
  // switch changeover to standard
  // idle 10 sec
  // integrate 8 sec
  // jump to 36
  // peak center
  // switch changeover to sample
  // idle 10 sec
  // integrate 8 sec
  // switch changeover to standard
  // idle 10 sec
  // integrate 8 sec

  // start FIRST GAS
  // nIntegrationTime=16000; // integration time in milliseconds
  // sGasName="N2/O2/Ar"; // set the gas configuration
  // name (must be identical to name in GasConfiguration!!)
  // nMassSelect=33; // select this mass on "
  // cChannel", next line
  // cChannel=1; // channel for mass select
  // call ResetChannelArr(); // clear array for channel in use
  // g_ChannelArr[0]=1;//40 // define channels in use; always
  // begin with g_ChannelArr[0]
  // if (i==0)
  // {
  // call MeasureGas (sGasName, "Pre", nMassSelect, cChannel,
  // nIntegrationTime, nStandardSide, CHANGE_GC, YES_PC, YES_BGD,
  // NO_PA);
  // }
// call MeasureGas (sGasName, "Sample", nMassSelect, cChannel, nIntegrationTime, nSampleSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
// call MeasureGas (sGasName, "Standard", nMassSelect, cChannel, nIntegrationTime, nStandardSide, KEEP_GC, NO_PC, NO_BGD, NO_PA);
// end FIRST GAS

// start THIRD GAS

nIntegrationTime = 16000; // integration time in milliseconds
sGasName = "O2_gaslab"; // set the gas configuration name (must be identical to name in GasConfiguration!!!)

nMassSelect = 18; // select this mass on "cChannel", next line
cChannel = 1; // channel for mass select

call ResetChannelArr(); // clear array for channel in use
// begin with g_ChannelArr[0]
// add or delete Channels depending on number of masses to be recorded
// g_ChannelArr[1]=1; //28
// g_ChannelArr[2]=2; //30
if (i == 0)
{
// call MeasureGas (sGasName, "Pre", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, YES_PC, NO_BGD, NO_PA);

// call MeasureGas (sGasName, "Sample", nMassSelect, cChannel, nIntegrationTime, nSampleSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);

call MeasureGas (sGasName, "Standard", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
}
// end THIRD GAS

// start FOURTH GAS

nIntegrationTime = 16000; // integration time in milliseconds
sGasName = "O2_gaslab"; // set the gas configuration name (must be identical to name in GasConfiguration!!!)
nMassSelect = 44; // select this mass on "cChannel", next line
cChannel = 1; // channel for mass select
call ResetChannelArr(); // clear array for channel in use
g_ChannelArr[0] = 1; // define channels in use; always begin with g_ChannelArr[0]
// g_ChannelArr[1] = 1; // add or delete channels depending on number of masses to be recorded
// g_ChannelArr[2] = 2; //

if (i == 0) {
    // call MeasureGas (sGasName, "Pre", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, YES_PC, NO_BGD, NO_PA);
call MeasureGas (sGasName, "Sample", nMassSelect, cChannel, nIntegrationTime, nSampleSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
call MeasureGas (sGasName, "Standard", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
}
// end FOURTH GAS

// start FIRST GAS

nIntegrationTime = 16000; // integration time in milliseconds
sGasName = "O2_gaslab"; // set the gas configuration name (must be identical to name in GasConfiguration !!!) /

nMassSelect = 32; // select this mass on "cChannel", next line
cChannel = 0; // channel for mass select
call ResetChannelArr(); // clear array for channel in use
g_ChannelArr[0] = 0; // define channels in use; always begin with g_ChannelArr[0]

if (i == 0) {
    // call MeasureGas (sGasName, "Pre", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
    // }
call MeasureGas (sGasName, "Sample", nMassSelect, cChannel, nIntegrationTime, nSampleSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
call MeasureGas (sGasName, "Standard", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
/// start SECOND GAS

nIntegrationTime = 16000; // integration time in milliseconds
sGasName = "O2_gaslab"; // set the gas configuration name (must be identical to name in GasConfiguration!!!)

nMassSelect = 28; // select this mass on "cChannel", next line
cChannel = 0; // channel for mass select

call ResetChannelArr(); // clear array for channel in use
g_ChannelArr[0] = 0; // define channels in use; always begin with g_ChannelArr[0]

if (i == 0)
{
// call MeasureGas (sGasName, "Pre", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
}
if (i < 3)
{
    call MeasureGas (sGasName, "Sample", nMassSelect, cChannel, nIntegrationTime, nSampleSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
    call MeasureGas (sGasName, "Standard", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA);
}

// end SECOND GAS

/// start THIRD GAS

nIntegrationTime = 16000; // integration time in milliseconds
sGasName = "N2"; // set the gas configuration name (must be identical to name in GasConfiguration!!!)

nMassSelect = 40; // select this mass on "cChannel", next line
cChannel = 1; // channel for mass select

call ResetChannelArr(); // clear array for channel in use
// g_ChannelArr[0]=1; // define channels in use; always begin with g_ChannelArr[0]
//
// if (i==0)
// {
// call MeasureGas (sGasName, "Pre", nMassSelect, cChannel, nIntegrationTime, nStandardSide, CHANGE_GC, YES_PC, YES_BGD, NO_PA);
//    }
// call MeasureGas (sGasName, "Sample", nMassSelect, cChannel, nIntegrationTime, nSampleSide, CHANGE_GC, NO_PC, NO_BGD, NO_PA) ;
//    call MeasureGas (sGasName, "Standard", nMassSelect, cChannel, nIntegrationTime, nStandardSide, KEEP_GC, NO_PC, NO_BGD, NO_PA);

// end THIRD GAS

}  // end of loop, measurement cycle ends here

}  // end of loop, measurement cycle ends here

if (_GetSequenceInfo(IS_LAST_SAMPLE_RUNNING, FALSE))
{
    call ChangeOverClose();
}

II  LIBRARY:LYNNOAX_LIB_WATERMS.ISL

//
// ISODAT NT SCRIPT LANGUAGE (ISL) : Dual Inlet Basic Script

// History list
// Author       Date       Reason
// changes

XIX
// place your includes here

#include "lib\stdisl.isl"
#include "lib\instrument.isl"
#include "lib\DualInlet_lib.isl"
#include "lib\math.isl"
#include "lib\InterferingMassLynnOax.isl"

// LynnOax
const number nMaxContractionTries = 10;
const number FlushingCycles = 3;
external number Success = 0;

external string sMultiportName = "Lynn Oax";
external string sTubeCrackerName = "Tube Cracker";
external string sLoadStd = "Lynn Oax/load O2std"
    ;
external string sInjectStd = "Lynn Oax/inject O2std"
    ;
external number LynnOax_SampleTransferTime = 180000;
external number LynnOax_PressureThreshold = 75; // for pure O2

external string g_sPortName = "";
external string g_sIdentifier1Name = "";
external string g_sMeasType = "";
external string g_sStdInj = "";
external string g_sChecks = "";
external string g_sEquilTime = "";
external number g_nAmountBellow = 0.0;
external number g_nPercentBellow = 1000;
external number nPa = 0;
external number PAfinalIntyStd = 0;
external number g_nSeqRowNumber = 0;
external number g_ExpansionDelay = 5000;
external number Press_read_waiting_time = 3000;
external number Flushing_Delay_Min = 60000; //
external number Flushing_Delay_10s = 10000;
external number Flushing_Delay_30s = 30000; //
external number Dual_Inlet_Fore_Vacuum_Threshold_LynnOax = 0.008;
external number Dual_Inlet_High_Vacuum_Threshold = 0.0015;
external number Dual_Inlet_System_High_Vacuum_Threshold = 0.0015;
external number Dual_Inlet_Standard_filling_High_Vacuum_Threshold = 0.0015;
external number Dual_Inlet_System_High_Vacuum_Pump_Time = 120000;
external number Dual_Inlet_StandardFilling_High_Vacuum_Pump_Time = 30000;
external number nMaxPumpCycles_LynnOax = 1000;
external number nStdFlushingDelay = 60000; // for O2 in air // 8000 for pure O2!! to ensure viscous flow

// Press Adjust related
const number PAinitial = 20000;
const number PAinitiald18O2N2 = 10000;
const number PAinitiald29N2 = 32000;
const number PAinterval = 5000;
const number PAmx = 45000;
const number PAtolerance = 30;
const number PAcup = 2; // m32
const channel chPa = 0; // m32
const number nMinPress = 55; // mbar
const number nMinPressd18O2N2 = 81; // mbar to reach 12000 mV(10G 02/2015)
const number nMinPressd29N2 = 30; // mbar 19 before amplifier added, 10G 02/2015
const number nMaxPressd29N2 = 60; // mbar 20 before amplifier added, 10G 02/2015

// this is the main point entry – this function is essential

function EquilibrationTime() // (string sEquilTime)
{
    if (_strcmp(g_sEquilTime, "cinq") == 0) { Flushing_Delay_Min = 5000; }
    if (_strcmp(g_sEquilTime, "dix") == 0) { Flushing_Delay_Min = 1000; }
    if (_strcmp(g_sEquilTime, "trente") == 0) { Flushing_Delay_Min = 30000; }
    if (_strcmp(g_sEquilTime, "soixante") == 0) { Flushing_Delay_Min = 60000; }
    _UserInfo("equilibration time is set to %0.2f s", 0, 0, (Flushing_Delay_Min / 1000));
}

