Advances in triple oxygen isotope analysis and applications for ice-core paleoclimate science

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Stable water-isotope measurements from ice cores reflect paleo-atmospheric thermodynamics along upstream moisture pathways. New analytical methods simplify the measurement of triple oxygen isotopes, which will improve measurement resolution and provide more complete information about the past atmosphere.

Water isotopes in ice cores ($\delta^{17}O$, $\delta^{18}O$, δD, deuterium excess, and ^{17}O excess) reflect past climate conditions

Stable water-isotope measurements (e.g. $\delta^{18}O$ and δD) from ice cores reflect temperature and other thermodynamic conditions of the past atmosphere. As atmospheric moisture moves poleward from evaporative source regions to eventual precipitation sites, mass-dependent fractionation processes progressively distill its isotopic composition. First-order, temperature-dependent equilibrium fractionation during precipitation is the dominant control on the observed ratio of heavy-to-light isotope abundance (i.e. $\delta^{17}O$, $\delta^{18}O$, or δD) at the ice-core site, and the water-isotope paleothermometer has consequently been a cornerstone of ice-core paleoclimate science for decades (e.g. Dansgaard 1964).

However, even these conventional applications of the water-isotope temperature proxy rely on quantitative models of upstream fractionation pathways. In other words, even though the condensation temperature exhibits large control on the water-isotope signal of the precipitation, the isotopic composition of the air parcel that condenses is predetermined by all upstream thermodynamic processes (e.g. Merlivat and Jouzel 1979). Modeling many unknown upstream fractionation processes (e.g. evaporation, atmospheric transport, and precipitation) is improved by the inclusion of additional water isotope observations that reflect those processes.

Second-order water-isotope quantities like deuterium excess (d) or ^{17}O excess ($\Delta^{17}O$) – which are defined by the relationships between δD and $\delta^{18}O$ (d) or $\delta^{17}O$ and $\delta^{18}O$ ($\Delta^{17}O$) as indicated in Figure 1a–b –, are dominated by these upstream kinetic fractionation events, and they can therefore provide information about the integrated history of an air parcel that has reached an ice-core site. While d and $\Delta^{17}O$ both depend on temperature and humidity variations in the atmosphere, the sensitivities of d and $\Delta^{17}O$ during fractionation are different, e.g. the relative effect of evaporation temperature is more important for d, and the relative effect of evaporation humidity is more important for $\Delta^{17}O$ (e.g. Uemura 2010). Therefore, measuring d and $\Delta^{17}O$ together should provide the most complete information about the past hydrosphere. The differences between d and $\Delta^{17}O$ are highlighted in Figures 1c–f, which show seasonally resolved measurements of d and $\Delta^{17}O$ from three ice-core sections from Greenland.

Despite the theoretical potential for $\Delta^{17}O$ to be a complementary tracer to d, traditional ice-core work has not included $\delta^{17}O$ or $\Delta^{17}O$ due to measurement limitations. Most commonly, $\delta^{18}O$ and d have been used to reconstruct past condensation-site and evaporation-source temperatures, but this method is imperfect because, in addition to the evaporation temperature, d is also influenced by other thermodynamic conditions during evaporation, atmospheric transport, and precipitation (Merlivat and Jouzel 1979). Including corresponding measurements of $\Delta^{17}O$ would provide an additional constraint for reconstructing the water-isotope fractionation pathways, and it is therefore desirable to produce records of $\Delta^{17}O$ and to develop climate models that account for $\Delta^{17}O$ (e.g. Markle and Steig 2022; Schoenemann and Steig 2016). The following sections describe recent improvements to $\Delta^{17}O$ measurement methodology and present existing ice-core records of $\Delta^{17}O$.

Recent advances in instrumentation improve temporal resolution of $\Delta^{17}O$ from ice cores

