Ice core methods: Water stable isotope ratios in ice cores

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Abstract

Both oxygen and hydrogen have different stable isotopes, which together can form multiple stable isotopologues of water. As water moves through the Earth's hydrologic system, these isotopologues respond differently to the same thermodynamic conditions. The processes that drive the hydrologic cycle distribute the isotopologues of water differentially between the phases of water, leading to variations in water-isotope ratios across the Earth. These processes are intimately linked to the functioning of Earth's climate system, and as that system changes so do the ratios of water isotopes in the reservoirs of water on Earth. The science of understanding the impact of the hydrologic cycle and climate on the distributions of water-isotope ratios developed along with interest in studying the stratigraphy of the world's glaciers and ice sheets. The intertwining of these disciplines ushered in the field of ice-core paleoclimatology. Water-isotope ratios are particularly useful for reconstructing past temperature, owing to the fundamental link between temperature, the distribution of water between phases, and the process of fractionation. Long continuous records of climate, enabled by the stable isotope ratios in ice cores, have revealed global changes in Earth's climate conditions, including the pattern of ice ages, their regional and interhemispheric expression, as well as abrupt shifts in Earth's climate that occurred repeatedly in the past. The records currently extend tens of thousand, and hundreds of thousands of years into the Earth's history, providing high latitude (and high altitude) counterparts to other paleoclimate archives.

Keywords

Atmosphere; Climate; Cryosphere; Energy cycle; Evaporation; Fractionation; Geochemistry; Hydrogen; Hydrologic cycle; Ice core; Ocean; Oxygen; Paleoclimate; Paleo-thermometer; Precipitation; Water isotopes

Key points
- The hydrologic cycle is a key component of Earth's climate system.
- The physical climate processes that drive the hydrological cycle, in particular the Clausius–Clapeyron relationship, influence the different isotopologues of water distinctly, leading to variations in their distribution across the Earth and through time.

- The study of water-isotope geochemistry and the hydrologic cycle developed simultaneously and complimentarily with the field of ice coring.
- Water-isotope records from ice cores have provided long and detailed histories and quantitative reconstructions of Earth's climate through time.

Introduction

Ice cores from the world's ice sheets can provide stratigraphic histories of Earth's climate. Since the first deep cores were recovered in the mid-20th century, the ratios of stable isotopes in water have formed the backbone of ice-core paleoclimatology (Langway, 1958; Epstein et al., 1970; Dansgaard et al., 1969) A robust theoretical framework guides the interpretation of ice-core water-isotope records as proxies for past climate, atmospheric temperature in particular (Dansgaard, 1964; Merlivat and Jouzel, 1979; Jouzel and Merlivat, 1984; Ciais and Jouzel, 1994), owing to fundamental climate processes (Dansgaard, 1964). These records lead to the quantification of climate changes on orbital timescales (Jouzel et al., 2007a) and the discovery of abrupt climate changes in the past (Dansgaard et al., 1982).

Stable isotope ratios are important and ubiquitous tools in Earth science. While isotopes of many elements can be measured on samples from ice cores, we will focus here on the elements that make up the ice itself, and the climate reconstructions derived from them. The water comprising the ice sheets, from which ice cores are extracted, arrived there through the processes of the global hydrologic cycle. The Earth's hydrologic cycle is a constant movement of water between phases and is both driven by and essential to the larger climate system. The various isotopologues of water experience the physical climate subtly differently. By understanding those differences, we can extract information about the past state of the hydrologic cycle and climate from ancient snow buried in the ice sheets.

Some definitions

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons, and are thus the same elements and have the same chemical properties, but have slightly different masses. Both hydrogen and oxygen have naturally occurring, stable isotopes, namely ^1H (a single proton nucleus representing about 99.985% of hydrogen), ^2H (often called deuterium and denoted D, with both a proton and a neutron in the nucleus, representing 0.0115% of hydrogen), ^{16}O (8 protons and 8 neutrons in the nucleus, 99.757% of oxygen), ^{18}O (with two extra neutrons in the nucleus, 0.205% of oxygen), and ^{17}O (with just one extra neutron, 0.038% of oxygen) (Sharp, 2006; Rosman and Taylor, 1998; Hoefs, 1997). Together these isotopes combine to form different isotopologues of water, with $H_2^{16}O$ being by far the most abundant (99.731% of all water), followed by water with a single rare isotope like $H_2^{18}O$ (about 0.2%) or $HD^{16}O$ (0.03146%) or $H_2^{17}O$ (0.03789%) (Sharp, 2006). Strictly speaking, "isotopes" refers to the atoms and "isotopologues" refers to the molecules containing different atoms. However, the reader will find these terms used somewhat loosely, particularly in paleoclimatology, though context almost always makes the meaning clear.

The number ratio, R, refers to the abundance of the heavier, rare isotopologue to the common, lighter one, within some group of water molecules: $^DR = {}^2H/{}^1H$ and $^{18}R = {}^{18}O/{}^{16}O$. The R values of Earth's waters are often small fractions owing to the rarity of heavier isotopes, and thus their abundance is often reported as delta values, which are normalized deviations of the R value in some sample of water from a well-known standard:

$$\delta = \frac{R_x - R_{std}}{R_{std}} \tag{1}$$

where R_x is the ratio in the sample and R_{std} is typically the Vienna Standard Mean Ocean Water (VSMOW) standard (Dansgaard, 1964; Craig, 1961; Sharp, 2006). The R values of SMOW are $^{18}R_{SMOW} = 0.00200520$, $^{17}R_{SMOW} = 0.0003799$, and $^DR_{SMOW} = 0.00015576$ (De Wit et al., 1980; Baertschi, 1976; Criss, 1999). As delta values are the small fractional deviation of an R value from some other well-known R value, they are commonly reported in per mil (‰ = 10^{-3}) though note that the unit of the delta value is the dimensionless 1; ‰ is not an SI unit (Coplen, 2011). Positive delta values indicate water enriched in the heavy isotope compared to mean ocean water while negative delta values signify water depleted in the heavy isotope.

Measurement techniques

Early measurements of the isotopes of water were made through density tests (Dole, 1935; Dansgaard, 1953) though after World War II, the availability of mass spectrometers leads to high quality measurements with relative ease (Dansgaard, 1953), and enabled precise disentanglement of the different isotopologues of water, which was previously unfeasible. In essence mass spectrometers work by ionizing a sample, accelerating the resulting ions across a voltage and then focusing the ions into a beam (Criss, 1999). The ion beam is then passed through a strong electric/magnetic field, forcing the beam into a circular path. Ions with distinct charge to mass ratios will follow paths with distinct radii, and thus the initial ion beam will be separated into different beams depending on

the presence of different isotopic masses. Collectors can then detect the relative amounts of these isotopes by measuring the currents resulting from the different ion beams (Criss, 1999). This technique formed the basis of studies of water-isotope ratios for over half a century (Nier, 1947; Dansgaard, 1953).

While historically water-isotope measurements were made using traditional mass spectrometry, in recent decades laser spectroscopy techniques are more commonly employed. Cavity ring-down spectroscopy (CRDS) is a widely used and important technique (Lis et al., 2008; Gupta et al., 2009; Guidotti et al., 2013) in which a specially tuned laser illuminates a cavity with enhanced intensity due to resonance, and a long path length owing to mirrors. When the laser is extinguished the intensity exponentially decays and that decay rate is increased by the presence of light absorbing gases within the cavity, in this case the different isotopologues of water which absorb at distinct wavelengths. Thus precise amounts of the different isotopologues of water can be quantified by measuring the decay or "ring down" times within the cavity.

This technique offers many benefits over other techniques. It can be measured quickly on very small amounts of water. It can be paired with continuous flow analysis (CFA) systems enabling the measurement of extremely high-resolution measurements in ice cores. Further, measurements of $\delta^{18}O$, $\delta^{17}O$, and/or δD can be measured effectively simultaneously from the same samples (Schauer et al., 2016).

Early history

The study of ice coring and the study of the relationships between water isotopes and climate developed simultaneously during the mid-20th century before combining in the 1960s. A number of good reviews of this history exist, including Langway (2008) and Jouzel (2013), to which the reader is enthusiastically directed.

The broad use of stable isotopes in Earth sciences exploded in the early 20th century (Rosenblum, 1940; Jensen, 1953). With the quantum and statistical mechanical framework for understanding fractionation processes built (e.g., Eyring, 1933, Urey, 1947), early work on the stable isotopes of hydrogen and oxygen in water showed their distinct vapor pressures (Dole, 1935; Lewis and Macdoland, 1933; Riesenfeld et al., 1936) and the influences of processes like evaporation (Tucholski, 1934; Jensen, 1953) on their distribution between phases, including speculation on processes specific to glacial ice (Jensen, 1953).

The 1950s and 1960s saw the development of the essential understanding of the role of the hydrologic cycle on the distributions of water-isotope ratios. In 1952, a researcher named Willi Dansgaard collected precipitation samples from a storm front passing over Copenhagen, Denmark (Dansgaard, 1953). Analyzing the oxygen isotope ratios in these samples, he identified many essential processes, including the role of progressive distillation, fractionation owing to differences in the vapor pressures of the isotopologues, and the potential influence of re-evaporation of the falling rain drops (Dansgaard, 1953). A broader picture of the role of the Earth's connected hydrologic cycle emerged when a wide range of stable isotopic measurements of ocean water were compared to that in precipitation (Epstein and Mayeda, 1953; Dansgaard, 1954). In particular Dansgaard (1954) identified the influence of the integrated condensation and evaporation history of water in the atmosphere and the important role of atmospheric temperature in driving these processes. These processes helped to explain the much wider range of water-isotope ratios found in meteoric water compared to that in the ocean. The small variations that were present in oceanic isotope ratios (Epstein and Mayeda, 1953) were found to be in-line with expectations from the influence of evaporation and precipitation (Dansgaard, 1954).

Over the next decade, a steady increase in observations and theoretical work drove an increased understanding of the relationships between climate, the processes of the hydrological cycle, and their role in driving the distributions of the stable isotopologues of water (e.g., Epstein, 1956, Craig, 1961, Craig et al., 1963, Craig and Gordon, 1965). Of particular note was the seminal work of Dansgaard (1964), who compiled a global dataset of measurements of the hydrogen and oxygen isotope ratios of precipitation. The large spatial scale helped elucidate the underlying physical processes. Clearly identified was the role of atmospheric transport of water vapor after evaporation, which leads to the progressive removal of water due to cooling and condensation, and the relative depletion of the heavy isotopes from the vapor. Dansgaard (1964) highlighted several features of the observational dataset correlated with this depletion of heavy isotopes, including the altitude, latitude, and continentality of the precipitation site, all of which stem from the physical influence of temperature in the atmosphere driving integrated condensation and distillation (Dansgaard, 1964; Gat, 1996).

Simultaneous to this work on water isotopes and the hydrologic cycle, the study of stratigraphy in the worlds glaciers and ice sheets was developing. Research on snow pits started in the 1930s (Sorge, 1933; Ahlmann, 1935) and developed further in the 1950s especially in Greenland and other Northern Hemisphere glaciers such as the Juneau Icefield (Bader, 1954; LaChapelle, 1954; Benson, 1960; Langway, 2008) and Antarctica (Epstein et al., 1963). Water-isotope ratios quickly became a tool in these snow pit studies (Epstein and Sharp, 1959a; Gonfiantini, 1959; Benson, 1960; Lorius, 1961). Early studies on the ice sheets showed that seasonal isotopic cycles were preserved in the snow pack (Epstein, 1956; Benson, 1960). Further research on the water-isotope ratios in Antarctica snow confirmed relationships to accumulation (Sharp and Epstein, 1962) and to atmospheric temperature through direct comparison with soundings (Picciotto et al., 1960), which were particularly advanced by multiyear observations at the South Pole (Epstein et al., 1965; Aldaz and Deutsch, 1967). The interest in water-isotope ratios as a tool for understanding much older glacial ice arose early and initially started with glacier margins and icebergs (Epstein and Sharp, 1959b; Sharp et al., 1960; Dansgaard et al., 1960; Langway, 2008; Jouzel, 2011).

After early studies using snow pit and shallow hand-auger coring, the initiative to drill deeper cores and access older glacier stratigraphy took off in the late 1940s and early 1950s (Bader, 1954; Benson, 1960; Langway, 1965, 1970; Langway, 2008). Three drilling projects to core deeper ice were launched in quick succession between 1949 and 1951 in three different regions around the

globe (Langway, 2008): in Antarctica (Swithinbank, 1957), on the Juneau Icefield in Alaska (Miller, 1954), and in Greenland (Heuberger, 1954). These efforts cored to depths between 100 and 150 m and were primarily used to study physical properties of the ice (Langway, 2008).