XXI
function GetIntPressStd_Introduction() : number
{
    bool success;
    channel chPA_channel = chPa;
call DiSetVolume(Dual_Inlet_Standard, 100.0); // set the volume to 100%
    // call DiSetVolume(Dual_Inlet_Standard, 100); // set the volume to 100%
call DiSwitchX(Dual_Inlet_Standard, 5, 1, 0); //
call SwitchChangeOver(Dual_Inlet_Standard);
_Delay(10000, 1, "Reaching constant voltage");
    number nStdStartPressure = call DiReadVolumePressure(Dual_Inlet_Standard);
    number nStdIntro = _GetIntensityEx(chPA_channel, 8000); // replace m32 channel by Dual_Inlet_g_nPaChannel?
    number nBVright = _GetCalc("Dual Inlet System / VolumeControl Right");
    _UserInfo("Fully expanded after intro, Standard Intensity %0.2f mV, pressure in bellow is %0.2f mbar at %0.2f percent", 0, 0,
        nStdIntro, nStdStartPressure, nBVright);
    return nStdStartPressure;
}

function GetIntPressSa_Introduction() : number
{
    bool success;
    channel chPA_channel = chPa;
call DiSetVolume(Dual_Inlet_Sample, 100.0); // set the volume to 100%
    // call DiSetVolume(Dual_Inlet_Standard, 100); // set the volume to 100%
call DiSwitchX(Dual_Inlet_Sample, 5, 1, 0); //
call SwitchChangeOver(Dual_Inlet_Sample);
_Delay(10000, 1, "Reaching constant voltage");
    number nSaStartPressure = call DiReadVolumePressure(Dual_Inlet_Sample);
    number nSaIntro = _GetIntensityEx(chPA_channel, 8000); // replace m32 channel by Dual_Inlet_g_nPaChannel?
    number nBVleft = _GetCalc("Dual Inlet System / VolumeControl Left");
    _UserInfo("Fully expanded after intro, Sample Intensity %0.2f mV, pressure in bellow is %0.2f mbar at %0.2f percent", 0, 0,
        nSaIntro, nSaStartPressure, nBVleft);
    return nSaStartPressure;
}

function GetIntPressStd_AfterPA_d29N2() : number

function GetIntPressSa_AfterPA_d29N2() : number
{
    bool success;
    channel chPA_channel = chPa;
    call DiSetVolume(Dual_Inlet_Sample,100.0); // set the volume to 100%
    // call DiSetVolume(Dual_Inlet_Sample,100); // set the volume to 100%
    call DiSwitchX(Dual_Inlet_Sample,5,1,0);//
    call SwitchChangeOver(Dual_Inlet_Sample);
    _Delay(10000,'"Reaching constant voltage"');
    number nSaPAPressure = call DiReadVolumePressure(Dual_Inlet_Sample);
    number nSaIntro = _GetIntensityEx(chPA_channel,8000);// replace m32 channel by Dual_Inlet_g_nPaChannel ?
    number nBVright = _GetCalc("Dual Inlet System/VolumeControl Right");
    _UserInfo("After N2 Press Adjust, Sample Intensity %0.2f mV, pressure in bellow is %0.2f mbar at %0.2f percent",0,0
    nSaIntro , nSaPAPressure , nBVright);
    return nSaPAPressure;
}

function DiWaitForHighVacuum(number nThreshold, number nPumpTime)
{  
  number nVacuum=0.009;
  number nCycle=0;
  while (nVacuum>nThreshold)
  {
    nVacuum=_GetCalc("Dual Inlet System/Fore Vacuum");
    _Delay(500);
    _UserInfo("DI: Waiting to reach Threshold %0.4f mBar [ %0.0f s ] : Pressure %0.4f mBar",19,3,nThreshold,nCycle,nVacuum);
    nCycle ++;
    if (nCycle>nMaxPumpCycles_LynnOax)
    {
      string sInfo=_strFormat("DI: Pressure Threshold %0.4f mBar not reached : %0.4f mBar",nThreshold,nVacuum);
      _ScriptError(sInfo,ERROR_TYPE_SCR_SEQ);
    }
    _Delay(nPumpTime,1,"Pump Multiport with Turbo Pump");
  }
}

//

function DiOpenHighVacPumpCR()
{
  //_Set("Dual Inlet System/Valve 39",0); //check if I really need this redondance
  call Switch_Valve39(0);
  _Delay(DI_DEFAULT_VALVE_DELAY);
  _Set("Dual Inlet System/Valve 40",1);
}

//

function OpenSide(int nSide)
{
  call DiSwitchX(nSide,3,1,200);
  call DiSwitchX(nSide,4,1,200);
  call DiSwitchX(nSide,6,1,200);
  call DiSwitchX(nSide,5,1,200);
}

//

function OpenAllValves()
{
  call OpenSide(Dual_Inlet_Sample);
  call DiSwitchX(Dual_Inlet_Sample,2,1,0);
```cpp
function PumpHighVacuum(number nThreshold, number nPumpTime)
{
    call DiOpenHighVacPumpCR();
    call DiWaitForHighVacuum(nThreshold, nPumpTime);
}

function CheckVacuum(int nSide, number nValveID, number nDelay):
    bool bOk=FALSE;
    call CloseVacPumps();
    call DiSwitchX(nSide, nValveID, 1, nDelay); // opens valve depending on the sample side
    _Delay(Press_read_waiting_time, 1, "Pump Flushed Standard with Rough Pump");
    if (_GetCalc("Dual Inlet System/Fore Vacuum") > Dual_Inlet_Fore_Vacuum_Threshold_LynnOax)
    {
        call DiOpenForeVacPump();
        call DiWaitForForeVacuum(Dual_Inlet_Fore_Vacuum_Threshold_LynnOax);
        _Delay(Press_read_waiting_time, 1, "4 s to get the right DI pressure");
    }
    call PumpHighVacuum(Dual_Inlet_Standard_filling_High_Vacuum_Threshold,
                         Dual_Inlet_StandardFilling_High_Vacuum_Pump_Time);
    bool bOK=TRUE;
    return bOk;
}

function DiExpandLynnOax(int nSide, number nThreshold, number nMaxTries):
    { bool
        number nPressure;
        number nTries;
        bool bOk=FALSE;
        string csSaStd;
    ...
```
call DiSetVolume(nSide,100);
for(nTries=0;nTries<nMaxTries;nTries++)
{
    nPressure = call DiReadVolumePressure(nSide);
    if (nSide == Dual_Inlet_Sample) { csSaStd=_strFormat("DiExpand Sample Pressure %0.2f mBar",nPressure);}
    if (nSide == Dual_Inlet_Standard) { csSaStd=_strFormat("DiExpand Standard Pressure %0.2f mBar",nPressure);}
    _UserInfo(csSaStd,0,0);
    if (nPressure <= nThreshold) {bOk=TRUE; break; }
    _UserInfo("Expand Sample Cycle (%0.0f)",0,0,(nTries+1));
call DiSwitchX(nSide,4,0,0);
call DiSwitchX(nSide,2,0,0);
call DiSwitchX(nSide,1,0,0); // valve needs to be closed to expand sample in cross and not in the whole LynnOax line
call CheckVacuum(nSide,3,5000); // close vac pumps, open specified valve and check vacuum
call DiSwitchX(nSide,3,0,0);
call DiSetVolume(nSide,50);
call DiSwitchX(nSide,4,1,0);
_Delay(30000,1,"Expand Sample − Equilibration");
call DiSwitchX(nSide,4,0,0); // added August2015 to isolate again the bellow (maybe there was a reason??)
call DiSetVolume(nSide,100); // added August 2015 to read new pressure after expansion at 100%!!!
_Delay(10000,1,"Wait a bit before reading new pressure"); // added August2015
}
return bOk;
} //

function DiBellowAdjust_Decrease(int nSide,number nThreshold,number nMaxTries) : bool
{ // contracts progressively bellow to expand more gas in the cross . Aim is to loose as little gas as possible, we may think about dicarding it. The threshold is 75 mbar
    number nPressure;
    number nTries;
    number nVolTries;
    bool bOk=FALSE;
    string csSaStd;
call DiSwitchX(nSide,4,0,0);
call DiSwitchX(nSide,2,1,0);
}
for (nTries = 0; nTries < nMaxTries; nTries++)
{
    nVolTries = (100 − (50 * nTries)); // modified August 2015, changed 10 by 50 to reduce cycle numbers that take time here
    nPressure = call DiReadVolumePressure(nSide);
    if (nSide == Dual_Inlet_Sample) { csSaStd = _strFormat("Sample Pressure %0.2f mBar", nPressure); }
    if (nSide == Dual_Inlet_Standard) { csSaStd = _strFormat("Standard Pressure %0.2f mBar", nPressure); }
    _UserInfo(csSaStd, 0, 0);
    if (nPressure <= nThreshold) { bOk = TRUE; break; }
    _UserInfo("Contract Bellow Cycle (%0.0f)", 0, 1, (nTries + 1));
    call DiSwitchX(nSide, 4, 1, 0); // first loop shouldn’t open this valve
    call DiSetVolume(nSide, nVolTries);
    _Delay(30000, 1, "Bellow just contracted – Wait a little bit");
    call DiSwitchX(nSide, 4, 0, 0);
    call DiSetVolume(nSide, 100);
    _Delay(30000, 1, "Bellow just expanded – Wait a little bit more");
}
return bOk;

// "un peu tire par les cheveux, mais ça devrait fonctionner"
function DiBellowAdjust_DecreaseN2(int nSide, number nThreshold, number nMaxTries) : bool
{
    number nPressure;
    number nTries;
    number nVolTries;
    bool bOk = FALSE;
    string csSaStd;
    call DiSwitchX(nSide, 4, 0, 0);
    call DiSwitchX(nSide, 2, 1, 0);
    call DiSwitchX(nSide, 3, 1, 0);
    call DiSwitchX(nSide, 1, 0, 0);
    call CheckVacuum(nSide, 3, Press_read_waiting_time); // close vac pumps, open specified valve and check vacuum
    return bOk;
}
call DiSwitchX(nSide,2,0,0);
call DiSwitchX(nSide,3,0,0);
call DiSwitchX(nSide,1,0,0);

for (nTries =0;nTries<nMaxTries;nTries ++;)
{
    nVolTries = (100-(50*nTries));
nPressure=call DiReadVolumePressure(nSide);

    if (nSide == Dual_Inlet_Sample) { csSaStd=_strFormat("Sample Pressure %0.2f mBar",nPressure);}
    if (nSide == Dual_Inlet_Standard) { csSaStd=_strFormat("Standard Pressure %0.2f mBar",nPressure);}

