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Water isotopes, climate variability, and the hydrological cycle: recent advances and new frontiers

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TOPICAL REVIEW

Water isotopes, climate variability, and the hydrological cycle: recent advances and new frontiers

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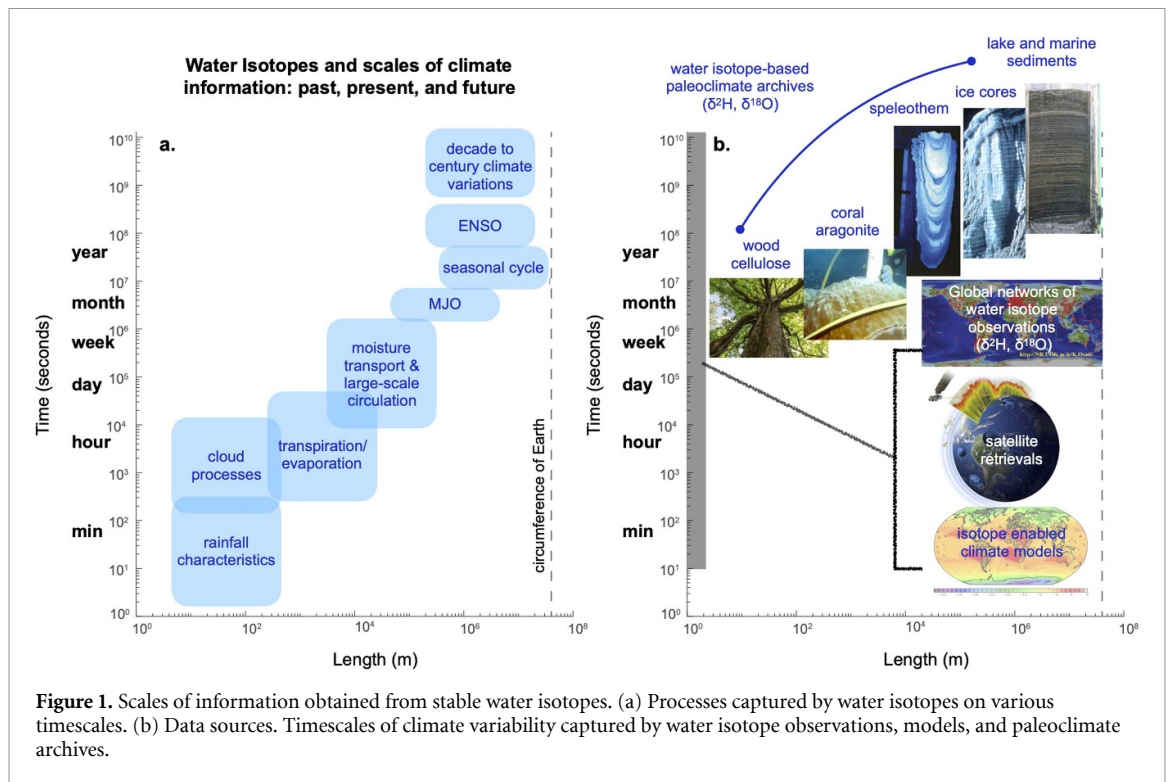
Abstract

The hydrologic cycle is a fundamental component of the climate system with critical societal and ecological relevance. Yet gaps persist in our understanding of water fluxes and their response to increased greenhouse gas forcing. The stable isotope ratios of oxygen and hydrogen in water provide a unique opportunity to evaluate hydrological processes and investigate their role in the variability of the climate system and its sensitivity to change. Water isotopes also form the basis of many paleoclimate proxies in a variety of archives, including ice cores, lake and marine sediments, corals, and speleothems. These records hold most of the available information about past hydrologic variability prior to instrumental observations. Water isotopes thus provide a ‘common currency’ that links paleoclimate archives to modern observations, allowing us to evaluate hydrologic processes and their effects on climate variability on a wide range of time and length scales. Building on previous literature summarizing advancements in water isotopic measurements and modeling and describe water isotopic applications for understanding hydrological processes, this topical review reflects on new insights about climate variability from isotopic studies. We highlight new work and opportunities to enhance our understanding and predictive skill and offer a set of recommendations to advance observational and model-based tools for climate research. Finally, we highlight opportunities to better constrain climate sensitivity and identify anthropogenically-driven hydrologic changes within the inherently noisy background of natural climate variability.