Although d has routinely been measured on ice cores for decades, measuring $\Delta^{17}O$ has only been possible for about 20 years (e.g. Barkan and Luz 2005), and observations of $\Delta^{17}O$ are limited in spatial and temporal resolution. However, new analytical methods have the potential to simplify the measurement of $\Delta^{17}O$ – which, when measured at all, is typically determined separately from other water-isotope quantities by discrete isotope-ratio mass spectrometry (e.g. Barkan and Luz 2005). Unlike d or $\delta^{18}O$, which vary in meteoric water by several or tens of "per mil" (‰, or parts per thousand), respectively, the natural variability of $\Delta^{17}O$ in precipitation is
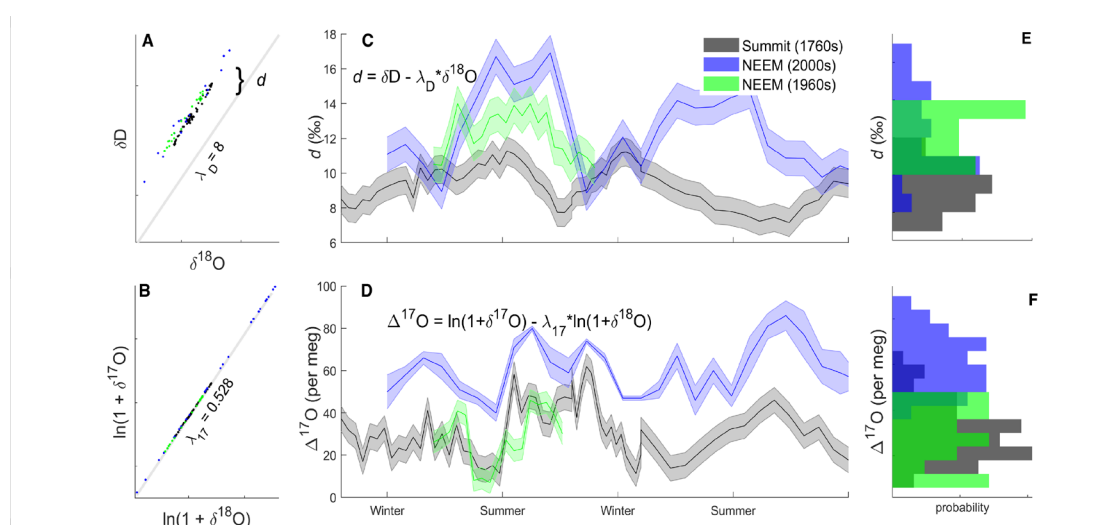

Figure 1: The relationships between δD or $\delta^{17}O$ and $\delta^{18}O$ – which define d and $\Delta^{17}O$ – are provided in **(A)** and **(B)**, respectively. Formal definitions of d and $\Delta^{17}O$ are given by the equations in **(C)** and **(D)**. (C) and (D) provide seasonally resolved records of d and $\Delta^{17}O$ from NEEM (Landais et al. 2012a) and Summit (Davidge et al. 2022), both ice-core sites in Greenland. The decade of the measured ice-core layers is provided in the legend – see the original publications for dating methodologies. All data were aligned to the seasonal cycle of corresponding $\delta^{18}O$ measurements to highlight seasonal patterns in d and $\Delta^{17}O$. Corresponding histograms of these same data are binned by the typical analytical uncertainty and highlight the differences in d **(E)** and $\Delta^{17}O$ **(F)** distribution observed at these sites.
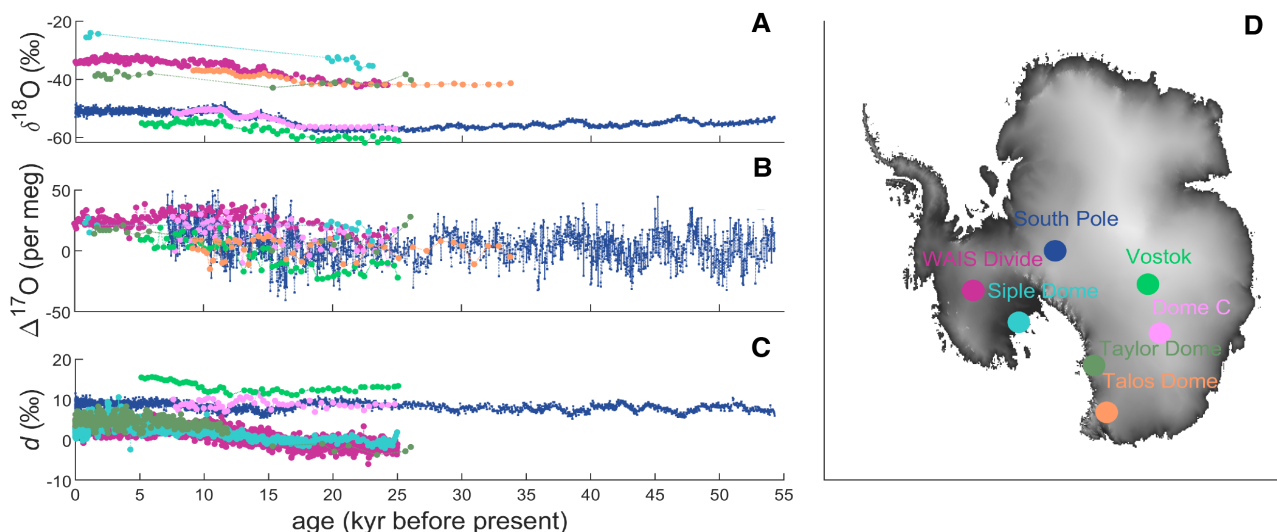
Figure 2: Corresponding measurements of $\delta^{18}O$ **(A)**, $\Delta^{17}O$ **(B)**, and d **(C)** for available Antarctic ice-core sites, whose locations are mapped in **(D)**. Continuously measured data from the South Pole is averaged to show 50 cm resolution for all isotope values (from Steig et al. 2021). All discrete data are shown at their measured resolutions. Details about data normalization protocols for $\Delta^{17}O$, and source information for all discretely measured data, are available from Schoenemann et al. (2013) and Schoenemann et al. (2014), respectively.