    _UserInfo(csSaStd,0,0);

    if (nPressure <=nThreshold) {bOk=TRUE;break;}

    _UserInfo("Contract Bellow Cycle (%0.0f)",0,1,(nTries+1));
call DiSwitchX(nSide,4,1,0); // first loop shouldn’t open this valve
    call DiSetVolume(nSide,nVolTries);
    _Delay(10000,1,"Bellow just contracted – Wait a little bit");
call DiSwitchX(nSide,4,0,0);
call DiSetVolume(nSide,100);
    _Delay(10000,1,"Bellow just expanded – Wait a little bit more");
}

if (nPressure >=nThreshold)
{
    call DiSwitchX(nSide,2,0,0);
call DiSwitchX(nSide,3,0,0);
call CheckVacuum(nSide,3,Press_read_waiting_time); // close vac pumps, open specified valve and check vacuum
    call DiSwitchX(nSide,3,0,0);

    number nTries2 =0;
    for (nTries2 =0;nTries2<nMaxTries;nTries2 ++;)
    {
        nVolTries = (100-(50*nTries2));
nPressure=call DiReadVolumePressure(nSide);

        if (nSide == Dual_Inlet_Sample) { csSaStd=_strFormat("Sample Pressure %0.2f mBar",nPressure);}
        if (nSide == Dual_Inlet_Standard) { csSaStd=_strFormat("Standard Pressure %0.2f mBar",nPressure);}

        _UserInfo(csSaStd,0,0);

        if (nPressure <=nThreshold) {bOk=TRUE;break;}

        _UserInfo("Contract Bellow Cycle (%0.0f)",0,1,(nTries+1));

XXVIII
call DiSwitchX(nSide,4,1,0); // first loop shouldn’t open this valve
call DiSetVolume(nSide,nVolTries);
_Delay(10000,1,"Bellow just contracted – Wait a little bit”);
call DiSwitchX(nSide,4,0,0);
call DiSetVolume(nSide,100);
_Delay(10000,1,"Bellow just contracted – Wait a little bit more”);
}

if (nPressure >= nThreshold)
{
call DiSwitchX(nSide,2,0,0);
call DiSwitchX(nSide,3,0,0);
call CheckVacuum(nSide,3,Press_read_waiting_time); // close vac pumps, open specified valve and check vacuum
call DiSwitchX(nSide,3,0,0);
number nTries3 = 0;
for (nTries3 = 0; nTries3 < nMaxTries; nTries3 ++)
{
  nVolTries = (100 − (50 * nTries3));
nPressure = call DiReadVolumePressure(nSide);

  if (nSide == Dual_Inlet_Sample) { csSaStd=_strFormat("Sample Pressure %0.2f mBar", nPressure); }
  if (nSide == Dual_Inlet_Standard) { csSaStd=_strFormat("Standard Pressure %0.2f mBar", nPressure); }

  _UserInfo(csSaStd,0,0);

  if (nPressure <= nThreshold) { bOk = TRUE; break; }

  _UserInfo("Contract Bellow Cycle (%0.0f)" , 0, 1, (nTries3 + 1));
call DiSwitchX(nSide,4,1,0); // first loop shouldn’t open this valve
call DiSetVolume(nSide,nVolTries);
_Delay(10000,1,"Bellow just contracted – Wait a little bit”);
call DiSwitchX(nSide,4,0,0);
call DiSetVolume(nSide,100);
_Delay(10000,1,"Bellow just contracted – Wait a little bit more”);
}

call DiSwitchX(nSide,2,0,0);
call DiSwitchX(nSide,3,0,0);
call CheckVacuum(nSide,3,Press_read_waiting_time); // close vac pumps, open specified valve and check vacuum
call DiSwitchX(nSide,3,0,0);
return bOk;

//
function DiBellowAdjust_Increase(int nSide, number nMaxTries): bool {
    number nPressure;
    number nStdPressure;
    number nStdStartPressure;
    number nTries;
    number nVolTries;
    number nStdInt;
    number nSaInt;
    number nBellowVolt;
    bool bOk=FALSE;
    string csSaStd;

    // this function is only use for the sample bellow in the current scripts last modified May 2016. Not part of standard refill for instance. It makes sure that the sample pressure will be higher than the standard one so a press adjust with sample as master is possible. IT SHOULD INCLUDE A STANDARD REFILL PROCEDURE in case Istd < 2000 but that should not occur.

    // channel chPA_channel = _GetChannelForCup(PAcup); // only exists with Isodat3.0
    channel chPA_channel = chPa;
    call DiSetVolume(Dual_Inlet_Sample, 100.0); // set the volume to 100%
    call DiSetVolume(Dual_Inlet_Standard, 100.0); // set the volume to 100%
    call DiSwitchX(Dual_Inlet_Standard, 5, 1, 0); //
    call SwitchChangeOver(Dual_Inlet_Standard);
    _Delay(10000, 1, "Reaching constant voltage");
    nStdStartPressure = call DiReadVolumePressure(Dual_Inlet_Standard);
    nStdInt = _GetIntensityEx(chPA_channel, 8000); // replace m32 channel by Dual_Inlet_g_nPaChannel ?
    _UserInfo("Start of DiBellowIncrease, Standard Intensity %.2f mV, pressure in bellow is %.2f at 100 percent", 0, 0, nStdInt, nStdStartPressure);

    if (nStdInt < StdMinVolt) // 8000mV but should be above 20 mbar for viscous flow
    {
        nStdInt = _SetBellowVolt(Dual_Inlet_Standard, StdMinVolt, chPA_channel, 500);
        if (nStdInt < 2000)
        {
            _UserInfo("Skip preliminary bellow adjustment cause standard has not been introduced yet. Standard intensisty is %.2f mV", 0, 0, nStdInt);
        }
    }
}
// [}
nStdPressure = call DiReadVolumePressure(Dual_Inlet_Standard);

for (nTries = 0; nTries < nMaxTries; nTries++)
{
   nVolTries = (100 - (10 * (nTries + 1)));
   call DiSwitchX(nSide, 5, 1, 0); // 15
   call SwitchChangeOver(nSide);
   _Delay(5000, 1, "Reaching constant voltage");
   nSaInt = _GetIntensityEx(chPA_channel, 8000);
   nPressure = call DiReadVolumePressure(nSide);
   // if (nSaInt == 0) {nSaInt = nStdInt;}
   if (nSide == Dual_Inlet_Sample)
      csSaStd = _strFormat("After DIBellowIncrease, Sample Intensity %4.2f mV Pressure %4.2f mBar, bellow contraction %0.0f ( cycle %0.0f)", nSaInt, nPressure, (nVolTries + 10), (nTries));
   if (nSide == Dual_Inlet_Standard)
      csSaStd = _strFormat("After DIBellowIncrease, Standard Intensity %4.2f mV Pressure %4.2f mBar, bellow contraction %0.0f ( cycle %0.0f)", nSaInt, nPressure, (nVolTries + 10), (nTries));
   _UserInfo(csSaStd, 0, 1);

   if (nPressure >= nStdPressure)
   {
      call DiSwitchX(nSide, 5, 1, 0); // 15
      call SwitchChangeOver(nSide);
      _Delay(3000, 1, "Reaching constant voltage"); // modifiedMay2016 from 10000 to 3000 ms
      nSaInt = _GetIntensityEx(chPA_channel, 8000);
      nPressure = call DiReadVolumePressure(nSide);
      if (nSide == Dual_Inlet_Sample)
         csSaStd = _strFormat("After DIBellowIncrease, Sample Intensity %4.2f mV Pressure %4.2f mBar, bellow contraction %0.0f ( cycle %0.0f)", nSaInt, nPressure, (nVolTries + 10), (nTries));
      if (nSide == Dual_Inlet_Standard)
         csSaStd = _strFormat("After DIBellowIncrease, Standard Intensity %4.2f mV Pressure %4.2f mBar, bellow contraction %0.0f ( cycle %0.0f)", nSaInt, nPressure, (nVolTries + 10), (nTries));
      _UserInfo(csSaStd, 6, 0);
      _UserInfo("Bellow contracted to %0.0f (Cycle %0.0f)", 0, 0, (nVolTries + 10), (nTries));
      call SwitchChangeOver(Dual_Inlet_Standard);
      bOk = TRUE;
      break;
   } // to avoid expanding bellow to 100%
   call DiSetVolume(nSide, nVolTries);
   _UserInfo("Contract Bellow to %0.0f (Cycle %0.0f)", 0, 1, nVolTries, (nTries + 1));

XXXI
function Pressureadjust_LynnOax() : number
{
  bool bPressAdjust=_GetSequenceFlag("Pressadjust",FALSE);
  // bool bPressAdjustOn=TRUE;
  number nSaInt;
  number nSaIntfullycompressed;
  number nPressure;
  channel chPA_channel = chPa; // _GetChannelForCup(PAcup);
  call DiSwitchX(Dual_Inlet_Sample,5,1,0);
  call ChangeOverLeft();
  call SwitchChangeOver(Dual_Inlet_Sample);
  nPressure= call DiReadVolumePressure(Dual_Inlet_Sample);
  nSaInt=_GetIntensityEx(chPA_channel,8000); // should be at 100%
  number nBVleft = _GetCalc("Dual Inlet System/VolumeControl Left");
  number nBVright = _GetCalc("Dual Inlet System/VolumeControl Right");
  // _UserInfo("After introduction and before pressAdjust, Sample Intensity %0.2f mV, Pressure in bellow %0.2f at %0.2f f ( cycle %0.0f) ",0,0, nSaInt, nPressure , nVolTries, (nTries+1));
    // _UserInfo(csSaStd,0,0);
      //}
    return bOk;
}
PAinitial);  
  _ChangePaMode(PRESS_AD_RIGHT); // so needs to be in manual first!!!  
  _ObjectPressAdjust(DualInlet_PressAdjust, csResult)  
  csInfo="Master is Sample PressAdjust: ";  
  csInfo+=csResult;  
  _UserInfo(csInfo,0,0);  
}  

else  
{  
  // alternative: use pressure instead of voltage in order not to affect filament with too high amount  
  call DiSetVolume(Dual_Inlet_Sample,0);  
  number nCurrPress=call DiReadVolumePressure(Dual_Inlet_Sample);  
  