Scientific ice drilling techniques rapidly developed after this, in particular led by what would become the US Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) (Bader, 1954; Langway, 2008; Jouzel, 2013). The first major accomplishments of this group were two cores drilled at Site 2 in Greenland, during 1956 and 1957, to depths of 305 m and 411 m, respectively (Langway, 1958, 1962, 1965; Langway, 2008). Deep coring at Byrd Station in West Antarctica and Little America V on the Ross Iceshelf between 1957 and 1959 returned two several hundred meter long cores (Langway, 2008; Jouzel, 2013). Russian-led drilling in the Antarctic also began in 1957 (Jouzel, 2013). Water-isotope measurements on the 1957 Site 2 Greenland core, which was thought to contain 900 years of stratigraphy, represent perhaps the first deep ice-core water-isotope studies (Epstein and Sharp, 1959a; Dansgaard, 1961; Langway, 1962, 1965, 1970; Langway, 2008). Relatively high-resolution water-isotope analyses on several distinct sections of this core revealed seasonal variations in water isotopes were preserved at depths to at least 400 m (Langway, 1965). Other coring efforts around this time in Antarctica used water-isotope measurements to quantify accumulation and recent decadal scale temperature change (Gonfiantini, 1965). After these successes, CRREL drilled the first truly deep (1388 m) core to bedrock at Camp Century in Greenland between 1960 and 1966 (Dansgaard et al., 1969) and went on to drill another core at Byrd Station in Antarctica, reaching bedrock at 2164 m in 1968 (Epstein et al., 1970; Langway, 2008; Jouzel, 2013). The culmination of these efforts was a series of papers that launched the field of ice-core water stable isotope research. Indeed water-isotope ratios have formed a backbone of ice-core paleoclimatology since.

Fundamentals of the relationship between water-isotope ratios and climate

Before outlining some of the major discoveries made from water-isotope ice-core records, we will discuss the essence of the interpretation of ice-core records as a proxy for past temperature. In some sense all interpretations of proxies require a model. Sometimes that model is statistical, based on a phenomenological observation about the geochemical measurement and the climate variable we'd like to reconstruct, while the underlying physical or biochemical processes may be partially or even completely unknown. A proxy interpretation may be backed by a conceptual model in which the core physical relationships are identified and support a qualitative interpretation, even if the details are unknown. As understanding of the underlying processes are developed, quantitative models, often numerical ones if the system is sufficiently complicated, allow quantitative interpretations and reconstructions, and importantly the objective assessment of uncertainty in those reconstructions.

A robust empirical relationship, a simple conceptual model, and nearly a century of research on the myriad underlying physical processes support the common interpretation of water-isotope ratios as a proxy for atmospheric temperature. The temperature of condensation is far from the only climatic variable that influences water-isotope ratios in polar snow, and it is not the only variable about whose past we can learn from ice-core records. The distribution of water-isotope ratios is fundamentally tied to the Earth's hydrologic cycle, the functioning of the climate system, and the definition of temperature itself. It is this core connection that makes the isotope ratios of water a particularly useful proxy for past climate.

Temperature and vapor pressure

It is perhaps most useful to start with the meaning of temperature. Temperature is a measure of the average kinetic energy of molecules in a substance. However not all molecules in a substance, for example a bowl of water, have the same kinetic energy. At a fixed temperature, there is a well-defined distribution of kinetic energies following the Maxwell–Boltzmann distribution (Maxwell, 1867; Hernandez, 2017) featuring a peak and a long skewed tail of positive kinetic energies (Fig. 1). As the temperature increases, the peak moves toward higher kinetic energies, and the likelihood of energies in the long, high-energy tail increases.

The liquid water molecules in our bowl are bound by strong intermolecular forces (Hoefs, 1997). Given the distribution of kinetic energies associated with the temperature of the water, some fraction of the water molecules will have enough energy to exceed the binding energy between molecules, leaving the liquid and becoming vapor. As the temperature increases, the fraction of molecules with enough energy to break these bonds increases (Fig. 1). Due to the random motions of the vapor molecules, some will collide with and reenter the liquid. If we keep our bowl at a constant temperature and in a closed container, the liquid and vapor phases of water will eventually reach an equilibrium in which the number of molecules leaving the liquid into the vapor and returning from the vapor to the liquid would balance. In this equilibrium, the vapor will exert a pressure, which is proportional to the number of molecules in the vapor, which is in turn proportional to the fraction of molecules with enough kinetic energy to exceed the binding energy between the molecules in the liquid, given the temperature. As the temperature increases, the number of molecules that can exceed the binding energy increases, the number of water molecules that can be in the vapor while in equilibrium with the liquid increases, and the pressure exerted by the vapor increases (Criss, 1999; Sharp, 2006; Hoefs, 1997).

The relationship between this equilibrium vapor pressure (P) and temperature has a distinct, nonlinear shape that is a direct result of the shape of the Maxwell–Boltzmann distribution of kinetic energies for different temperatures, and is known as the Clausius–Clapeyron relationship:
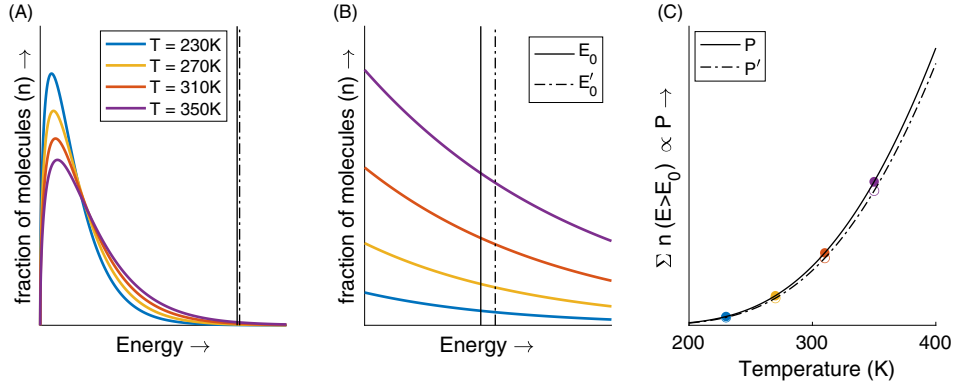
Fig. 1 Schematic of the relationship between temperature, energy, and vapor pressure. (A) the distributions of kinetic energies for different temperatures are shown *colored lines* (in Kelvin), following the Maxwell–Boltzmann equations. At warmer temperatures, the mean kinetic energies are higher and the distributions are broader. The idealized binding energy of liquid water (the common, light isotopologue) is shown in the *vertical solid line* (E_0). The higher binding energy of a heavy isotopologue (E_0') is shown in the *dashed line*. (B) Detail of panel (A) showing the energy distributions for different temperatures near the binding energies. At higher temperatures, more molecules have enough kinetic energy to exceed the binding energy. (C) The sum of the number of molecules exceeding the binding energy of (common) liquid water as a function of temperature is shown in the *solid line*, which is proportional to the saturated vapor pressure of water (P). The *colored dots* show the points associated with the temperature curves from panels (A) and (B). The equivalent curve for the heavier isotopologue is shown in the *dashed line* (P').

$$\ln\left(\frac{P}{P_0}\right) = -\Delta H \bar{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{2}$$

in which $\bar{R}$ is the gas constant (8.3145 J mol^{-1} K^{-1}), ΔH is the change in enthalpy of the reaction, the latent heat of vaporization, $\Delta H_{vap} = L = 2.45 \times 10^6$ J kg^{-1}, and P_0 and T_0 are a reference pressure and temperature, respectively. Given an atmospheric pressure, this defines the saturated specific humidity of the atmosphere (Fig. 2).

Such a relationship can be defined for the other phase changes of water as liquid, vapor, and ice can all exist at Earthly temperatures and pressures, by application of Van't Hoff's equation (Van't Hoff, 1884) and the appropriate change in enthalpy of the reaction (Criss, 1999). The Clausius–Clapeyron relationship turns out to be especially critical to understanding the Earth's
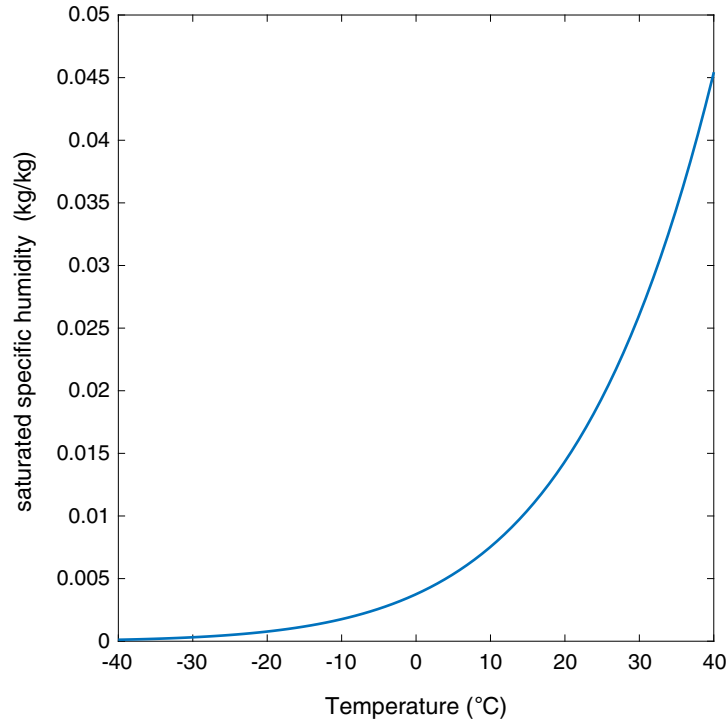

Fig. 2 The Clausius–Clapeyron relationship. The saturated specific humidity as a function of temperature, in units of kg of water per kg of air.

climate, hydrological cycle, the distribution of the stable isotopes of water, and the interpretation of water-isotope ratios as proxies for the climate in the past. The nonlinearity of this curve is critical: warm air holds much more water vapor in it than cold air, and the capacity grows exponentially with temperature.

Fractionation

We've been considering here the common isotopologue of water, H_2O. The other isotopologues of water behave similarly but with a key difference. The presence of an extra neutron or two within one of the atoms of a water molecule leads to differences in the mass of the molecule, which in turn leads to subtle differences in the vibrational and rotational energies of the molecule (Urey, 1947; O'Neil, 1986; Criss, 1999). In particular the extra mass leads to a reduction of the lowest quantized vibrational energy, the zero point energy (Eyring, 1933; Criss, 1999; Scheiner, 2000). This in turn leads to a change in the enthalpy of reaction; because the heavier isotopologues of water have lower zero point energies, they require more energy to be incorporated into reactions than the light isotopologues (Criss, 1999; Scheiner, 2000).

Imagine our bowl of water, but now filled with HDO ($^1H^2HO$), instead of common H_2O. These molecules require more energy to exceed the binding energy of the liquid and enter the vapor, compared to the lighter H_2O molecules. For a given temperature, fewer HDO molecules will enter the vapor and thus exert a lower vapor pressure at equilibrium (Fig. 1). Each isotopologue of water has its own subtly different version of Eq. (2). Fig. 3A shows this for H_2O and HDO.