only tens of "per meg" (or parts per million), which exacerbates measurement difficulties. However, recent advances in cavity ring-down laser spectroscopy (CRDS) enable the simultaneous measurement of all stable water isotopes (i.e. $\delta^{17}O$, $\delta^{18}O$, δD, $\Delta^{17}O$, and d) with precision that meets or exceeds that of traditional methods (see Steig et al. 2014). CRDS is an appealing method not only because it can measure all water isotopes at once, but also because it can be combined with continuous sample melting strategies that are already in use for other ice-core analyses. Over the last 10 years, continuous-flow analysis (CFA) has been widely adopted by ice-core laboratories, and measurements of $\delta^{18}O$, δD, and d by CFA-CRDS are already routine for ice-core measurement campaigns (e.g. Emanuelsson et al. 2015). Recent work (Davidge et al. 2022; Steig et al. 2021) demonstrates that CFA-CRDS for all stable water isotopes can greatly reduce the analysis time for $\Delta^{17}O$ and it can therefore improve the time resolution of $\Delta^{17}O$ measurements. CFA-CRDS methods will be useful for improving the temporal and spatial resolution of $\Delta^{17}O$ to characterize the natural variability of meteoric $\Delta^{17}O$.

Recent work demonstrates that CFA-CRDS for $\Delta^{17}O$ can indeed improve the resolution of $\Delta^{17}O$ observations with high precision (<10 per meg), especially when CFA for $\Delta^{17}O$ is developed with specific attention to calibration strategies (Davidge et al. 2022; Steig et al. 2021). Steig et al. (2021) measured the lower 1200 m of the South Pole ice core by CFA-CRDS for all stable water isotopes, revealing significant millennial-scale variability in $\Delta^{17}O$ that is not observed in coarser records of $\Delta^{17}O$ from other ice-core sites, but that is co-incident with other climatic events recorded by d and $\delta^{18}O$ (Figs. 2a–c). However, they also identify the importance of frequent (i.e. daily) data calibration against multiple reference waters, adopting a new calibration method that utilizes more reference water measurements than typical CRDS strategies. Davidge et al. (2022) demonstrated that CFA-CRDS for $\Delta^{17}O$ performs as well as discrete methods by measuring replicate sections of an ice core

from Greenland; annually resolved data from that study are provided in Figure 1c–d. They also found that, though small, the greatest source of uncertainty for $\Delta^{17}O$ by CFA-CRDS is the calibration technique. Both studies suggest that the measurement resolution depends on the desired precision for $\Delta^{17}O$ and the rate of the continuous melter. Continuing to develop and implement CFA-CRDS methods so that more existing ice cores can be measured for $\Delta^{17}O$ will improve the spatial and temporal resolution of $\Delta^{17}O$, which is a critical step for studying atmospheric controls on second-order water-isotope quantities and refining interpretations of the paleoclimate record.

$\Delta^{17}O$ data varies on seasonal, millennial, and glacial timescales
Utilizing CFA-CRDS to characterize the full range of variability in both d and $\Delta^{17}O$ – and the differences between them – should allow the decoupling of equilibrium and kinetic fractionation during evaporation, which will improve reconstructions made from water-isotope measurements. Because the signal-to-noise ratios for both d and $\Delta^{17}O$ are generally quite small, quantifying the relationship between them will be most straightforward on timescales and at locations where variability is greatest. Existing ice-core records of $\Delta^{17}O$ from both Greenland and Antarctica are provided in Figures 1 and 2. Figure 1c–d shows the seasonality of $\Delta^{17}O$ and d in Greenland glacial ice and indicates a seasonal magnitude of 40–50 per meg for $\Delta^{17}O$. Similar seasonal magnitudes have been observed over Antarctica (e.g. Landais et al. 2012b; Schoenemann and Steig 2016). Figure 2 presents deep ice-core records of $\Delta^{17}O$, d, and $\delta^{18}O$ from Antarctica, where the observed increase in $\Delta^{17}O$ between the last glacial period and the Holocene range from four to five per meg at some coastal sites (e.g. Taylor Dome or Siple Dome) to more than 20 per meg at inland locations like Vostok. The amplitude of millennial-scale variations observed in the CFA-CRDS record from the South Pole is more than 30 per meg (Steig et al. 2021). Efforts to pinpoint the specific controls on d and $\Delta^{17}O$ by comparing

measurements with climate reanalysis products (e.g. Landais et al. 2012a) or isotope-enabled climate simulations (e.g. Dütsch et al. 2019; Schoenemann et al. 2014) will be facilitated by corresponding, high-resolution measurements of all first- and second-order water-isotope quantities, and CFA-CRDS techniques provide a method for developing those data.

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