  if ((nCurrPress<nMinPress)==TRUE) //2  
  {  
    _UserInfo("Sample intensity too low at full expansion for Manual Pressure Adjustment at %0.0f mV; switched to PA with master as sample",0,0,PAinitial);  
    call DiBellowAdjust_Increase(Dual_Inlet_Sample, nMaxContractionTries);  
    _ChangePaMode(PRESS_AD_RIGHT); // so needs to be in manual first!!!  
    _ObjectPressAdjust(DualInlet_PressAdjust, csResult)  
    csInfo="Master is Sample PressAdjust: ";  
    csInfo+=csResult;  
    _UserInfo(csInfo,0,0);  
  }  
  else  
  {  
    call DiSetVolume(Dual_Inlet_Sample,100.0);  
    _ObjectPressAdjust(DualInlet_PressAdjust, csResult)  
    csInfo="Manual PressAdjust: ";  
    csInfo+=csResult;  
    _UserInfo(csInfo,0,0);  
  }  
  else  
  {  
    _UserInfo("Pressure Adjustment skipped",1,0);  
  }  
return TRUE;  
}
function Pressureadjust_LynnOaxd18O2N2() : number
{
  bool bPressAdjust = _GetSequenceFlag("Pressadjust",FALSE);
  // bool bPressAdjustOn=TRUE;
  number nSaInt;
  number nSaIntfullycompressed;
  number nPressure;
  channel chPA_channel = chPa; // _GetChannelForCup(PAcup);
  call DiSwitchX(Dual_Inlet_Sample,5,1,0);
  call ChangeOverLeft();
  call SwitchChangeOver(Dual_Inlet_Sample);
  nPressure= call DiReadVolumePressure(Dual_Inlet_Sample);
  nSaInt= _GetIntensityEx(chPA_channel,8000); // should be at 100%
  number nBVleft = _GetCalc("Dual Inlet System/VolumeControl Left");
  number nBVright = _GetCalc("Dual Inlet System/VolumeControl Right");
  _UserInfo("After introduction and before pressAdjust, Sample Intensity %0.2f mV, Pressure in bellow %0.2f at %0.2f ",0,1,
    nSaInt,nPressure ,nBVleft);
  // consider to remove the upper line as it will be anyway measured in the IntPress_Intro function
  if (bPressAdjust==TRUE)
  {
    call DiSwitchX(Dual_Inlet_Standard,5,1,0);
    call SwitchChangeOver(Dual_Inlet_Standard);
    _UserInfo("Start Pressure Adjustment",0,1);
    string csResult="?";
    string csInfo=""
    nPa=PAinitiald18O2N2 ;
    if ((nSaInt>nPa)==TRUE)
    {
      _UserInfo("Sample intensity too high for Manual Press Adjust at %0.0f mV, switched to PA with master as sample",0,0,
        PAinitiald18O2N2);
      // _ChangePaMode(PRESS_AD_RIGHT); // so needs to be in manual first !!!
      call DiBellowAdjust_Increase(Dual_Inlet_Sample,
        nMaxContractionTries); // added line but should not happen that modifiedMay2016 CR
      _ChangePaMode(PRESS_AD_LEFT); // modifiedMay2016 CR to LEFT
      _ObjectPressAdjust(DualInlet_PressAdjust ,csResult)
      csInfo="Master is Sample PressAdjust: ";
      csInfo+=csResult;
      _UserInfo(csInfo,0,0);
  }
else
{
    // alternative: use pressure instead of voltage in order not to affect filament with too high amount
    call DiSetVolume(Dual_Inlet_Sample, 0);
    number nCurrPress = call DiReadVolumePressure(Dual_Inlet_Sample);

    if ((nCurrPress < nMinPressd18O2N2) == TRUE) // 2
    {
        _UserInfo("Sample intensity too low at full expansion for Manual Pressure Adjustment at %0.0f mV ; switched to PA with master as sample", 0, 0, PAinitiald18O2N2);
        call DiBellowAdjust_Increase(Dual_Inlet_Sample, nMaxContractionTries); // some time may be gained here as the called function expands bellow to 100% while it should not be needed. On the other hand
        // _ChangePaMode(PRESS_AD_RIGHT); // so needs to be in manual first !!!
        _ChangePaMode(PRESS_AD_LEFT); // so needs to be in manual first !!! changed to left on 100815 by Isabell
        _ObjectPressAdjust(DualInlet_PressAdjust, csResult)
        csInfo = "Master is Sample PressAdjust: ";
        csInfo += csResult;
        _UserInfo(csInfo, 0, 0);
    }
    else
    {
        call DiSetVolume(Dual_Inlet_Sample, 100.0);
        _ObjectPressAdjust(DualInlet_PressAdjust, csResult)
        csInfo = "Manual PressAdjust: ";
        csInfo += csResult;
        _UserInfo(csInfo, 0, 0);
    }
}

// this function requires Standard Intensity to be always lower than PAinitiald18O2N2 at 100% otherwise PA manual or PA with sample as master will fail.
else
{
    _UserInfo("Pressure Adjustment skipped", 1, 0);
}
return TRUE;

//
function Pressureadjust_LynnOaxd29N2() : number
{
    bool bPressAdjust=_GetSequenceFlag("Pressureadjust",FALSE);
    // bool bPressAdjustOn=TRUE;
    number nSaInt;
    number nStdInt;
    number nSaIntfullycompressed;
    number nPressure;
    number nStdPAPressure;
    number nSaPAPressure;

    channel chPA_channel = chPa; // _GetChannelForCup(PAcup);
    call DiSwitchX(Dual_Inlet_Sample,5,1,0);
    call ChangeOverLeft();
    call SwitchChangeOver(Dual_Inlet_Sample);
    nPressure=call DiReadVolumePressure(Dual_Inlet_Sample);
    nSaInt=_GetIntensityEx(chPA_channel,8000); // should be at 100%

    _UserInfo("After introduction and before pressAdjust, Sample Intensity %0.2f mV, Pressure in bellow %0.2f at %0.2f",0,1,
        nSaInt,nPressure,nBVleft);

    // consider to remove the upper line as it will be anyway measured in the IntPress_Intro function

    if (bPressAdjust==TRUE)
    {
        call DiSwitchX(Dual_Inlet_Standard,5,1,0);
        call SwitchChangeOver(Dual_Inlet_Standard);
        nStdInt=_GetIntensityEx(chPA_channel,8000); // should be at 100%

        _UserInfo("Start Pressure Adjustment",0,1);
        string csResult="?";
        string csInfo="";
        nPa=PAinitiald29N2;

        if ((nStdInt>nPa)==TRUE)
        {
            _UserInfo("Standard intensity too high for Manual Press Adjust at %0.0f mV, check if gas needs to be removed from bellow",0,0,PAinitiald29N2);
            call DiBellowAdjust_DecreaseN2(Dual_Inlet_Standard,nMaxPressd29N2,3);
        }

        nPressure=call DiReadVolumePressure(Dual_Inlet_Standard);
        if nPressure>nMaxPressd29N2
        {
            call DiBellowAdjust_DecreaseN2(Dual_Inlet_Standard,nMaxPressd29N2,3);
        }
        nPressure=call DiReadVolumePressure(Dual_Inlet_Standard);
        if nPressure>nMaxPressd29N2

        XXXVI
```c
{ call DiBellowAdjust_DecreaseN2(Dual_Inlet_Standard, nMaxPressd29N2, 3); }

nStdPAPressure = call GetIntPressStd_AfterPA_d29N2();
}

if ((nSaInt>nPa)==TRUE)
{
    _UserInfo("Sample intensity too high for Manual Press Adjust at %0.0f mV, check if gas needs to be removed from bellow",0,0,PAinitiald29N2);
    call DiBellowAdjust_DecreaseN2(Dual_Inlet_Sample, nMaxPressd29N2, 3);

    nPressure= call DiReadVolumePressure(Dual_Inlet_Sample);
    if nPressure>nMaxPressd29N2
    {
        call DiBellowAdjust_DecreaseN2(Dual_Inlet_Sample, nMaxPressd29N2, 3);
    }
    nPressure= call DiReadVolumePressure(Dual_Inlet_Sample);
    if nPressure>nMaxPressd29N2
    {
        call DiBellowAdjust_DecreaseN2(Dual_Inlet_Sample, nMaxPressd29N2, 3);
    }

    call DiSwitchX(Dual_Inlet_Sample,5,1,0);
    //call ChangeOverLeft();
    call SwitchChangeOver(Dual_Inlet_Sample);
    nSaPAPressure = call GetIntPressSa_AfterPA_d29N2();

    call DiSetVolume(Dual_Inlet_Sample,100.0);
    _ObjectPressAdjust(DualInlet_PressAdjust,csResult)
    csInfo="Manual PressAdjust: ";
    csInfo+=csResult;
    _UserInfo(csInfo,0,0);
}
else
{
    // alternative: use pressure instead of voltage in order not to affect filament with too high amount
    call DiSetVolume(Dual_Inlet_Sample,0);
    number nCurrPress=call DiReadVolumePressure(Dual_Inlet_Sample);

    if ((nCurrPress<nMinPressd29N2)==TRUE) //2
    {
        _UserInfo("Sample intensity too low at full contraction for Manual Pressure Adjustment at %0.0f mV; switched to PA with master as sample",0,0,PAinitial);
    }
```
call DiBelowAdjust_Increase(Dual_Inlet_Sample, nMaxContractionTries);

_changePaMode(PRESS_AD_RIGHT); // so needs to be in manual first !!!
_ObjectPressAdjust(DualInlet_PressAdjust, csResult)
_csInfo="Master is Sample PressAdjust: ";
_csInfo+=csResult;
_UserInfo(csInfo,0,0);
}
else
{

call DiSetVolume(Dual_Inlet_Sample,100.0);
_ObjectPressAdjust(DualInlet_PressAdjust, csResult)
_csInfo="Manual PressAdjust: ";
_csInfo+=csResult;
_UserInfo(csInfo,0,0);
}
else
{