Of course natural waters are a mixture of the common $H_2^{16}O$ molecule and trace amounts of the rare heavier isotopologues, predominantly $H_2^{18}O$, $HD^{16}O$, and $H_2^{17}O$. The relative amounts of each isotopologue change as water changes phase, a process called fractionation, which results from precisely the physics described above. Consider liquid water in equilibrium with vapor at a given temperature. If there were no mass difference (somehow) between, for example, H_2O and HDO, the proportion of HDO molecules to H_2O molecules in the vapor would be the same as that in the liquid. However, because of the higher energetic requirement to leave the liquid, at a given temperature the ratio of HDO to H_2O molecules in the vapor will be lower than in the liquid; fewer molecules will have enough energy to exceed the higher binding energy of the heavier isotopologue. At a given temperature, each isotopologue has different vapor pressures. The ratio of the idealized vapor pressures of the different
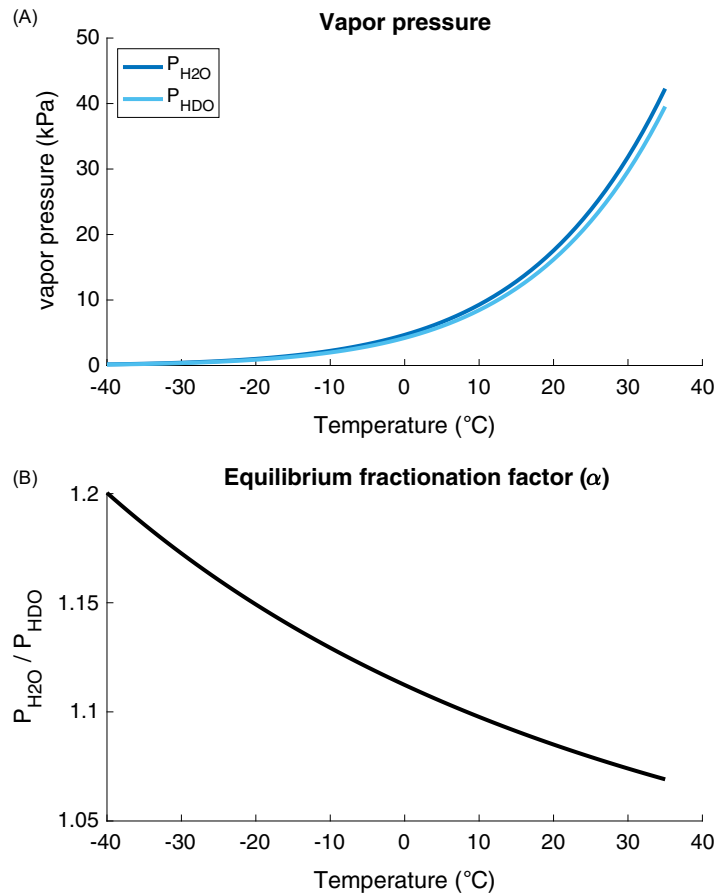

Fig. 3   (A) The saturated vapor pressures of H_2O and HDO following Criss (1999). (B) The ratio of the saturated vapor pressures of H_2O and HDO is the equilibrium fractionation factor, α_{eq}.

isotopologues (shown in Fig. 3) describes the partitioning of the isotopologues and exactly gives the ratio of the R values between each phase in equilibrium with each other, also known as the equilibrium fractionation factor (Criss, 1999; Sharp, 2006; Hoefs, 1997):

$$\alpha_{eq} = R_{\text{liquid}}/R_{\text{vapor}} \tag{3}$$

For example for H_2O and HDO ($^1H^2HO$) in liquid and vapor:

$$\frac{^2H}{^1H}_{\text{liquid}} = {}^D\alpha_{eq} \frac{^2H}{^1H}_{\text{vapor}} \tag{4}$$

Equilibrium fractionation factors exist for all the other isotopologues and phase changes of water (Criss, 1999). Note that the equilibrium fractionation factors are inherently temperature dependent, which results from the shape of the temperature-dependent vapor pressures for each isotopologue, which in turn results from the shape of the Maxwell–Boltzmann distribution and how the enthalpies of reaction vary with the mass of the isotopologue. The fractionation factors generally decrease with increasing temperature, meaning there is less discrimination between the different isotopologues of water during phase change at warmer temperatures.

In addition to these steady-state equilibrium effects, there are nonequilibrium (or kinetic) fractionation effects owing to the difference in masses between isotopes. For a given temperature (and thus average kinetic energy), the average velocities of lighter isotopologues are higher compared to heavier isotopologues, and likewise the rate of chemical reactions in which bonds are broken is higher for the lighter isotopologues compared to heavier isotopologues (Melander, 1960). The resulting kinetic fractionation effects are an important aspect of nonequilibrium phase changes and processes like diffusion. Such processes are ubiquitous in Earth's hydrologic cycle and important for understanding the water-isotope ratios of polar snow. For example, evaporation from the world's oceans is the dominant source of atmospheric water vapor, and ultimately precipitation, and predominantly happens in undersaturated, nonequilibrium, conditions. These effects can modify and amplify the equilibrium discrimination between isotopologues of water during phase changes.

Water and climate

While paleoclimate interpretations of water-isotope ratios in ice often focus on conditions at a single instance of phase change, e.g., the temperature during condensation above the ice sheet, it's the integrated water cycle, tied to the fundamental processes of the climate system, that enables the proxy interpretation.

The ultimate source of energy driving Earth's climate is the light from the Sun. The Earth system gains more energy from the Sun than it loses to space at the low latitudes, and loses more than gained at the high latitudes. To balance this, the climate system transports energy from the low to high latitudes (Hartmann, 2015). Water plays an essential role in most aspects of this climatic heat engine. The intensity of absorbed incoming insolation from the Sun is not the same at all locations on the Earth. This is primarily because Earth is spheroidal. The next most important reason is the intersection of temperature, the phases of water, and their albedo. The liquid oceans are dark and absorb shortwave radiation from the Sun, while frozen water in the ice sheets and sea ice at the poles is bright and reflective, as are droplets that make up clouds. Water vapor is largely transparent to this incoming energy. These properties set the dominant global patterns of Earth's surface albedo and the absorbed energy from the Sun.

The Sun's rays heat the Earth's surface where absorbed, which in turn heats the atmosphere through the transfer of energy, the majority of which is accomplished through the latent heat associated with evaporating water from the ocean to the atmosphere (Hartmann, 2015), primarily in the low latitudes. The amount of water vapor in the Earth's atmosphere varies by orders of magnitude depending on location due to the strong nonlinear dependence of the water's vapor pressure and temperature. In the atmosphere, water vapor absorbs the long-wave energy emitted by the Earth's surface (Wallace and Hobbs, 2006; Hartmann, 2015) and is the most important and abundant greenhouse gas. This effect is another route through which the surface heats the atmosphere, which in turn warms and reradiates to the surface.

Eventually, the water in the atmosphere will return to the oceans through precipitation. The residence time of water in the atmosphere has a mean of 8–10 days (Gimeno et al., 2021). The spatial patterns of evaporation and precipitation are not identical (Hartmann, 2015). Generally, atmospheric motions transport water from regions of evaporation poleward and upward, leading to cooling and saturation, again owing to the strong temperature dependence of the Clausius–Clapeyron relationship. This process results in condensation, precipitation, and the release of the latent heat. Water vapor thus accounts for a significant fraction of total heat transport and convergence in the atmosphere, balancing energy gain and loss between the equator and the poles (Hartmann, 2015). Atmospheric motions drive the surface ocean currents. The patterns of evaporation, precipitation, and freezing of surface oceans, together with the pattern of heating, drive the large-scale deep ocean circulation through altering the buoyancy of the surface (Ferreira and Marshall, 2006; Hartmann, 2015).

The global hydrologic cycle, the transport and phase changes of water, is fundamental to the global climate system and the patterns of temperature on the Earth. Governing this role is the pressure–temperature relationships between the phases of water, typified by the Clausius–Clapeyron curve between vapor and liquid. Each isotopologue of water has its own subtly different set of pressure–temperature relationships between phases. There are thus slightly different global water cycles for each isotopologue.

The study of water-isotope ratios in ice cores is a comparative study of these multiple water cycles and the differences in how they have changed through Earth's climate history.

First-order interpretation

The basis of the interpretations of water-isotope ratios in polar ice cores is the essential role of water in the climate system, in particular the net transport of water from the low latitudes to the high latitudes through the atmosphere and the relationships between temperature, vapor pressure, and phase change. Since the early foundations of this field (e.g., Dansgaard, 1953, Dansgaard, 1964), there has been decades of refinement of the core interpretations, and many excellent texts and reviews can provide the reader with important history and details (e.g., Hoefs, 1997, Sharp, 2006, Criss, 1999, Gat, 1996, Galewsky et al., 2016, Bowen et al., 2019, Dee et al., 2023).

The essential conceptual model to describe the distributions of water-isotope ratios in meteoric water is straightforward. Water evaporating into the atmosphere is relatively depleted in heavy isotopes compared to the underlying ocean water. The basic functioning of the atmospheric circulation is to move heat (including the latent heat of this water vapor) from the low latitudes, where the majority of evaporation occurs, to the high latitudes. From the edge of the tropics poleward, this net transport is down-gradient from regions of high temperature and high atmospheric water concentration to regions of low temperature and low water concentration. This drives the integrative removal of water from the atmosphere, and the progressive distillation of the vapor of heavier isotopes. As water vapor is driven poleward, it cools, reaches saturation, and some of the water in the atmosphere will condense and precipitate. During condensation, relatively more of the heavy isotopes will be in the condensate, whether liquid or solid, compared to the vapor. Since this water will be removed by precipitation, the vapor will preferentially lose the heavy isotopes compared to the light. As water is broadly transported from the low latitudes to the high latitudes, the vapor will become increasingly depleted of the heavier isotopes, as will the precipitation falling from it. While many factors may drive additional variation in water-isotope ratios of precipitation at any point or during any event, over long periods of time and many events, this essential process will lead to a persistent pattern of more negative delta values of precipitation at higher latitudes (Dansgaard, 1964). Should the mean climate at a high latitude site, for example, decrease over time, water vapor reaching that site will on average have cooled more to get there, more total water will have been wrung from the atmosphere, and preferentially more of the heavy isotopologues compared to the lighter ones will have been lost along the way. The delta values of precipitation falling at that site would get even more negative. Conversely if the same site were to warm up, there would be less distillation of water from the atmosphere on average to get there, less total fractionation of the water-isotope ratios, and the delta values of precipitation at the site would get less negative.

This is the essence of the qualitative interpretation of water-isotope ratios for variability in temperature at a precipitation site. There are many details, nuances, and complications to this relatively simple picture. A key to this interpretation is that the changes in climate are large enough in magnitude or persistent enough in time to be detectable among the myriad of other influences on the water-isotope ratios of vapor and precipitation. Aiding the robustness of this simple interpretation is that the underlying process (large-scale moisture transport down temperature and specific humidity gradients) is fundamental to the operation of the climate system. We'll now take a tour of some of the details.

Evaporation

Evaporation from the ocean into the atmosphere is the ultimate source of water for the hydrological cycle. At any moment around 1.35×10^9 km^3 of water is in Earth's oceans, while less than 13,000 km^3 is in the atmosphere (Gleick, 1996). The air above the global oceans is, on average, below saturation (relative humidity around 80%) (Hartmann, 2015). Kinetic fractionation processes will thus be important in the partitioning of water isotopes during evaporation (Von Ehhalt and Knott, 1965). Craig and Gordon (1965) developed a model for this process, which has since been adapted or modified for many related circumstances (Von Ehhalt and Knott, 1965; Craig and Gordon, 1965; Merlivat and Jouzel, 1979; Gat, 1996; Criss, 1999; Galewsky et al., 2016).

In general, the fractionation during evaporation depends on the isotopic ratios of the liquid water at the ocean surface and of vapor in the atmosphere. The relative humidity of the atmosphere (RH) is also important, as is the air temperature (T_a), and the temperature of the sea surface (SST). A parameter called the normalized relative humidity (RH$_n$) brings these three variables together to quantify the relevant degree of nonequilibrium, making it particularly useful for understanding kinetic fractionation (Merlivat and Jouzel, 1979; Risi et al., 2010):

$$\mathrm{RH}_n = \frac{\mathrm{RH} \times e_s(T_a)}{e_s(\mathrm{SST})}$$

(5)

where $e_s(T_a)$ and $e_s(\mathrm{SST})$ are the saturated vapor pressures of air at the surface air temperature and at the sea surface temperature, respectively.

The kinetic effects of this process have to do with the relative diffusivities, D and D^*, of the light and heavy isotopes, respectively (Merlivat, 1978), which define an effective diffusive fractionation factor:

$$\alpha_{diff} = \left(\frac{D}{D^*}\right)^n$$

(6)

where the exponent, n, varies between 0 and 1 and relates to the wind regime, specifically the amount of turbulent mixing (Merlivat and Jouzel, 1979). In the case of high wind speed over rough surfaces, pure turbulence would dominate and $n = 0$, while in stagnant conditions molecular diffusion dominates and $n = 1$ (Merlivat and Jouzel, 1979; Gat, 1996). The value of the exponent appropriate for different scenarios can be determined from theory or empirical studies (Gat, 1996; Criss, 1999; Uemura et al., 2008).

Bringing these ideas together and following Craig and Gordon (1965), Merlivat and Jouzel (1979), Criss (1999), and Luz et al. (2009), the fractionation factor during nonequilibrium evaporation is

$$\alpha_{evap} = \frac{R_o}{R_e} = \frac{\alpha_{eq}\alpha_{diff}(1 - \mathrm{RH}_n)}{1 - \alpha_{eq}\mathrm{RH}_n(R_v/R_o)} \tag{7}$$

where R_e is the isotope ratio of the evaporate, R_o is that of the ocean, R_v is that of the free atmosphere. The isotope ratios of the surface ocean vary globally (Epstein and Mayeda, 1953; Craig and Gordon, 1965; Schmidt et al., 1999; Bonne et al., 2019), though generally are fairly close to 0 (in both $\delta^{18}O$ and δD), and vary substantially less than the isotope ratios in vapor and precipitation. The isotopic ratios of the ocean do change through time, particularly as the reservoir size of grounded ice sheets grow and shrink over glacial cycles (e.g., Lisiecki and Raymo, 2005, Bintanja and Van de Wal, 2008). As the ice sheets grow, more of light isotopologues of water are locked up in the ice while the heavier isotopologues accumulate in the oceans. It can be useful to correct the water-isotope records in ice cores for such changes when possible (Petit et al., 1999; Stenni et al., 2010; Uemura et al., 2012; Markle and Steig, 2022).