1. Introduction: water isotopes and the global water cycle

The hydrologic cycle is a fundamental component of the climate system with critical societal and ecological relevance. Yet gaps persist in our understanding of water fluxes and their response to increased greenhouse gas forcing (Sherwood *et al* 2010, Burls and Fedorov 2017). The response of the hydrologic cycle to natural radiative forcing factors, such as volcanic eruptions, is also uncertain, as is the full range of hydrologic variability internal to the Earth system, particularly on decadal and longer timescales. Since water vapor, clouds, and precipitation all modify Earth’s radiative balance, the ability to characterize and simulate both internal and forced hydrologic variability is essential to accurately predict the pace and pattern of climate change.

Part of our uncertainty about how the hydrologic cycle has changed in the past and will change in the future is due to the short length of the instrumental record, which is limited to several decades (even in the



most highly sampled regions). This uncertainty is also a consequence of poorly constrained hydrologic parameterizations in numerical models, resulting from limitations in our understanding of the myriad processes involved in the water cycle. Nowhere is the impact of these poorly constrained parameterizations more clear than in our decades-long struggle to simulate clouds and constrain climate sensitivity in global simulations. Estimates of climate sensitivity in state-of-the-art coupled general circulation models (GCMs) diverge widely in large part due to the diverse and uncertain treatment of clouds, precipitation, and other hydrologic processes that are not resolved on the coarse scale of model grids (Arias *et al* 2021). Overcoming these obstacles and improving our understanding of the global water cycle and how it responds to external changes in climate thus necessitates new approaches that leverage diverse data sources, integrate information over long time periods, and include robust data-model synthesis efforts.

The stable isotope ratios of oxygen and hydrogen in water provide a unique opportunity to evaluate hydrological processes and investigate their role in the variability of the climate system and its sensitivity to change. Since heavy and light isotopes move through phase changes at distinct rates—a result of different atomic masses, diffusivities, and vapor pressures (Dansgaard 1964)—their ratio provides an integrated history of moisture exchange (Gat 1996, Galewsky *et al* 2016). This history records the fluxes of water that connect land, sea, and air, regulating the basic states of the biosphere, ocean, and atmosphere. Water isotopes thus act as an additional ‘degree of freedom’ for understanding the complex hydroclimate system, providing information beyond what standard hydrologic variables, such as specific humidity or precipitation amount, can offer (Lee and Fung 2008, Bailey *et al* 2015, Nusbaumer *et al* 2017, Wright *et al* 2017, Risi *et al* 2012a, Wright *et al* 2009).

Water isotopes also form the basis of many paleoclimate proxy measurements in a variety of archives, including ice cores, lake and marine sediments, corals, and speleothems. These records hold most of the available information about past hydrologic variability prior to instrumental observations (and see Konecky *et al* 2020 for a review). Water isotopes thus provide a ‘common currency’ that links paleoclimate archives to modern observations, allowing us to evaluate hydrologic processes and their effects on climate variability on a wide range of time and length scales (figure 1).

Indeed, stable water isotope ratios also create a common unit that uniquely links paleoclimate reconstructions, modern climate observations, and isotope-enabled model simulations. Interpretation of both paleoclimate and modern observations is bolstered by the integration of water isotopes in GCMs (Joussaume *et al* 1984), from models of intermediate complexity (Brennan 2012, Roche 2013, Dee *et al* 2015b, Mathieu *et al* 2002) to fully coupled GCMs (Werner *et al* 2001, Noone and Simmonds 2002, Schmidt *et al* 2007, Lee and Fung 2008, Tindall *et al* 2009, Risi *et al* 2010, Kurita *et al* 2011, Werner *et al* 2011, Field *et al* 2014, Nusbaumer *et al* 2017, Brady *et al* 2019, Cauquoin *et al* 2019, Yoshimura *et al* 2008). Such efforts

have facilitated many new developments in the interpretation of proxy records—moving the field away from interpreting individual records in isolation toward identifying changes in the global climate state that are consistent with the isotopic variability captured by large networks of proxy records (Steiger *et al* 2017, Zhu *et al* 2017, Hu *et al* 2019, Zhu *et al* 2020, Dee *et al* 2017, Thompson *et al* 2021, Du *et al* 2021, Falster *et al* 2021, He *et al* 2021, and many others). Water isotope enabled models have also created opportunities to evaluate the performance of climate models, identifying deficiencies in numerical representations of key processes such as moisture transport, circulation, cloud physics, and precipitation efficiency (Nusbaumer *et al* 2017, Düttsch *et al* 2019, Hu *et al* 2020, Risi *et al* 2012a).