_UserInfo("Pressure Adjustment skipped",1,0);
}
return TRUE;
}
//

function WaitForScanEnd() : bool
{

while (_IsScanning()==TRUE)
{
    _Delay(1000);
}
return FALSE;
}
//

function MassScanning() : bool
{
    bool sOK = _StartDACScan(MAGNET,2000,12000,100);
    call WaitForScanEnd();
    // sOK=_SaveFile("C:\Thermo\Isodat NT\Global\User\Dual Inlet System \Results\ACQ_O2_Results\Scans" 
    return sOK;
}
function MpReadMultiportPressure() : number
{
    string sGauge="Isotope MS/";
    sGauge+=sMSInstMultiportName;
    number nPressure=_GetCalc(sGauge);
    return nPressure;
}

function MpSwitchValve(string sValveName, int nState)
{
    string sValve=sMultiportName;
    sValve+="/";
    sValve+=sValveName;
    _Set(sValve, nState);
}

function MpCrackTube(string sPort)
{
    string sNumber=_strright(sPort,(_strlen(sPort) - 6));
    string sCracker=sTubeCrackerName;
    sCracker="/Cracker";
    sCracker+=sNumber;
    _Set(sCracker, 1);
    _Delay(1000);
    _Set(sCracker, 0);
}

function MpSampleValve(string sPort, int nState)
{
    string sNumber=_strright(sPort,(_strlen(sPort) - 6)); //get rid of sample string and keeps number
}
string sSwitch=sMultiportName;
sSwitch+="/Valve";
sSwitch+=sNumber;
_set(sSwitch,nState);
}
//

function MpConnect(bool bConnect)
{
    int nState=bConnect;
    _ConnectDev("Lynn Oax",bConnect);
call MpSwitchValve("Dual Inlet System/Valve 11",nState);
}
//

function MpPump()
{
    _UserInfo("Pump Sample Side",0,1);
    //
    // Multiport
    //
call DiSetVolume(Dual_Inlet_Sample,100.0); // set the volume to 100%
    // call MpConnect(1); see below for substitution
call DiSwitchX(Dual_Inlet_Sample,1,1,0); // opens either 11 or 21 depending on the sample side
    if (_GetCalc("Dual Inlet System/Fore Vacuum")>
        Dual_Inlet_Fore_Vacuum_Threshold_LynnOax)
    {
        call DiPumpSide(Dual_Inlet_Sample,
                        Dual_Inlet_Fore_Vacuum_Threshold_LynnOax);
        _Delay(Dual_Inlet_Fore_Vacuum_Pump_Time,1,"Pump Multiport with Rough Pump");
    }
    else
    {
        call DiOpenHighVacPumpCR();
call OpenSide(Dual_Inlet_Sample); // opens 13 14 15 16
    }
call PumpHighVacuum(Dual_Inlet_High_Vacuum_Threshold,
                        Dual_Inlet_System_High_Vacuum_Pump_Time);
    // call MpSwitchValve("Waste",o); not needed

XL
// call MpConnect(0);
call DiSwitchX(Dual_Inlet_Sample, 1, 0, 0); // closes either 11 or 21 depending on the sample side
call DiCloseSide(Dual_Inlet_Sample); // 13, 14, 15, and 16 closed
_Delay(DI_DEFAULT_VALVE_DELAY);
}

function Vacuuming()
{
    _UserInfo("Pump Dual Inlet System yeah", 0, 1);
call ChangeOverClose();
call DiSetVolume(Dual_Inlet_Sample, 100.0); // set the volume to 100%
call DiSetVolume(Dual_Inlet_Standard, 100.0); // set the volume to 100%
call CloseVacPumps();
call OpenAllValves();
_Delay(Press_read_waiting_time, 1, "4 s to get the right DI pressure");

    if (_GetCalc("Dual Inlet System/Fore Vacuum") > Dual_Inlet_Fore_Vacuum_Threshold_LynnOax)
    {
        call DiOpenForeVacPump();
call DiWaitForForeVacuum(Dual_Inlet_Fore_Vacuum_Threshold_LynnOax);
_Delay(Dual_Inlet_Fore_Vacuum_Pump_Time, 1, "Pumping Dual Inlet System with Rough Pump");
    }
call PumpHighVacuum(Dual_Inlet_System_High_Vacuum_Threshold, Dual_Inlet_High_Vacuum_Pump_Time);
_Delay(DI_DEFAULT_VALVE_DELAY);
}

function GetPortName() : bool
{
    bool bResult=TRUE; // Do I need to add IsDeviceAvailable ?
g_sPortName=_GetSequenceText("Lynn Oax Inlet", "none");
g_sIdentifier1Name=_GetSequenceText("Identifier 1", "none");
string sSampleIDnumber = _strright(g_sPortName, (_strlen(g_sPortName) - _strlen("sample"))); // get rid of sample string and keeps number
string sSampleIDstring = _strleft(g_sPortName, (_strlen(g_sPortName) - (_strlen(sSampleIDnumber))));
string sSampleID = "ID of measured sample is ";
if (_strcmp(sSampleIDstring,"sample") == 0) {sSampleID += sSampleIDnumber; }
else {sSampleID += "none"; } // mars2013 : replaced standard by none, does not make sense to keep standard here as there is another column for identification
sSampleID += "; ";
sSampleID += g_sIdentifier1Name;
UserInfo(sSampleID,0,0);
return bResult;

function MpTransferMp() : bool
{
call SwitchChangeOver(Dual_Inlet_Standard);
call MpPump();
bool bOk=FALSE;
call DiSetVolume(Dual_Inlet_Sample,100.0);
call DiSwitchX(Dual_Inlet_Sample,1,1,0); // 11 call MpConnect (1);
call DiSwitchX(Dual_Inlet_Sample,4,1,0); // 14
call DiSwitchX(Dual_Inlet_Sample,2,0,0); // 12 to be safe

call MpSampleValve(g_sPortName,0); // open Lynn Oax valve (0 cause inversed normal state)
_Delay(LynnOax_SampleTransferTime,1,"Sample Transfertime");
bOk = call DiBellowAdjust_Decrease(Dual_Inlet_Sample, LynnOax_PressureThreshold,3); // modified August2015
if (bOk==FALSE) {
call DiSetVolume(Dual_Inlet_Sample,100); // put the bellow back to 100% before press adjust
call CloseVacPumps();
bOk= call DiExpandLynnOax(Dual_Inlet_Sample, LynnOax_PressureThreshold,nMaxContractionTries); // modified August2015
call DiSwitchX(Dual_Inlet_Sample,4,0,0); // close 14
if (bOk==FALSE) { _ScriptError("Multiport Expansion failed!",ERROR_TYPE_SCR_SEQ);}
}
call MpSampleValve(g_sPortName,1); // close Lynn Oax valve (1 cause inversed normal state)
function MpTransfer(): boolean {
    call DiSwitchX(Dual_Inlet Sample, 1, 0, 0);
call CloseVacPumps();
call DiSwitchX(Dual_Inlet Sample, 4, 1, 0);
call DiSwitchX(Dual_Inlet Sample, 3, 1, 0);
_Delay(1000, 1, "Check if bellow is empty");
call DiSwitchX(Dual_Inlet Sample, 4, 0, 0);

    bool bMeasure = call GetPortName();
    if (bMeasure) { call MpTransferMp();}
    return true;
}

function checkVacStdAA(): boolean {
    bool bOk = false;
call CloseVacPumps();
// isolate standard aliquot line to pump
    call DiSwitchX(Dual_Inlet Standard, 2, 0, DI_DEFAULT VALVE_DELAY);
call DiSwitchX(Dual_Inlet Standard, 4, 0, DI_DEFAULT VALVE_DELAY);
call DiSwitchX(Dual_Inlet Standard, 6, 0, DI_DEFAULT VALVE_DELAY);
call DiSwitchX(Dual_Inlet Sample, 3, 0, DI_DEFAULT VALVE_DELAY);
call DiSwitchX(Dual_Inlet Sample, 6, 0, DI_DEFAULT VALVE_DELAY);
call DiSwitchX(Dual_Inlet Standard, 1, 1, DI_DEFAULT VALVE_DELAY);
call DiSwitchX(Dual_Inlet Standard, 3, 1, DI_DEFAULT VALVE_DELAY);
_Set(sLoadStd, 1); // closing Std upstream
_Set(sInjectStd, 0); // opening aliquot StdAA
_Delay(Press_read_waiting_time, 1, "Be patient, getting the right pressure");

    if (_GetCalc("Dual Inlet System/Fore Vacuum") >
        Dual_Inlet_Fore_Vacuum_Threshold_LynnOax) {
        call DiOpenForeVacPump();
call DiWaitForForeVacuum(
            Dual_Inlet_Fore_Vacuum_Threshold_LynnOax);
    }
call PumpHighVacuum(
    Dual_Inlet_Standard_filling_High_Vacuum_Threshold,
    Dual_Inlet_StandardFilling_High_Vacuum_Pump_Time);
    //back to initial valve configuration. Better to ensure v4’s and v6’s are still closed
_set(sInjectStd,1); // closing (inversed too?)
call CloseVacPumps(); // added cause comes before checking inner lines
_set(sLoadStd,1); // opening
_delays(eq_delay,1,"Loading Standard to StdAA");
_set(sLoadStd,0); // opening
_delays(eq_delay,1,"Standard equilibrating in StdAA");
return bOk;
}

function StdAA_introduction (number eq_delay) : bool
{
bool bintOk=FALSE;
_set(sInjectStd,1); // closing
_set(sLoadStd,1); // closing
_delays(1000);
_set(sLoadStd,0); // opening
_delays(eq_delay,1,"Loading Standard to StdAA");
_set(sLoadStd,1); // closing
_delays(eq_delay,1,"Standard equilibrating in StdAA");
return bintOk;
}