Moisture transport and precipitation

Once evaporated, the motions of the atmosphere will generally transport water vapor upward and poleward, on average, in the climate system's ceaseless, Sisyphean objective to satisfy global energy balance (Hartmann, 2015). On this journey the air will lift and cool, and the saturated vapor pressure will decrease nonlinearly. Initially undersaturated air will saturate forming condensation, which will leave the system as precipitation. Additional cooling leads to further condensation and precipitation, progressively removing water from the atmosphere.

This progressive, fractional removal of constituents from a large reservoir is called a Rayleigh distillation process (Rayleigh, 1902) and is responsible for describing the distributions of water-isotope ratios in vapor and precipitation (Dansgaard, 1953, 1964). The relationship describing how water-isotope ratios fractionate under these conditions is straightforward:

$$\frac{d \ln (R_v)}{d \ln (f)} = \alpha - 1 \tag{8}$$

where R_v is the isotope ratio of the vapor, α is the appropriate fractionation factor, and f is the fraction of initial water remaining in the air parcel. In a pseudo-adiabatic cooling process, which can be roughly applied to average poleward moisture transport (Bailey et al., 2019), the fraction of initial vapor remaining simply follows the nonlinear decline of the Clausius–Clapeyron relationship given the temperature gradient through which it is cooled (Dansgaard, 1953, 1964), or something close to it (Criss, 1999; Markle and Steig, 2022), though of course in reality atmospheric mixing can modify this picture (Risi et al., 2013; Bailey et al., 2019; Markle and Steig, 2022).

If condensation is happening at saturation, then the appropriate α is simply the equilibrium fractionation factor. Non-equilibrium conditions and thus kinetic fractionation can exist in the presence of both liquid and ice condensate, owing to the difference of the saturation vapor pressures over each phase, or in the absence of condensation nuclei (Jouzel and Merlivat, 1984; Ciais and Jouzel, 1994; Hong et al., 2004; Hu et al., 2010). In these supersaturated conditions, Eq. (8) becomes:

$$d \ln (R) = (\alpha_{eq}\alpha_k - 1)d \ln (f) \tag{9}$$

where the kinetic fractionation factor, α_k, depends on the ratio of the diffusivities of the isotopologues and the supersaturation of vapor over ice, S_i (Jouzel and Merlivat, 1984):

$$\alpha_k = \frac{S_i}{\alpha_{eq} \times \frac{D}{D^*}(S_i - 1) + 1} \tag{10}$$

Falling condensation may continue to interact with the atmosphere (Dansgaard, 1964). Re-evaporation can enrich the precipitation in the heavier isotope if the atmosphere is undersaturated (Dansgaard, 1964; Bony et al., 2008; Risi et al., 2010; Galewsky et al., 2016).

It is this integrative, progressive distillation process, driven by large-scale poleward moisture transport, that enables polar precipitation to become so dramatically depleted in heavy isotopes and reach such negative delta values (Dansgaard, 1953, 1964). Indeed, the delta values of typical snow on the polar ice sheets are far too negative, far too removed from average ocean water, to be produced without the integrative distillation achieved by atmospheric moisture transport.

This distillation process is inherently nonlinear; the change in the isotope ratio during condensation depends on the ratio itself, the definition of exponential decay. The fraction of water remaining, f, is a nonlinear function of temperature following the temperature dependence of Clausius–Clapeyron. These two nonlinear effects combine to result in a relationship between the δ values of precipitation and condensation temperature that is approximately linear (Dansgaard, 1954, 1964) [though not exactly
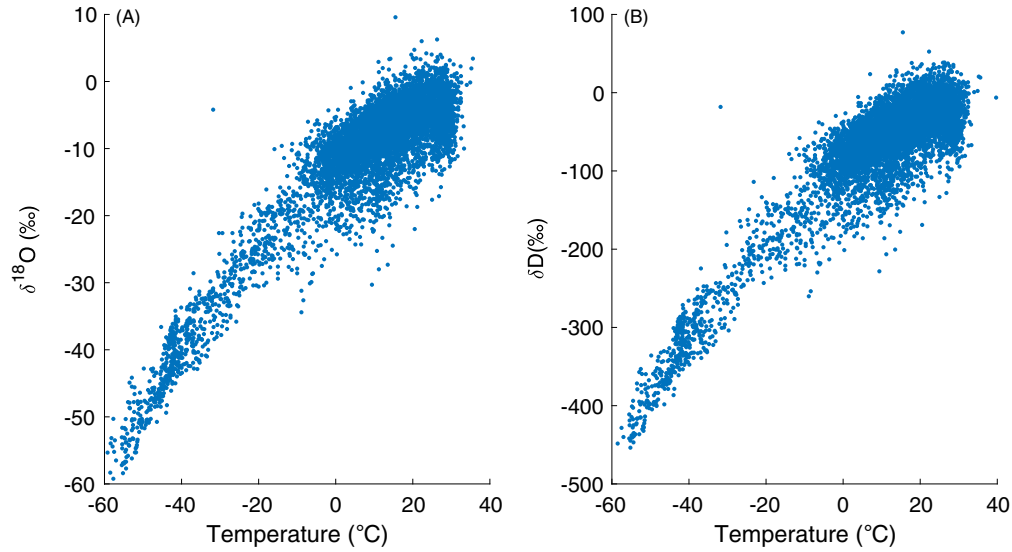
Fig. 4   The relationship between monthly surface temperature and (A) the $\delta^{18}O$ of monthly precipitation and (B) the δD of monthly precipitation. Precipitation isotope data from the GNIP database (IAEA, 2001) and Antarctic surface snow (Masson-Delmotte et al., 2008).
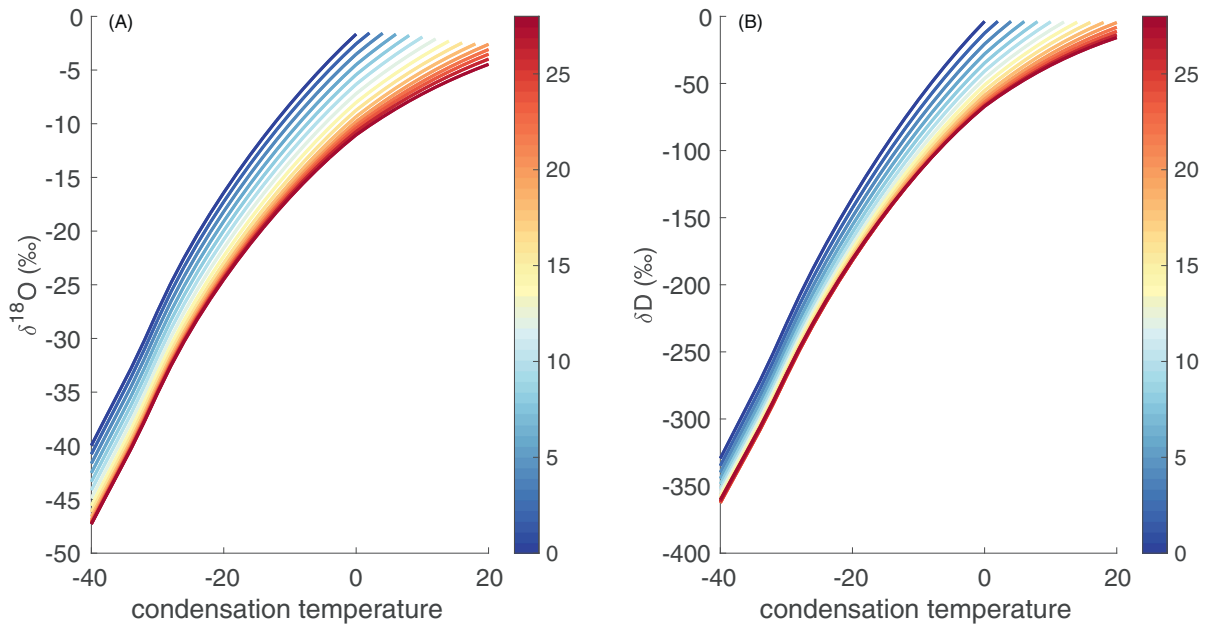

Fig. 5   A simple water-isotope distillation model (Markle and Steig, 2022). (A) The relationship between the $\delta^{18}O$ of precipitation and air temperature at condensation for multiple different pseudo-adiabatic cooling pathways, given by different initial air temperatures (*color of lines*, °C). The differing initial air temperatures also set the initial vapor isotope composition. (B) Same as the left panel but for the relationship between the δD of precipitation and air temperature at condensation.

linear (Markle and Steig, 2022)] and drive the long-observed and compelling relationship between decreasing δ values of precipitation and decreasing surface temperature (Dansgaard, 1964) (Fig. 4).

Simple water-isotope distillation models (Dansgaard, 1964; Aldaz and Deutsch, 1967; Jouzel and Merlivat, 1984; Ciais and Jouzel, 1994; Kavanaugh and Cuffey, 2003; Markle and Steig, 2022) can take into account these essential processes and capture the basic relationships between climate and water-isotope ratios (e.g., Fig. 5) as can intermediate complexity models (Dee et al., 2015, 2023) and water-isotope-enabled Global Climate Models (e.g., Hoffmann et al., 1998, Hoffmann et al., 2000, Brady et al., 2019, Bailey et al., 2019).

The strong empirical relationship between δ values of precipitation and air temperature (Fig. 4) is the result of fundamental aspects of climate and water. First, the temperature dependence of the saturated vapor pressure of water arises from the binding

energy between water molecules and the definition of temperature. Next, the climate system moves heat down energy gradients, which leads water to be condensed from the atmosphere owing to the temperature-dependent saturated vapor pressure. Third, the differences in the saturated vapor pressures of different isotopologues of water cause fractionation, which, combined with Rayleigh distillation, links water transport, precipitation, and the distillation of isotopologues. The temperature dependence of the fractionation factors does not drive the relationship between δ values and temperature, though it do amplify it (it should be noted that the temperature dependence of the equilibrium fractionation factors results from the same physics that result in fractionation factors in the first place). In this view the temperature at condensation is important, though largely because it represents the thermodynamic end of interconnected large-scale moisture transport. Processes in addition to simple distillation influence the water-isotope values of polar precipitation. However, large-scale moisture transport is so fundamental to the functioning of the climate system that over long enough timescales, large enough spatial scales, or in the presence of large enough forcing, it exerts a very strong lever on the water-isotope ratios of polar precipitation.

Second-order water-isotope parameters

The oxygen and hydrogen water-isotope systems largely behave the same within meteoric waters, though there are some key differences, namely that the δD fractionates proportionally more than the $\delta^{18}O$. Craig (1961) first quantified the relationship in global precipitation as $\delta D = 8 \times \delta^{18}O + 10$. Deviations from this line of best fit (Fig. 6) define the "deuterium excess" parameter (Dansgaard, 1964), the amount of deuterium in excess of the global relationship:

$$d_{xs} = \delta D - 8 \times \delta^{18}O \qquad (11)$$

The deuterium excess is a second-order water-isotope parameter, which is sensitive to, among other things, nonequilibrium process like kinetic fractionation. The linear slope of 8 is not fundamental; though the rough magnitude may stem from relative mass differences between isotopes (Hoefs, 1997) (though not isotopologues), it is not the result of theoretical equilibrium fractionation (Craig, 1961). In a Rayleigh process occurring solely under equilibrium conditions, the slope of the $\delta^{18}O$ and δD relationship is not linear. The relationship between $\ln(1 + \delta^{18}O)$ and $\ln(1 + \delta D)$ would, under such a process, show a slope of $\frac{1 - {}^{D}\alpha_{eq}}{1 - {}^{18}\alpha_{eq}}$ (Craig, 1961), which is a number close to 8, but even here the slope isn't precisely 8 and is variable as the equilibrium fractionation factors are fundamentally functions of temperature.

