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On the use of $\delta^{18}O_{atm}$ for ice core dating

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ABSTRACT

Deep ice core chronologies have been improved over the past years through the addition of new age constraints. However, dating methods are still associated with large uncertainties for ice cores from the East Antarctic plateau where layer counting is not possible. Indeed, an uncertainty up to 6 ka is associated with AICC2012 chronology of EPICA Dome C (EDC) ice core, which mostly arises from uncertainty on the delay between changes recorded in $\delta^{18}O_{atm}$ and in June 21st insolation variations at 65°N used for ice core orbital dating. Consequently, we need to enhance the knowledge of this delay to improve ice core chronologies.

We present new high-resolution EDC $\delta^{18}O_{atm}$ record (153–374 ka) and $\delta O_2/N_2$ measurements (163–332 ka) performed on well-stored ice to provide continuous records of $\delta^{18}O_{atm}$ and $\delta O_2/N_2$ between 100 and 800 ka. The comparison of $\delta^{18}O_{atm}$ with the $\delta^{18}O_{calcite}$ from East Asian speleothems shows that both signals present similar orbital and millennial variabilities, which may represent shifts in the InterTropical Convergence Zone position, themselves associated with Heinrich events. We thus propose to use the $\delta^{18}O_{calcite}$ as target for $\delta^{18}O_{atm}$ orbital dating. Such a tuning method improves the ice core chronology of the last glacial inception compared to AICC2012 by reconciling NGRIP and mid-latitude climatic records. It is especially marked during Dansgaard-Oeschger 25 where the proposed chronology is 2.2 ka older than AICC2012. This $\delta^{18}O_{atm} - \delta^{18}O_{calcite}$ alignment method applied between 100 and 640 ka improves the EDC ice core chronology, especially over MIS 11, and leads to lower ice age uncertainties compared to AICC2012.

1. Introduction

The EPICA Dome C (EDC) ice core provides a continuous 800 ka (thousands of years before 1950) record of past atmospheric greenhouse gases concentrations (Spahni et al., 2005; Loulergue et al., 2008; Lüthi et al., 2008) and Antarctic surface temperature (Jouzel et al., 2007), contributing to paleoclimatic and paleoenvironmental information. However the uncertainties arising from ice core dating methodologies limit the interpretation of records in terms of past climate dynamics, especially on long time scales. Establishing a causal relationship between orbital forcing (precession or obliquity) and polar temperature over deglaciations, or making the link between polar ice cores and low latitudes climate archives is particularly critical in this context. The EDC3 chronology (Parrenin et al., 2007) has been developed using ice flow modeling, peaks in ^{10}Be record and orbital dating constraints based on air content and $\delta^{18}O_{atm}$ ($\delta^{18}O$ of atmospheric O_2), especially in the deeper part of the ice core (300–800 ka, Dreyfus et al., 2007). The more recent AICC2012 chronology (Bazin et al., 2013; Veres et al., 2013) was built using revised and additional age constraints compared to EDC3, especially through the addition of numerous gas and ice stratigraphic links, combined with the inverse dating method DATICE (Lemieux-Dudon et al., 2010) to provide a coherent chronology for four Antarctic ice cores (EDC, Vostok, EPICA Dronning Maud Land - EDML, TALos Dome ICE core - TALDICE) and one Greenland ice core (NorthGRIP - NGRIP). An uncertainty of up to 6 ka is associated with the AICC2012 EDC chronology for the oldest part (Bazin et al., 2013).

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Despite the numerous dating constraints implemented in the EDC3 and AICC2012 chronologies, there are evidences that these chronologies should be revised. First, the comparison of Dome F (DFO2006) and AICC2012 age scales over the Marine Isotope Stage (MIS) 5 features an age difference with maximum values of 4.5 and 3.1 ka over MIS 5d and MIS 5b respectively (Fujita et al., 2015). Second, the comparison of the NGRIP $\delta^{18}O_{ice}$ record on the AICC2012 chronology with lower latitudes records such as the Northern rim of the Alps speleothems - NALPS (Boch et al., 2011) highlights inconsistencies of several millennia between chronologies over the last glacial inception (Veres et al., 2013).

Total air content has largely been used for the establishment of EDC chronologies (Parrenin et al., 2007) based on its link with the integrated local summer insolation (Raynaud et al., 2007). Another ice core parameter, the $\delta O_2/N_2$, was proposed as an orbital tuning tool (Bender, 2002). Indeed, the $\delta O_2/N_2$ outlines variations at orbital scale that are in phase with the local summer insolation (Bender, 2002; Kawamura et al., 2007; Suwa and Bender, 2008; Landais et al., 2012; Bazin et al., 2016). The relationship between $\delta O_2/N_2$ and the local summer insolation is likely established through the near-surface snow metamorphism (Hutterli et al., 2010) that influences snow density down to the pore close-off depth during firnification (Fujita et al., 2009). Then, at close-off, trapping process favors the loss of O_2 compared to N_2 molecules (Battle et al., 1996; Huber et al., 2006; Severinghaus and Battle, 2006). This link can be used to build ice core chronologies when associated with an appropriate error bar.