function Flushing (number nMaxFlush) : bool
{
    number nFlush;
bool bOk=FALSE;
    // 1.
    // string szActionMessage = "Please open the standard line (3 SS4H valves, one is upstream the pressure regulator ) and make sure P regulator not above .2 bar overpressure ";
    // _MessageBox(szActionMessage,MB_OK,MB_ICONEXCLAMATION);
    _UserInfo("Hope you didn’t forget to open the standard line, check that pressure is at 1.2 bar overpressure",0,1);
    for (nFlush=0;nFlush<nMaxFlush;nFlush++)
{ call DiSwitchX(Dual_Inlet_Sample,1,0,0); call DiSwitchX(Dual_Inlet_Sample,4,0,0); call DiSwitchX(Dual_Inlet_Sample,2,1,0); call DiSwitchX(Dual_Inlet_Standard,2,1,0); // make sure DI ext right is evacuated _Set(sLoadStd,1); // closing Std upstream _Set(sInjectStd,0); // opening aliquot StdAA call DiSwitchX(Dual_Inlet_Standard,1,1,0);
bool bOk = call CheckVacuum(Dual_Inlet_Standard,3,DI_DEFAULT_VALVE_DELAY); // close vac pumps, open specified valve and check vacuum
call DiSwitchX(Dual_Inlet_Standard,4,0,0);
call DiSwitchX(Dual_Inlet_Standard,6,0,0);
call DiSwitchX(Dual_Inlet_Sample,6,0,0);
call DiSwitchX(Dual_Inlet_Sample,3,0,0);
call DiSwitchX(Dual_Inlet_Standard,3,0,0);
call StdAA_introduction(Flushing_Delay_10s);
_set(sInjectStd,0); // opening StdAA to MS
string sFlushMessage = _strFormat("Std Wall Equilibration cycle %0.0f",(nFlush+1));
call CloseVacPumps();
_Delay(Flushing_Delay_10s,1,sFlushMessage);
call CloseVacPumps();
// call DiSwitchX(Dual_Inlet_Standard,1,0,0);
call DiSwitchX(Dual_Inlet_Standard,3,1,Press_read_waiting_time);
_Delay(Press_read_waiting_time,1,"3 s to get the right DI pressure");
if (_GetCalc("Dual Inlet System/Fore Vacuum")>
Dual_Inlet_Fore_Vacuum_Threshold_LynnOax)
{
call DiOpenForeVacPump();
call DiWaitForForeVacuum(Dual_Inlet_Fore_Vacuum_Threshold_LynnOax);
_Delay(Dual_Inlet_Fore_Vacuum_Threshold_LynnOax,1,"Pumping Flushed Standard with Rough Pump");
}
else
{
_MessageBox("You probably forgot to introduce the standard in the line... Try again",MB_OK,MB_ICONEXCLAMATION);
call Flushing(nMaxFlush);
}
call PumpHighVacuum(Dual_Inlet_Standard_filling_High_Vacuum_Threshold,
Dual_Inlet_StandardFilling_High_Vacuum_Pump_Time);
call DiSwitchX(Dual_Inlet_Standard,1,0,0);
_set(sInjectStd,1); // closing
return bOk;
function CompressBellowOption(int nSide, number nCompression) : bool{
    bool bOk = FALSE;
    bool bPILeft = _GetSequenceFlag("Pleft+",FALSE);
    bool bPIRight = _GetSequenceFlag("Pright+",FALSE);

    if bPILeft
    {
        call DiSetVolume(Dual_Inlet_Sample,nCompression);
        _UserInfo("Left (Sa) Bellow has been set to %0.2f percent",0,0,nCompression);
    }
    if bPIRight
    {
        call DiSetVolume(Dual_Inlet_Standard,nCompression);
        _UserInfo("Right (Std) Bellow has been set to %0.2f percent",0,0,nCompression);
    }
    return bOk;
}

function StdTransferDIRIGHT() : bool{
    bool bOk = FALSE;
    bool boOk = FALSE;

    call Flushing(1); // line added to ensure flushing at each std introduction
    call DiSetVolume(Dual_Inlet_Standard,100.0);
    call DiSwitchX(Dual_Inlet_Sample,4,0,0); // should be closed
    call DiSwitchX(Dual_Inlet_Sample,1,0,0); // should be closed
    call DiSwitchX(Dual_Inlet_Sample,6,0,0); // should be closed
    call CloseVacPumps();
    call DiSwitchX(Dual_Inlet_Sample,2,1,0);
    call OpenSide(Dual_Inlet_Standard);
    call DiSwitchX(Dual_Inlet_Sample,3,1,0);
    // make sure DI ext right is evacuated
    _Set(sLoadStd,1); // closing Std upstream
    _Delay(1000);
    _Set(sInjectStd,0); // opening aliquot StdAA
    call DiSwitchX(Dual_Inlet_Standard,1,1,0);
    // call checkVacStdAA();
    boOk = call CheckVacuum(Dual_Inlet_Standard,2,
    Press_read_waiting_time); // close vac pumps, open specified
valve and check vacuum

//**** currently 1 2 3 4 5 6 std side and 2 3 sample side opened *****/

// Amount in bellow

if (g_nAmountBellow == 0.5) //16 mbar
{
    call DiSwitchX(Dual_Inlet_Standard, 2, 0, 0);
}

if (g_nAmountBellow == 0.6)
{
    call DiSetVolume(Dual_Inlet_Standard, 80.0);
}

if (g_nAmountBellow == 1.0) //28 mbar
{
    call DiSetVolume(Dual_Inlet_Standard, 100.0);
}

if (g_nAmountBellow == 1.3) //34 mbar
{
    call DiSetVolume(Dual_Inlet_Standard, 100.0);
}

if ((g_nAmountBellow == 0.0) || (g_nAmountBellow == 0.1) || (g_nAmountBellow == 0.2) || (g_nAmountBellow == 0.3) || (g_nAmountBellow == 0.4) || (g_nAmountBellow == 0.7) || (g_nAmountBellow == 1.1) || (g_nAmountBellow == 1.2) || (g_nAmountBellow == 1.4) || (g_nAmountBellow == 1.5) || (g_nAmountBellow == 1.6) || (g_nAmountBellow == 1.7) || (g_nAmountBellow == 1.8))
{
    call DiSetVolume(Dual_Inlet_Standard, 8.0);
    call DiSetVolume(Dual_Inlet_Sample, 8.0);
    _UserInfo("this amount hasn’t been stricto sensu defined “,0,1);
}

// common introduction
    // call at last to respect equilibration time between runs
if (g_nPercentBellow != 1000) { call CompressBellowOption(Dual_Inlet_Standard, g_nPercentBellow);}
    call StdAA_introduction(Flushing_Delay_Min);
// isolate standard aliquot line to pump
call DiSwitchX(Dual_Inlet_Sample, 3, 0, 1000);
call DiSwitchX(Dual_Inlet_Standard, 4, 0, DI_DEFAULT_VALVE_DELAY);
call DiSwitchX(Dual_Inlet_Standard,3,0,DI_DEFAULT_VALVE_DELAY);
_set(sInjectStd,0); // opening (inversed too)
_Delay(Flushing_Delay_Min,1,"Standard Transfer to Standard,
Sample Cross and inner line, IT as good as it can be in
separate filling");
(userInfo("amount introduced in right standard bellow is roughly
%0.2f cc",0.1,g_nAmountBellow);
call DiSwitchX(Dual_Inlet_Standard,1,0,DI_DEFAULT_VALVE_DELAY);
_Delay(Flushing_Delay_Min,1,"DI Ext right closed");
call DiSwitchX(Dual_Inlet_Standard,5,0,1000);
call DiSetVolume(Dual_Inlet_Standard,100.0);
_Delay(Flushing_Delay_Min,1,"Standard Transfer to Bellows");
call DiSwitchX(Dual_Inlet_Standard,4,0,DI_DEFAULT_VALVE_DELAY);
call DiSwitchX(Dual_Inlet_Standard,4,1,DI_DEFAULT_VALVE_DELAY);
_Delay(Standard Equilibration Bellows");
call DiSwitchX(Dual_Inlet_Standard,6,0,1000);
// call CloseVacPumps(); done with DiExpand
bOk= call DiExpandLynnOax(Dual_Inlet_Standard,
LynnOax_PressureThreshold,nMaxExpansionTries);
call DiSwitchX(Dual_Inlet_Standard,4,0,DI_DEFAULT_VALVE_DELAY);
// bOkbis=call DiBellowAdjust_Increase(Dual_Inlet_Standard,
// nMaxContractionTries);
call DiSwitchX(Dual_Inlet_Standard,5,1,DI_DEFAULT_VALVE_DELAY);
return bOk;
}

function StdRefill(): bool {
bool bOk = FALSE;
g_sPortName=_GetSequenceText("Lynn Oax Inlet","none");
channel chPA_channel = chPa;
call DiSetVolume(Dual_Inlet_Standard,100.0);
// call DiSwitchX(Dual_Inlet_Standard,5,1,0); // Switch Change Over
number nRefill = call DiReadVolumePressure(Dual_Inlet_Standard);
if (nRefill <25) {

// call Flushing(1); // FlushingCycles default =3 Line removed
modified May 2016

call StdTransferDIRIGHT();
}
return bOk;
}
function StdTransferDILEFT() : bool {
    bool bOk = FALSE;
    bool bOkbis = FALSE;
    bool boOk = FALSE;

    call Flushing(1);
    call DiSetVolume(Dual_Inlet_Sample,100.0); // put the bellow back to 100% before press adjust
    call DiSwitchX(Dual_Inlet_Sample,1,0,0);
    call DiSwitchX(Dual_Inlet_Sample,1,1,0);
    call DiSwitchX(Dual_Inlet_Standard,6,0,0);
    call CloseVacPumps();
    call DiSwitchX(Dual_Inlet_Sample,1,0,0);
    call OpenSide(Dual_Inlet_Sample); // 3 4 5 6
    call DiSwitchX(Dual_Inlet_Sample,1,0,0);
    // make sure DI ext right is evacuated
    _Set(sLoadStd,1); // closing Std upstream
    _Delay(1000);
    _Set(sInjectStd,0); // opening aliquot StdAA
    boOk = call CheckVacuum(Dual_Inlet_Sample,2,
        Press_read_waiting_time); // close vac pumps, open specified valve and check vacuum
    // ***** currently 2 3 4 5 6 sample side and 1 2 3 standard side opened *****/
}

    //Amount in bellow
    // if (_strcmp(g_sAmountBellow,"na")==0)
    if (g_nAmountBellow == 0.6) //16mbar
        {
            call DiSetVolume(Dual_Inlet_Sample,80.0);
        }
    if (g_nAmountBellow == 1.0) //28 mbar
        {
            call DiSetVolume(Dual_Inlet_Sample,100.0);
        }
    if (g_nAmountBellow == 1.3) //34 mbar
        {
            call DiSetVolume(Dual_Inlet_Sample,100.0);
        }
    if ((g_nAmountBellow == 0.0) || (g_nAmountBellow == 0.1) || (g_nAmountBellow == 0.2) || (g_nAmountBellow == 0.3) || (g_nAmountBellow == 0.4) || (g_nAmountBellow == 0.5) || (g_nAmountBellow == 0.7) || (g_nAmountBellow == 0.8) || (g_nAmountBellow == 0.9) || (g_nAmountBellow == 1.1) || (g_nAmountBellow == 1.2) || (g_nAmountBellow == 1.4) || (g_nAmountBellow ==
1.6) || (g_nAmountBelow == 1.7) || (g_nAmountBelow ==
1.8))
{
    call DiSetVolume(Dual_Inlet_Sample, 8.0);
    call DiSetVolume(Dual_Inlet_Sample, 8.0);
    _UserInfo("this amount hasn’t been defined yet", 0, 1);
}