The approximate linearity of $\delta^{18}O$ and δD is largely a coincidence (Craig, 1961) of competing processes that are each slightly nonlinear over the range of conditions most commonly experienced by meteoric waters, but compensating. However the underlying nonlinearities can be important. The linearly defined deuterium excess is not a conserved quantity; even under equilibrium-only
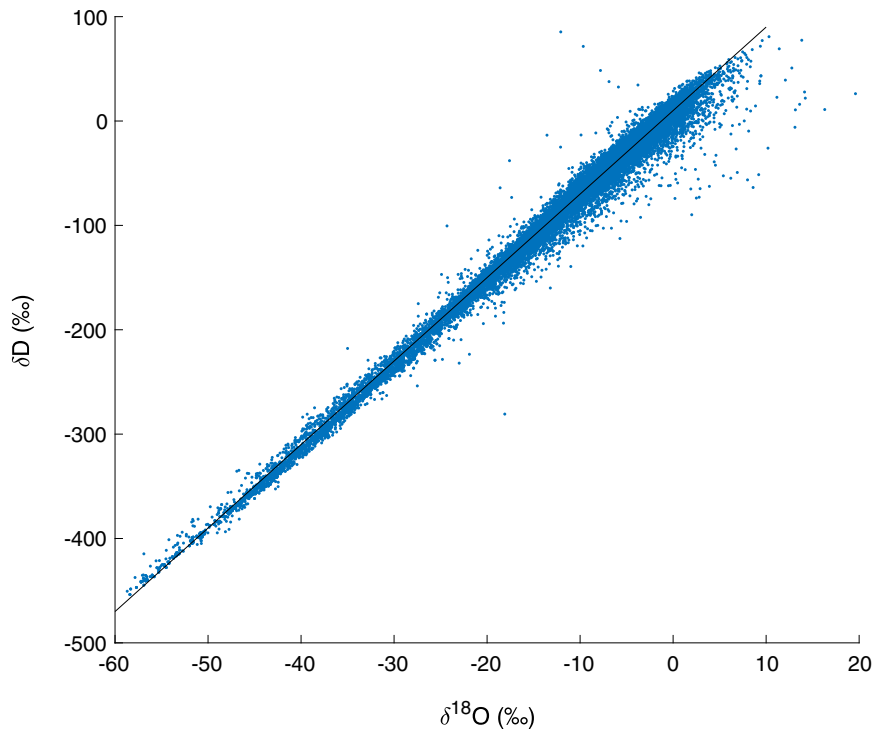

Fig. 6 The global relationship between δD and $\delta^{18}O$ in precipitation. A line with a slope of 8 is shown in *black*. Data come from the GNIP database (IAEA, 2001), the Waterisotopes.org database (Bowen, 2023; West et al., 2009), and a compilation of surface Antarctic snow from Masson-Delmotte et al. (2008). A comparatively small amount of additional data from Markle and Steig (2022) is also included.

conditions, the parameter has nonlinear biases that become increasingly important as precipitation becomes increasingly depleted in the heavy isotope, as in Antarctic precipitation (Uemura et al., 2012; Markle et al., 2017; Dütsch et al., 2017; Markle and Steig, 2022). Recognizing these limitations, Uemura et al. (2012) fit a second-order polynomial to a compilation of $\ln(1 + \delta^{18}O)$ and $\ln(1 + \delta D)$ data to define a phenomenological, nonlinear deuterium excess parameter:

$$d_{ln} = \delta'D - \left(A \times \left(\delta'^{18}O \right)^2 + B \times \delta'^{18}O \right) \tag{12}$$

where $\delta'_x = ln(1 + \delta_x)$ is a modified form of the delta value more directly related to the distillation process (Craig, 1961), $A = -28.5$, and $B = 8.47$ (note that the coefficients and δ' values are unitless; for example $\delta'^{18}O = -0.020$, not -20 with the ‰ dropped). This empirical nonlinear parameter reduces many of the biases of the linear parameter making it a more useful proxy for many paleoclimate and ice core applications (Uemura et al., 2012; Markle et al., 2017; Markle and Steig, 2022).

Another second-order water-isotope parameter similarly relates the weighted difference between the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios (Angert et al., 2004; Barkan and Luz, 2005, 2007),

$$^{17}O_{xs} = \delta'^{17}O - 0.528 \times \delta'^{18}O \tag{13}$$

Water with ^{17}O and water with ^{18}O largely behave similarly, though again there are subtle differences, which the $^{17}O_{xs}$ attempts to quantify. In particular, kinetic effects should be especially quantifiable by this metric though it requires very precise measurements as the deviations from the expected relationships are around three orders of magnitude smaller than for the deuterium excess (e.g., Angert et al., 2004, Barkan and Luz, 2005, Uemura et al., 2010).

Postdepositional effects

Once snow precipitates onto the ice sheets, it continues to interact with vapor, which can modify it's water-isotope ratios. The idea that sublimation in particular may have a fractionation effect on snow in the formation of glacier ice is far from new (Jensen, 1953), though details about these interactions are an increasing focus of study. Researchers have demonstrated the constant interaction of the vapor and the surface snow on glaciers with both sublimation and condensation leading to fractionation (Landais et al., 2012; Steen-Larsen et al., 2013; Wahl et al., 2021). As vapor just above the surface is often saturated with respect to ice, many of these interactions may tend toward equilibrium isotopic exchange, though in the presence of supersaturation, kinetic fractionation processes may also affect the snow (Steen-Larsen et al., 2011, 2013; Casado et al., 2016; Wahl et al., 2021, 2022), just as they do aloft in the atmosphere. These processes are not well accounted for in many models used to guide the quantitative interpretation of water-isotope ratios in ice cores.

While direct interactions between the snow and the free atmosphere penetrate a few centimeters into the polar snowpack, this can potentially represent a nontrivial amount of stratigraphic time in low accumulation areas. Further, the upper 10s of meters of snowpack, the firn, are porous and water vapor in these pore spaces interacts with the surrounding ice matrix. In particular above the depth at which the pore spaces close into bubbles, water vapor diffuses and equilibrates with the surrounding ice (Johnsen, 1977; Whillans and Grootes, 1985). An impact of this process is to smooth out variability in the initially deposited isotope stratigraphy (Johnsen, 1977; Whillans and Grootes, 1985; Cuffey and Steig, 1998; Johnsen et al., 2000). The amount of total smoothing increases over the time between deposition and compaction to glacial ice, which diminishes initial water-isotope signals at depth, a feature noted from the earliest water-isotope measurements from ice cores (Langway, 1965). Water isotopes continue to diffuse in solid ice though the rates are extremely slow (Johnsen et al., 2000). Ultimately the diffusion processes in the firn are driven by similar fractionation physics that influence water elsewhere in the climate system and are sensitive to variables such as temperature. Vapor diffusion in the firn can be constrained from the spectra of high-frequency variance in water-isotope ratios and used to better understand local climate (Johnsen et al., 2000; Holme et al., 2018; Jones et al., 2017a; Kahle et al., 2021; Gkinis et al., 2021a).

Key advances in understanding climate history from water-isotope records in ice cores

We now return to the advances in understanding past climate made though the recovery, analysis, and interpretation of ice-core water-isotope records. The amount we learned from the first two deep ice-core water-isotope records, from Camp Century in Greenland (Dansgaard et al., 1969) and Byrd Station in Antarctica (Epstein et al., 1970), is remarkable. In some ways, it is surprising how little we have learned since. While that may be a bit of hyperbole, these first records show the essential features, mysteries, and challenges of many future ice-core records.

The 1390-m Camp Century record from Greenland contains 100,000 years of climate history (Dansgaard et al., 1969). This record captures the relatively stable Holocene, the last deglaciation and warming out of the last ice age, including the Bølling and Aleroed interstadials, the Last Glacial Maximum, multimillennial variations the authors thought might be related to orbital precession during the last glacial period, and a preceding warm interval which the authors interpret to be the Eemian interglacial. Dansgaard et al. (1969) found remarkable correspondence between this novel climate record and existing paleoclimate evidence such as a pollen record, an ocean oxygen isotope record, and evidence of the timing of the advance and retreat of the Laurentide ice sheet. The authors broadly interpreted the $\delta^{18}O$ record as relative local temperature change though they did not make an explicit, quantitative reconstruction of temperature. This was due to a number of potential competing influences that could limit their quantitative certainty including flow of the ice in deeper layers from a different deposition site and potential changes in ice flow

through time, potential changes in the thickness of the ice sheet, potential changes in the isotopic signature of seawater through time (Dansgaard and Tauber, 1969), and potential changes in seasonality of precipitation. All of these remain challenges for ice core interpretation today.

The 2164-m record from Byrd Station on the West Antarctic Ice Sheet was published soon after the Camp Century record (Epstein et al., 1970). Despite the vastly greater depth reached in Antarctica, the authors believed this record also reached back approximately 100,000 years. Epstein et al. (1970) presented both $\delta^{18}O$ and, for the first time on a deep ice core, δD for the Byrd record (while both isotopes were measured on Camp Century, the δD measurements were only made on a comparatively small sample, while $\delta^{18}O$ was measured for the whole record). The Byrd $\delta^{18}O$ and δD show extremely similar changes through time and a relative scaling (a slope of $\delta D = 7.9 \times \delta^{18}O$) slightly different than was then known for other regions. The authors noted that these slight differences may, in the future, be used to discern additional, subtle information about environmental conditions in the past (indeed, using exactly these differences in the $\delta^{18}O$ and δD has proved remarkably useful since, as we shall see). They found that the timing of the last ice age and deglaciation was largely synchronous between Antarctica and Greenland. While noting many of the same complications as Dansgaard et al. (1969), they make, for the first time, a quantitative temperature estimate for the warming from the last glacial period to the Holocene for Antarctica, suggesting it warmed 7–8°C, using an empirical $\delta^{18}O$ to temperature scaling from the South Pole (Aldaz and Deutsch, 1967). They note interstadial variations in Antarctica that appeared to correspond in timing to interstadial anomalies in the Greenland core (again, a prescient observation).

After these initial cores, an open question remained as to how much of the variability found in these water-isotope records could be tied to large-scale climate changes versus local, site-specific effects (Dansgaard et al., 1982). While broad-scale changes were observed both in Greenland and Antarctica (Epstein et al., 1970), questions remained, particularly when an ice core from the Devon ice cap showed only some shared features with the Camp Century core (Paterson and Clarke, 1978; Dansgaard et al., 1982). Subsequent ice-core water-isotope records from both ice sheets removed any doubt that the water-isotope ratio proxy could record at least regional changes in climate and the hydrologic cycle. Deep ice-core drilling in the 1970s in Antarctica at Vostok Station and Dome C produced important water-isotope records that, in comparison with the earlier Byrd record, confirmed Antarctic-wide changes in climate, spanning both the East and West Antarctic ice sheets rather than site-specific or ice-sheet related changes (Lorius et al., 1979). These records further revealed potentially synchronous millennial-scale oscillations in climate at the end of the deglaciation (through the Younger Dryas and Bølling–Allerod periods) also seen in the Camp Century core and provided estimates of surface temperature change in East Antarctica for the warming since the last glacial period (Barkov, 1977; Lorius et al., 1979; Jouzel et al., 1981).

In Greenland, a new water-isotope record was produced from the Greenland Ice Sheet Project (GISP), drilled at the Dye-3 station (Dansgaard et al., 1982), and provided important and surprising results. Essentially all of the $\delta^{18}O$ oscillations in the Dye 3 core down to 50 m can be correlated to the previously found oscillations in the Camp Century core (to 75 m), which suggested that the oscillations could be attributed to changes in climate in the North Atlantic region as opposed to any local effects. The Dye-3 isotope record also showed convoluted influence of ice flow and folding near the bottom of the ice sheet (Dansgaard et al., 1982). The records of both Dye-3 and Camp Century revealed rapid, large amplitude millennial-scale jumps in $\delta^{18}O$ during the last glacial period, synchronous at both sites (Dansgaard et al., 1982; Oeschger, 1985; Langway et al., 1985). Dansgaard et al. (1982) suggested that these oscillations indicated rapid changes in climate in the North Atlantic region that could be related to shifts between two different quasistationary modes of atmospheric circulation or climate, and established a tentative link to marine records of climate (Oeschger, 1985). These features were later found to be synchronous with other paleoclimate archives from ice cores and elsewhere, now known as Dansgaard–Oeschger (D-O) events, representing intriguing oscillations of the coupled climate system that remain incompletely understood even decades later.

The general patterns of climate indicated by water-isotope ratios in Greenland, including all the rapid D-O events, have been found to be broadly coherent across all subsequent cores drilled in Greenland (Johnsen et al., 2001) (Fig. 7). The GRIP and GISP2 cores, drilled just 30 km apart (Jouzel, 2013), allow the assessment of the shared and unshared variability in water-isotope ratios, and that which could be related to local and regional climate rather than noise within the proxy (Grootes and Stuiver, 1997; Stuiver et al., 1995; Grootes et al., 1993; Johnsen et al., 2001).

