Abstract

Owing to its 1200 yr lifetime, atmospheric oxygen (O\textsubscript{2}) is a global tracer of biological and hydrological processes. The dominant source of O\textsubscript{2} is located in the low latitudes, where most of the O\textsubscript{2} production/uptake occurs. Atmospheric O\textsubscript{2} 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 O\textsubscript{2} is enriched in heavy isotopologues (\(\delta^{17}O\), \(\delta^{18}O\)) relative to O\textsubscript{2} in ocean water, the ultimate source of O\textsubscript{2} for photosynthesis. The processes causing enrichment of \(^{17}O/^{16}O\) and \(^{18}O/^{16}O\) 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 O\textsubscript{2} 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 O\textsubscript{2} 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 O\textsubscript{2} isotope ratios to the interpretation of their past variations. First, we present the O\textsubscript{2} cycle and describe the results of process-based modeling studies aiming at reproducing the observed enrichment in atmospheric \(\delta^{18}O\) and \(\Delta^{17} (\Delta^{17}_{\text{atm}} = \ln(\delta^{17}O_{\text{atm}}) - 0.516 \cdot \ln(\delta^{18}O_{\text{atm}})).\) We review the current understanding of past orbital and millennial time-scale variations of atmospheric O\textsubscript{2} 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 \(\delta^{18}O_{\text{atm}}\) and especially \(\Delta^{17}_{\text{atm}}\) preserved in ice core bubbles. One must primarily have the ability to measure variations as small as 10 permeg (0.01 \text{%,}) corresponding to the millennial-scale changes observed in \(\Delta^{17}_{\text{atm}}.\) O\textsubscript{2} needs to be separated from other atmospheric constituents to achieve such a level of precision. This motivated us to develop a new method of O\textsubscript{2} separation, based on membrane technology. We verify its 100 % selectivity to O\textsubscript{2}, and estimate its O\textsubscript{2} permeability. This method is currently not applicable to \(\Delta^{17}_{\text{atm}}\) measurements due to sealing issues and variable isotope fractionation during O\textsubscript{2} permeation across the membrane.
Third, a semi-automated, offline experimental setup for $\delta^{18}$O$_{\text{atm}}$ and $^{17}\Delta_{\text{atm}}$ measurements was built 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$_{\text{atm}}$ 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$_{\text{atm}}$ 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 ($\approx$ 30 g) and $\delta^{18}$O$_{\text{atm}}$, $\delta$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 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$_{\text{atm}}$ 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‰ (1σ) and 0.005‰ (1σ). 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$_{\text{atm}}$ and $\delta$O$_2$/N$_2$ is estimated as 0.028‰ (1σ) and 0.021‰ (1σ), respectively.

Fifth, thanks to improving isotope measurement techniques, millennial scale variations of $\delta^{18}$O$_{\text{atm}}$ and $^{17}\Delta_{\text{atm}}$ preserved in polar ice cores have been revealed. In particular, a systematic $\delta^{18}$O$_{\text{atm}}$ increase is recorded during Heinrich stadials (Greenland stadials during which a Heinrich event occurs). Because of its global character, $\delta^{18}$O$_{\text{atm}}$ 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$_{\text{atm}}$ has been established, which limits the use of $\delta^{18}$O$_{\text{atm}}$ as a quantitative indicator for past biospheric production or variations of the hydrological cycle. Here, we quantify the response of $\delta^{18}$O$_{\text{atm}}$ 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 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.