// common introduction
// call at last to respect equilibration time between runs
if (g_nPercentBellow!=1000) { call CompressBellowOption(
    Dual_Inlet_Sample, g_nPercentBellow);}

    call StdAA_introduction(Flushing_Delay_Min);
    _UserInfo("amount introduced is roughly %0.2f cc", 0.1, g_nAmountBellow);
    _Delay(Flushing_Delay_Min,1,"DI Ext right closed");
    call DiSwitchX(Dual_Inlet_Sample,5,0,1000);
    _Delay(Flushing_Delay_Min,1,"Standard Transfer to left Bellow");
    call DiSwitchX(Dual_Inlet_Sample,5,1,DI_DEFAULT_VALVE_DELAY);
    call DiSetVolume(Dual_Inlet_Standard,100.0);
    _Delay(Flushing_Delay_Min,1,"Standard Equilibration in left Bellow");
    call DiSwitchX(Dual_Inlet_Sample,6,0,1000);

    bOkbis= call DiExpandLynnOax(Dual_Inlet_Sample,
        LynnOax_PressureThreshold, nMaxExpansionTries);
    call DiSwitchX(Dual_Inlet_Sample,4,0,DI_DEFAULT_VALVE_DELAY);
    bOkbis= call DiBellowAdjust_Increase(Dual_Inlet_Sample,
        nMaxContractionTries);
    call DiSwitchX(Dual_Inlet_Sample,4,1,DI_DEFAULT_VALVE_DELAY);

    return bOkbis;
    return bOk;

    // *** Mass Spec Droite ***
    // call DiSwitchX(Dual_Inlet_Standard,1,1,DI_DEFAULT_VALVE_DELAY);
    _Delay(Flushing_Delay_Min,1,"Standard Transfer to Standard Cross");
    call DiSwitchX(Dual_Inlet_Standard,1,0,0);
    call DiSwitchX(Dual_Inlet_Sample,3,0,DI_DEFAULT_VALVE_DELAY);
function LinearityBellowImbalance() : bool
{
    bool bOk = FALSE;
    bool bPILeft = _GetSequenceFlag("Pleft",FALSE);
    bool bPIRight = _GetSequenceFlag("Pright",FALSE);
    number nSigInt;
    channel chPA_channel = chPa;

    /*
     * if (bPILeft) // alternative 1
     *
     * call DiSwitchX(Dual_Inlet_Standard,5,1,0); // actually decrease on std side
     * if (bPIRight) // alternative 1
     * {
     *    call DiSwitchX(Dual_Inlet_Sample,5,1,0);
     * }
     */
    if (bPILeft) // alternative 2
    {
        call DiSwitchX(Dual_Inlet_Standard,5,1,0); //
        call DiSwitchX(Dual_Inlet_Sample,5,1,0); //
        call SwitchChangeOver(Dual_Inlet_Standard);
        _Delay(10000,1,"Reaching constant voltage");
        nSigInt = _GetIntensityEx(chPA_channel,8000); // replace m32 channel by Dual_Inlet_g_nPaChannel
        // if (nStdInt<StdMinVolt)
        // {
        //    nStdInt = _SetBellowVolt(Dual_Inlet_Standard,StdMinVolt,
        //                            chPA_channel,50);
        // }
        // if (nStdInt<2000)
    }
// {  _UserInfo("Skip preliminary bellow adjustment cause standard has not been introduced yet. Standard intensity is %0.2f mV",0,0,nStdInt);  }
call DiSwitchX(Dual_Inlet_Standard,4,0,0);
call DiSwitchX(Dual_Inlet_Sample,4,0,0);
call SwitchChangeOver(Dual_Inlet_Sample);

number deltaVoltage = 1000;
number VoltTarget = (nSigInt+deltaVoltage);
number nSaInt_linearity = _SetBellowVolt(Dual_Inlet_Sample, VoltTarget,chPA_channel,50);

}  

if (bPIRight)
{

call DiSwitchX(Dual_Inlet_Standard,5,1,0);
call DiSwitchX(Dual_Inlet_Sample,5,1,0);
call SwitchChangeOver(Dual_Inlet_Sample);
_Delay(10000,1,"Reaching constant voltage")
nSigInt = _GetIntensityEx(chPA_channel,8000);  // replace m32 channel by Dual_Inlet_g_nPaChannel ?
call DiSwitchX(Dual_Inlet_Standard,4,0,0);
call DiSwitchX(Dual_Inlet_Sample,4,0,0);
call SwitchChangeOver(Dual_Inlet_Standard);

number deltaVoltage = 1000;
number VoltTarget = (nSigInt+deltaVoltage);
number nStdInt_linearity = _SetBellowVolt(Dual_Inlet_Standard, VoltTarget,chPA_channel,50);

return bOk;
}

//--

function StdTransferEQINNERLINE() : bool
{

bool bOk = FALSE;
bool bOkbis = FALSE;
bool boOk = FALSE;
number nStdInt;
number nSaInt;
_UserInfo("You are currently in simultanuous introduction, with equilibration in inner line",0,0);
call DiSetVolume(Dual_Inlet_Sample,100.0);  // put the bellow back to 100% before press adjust
call DiSetVolume(Dual_Inlet_Standard, 100.0); // put the bellow back to 100% before press adjust

call DiSwitchX(Dual_Inlet_Sample, 1, 0, 0);
call CloseVacPumps();
call DiSwitchX(Dual_Inlet_Standard, 1, 1, 0);
_set(sInjectStd, 0); // opening (inversed too?)
call DiSwitchX(Dual_Inlet_Standard, 2, 1, 0);
call OpenSide(Dual_Inlet_Standard); // 3 4 5 6
call OpenSide(Dual_Inlet_Sample); // 3 4 5 6

boOk = call CheckVacuum(Dual_Inlet_Sample, 2, Press_read_waiting_time); // close vac pumps, open specified valve and check vacuum

// here we need to make sure 13 15 23 25 are closed
call DiSwitchX(Dual_Inlet_Sample, 3, 0, 0);
call DiSwitchX(Dual_Inlet_Standard, 3, 0, 0);

//Amount in bellow

if (g_nAmountBellow == 1.0)
{
call DiSetVolume(Dual_Inlet_Standard, 6.0);
call DiSetVolume(Dual_Inlet_Sample, 6.0);
}

if (g_nAmountBellow == 0.8)
{
call DiSetVolume(Dual_Inlet_Standard, 4.0);
call DiSetVolume(Dual_Inlet_Sample, 4.0);
}

if (g_nAmountBellow == 0.4)
{
call DiSetVolume(Dual_Inlet_Standard, 2.0);
call DiSetVolume(Dual_Inlet_Sample, 2.0);
}

if (g_nAmountBellow == 0.0) || (g_nAmountBellow == 0.1) || (g_nAmountBellow == 0.2) || (g_nAmountBellow == 0.3) || (g_nAmountBellow == 0.5) || (g_nAmountBellow == 0.6) || (g_nAmountBellow == 0.7) || (g_nAmountBellow == 0.9) || (g_nAmountBellow == 1.1) || (g_nAmountBellow == 1.2) || (g_nAmountBellow == 1.3) || (g_nAmountBellow == 1.4) || (g_nAmountBellow == 1.5) || (g_nAmountBellow == 1.6) || (g_nAmountBellow == 1.7) || (g_nAmountBellow == 1.8))
{
call DiSetVolume(Dual_Inlet_Standard, 100.0);
call DiSetVolume(Dual_Inlet_Sample, 100.0);
}

// common introduction with stdAA
call StdAA_introduction(Flushing_Delay_Min); // introduction to stdAA
call DiSwitchX(Dual_Inlet_Sample, 4, 0, 0);

LIII
call DiSwitchX (Dual_Inlet_Standard, 4, 0, 0);
_UserInfo ("amount introduced in left sample bellow is roughly %0.2f cc", 0, 1, g_nAmountBellow);
_Set (sInjectStd, 0); // opening StdAA to MS
_Delay (Flushing_Delay_Min, 1, "Equilibrating in inner line and StdAA");
_Set (sInjectStd, 1); // closing (inversed too?)
call DiSwitchX (Dual_Inlet_Standard, 1, 0, DI_DEFAULT_VALVE_DELAY);
_Delay (Flushing_Delay_Min, 1, "Equilibrating in inner line, DI Ext right closed");
call DiSwitchX (Dual_Inlet_Standard, 5, 0, DI_DEFAULT_VALVE_DELAY);
call DiSwitchX (Dual_Inlet_Sample, 5, 0, DI_DEFAULT_VALVE_DELAY);
call DiSwitchX (Dual_Inlet_Sample, 4, 1, 0);
call DiSwitchX (Dual_Inlet_Sample, 4, 1, 0);
_Delay (Flushing_Delay_Min, 1, "Equilibrating in inner line and bellows");
call DiSwitchX (Dual_Inlet_Sample, 4, 0, 0);
call DiSwitchX (Dual_Inlet_Sample, 4, 0, 0);
call DiSetVolume (Dual_Inlet_Sample, 100.0);
call DiSetVolume (Dual_Inlet_Standard, 100.0);
call DiSwitchX (Dual_Inlet_Sample, 6, 0, DI_DEFAULT_VALVE_DELAY);
call DiSwitchX (Dual_Inlet_Standard, 6, 0, DI_DEFAULT_VALVE_DELAY);
bOkbis = call DiExpandLynnOax (Dual_Inlet_Sample, LynnOax_PressureThreshold, nMaxExpansionTries);
call DiSwitchX (Dual_Inlet_Sample, 4, 0, DI_DEFAULT_VALVE_DELAY);
return bOk;