The rapid and unexplained climate changes revealed in the Greenland water-isotope records were revelations, though because of the age of the ice sheet, clear records through and beyond the last interglacial period have not been recovered. However, researchers in Antarctica steadily pushed the frontier of deeper time for ice-core water-isotope records. A series of cores from Vostok Station lead the way in these discoveries (Jouzel, 2013). Records of $\delta^{18}O$ (Lorius et al., 1985) and δD (Jouzel et al., 1987) on the second deep Vostok ice core were able to reach back over 150,000 years revealing an entire glacial cycle. Using both the $\delta^{18}O$ and δD records, Jouzel et al. (1987) improved isotope-based temperature reconstructions, probing the validity of using modern isotope–temperature relationships for reconstructions of the past. New deep Vostok cores extended the record even further to the penultimate glacial period 200,000 years ago (Jouzel et al., 1993), then to 260,000 years (Jouzel et al., 1996), and finally to over 420,000 years and a total depth of 3350 m (Petit et al., 1999; Jouzel, 2013). Using local empirical water-isotope-temperature scaling, and correcting for changes in the oxygen isotope ratios of global seawater, then known from marine sediment cores, Petit et al. (1999) reconstruct temperature for the Vostok site, both of the effective condensation temperature in the atmosphere and at the surface, finding glacial–interglacial changes of about 8°C and 12°C for each, respectively. They were thus able to make detailed study of climatic changes between multiple glacial cycles, finding the consistent sawtooth pattern of these cycles with comparatively rapid warming out of glacial periods and slower cooling into them. They found somewhat different durations for some glacial cycles, common minimum temperature during glacial periods but relatively different maximum temperature during interglacials.
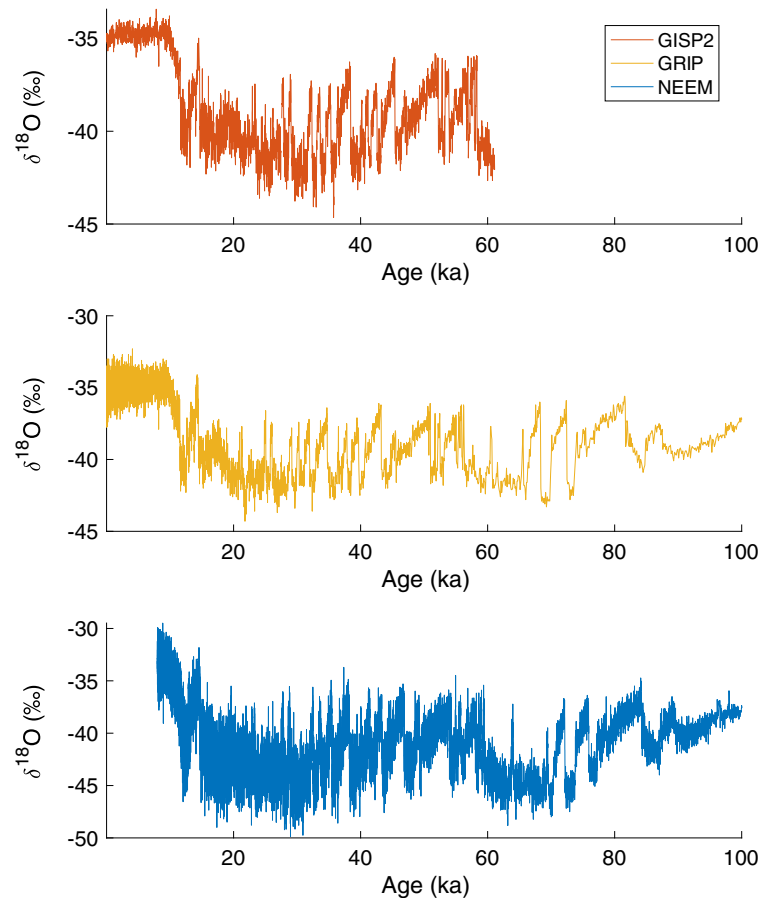
Fig. 7 Ice-core records of δ^{18}O from a few Greenland ice cores: the GISP2 ice core (Grootes and Stuiver, 1997; Stuiver et al., 1995) (in *red*), the GRIP core (Grootes et al., 1993; Johnsen et al., 2001) (in *gold*), and the more recent (very high resolution) NEEM ice core Gkinis et al. (2020, 2021b) (*blue*). All records show the warming from the Last Glacial Maximum (20,000 years ago) into the Holocene as well as a series of abrupt climate change events throughout the last glacial period.

Petit et al. (1999) suggested that the record indicated relative stability of the West Antarctic Ice Sheet (WAIS) across glacial cycles, or at least a remarkable insensitivity of East Antarctic climate to large changes in the WAIS. Importantly these records also demonstrated the robust coherence of water-isotope records of climate with other paleo-proxies from ice cores, perhaps most importantly those of the greenhouse gases CH_4 and CO_2 (Genthon et al., 1987; Petit et al., 1999). They showed that both temperatures at Vostok, as indicated by the water-isotope ratios, as well as these gases were higher in two previous interglacial periods than during the Holocene.

The age limit for continuous ice-core water-isotope records was pushed significantly further by two more East Antarctic efforts. The European Project for Ice Coring in Antarctica (EPICA) returned to Dome C, recovering a core to 3260 m, providing a more than 800,000-year-long record (EPICA Community Members, 2004). At Dome Fuji, the Japanese National Institute for Polar Research drilled two cores, covering multiple glacial cycles (Watanabe et al., 2003; Kawamura et al., 2007; Uemura et al., 2012), with the deepest to 3035 m and 720,000 years of water-isotope history (Motoyama, 2007). The Dome C record of eight glacial cycles (EPICA Community Members, 2004) (Fig. 8) provided tremendous and detailed insight on changes to Earth's climate in response to orbital forcing (Jouzel et al., 2007a; Masson-Delmotte et al., 2010) and presented a test for Earth system modeling (Wolff et al., 2004). Indeed, as water isotopes have been included into complex climate models, ice-core records such as these have provided critical tests cases (Jouzel et al., 2000; Werner et al., 2018). These records represent the longest continuous ice-core water-isotope record to date, though snapshots from even older ice (at least 2 million years old) have been recovered from other Antarctic sites (e.g., Yan et al., 2019).

Water-isotope records from temporally shorter, but higher-resolution Antarctic ice cores, paired with finely resolved age-scales, enabled researchers to examine detailed questions about relative phasing of climate. For example, the next EPICA project at Dronning Maud Land confirmed that every rapid climate change event in Greenland had a corresponding, though different in magnitude and temporal character, isotope signal in Antarctica (EPICA Community Members et al., 2006). An extremely high-resolution record from the West Antarctic Ice Sheet Divide (WAIS Divide Project Members et al., 2013), with very well-constrained synchronization to the Greenland ice-core records, was able to determine the precise phasing between the hemispheres during these events (WAIS Divide Project Members et al., 2015) and identified both synchronous (Markle et al., 2017) and lagged (WAIS Divide Project Members et al., 2015) aspects of Southern Hemisphere climate, compared to North Atlantic climate, using water-isotope records.
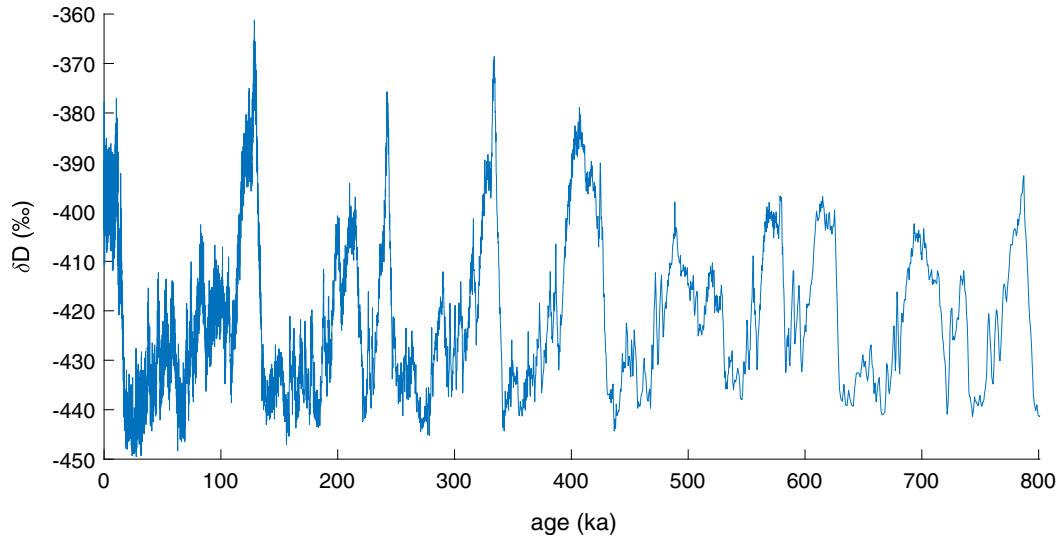
Fig. 8 The 800,000-year-long Dome C δD record (Jouzel et al., 2007a). Along with corresponding δ^{18}O measurements (e.g., Landais et al., 2021, not shown), these are the longest continuous ice-core water-isotope records, revealing eight glacial cycles.

A number of deep Antarctic records have been developed that span at least through the last deglaciation and into the last ice age (Fig. 9). As in Greenland (Fig. 7), these records largely show coherent climatic histories.

Rapid advances in measurement techniques (e.g., Gkinis et al., 2011, Jones et al., 2017b) are opening frontiers in water-isotope resolution in ice cores, enabling studies of high-frequency climate variability over long periods of time (e.g., Jones et al., 2018) and quantification of postdepositional changes (e.g., Gkinis et al., 2014). As an example, Fig. 10 shows the first published discrete δD record from the WAIS Divide ice core (light blue) (WAIS Divide Project Members et al., 2013; Markle et al., 2017), which at the time
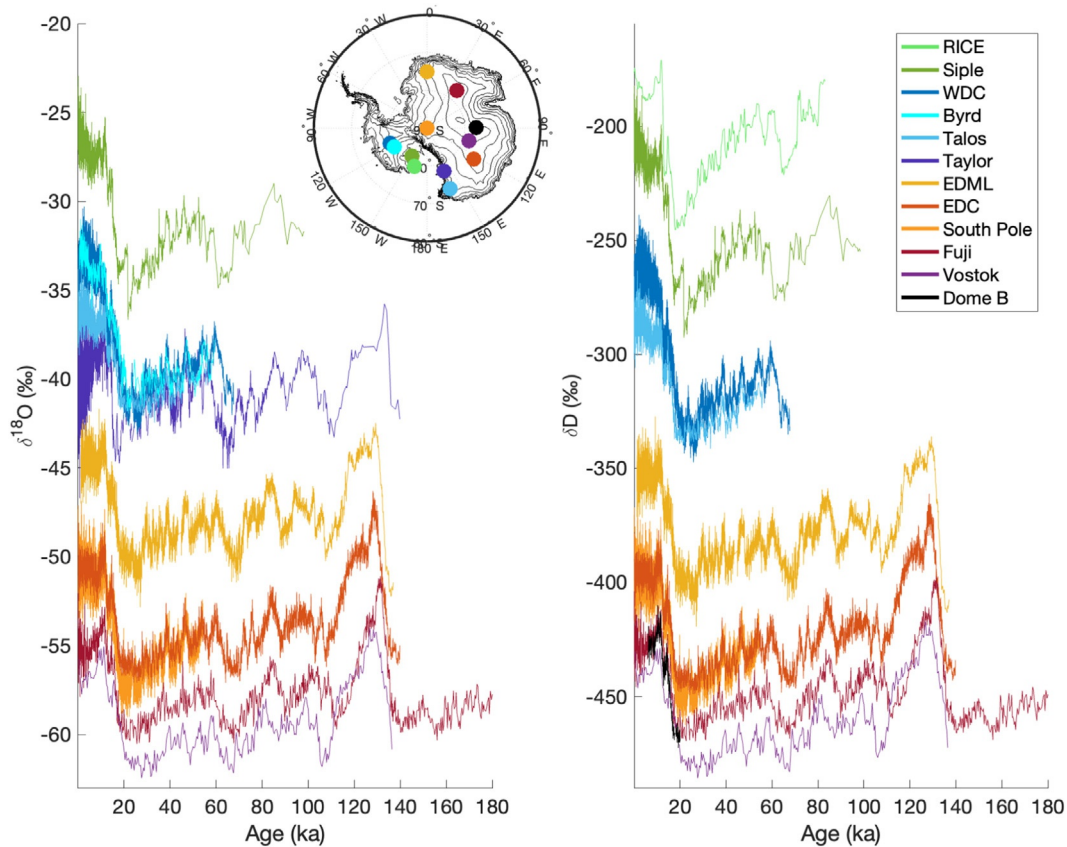