The $\delta^{18}O_{atm}$ measured in ice cores is a complex signal that can still be related to the low latitude water cycle (Landais et al., 2010; Seltzer et al., 2017). This marker combines variations in biospheric and low latitude water cycle processes, thus integrating changes in global sea level, water cycle and biosphere productivity through photosynthesis and respiration fluxes (Bender et al., 1994). Although the drivers of $\delta^{18}O_{atm}$ variations over the last 800 ka remain poorly known, several studies have highlighted the resemblance between those variations and the precession signal or mid-June 65°N insolation (Jouzel et al., 1996; Petit et al., 1999; Dreyfus et al., 2007; Landais et al., 2010). A 5–6 ka lag is classically applied between precession and $\delta^{18}O_{atm}$ minima, as primarily observed over Termination I (Bender et al., 1994; Jouzel et al., 1996, 2002; Petit et al., 1999; Dreyfus et al., 2007). The existence of this lag and the difficulty to explain it due to the complexity of the $\delta^{18}O_{atm}$ signal are the main reasons why EDC ice core chronologies are associated with a 6 ka uncertainty. A reduction of this error bar would allow the use of $\delta^{18}O_{atm}$ as a better dating tool.

Advances in the use of $\delta^{18}O_{atm}$ for chronology construction goes through a better understanding of processes affecting the $\delta^{18}O_{atm}$. It has been suggested that precessional variations in solar input can play a key role in influencing the low latitude water cycle and hence $\delta^{18}O_{atm}$ through changes of the ITCZ (InterTropical Convergence Zone) position (Bender et al., 1994; Landais et al., 2010). The role of precession or northern summer insolation on ITCZ shifts is expected from interhemispheric atmospheric energy balance (Cheng et al., 2016). It is visible in East Asian $\delta^{18}O_{calcite}$ record with the additional imprint of millennial scale variability. The resemblance between $\delta^{18}O_{atm}$ and East Asian $\delta^{18}O_{calcite}$ has already been highlighted (Wang et al., 2008; Severinghaus et al., 2009; Landais et al., 2010). A recent speleothem composite $\delta^{18}O_{calcite}$ record from Chinese caves supports the idea that the last seven glacial terminations recorded in $\delta^{18}O_{calcite}$ were driven by Northern Hemisphere summer insolation changes (Cheng et al., 2016). Since speleothem records are precisely dated, this composite record is a good candidate to progress in our use of $\delta^{18}O_{atm}$ as a dating constraint.

In this paper we first present new high-resolution $\delta^{18}O_{atm}$ and $\delta O_2/N_2$ reference records from EDC ice core over the last 400 ka and hence complement the study of Bazin et al. (2016) focused on the 300–800 ka period. We use these composite records to decipher the orbital and millennial components of the $\delta^{18}O_{atm}$ signal and explore mechanisms driving the $\delta^{18}O_{atm}$ variations in comparison with East Asian $\delta^{18}O_{calcite}$. We thus propose a novel method using the $\delta^{18}O_{atm}$ data to improve the ice core dating and find support for it through an application over the last 640 ka.

2. Methods

2.1. Analytical method

All analyzed samples come from the EPICA Dome C deep ice core from Antarctica. 75 samples were stored at −50 °C and could be used for both $\delta^{18}O_{atm}$ and $\delta O_2/N_2$ measurements. Additional 333 samples, stored at −20 °C, completed the $\delta^{18}O_{atm}$ series. Except for the 56 samples measured at Princeton University by Dreyfus (2008) for $\delta^{18}O_{atm}$, following the analytical method given in Dreyfus et al. (2010), most of the $\delta^{18}O_{atm}$ and all $\delta O_2/N_2$ analyses have been performed at LSCE using a semi-automatic extraction line (Capron et al., 2010). Before measurement, 3–5 mm of ice are removed from each sample face in order to prevent contamination from exchanges with ambient air. Each day, three ice samples with duplicates are placed in cold flasks and the air in the flask is evacuated. The samples are then melted and left at room temperature for at least 1h30 in order to extract the air trapped in ice samples. The air samples are transferred through water vapor and CO_2 traps one by one and are cryogenically trapped into a manifold immersed in liquid helium (Capron et al., 2010; Bazin et al., 2016). Two exterior air samples are analyzed for each daily batch of measurements. These exterior air samples serve as standard for $\delta O_2/N_2$, $\delta^{18}O_{atm}$ and atmospheric $\delta^{15}N$ measurements, and are used to check the evolution of our internal laboratory standard and the proper functioning of our analytical set-up.

The measurements of the isotopic composition of air extracted from the ice are then performed using a dual inlet Delta V plus (Thermo Electron Corporation) mass spectrometer. A run is composed of 16 measurements for each sample and allows measurements of the composition of $\delta^{18}O$, $\delta^{15}N$, $\delta O_2/N_2$ and CO_2 (mass 44) simultaneously.

2.2. Corrections

The raw data are corrected for several processes such as pressure imbalance and mass interferences following procedures described in Landais et al. (2003a) and Severinghaus et al. (2003). They also need to be calibrated against the mean exterior air values in order to express the $\delta^{18}O_{atm}$, $\delta^{15}N$ and $\delta O_2/N_2$ with respect to the composition of atmospheric air, i.e. the standard of reference for these isotopic and elemental ratios. As we did not observe any evolution in the isotopic measurements of atmospheric air through the period of measurements, the correction with respect to atmospheric air was done using a constant value for each period of measurements. In addition to these standard corrections, we also account for firn fractionation and gas loss effects.

2.2.1. Firn fractionation correction due to diffusive processes

The $\delta^{18}O$ of O_2 and $\delta O_2/N_2$ records must be corrected for processes in the firn diffusive column that directly affect the distribution of isotopes. The associated fractionations are driven either by the Earth's gravity field or by the temperature gradient within the firn column (Severinghaus et al., 1998). In our case, the thermal fractionation correction in East Antarctica is neglected because temperature changes are too slow to create large transient temperature gradients, which lead to the migration of the heavier