//

function GetVoltage_Pressure_diff (number nSaStartPressure, number nStdStartPressure) {
   // number nSaStartPressure;
   // number nStdStartPressure;
   channel chPA_channel = chPa;
call DiSwitchX (Dual_Inlet_Standard, 5, 1, 0);
call ChangeOverRight ();
call SwitchChangeOver (Dual_Inlet_Standard);
call DiSwitchX (Dual_Inlet_Standard, 5, 1, 0);
   // call PeakCenter ();
   _Delay (10000, 1, "Reaching constant voltage Std");
   number StdSig = _GetIntensityEx (chPA_channel, 8000); //
call SwitchChangeOver (Dual_Inlet_Sample);
call DiSwitchX (Dual_Inlet_Sample, 5, 1, 0);
   _Delay (10000, 1, "Reaching constant voltage Sa");
   number SaSig = _GetIntensityEx (chPA_channel, 8000); //
   chPA_channel
   call ChangeOverClose ();
   number diffVolt = (SaSig - StdSig);
number nRPress = call DiReadVolumePressure(Dual_Inlet_Standard);
number nLPress = call DiReadVolumePressure(Dual_Inlet_Sample);
number nLRpress = (nLPress - nRPress); // always sample - standard
number nVleft = _GetCalc("Dual Inlet System/VolumeControl Left");
number nVright = _GetCalc("Dual Inlet System/VolumeControl Right");
number nLRV = (nVleft - nVright);
// number BelVolDiff = ((38*nSaStartPressure/nLPress) - (38*nStdStartPressure/nRPress));
// number LBelVol = (38*nSaStartPressure/nLPress);
if ((_GetSequenceFlag("Pressadjust",FALSE)) == TRUE)
{
    _UserInfo("Voltage difference (Sa-Std) at acquisition start %4.1f mV: Sa:%4.1f mV Std:%4.1f mV",3,0,diffVolt,SaSig,StdSig);
    _UserInfo("Pressure difference (Sa-Std) at acquisition start %4.1f mbar: Sa:%4.1f mbar Std:%4.1f mbar",3,0,nLRV,nLPress,nRPress);
    _UserInfo("Bellow percentage difference (Left-Right) at acquisition start %4.1f: Sa:%4.1f Std:%4.1f",3,0,nLRV,nVleft,nVright);
}
if ((_GetSequenceFlag("Pressadjust",FALSE)) == FALSE)
{
    _UserInfo("work in progress, bellow calib needed",3,0);
    _UserInfo("work in progress, bellow calib needed",3,0);
    // _UserInfo("Bellow volume difference (Left-Right) at acquisition start %4.2f cc: Sa:%4.2f cc Std:%4.2f cc",3,0,((38*nSaStartPressure/nLPress) - (38*nStdStartPressure/nRPress)),(38*nSaStartPressure/nLPress),(38*nStdStartPressure/nRPress));
    // _UserInfo("Amount difference (STP) (Left-Right) in bellow at acquisition start %4.3f cc: Sa:%4.3f cc Std:%4.3f cc",3,0,((38*nSaStartPressure/1013.15) - (38*nStdStartPressure/1013.15)),(38*nSaStartPressure/1013.15),(38*nStdStartPressure/1013.15));
}
if ((_GetSequenceFlag("Pressadjust",FALSE)) == FALSE)
{
    _UserInfo("work in progress, bellow calib needed",3,0);
    _UserInfo("work in progress, bellow calib needed",3,0);
    // _UserInfo("Bellow volume difference (Left-Right) at acquisition start %4.2f cc: Sa:%4.2f cc Std:%4.2f cc",3,0,((38*nSaStartPressure/nLPress) - (38*nStdStartPressure/nRPress)),(38*nSaStartPressure/nLPress),(38*nStdStartPressure/nRPress));
    // _UserInfo("Amount difference (STP) (Left-Right) in bellow at acquisition start %4.3f cc: Sa:%4.3f cc Std:%4.3f cc",3,0,((38*nSaStartPressure/1013.15) - (38*nStdStartPressure/1013.15)),(38*nSaStartPressure/1013.15),(38*nStdStartPressure/1013.15));
}
function Preparation_DualInletSystem () : bool
{
    call checkVacStdAA ();
    call DiSwitchX (Dual_Inlet_Standard,1,0,0); //
    call DiSwitchX (Dual_Inlet_Sample,1,0,0); //
    call Vacuuming();
    call Flushing (FlushingCycles); // FlushingCycles=3 flush std
    line 3 times by default
    return 1;
}

function MonitorMass ()
{
    bool bMonitormass = _GetSequenceFlag ("MonitorMass",FALSE);
    if (bMonitormass==TRUE)
    {
        _UserInfo ("Mass Monitoring",0,1);
        call DiMeasureInterferingMasses (Ms_PeakCenterChannel,
        Ms_IntegrationTime);
    }
}

function MagnetScan ()
{
    bool bMagnetScan  = _GetSequenceFlag ("MagnetScan",FALSE);
    if (bMagnetScan==TRUE)
    {
        _UserInfo ("Mass scanning",0,1);
        call MassScanning();
    }
}
Python code to calculate $\delta O_2/N_2$ obtained by peak jumping

```python
#!/usr/bin/env python

# Simple python script to calculate delta O2/N2 (peak jumping).
#
# Author: Isabell Lubanski
# Date: 15-09-2015

from ROOT import *
import math
from array import array

SavePlots = True  # Determining if plots are saved or not

# Read the data:
# Define eight arrays containing 16O and 15N values for both sample and standard gas:

T_16O_sample = array("f")
T_16O_sample = array("f")
T_16O_standard = array("f")
T_14N_sample = array("f")
T_14N_sample = array("f")
T_14N_standard = array("f")
V_16O_standard = array("f")
V_16O_sample = array("f")
V_14N_sample = array("f")
V_14N_standard = array("f")

c = []
for line in fileinput.input():
    content.append(line)

for blokNo in range(1,6+1):  # Reads 6 blocks (+1 because the last is not included) Change here you want e.g. 3 instead of 6 runs
```

LVII
```python
line1 = content[4*blockNo+4].split("",") #line1 = 16O_sample and so forth. This splits the line at all ",", so that we now have a list of numbers in "content" that consist of a block
line2 = content[4*blockNo+5].split("",")
line3 = content[4*blockNo+6].split("",")
line4 = content[4*blockNo+7].split("",")

T_16O_sample.append(float(line1[1])) #Here we fill in the times where 16O is measured into the already defined array 'T_16O_sample' and so forth. Entry [1] corresponds to number two entry because the first is 0
V_16O_sample.append(float(line1[5]))
T_14N_sample.append(float(line2[1]))
V_14N_sample.append(float(line2[5]))
T_14N_standard.append(float(line3[1]))
V_14N_standard.append(float(line3[5]))
T_14N_standard.append(float(line4[1]))
V_14N_standard.append(float(line4[5]))

# Fit the linearity of 16O sample:
canvas_16O_standard = TCanvas("canvas_O16_standard", "canvas_O16_standard", 50, 50, 1200, 600)

graph_16O_standard = TGraph(len(T_16O_standard), T_16O_standard, V_16O_standard)
graph_16O_standard.SetMarkerStyle(2)

fit_16O_standard = TF1("fit_16O_standard", "1.0 + x", 0, T_16O_standard[-1]) # A line as fitting function.
# fit_16O_standard = TF1("fit_16O_standard", "[0] + [1]*x", 0, T_16O_standard[-1]) # A line as fitting function.
# fit_16O_standard.SetParameters(7000.0, -0.2) # Set the starting values of [0] and [1] to 7000 and -0.2
fit_16O_standard.SetLineColor(kRed) # Set the line color to red.
fit_16O_standard.SetLineWidth(2) # Set the line width to 4.

graph_16O_standard.Fit("fit_16O_standard", "R") # Make the fit with the range as set.
graph_16O_standard.Draw("AP") # Draw the axis and points of the graph.

# print fit_16O_standard.GetParameter(0)
# print fit_16O_standard.GetParameter(1)
# print fit_16O_standard.Eval(800)

if (SavePlots):
canvas_16O_standard.SaveAs("fit_16O_standard.png") # Save plot as "fit_16O_standard.png" (format follow extension name)

# Fit the linearity of 14N sample:
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canvas_14N_sample = TCanvas( "canvas_14N_sample", "canvas_14N_sample", 50, 50, 1200, 600 )

graph_14N_sample = TGraph( len(T_14N_sample), T_14N_sample, V_14N_sample )

graph_14N_sample.SetMarkerStyle(2)

fit_14N_sample = TF1("fit_14N_sample", "1.0 ++ x", 0, T_14N_sample[-1]) # A line as fitting function.

fit_14N_sample.SetLineColor(kRed) # Set the line color to red

fit_14N_sample.SetLineWidth(2) # Set the line width to 4.

graph_14N_sample.Fit("fit_14N_sample", "R") # Make the fit with the range as set.

graph_14N_sample.Draw("AP") # Draw the axis and points of the graph.

if (SavePlots):
    canvas_14N_sample.SaveAs("fit_14N_sample.png") # Save plot as "fit_16O_standard.png" (format follow extension name)

# Fit the linearity of 14N standard:

canvas_14N_standard = TCanvas( "canvas_14N_standard", "canvas_14N_standard", 50, 50, 1200, 600 )

graph_14N_standard = TGraph(len(T_14N_standard), T_14N_standard, V_14N_standard)

graph_14N_standard.SetMarkerStyle(2)

fit_14N_standard = TF1("fit_14N_standard", "1.0 ++ x", 0, T_14N_standard[-1]) # A line as fitting function.

fit_14N_standard.SetLineColor(kRed) # Set the line color to red.

fit_14N_standard.SetLineWidth(2) # Set the line width to 4.

graph_14N_standard.Fit("fit_14N_standard", "R") # Make the fit with the range as set.

graph_14N_standard.Draw("AP") # Draw the axis and points of the graph.

if (SavePlots):
    canvas_14N_standard.SaveAs("fit_14N_standard.png") # Save plot as "fit_16O_standard.png" (format follow extension name)

Delta_O2_N2 = array(f)

for blokNo in range(1,6+1):
    # Reads 6 blocks (+1 because the last is not included). Change here if less cycles
Time_of_sample_16O = T_16O_sample[blokNo-1]
Numerator = V_16O_sample[blokNo-1]/fit_14N_sample.Eval(Time_of_sample_16O)
Delta_O2_N2.append(((Numerator/Denominator)-1)*1000.0)

# print Delta_O2_N2

# print sum(Delta_O2_N2)
# print len(Delta_O2_N2)

Delta_O2_N2_average = sum(Delta_O2_N2)/len(Delta_O2_N2)

Sum_of_squares = 0.0
for blokNo in range(1,6+1): # Reads 6 blocks (+1 because the last is not included). Change here!! if less cycles
    Sum_of_squares = Sum_of_squares + ((Delta_O2_N2_average - Delta_O2_N2[blokNo-1])**2)/len(Delta_O2_N2)

Delta_O2_N2_std_dev = math.sqrt(Sum_of_squares)

print Delta_O2_N2_average
print Delta_O2_N2_std_dev

raw_input('Press Enter to exit')
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