Fig. 9 Ice-core records of δ^{18}O and δD from several deep Antarctic ice cores. The records include WDC (Markle et al., 2017; WAIS Divide Project Members et al., 2013; Steig et al., 2013), Siple Dome (Brook et al., 2005; Schilla, 2007), EDML (Stenni et al., 2010), EDC (Stenni et al., 2010), Vostok (Vimeux et al., 2002), Dome Fuji (Uemura et al., 2012), Talos Dome (Stenni et al., 2011), Taylor Dome (Steig et al., 2000; Steig, 2006), South Pole (SP, Steig et al., 2021), Byrd (Epstein et al., 1970), Roosevelt Island is also plotted (RICE, Lee et al., 2020), and Dome B (Jouzel et al., 1995). *Inset* shows location of cores on the continent.
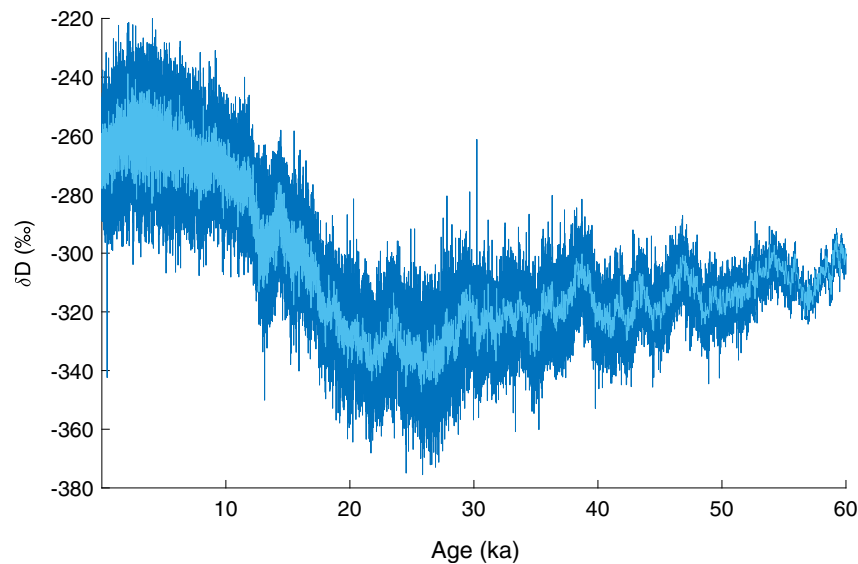
Fig. 10   Records of δD from WAIS Divide, showing the comparative resolution of discretely measured 0.5-m samples (*light blue*) (WAIS Divide Project Members et al., 2013; Markle et al., 2017), and continuously measured (approximately 0.01 m) samples (*dark blue*) (Jones et al., 2018).

of publication was the highest resolution Antarctic record spanning the last deglaciation. Also shown is the continuously measured δD from the same core in extraordinarily high resolution, published just a few years later (dark blue) (Jones et al., 2018).

Moisture source reconstructions

Although the potential to make use of the differential influence of the hydrologic cycle on the oxygen and hydrogen isotopes of water was identified early on (Dansgaard, 1964; Epstein et al., 1970), δ^{18}O and δD were largely used independently or in a corroborative sense, for early ice-core water-isotope studies. With increased theoretical understanding of the important processes, particularly at the moisture source (Merlivat and Jouzel, 1979) and during atmospheric transport (Jouzel and Merlivat, 1984), researchers began to use the deuterium excess parameter to understand more about global climate than just temperatures over the ice sheet. To highlight just a few examples, the deuterium excess signal in the original Dome C core (Jouzel et al., 1981, 1982) suggested higher relative humidity over the Southern Ocean during the last glacial period compared to the Holocene. In alpine ice cores, the deuterium excess could better resolve seasonal signals than either isotope ratio independently (Stichler et al., 1982). Deuterium excess measurements from modern snow and from the Dye-3 ice core (White et al., 1988; Johnsen et al., 1989) were used to determine the moisture source origins of Arctic precipitation, as well as Antarctic precipitation (e.g., Ciais et al., 1995, Uemura et al., 2008). Deuterium excess records also later showed abrupt changes in the moisture origins of precipitation reaching Greenland during D-O events (Masson-Delmotte et al., 2005; Jouzel et al., 2005, 2007b; Steffensen et al., 2008), and corresponding rapid changes in Antarctic moisture sources (Buiron et al., 2012; Markle et al., 2017; Buizert et al., 2018) related to global shifts in atmospheric circulation. Deuterium excess records have shown longer, orbital scale changes in moisture source conditions in Antarctica (e.g., Stenni et al., 2010, Uemura et al., 2012) and have been used to improve local temperature reconstructions to better resolve covariance between climate and the carbon cycle (Cuffey and Vimeux, 2001) .

While the linearly defined deuterium excess parameter has issues of artifacts and bias in waters that are particularly depleted in heavy isotopes such as in Antarctic precipitation (Uemura et al., 2012; Markle et al., 2017; Markle and Steig, 2022), the nonlinear deuterium excess parameter, d_{ln}, more faithfully preserves initial moisture source conditions (Markle and Steig, 2022). In fact, d_{ln} records are remarkably more coherent across timescales and across the Antarctic continent (Markle et al., 2017; Markle and Steig, 2022) (Fig. 11).

As measurement techniques improved to allow precise measurements of δD, δ^{18}O, and δ^{17}O (Barkan and Luz, 2005; Uemura et al., 2010; Steig et al., 2021), the $^{17}O_{excess}$ in polar ice cores has, for example, been used to understand changes in moisture source relative humidity (Landais et al., 2008; Risi et al., 2010), and the effects of supersaturated condensation formation and sea ice changes (Schoenemann et al., 2014).

Advances in quantitative temperature reconstructions

Reconstructing temperature from water-isotope records ultimately rests on the fundamental relationships between air temperature, the hydrologic cycle and its role in climate, and the physics of isotope fractionation, as described above. Quantitative reconstructions of temperature ultimately rely on models, for example statistical models using the observed relationship between temperature and isotope ratios in modern snow (Epstein et al., 1970; Petit et al., 1999; Jouzel et al., 2007a). Such an approach has the potential issue that it can conflate changes in other aspects of the hydrological cycle that also influence water-isotope ratios at the ice core site, such as changes in moisture source conditions, with changes in condensations site temperature (Jouzel et al., 2007a).
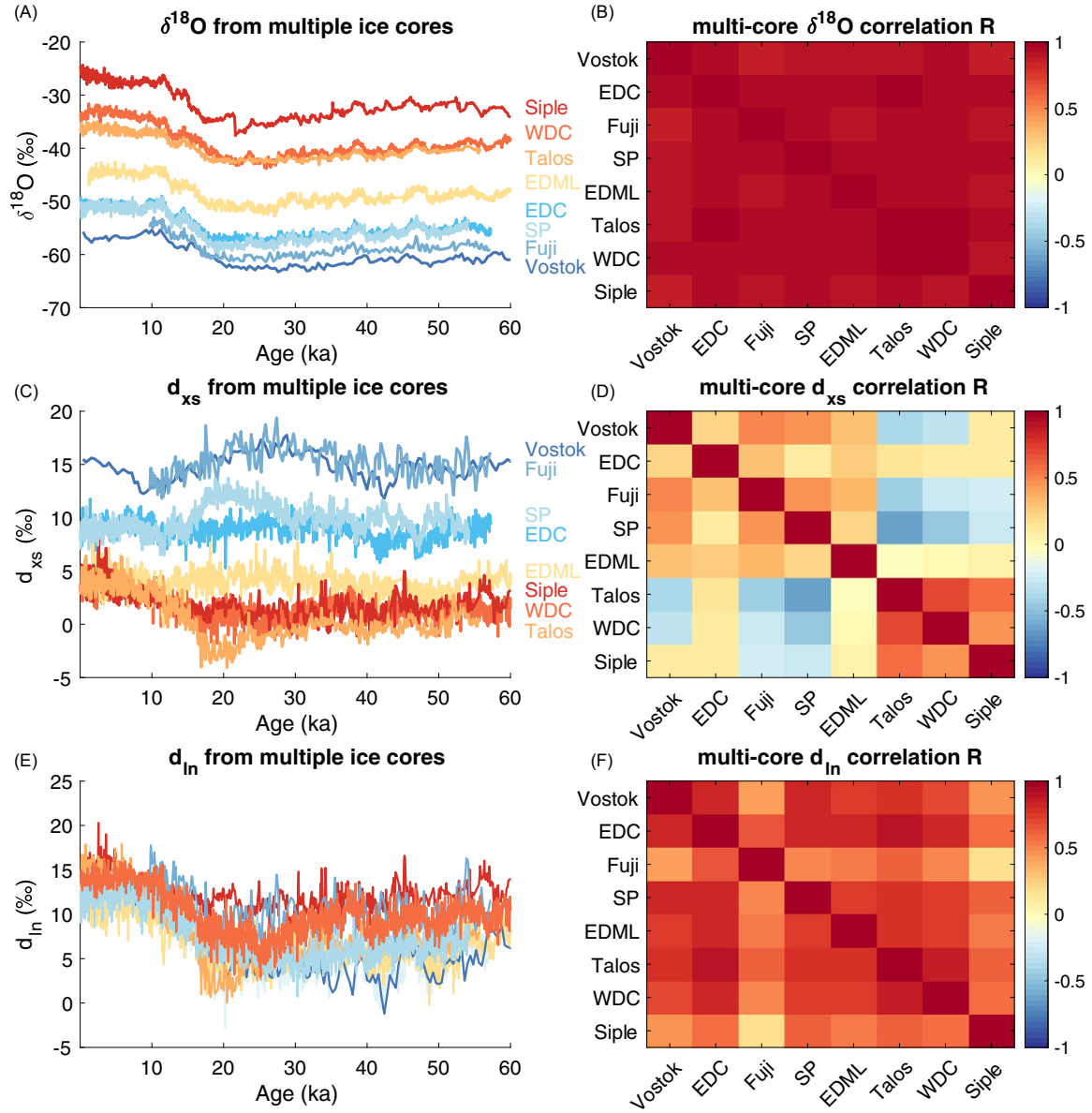
Fig. 11 Time series and cross-correlation matrices for eight different deep Antarctic ice core sites adapted from Markle and Steig (2022). The records include WDC (Markle et al., 2017; WAIS Divide Project Members et al., 2013; Steig et al., 2013) and Siple Dome (Brook et al., 2005; Schilla, 2007) from West Antarctica, as well as the EDML (Stenni et al., 2010), EDC (Stenni et al., 2010), Vostok (Vimeux et al., 2002), Dome Fuji (Uemura et al., 2012), Talos Dome (Stenni et al., 2011), and South Pole (SP, Steig et al., 2021) records from East Antarctica. (A, B) δ^{18}O; (C, D) d_{xs}; and (E, F) d_{ln}. In the time-series plots, each record is colored by its Holocene average δ^{18}O value. All records are ordered by their approximate modern surface temperature in the cross-correlation matrices. All original records are interpolated to even 50-yr time spacing on the Buizert et al. (2018) synchronized timescale where possible, or they are plotted on original published timescales. The cross-correlation pattern in (D) shows that d_{xs} correlations switch sign as a function of the total depletion at the site, an artifact of biases inherent to the linear definition (Markle and Steig, 2022).

Moisture source conditions (e.g., relative humidity, air and sea surface temperature, sea surface isotope ratios) are not the only potential confounding variables but they are important as they can drive the total amount of distillation and initial isotope ratios of vapor.

Because of the integrated influence on moisture transport in the atmosphere, a common approach to quantitative temperature reconstructions from water-isotope records requires reconstructing both changes in moisture source and deposition site conditions. Reconstructing these two unknowns requires two constraints, which is possible since both the oxygen and hydrogen isotope ratios are influenced by this same process in subtly different ways. One can construct a system of equations to disentangle the confounding influence of site and source conditions on changes ice-core water-isotope ratios (Petit et al., 1999; Jouzel et al., 1997; Cuffey and Vimeux, 2001; Vimeux et al., 2002; Kavanaugh and Cuffey, 2002; Stenni et al., 2010; Uemura et al., 2012). For example,

$$\Delta\delta^{18}O = \gamma_1 \Delta T_{site} + \gamma_2 \Delta T_{source} \tag{14}$$

$$\Delta d_{xs} = \beta_1 \Delta T_{site} + \beta_2 \Delta T_{source} \tag{15}$$

where $\Delta\delta^{18}O$ and Δd_{xs} are changes in isotope ratios driven by changes in both precipitation site temperature and evaporation source temperature, ΔT_{site} and ΔT_{source}. Here, β and γ are the scaling relationships of $\delta^{18}O$ and d_{xs} with site and source temperature, respectively, which can be determined from observations or distillation models (Vimeux et al., 2002; Kavanaugh and Cuffey, 2002; Stenni et al., 2010; Uemura et al., 2012). This system of equations is then simply solved for ΔT_{site} and ΔT_{source} (Vimeux et al., 2002; Stenni et al., 2010; Uemura et al., 2012).

In the most general sense the "site" temperature is the vertically integrated, condensation-weighted (including interaction between the precipitate and vapor either during snowfall or at the ice sheet surface) air temperature, over some suitably long time interval rather than the surface temperature or, for example, the inversion temperature. Relationships between the surface temperature and the condensation temperature can be derived from observations and reanalysis data (e.g., Masson-Delmotte et al., 2008, Markle and Steig, 2022). Similarly the "source" temperature is the spatially integrated, evaporation-weighted air temperature over the region that contributes moisture to the precipitation site, which can be estimated to some extent from back-trajectory modeling and water-tagged climate modeling (Sodemann and Stohl, 2009; Markle et al., 2017; Bailey et al., 2019). The spatial distributions of these moisture sources may change through time (e.g., Markle et al., 2017).

Markle and Steig (2022) showed that because the underlying relationships that cause water-isotope ratios in polar precipitation to change with temperature are nonlinear, a linear system of equations like those above can lead to artifacts in some temperature reconstructions, particularly for the moisture source. By inverting a numerical water-isotope distillation model, which accounts for the underlying temperature dependencies, and using the logarithmic deuterium excess parameter, temperature reconstructions can be improved (Markle and Steig, 2022), especially for reconstructions of moisture source conditions. Condensation temperature anomaly reconstructions averaged across eight Antarctic ice-core records, taking into account inherent nonlinearities, are shown in Fig. 12A, while moisture source SST reconstructions using the same method are shown in Fig. 12B. The ice-core-based estimates of Southern Ocean SSTs are compared to a compilation of Southern Ocean SST reconstructions from marine sediment cores (Chandler and Langebroek, 2021) and are remarkably coherent, given that they come from completely independent proxies. Self-consistent reconstructions of temperature change over the poles and over the midlatitude oceans also show coherence (e.g., Fig. 12) and allow us to quantify patterns of polar amplification through time (Markle and Steig, 2022).

There is a considerable interest in how best to refine quantitative climate reconstructions from water-isotope records, whether using modern empirical relationships of water-isotope ratios and temperature, estimates based on physical understanding aided by numerical models (e.g., Jouzel et al., 1997, Uemura et al., 2012, Markle and Steig, 2022, Servettaz et al., 2023) as well as interest in what role processes not yet well-represented in such models (particularly between the ice sheet and the overlying vapor) could play in modifying these relationships (e.g., Town et al., 2024). In some cases, water-isotope-temperature reconstructions can be
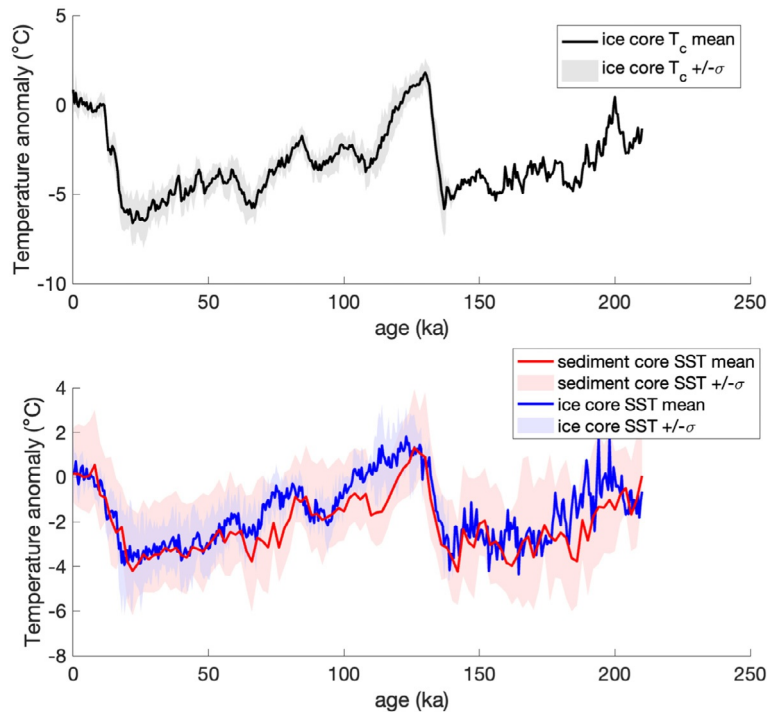

Fig. 12   (Top) Average ice-core site condensation temperature anomaly (*black*) for eight ice-core records (Markle and Steig, 2022); *shading* indicates the standard deviation of the spread from all records. (Bottom) Moisture source SST anomaly from the same ice-core records (*blue*) compared to SST reconstructions from about 32 Southern Ocean marine sediment cores (Chandler and Langebroek, 2021). Note the agreement between the ocean-based and ice-core-based estimates of Southern Ocean SSTs, particularly between 0 and 60 ka, beyond which there are only about half of the ice-core records.

constrained by independent information such as borehole temperature profiles (e.g., Werner et al., 2000, Cuffey et al., 2016), or isotope fractionation in gases (e.g., Buizert et al., 2014), the diffusion process of water isotope within the firn (e.g., Kahle et al., 2021), the combined influence of the hydrologic cycle on water isotopes and other ice-core measurements like aerosols (Markle et al., 2018), or potentially other information.

Robustness of water-isotope records

Water-isotope records from both Greenland and Antarctica share an interesting set of features that tells us something about the nature of the proxy. While ice-core water isotopes can preserve incredibly high-resolution records (indeed, the latest measurement techniques at high accumulation sites can reveal subannual water-isotope variability for thousands of years (Jones et al., 2023)), those records are not generally coherent with other records from the same ice sheet, at the highest frequencies, for example, from interannual to even centennial timescales. The ITASE ice core array from West Antarctica (Steig et al., 2005) provides a useful example of this. While average information from the ice sheet (Steig et al., 2013) and even regional and seasonal information (Küttel et al., 2012) can be readily extracted from the network of cores, they are not particularly well correlated at interannual to interdecadal timescales, and less well correlated than physically related climate variables like temperature (Fig. 13). And this makes
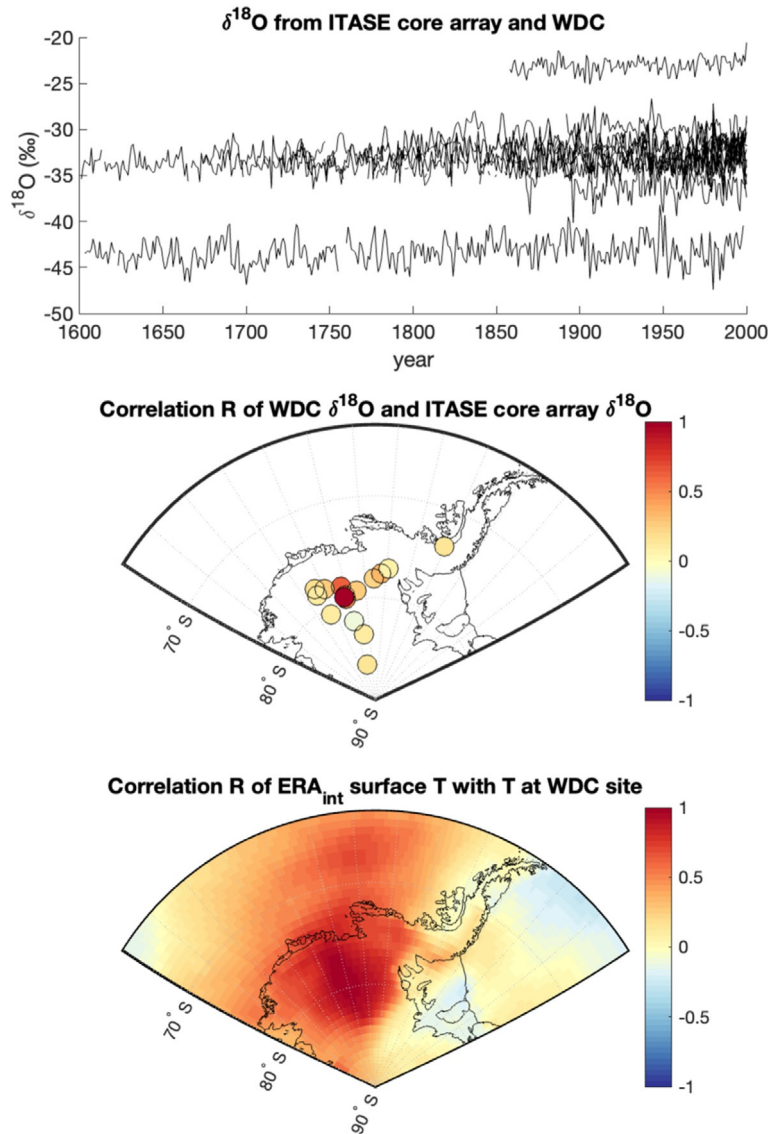

Fig. 13   (Top) Ice core δ^{18}O records from the ITASE array, other shallow cores, and the WAIS Divide ice core (Steig et al., 2013) . (Middle) The correlation R between water isotopes at the WDC site with WDC (*red dot* at center, $R = 1$) and with water isotopes from a collection of shallow cores. Temporal overlap of the records is different for each comparison, but ranges from multidecadal to multicentennial scales. (Bottom) The spatial autocorrelation of annual mean surface air temperature at the WDC site with surface air temperature across the region [from 38 years of the ERA interim reanalysis project, Dee et al. (2011)].

a lot of sense. First, there are confounding factors, such as age scale alignment and uncertainty, that might lead to disagreement at higher temporal frequencies but not at lower ones. Further, there are many influences on the water-isotope ratios that would not be expected to be shared across the ice sheet at high frequencies, but which should average out at low frequencies. These include the details of local postdepositional processes, local stochastic variability in temperature, pressure, precipitation, storm paths, and the various processes leading to accumulation such as wind redistribution (each core is after all just a few inches across).

However, if we zoom out on the spatial-temporal cone, once we get to multicentennial (and certainly millennial) variability, all ice-core records from an ice sheet are remarkably coherent (e.g., Figs. 7 and 9). While there are some notable and interesting differences at these scales (e.g., WAIS Divide Project Members et al., 2013), they are relatively minor and the large-scale patterns are largely shared by all cores within Antarctica, and likewise within Greenland. Fig. 11 shows a number of Antarctic δ^{18}O records spanning the last 60,000 years as well as a cross-correlation matrix, following Markle and Steig (2022); all records are extremely well correlated. The figure also shows times series and cross-correlation matrices for the linear d_{xs} parameter, which is degraded by nonlinear biases and artifacts, and the logarithmic d_{ln} parameter, which greatly reduces those biases, showing a much more coherent picture (Markle and Steig, 2022). The ice-core water-isotope records within each continent are, for example, more coherent than comparable proxies from marine sediment records from the Southern Ocean over shared timeframes, despite the larger number of marine records (Fig. 12) (Chandler and Langebroek, 2021).

Only large-scale processes common to all sites could produce such coherent results. The thermodynamic processes tied to meridional atmospheric water transport provide a useful framework (Dansgaard, 1964). Indeed, these processes certainly are happening and certainly wield a large lever. There are also numerous processes not particularly tied to local temperature or large-scale climatological temperature gradients and moisture transport that can lead to large variations. Better understanding all the relevant processes will continue to improve our quantitative reconstructions of climate variables like temperature from water-isotope ratios in ice.

Conclusions and summary

The ice sheets exist because frozen water precipitated from the atmosphere steadily accumulates in polar regions. This enables the recovery of ice-core records and is the result of large-scale atmospheric moisture transport, the centerpiece of the global hydrological cycle. This same hydrologic cycle, the movement of water between phases and reservoirs on Earth, plays a key role in the patterns of Earth's temperature and other aspects of climate, as well as in how those patterns change in response to a forcing on the system.

We can understand the study of water-isotope ratios as detailing the (sometimes odd) behavior of a trace constituent of water; how the very rare isotopologues are lost or gained as water moves through the hydrologic cycle. However, there is another way to think about the problem. Earth has several different isotopologues of water and thus has several different hydrologic cycles. Water-isotope ratios inform us about the relative behavior of these hydrologic cycles.

The processes of water transport and phase change lead to fractionation of water isotopes, divergence of the various hydrologic cycles on Earth, though those cycles are influenced by, and are fundamental to, the same climate and variations in climate. Through the atmospheric transport of water toward the poles, many climate processes are recorded in the ice sheets by the relative amount of the different waters that make it to (and, in fact, constitute) the ice sheets. By understanding these processes, often leveraging long temporal scales or large spatial scales, we can extract useful, quantitative information about Earth's temperature and climate history.

Indeed ice-core water-isotope records have provided extremely detailed and long histories of Earth's climate. They have revealed the terrestrial patterns of ice age cycles, and the relationships and phasing between the hemispheres. They allow us to quantify the hemispheric patterns of temperature change and polar amplification, and demonstrated the climate system's ability for abrupt and rapid change in the past.

Acknowledgment

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