Building on previous reviews that report advancements in water isotopic measurements and modeling and describe water isotopic applications for understanding hydrological processes (Galewsky *et al* 2016, Jones and Dee 2018, Bowen *et al* 2019), this paper reflects on insights about climate variability generated from isotopic studies. We highlight new work and opportunities to enhance our understanding and predictive skill. Progressing from long to short timescales, we discuss how water isotopes have improved our understanding of internal variability and externally-forced changes in the climate system, including changes in the large-scale circulation and global teleconnection patterns. We also highlight how water isotopic information has allowed us to detect variations in inherently noisy systems like the El Niño–Southern Oscillation (ENSO), and to better understand the complex interplay of moistening and drying that governs the Madden–Julian Oscillation (MJO). Our review is further organized by dominant proxy or measurement type, even though multi-proxy syntheses, model-data comparisons, and studies combining proxies and modern observations are becoming increasingly common and necessary. Based on our synthesis of the literature, we offer a set of recommendations to advance observational and model-based tools for climate research, and highlight opportunities to 1) better constrain climate sensitivity and 2) identify anthropogenically-driven hydrologic changes within the inherently noisy background of natural climate variability.

2. Background: tools of the trade

2.1. Understanding oxygen and hydrogen isotopes and fractionation

Three stable isotopes of oxygen (^{16}O , ^{17}O , ^{18}O) and two stable isotopes of hydrogen (^1H , ^2H) exist in nature. Isotopologues of water molecules thus have multiple potential configurations with different atomic masses, including the most abundant $^1\text{H}^1\text{H}^{16}\text{O}$ and the more rare $^1\text{H}^1\text{H}^{18}\text{O}$, $^1\text{H}^1\text{H}^{17}\text{O}$, and $^2\text{H}^1\text{H}^{16}\text{O}$. Ratios of the heavier (more rare) isotope to the lighter (most abundant) isotope are expressed in delta notation relative to a standard—in this case, the International Atomic Energy Agency Vienna Standard Mean Ocean Water:

$$\delta^{18}\text{O}, \delta^2\text{H}[\text{‰}] = \left(\frac{R_{\text{SAMPLE}}}{R_{\text{STANDARD}}} - 1 \right) \cdot 1000 \quad (1)$$

where R_{SAMPLE} and R_{STANDARD} are the ratios of the concentrations of ($^{18}\text{O}/^{16}\text{O}$) or ($^2\text{H}/^1\text{H}$) in the sample and the standard, respectively ($R = ^{18}\text{O}/^{16}\text{O}$). The resulting δ value, with units permil (‰), can be negative or positive. While seawater values are typically within several permil of zero, atmospheric vapor and precipitation values are often negative. δ values may be considered ‘high’ (and their medium ‘enriched’) even if they are negative, so long as the abundance of the heavy isotope relative to the light isotope is higher than expected. Likewise, δ values are considered ‘low’ (and their medium ‘depleted’) so long as the relative abundance of the heavy isotope is lower than expected.

Water isotopes are valuable tools to understand the hydrologic cycle due to their fractionation—or relative partitioning—during phase changes. This isotopic imprint is conserved, providing a way to characterize and trace air and ocean masses in the absence of further phase changes or mixing (Noone *et al* 2011, Galewsky *et al* 2016, Gedzelman and Arnold 1994, LeGrande and Schmidt 2006). One form of mass-dependent fractionation—*equilibrium* fractionation—results from the fact that the saturation vapor pressures of water isotopologues decrease with increasing atomic mass (i.e. heavier isotopologues have lower vapor pressures). Thus, during evaporation, water molecules that contain a heavy isotope preferentially remain in the condensed phase relative to water molecules containing only lighter isotopes. Similarly, water molecules that contain a heavy isotope preferentially condense. Importantly, this type of fractionation is only sufficient for describing isotopic partitioning under conditions of thermodynamic equilibrium (e.g. during the condensation of water vapor from saturated air parcels).

The Rayleigh distillation model (figure 2) provides one of the simplest ways to quantify the effect of equilibrium fractionation on atmospheric water vapor during condensation (Dansgaard 1964, Gat 2010):

$$R_t = R_0 f^{(\alpha-1)}. \quad (2)$$

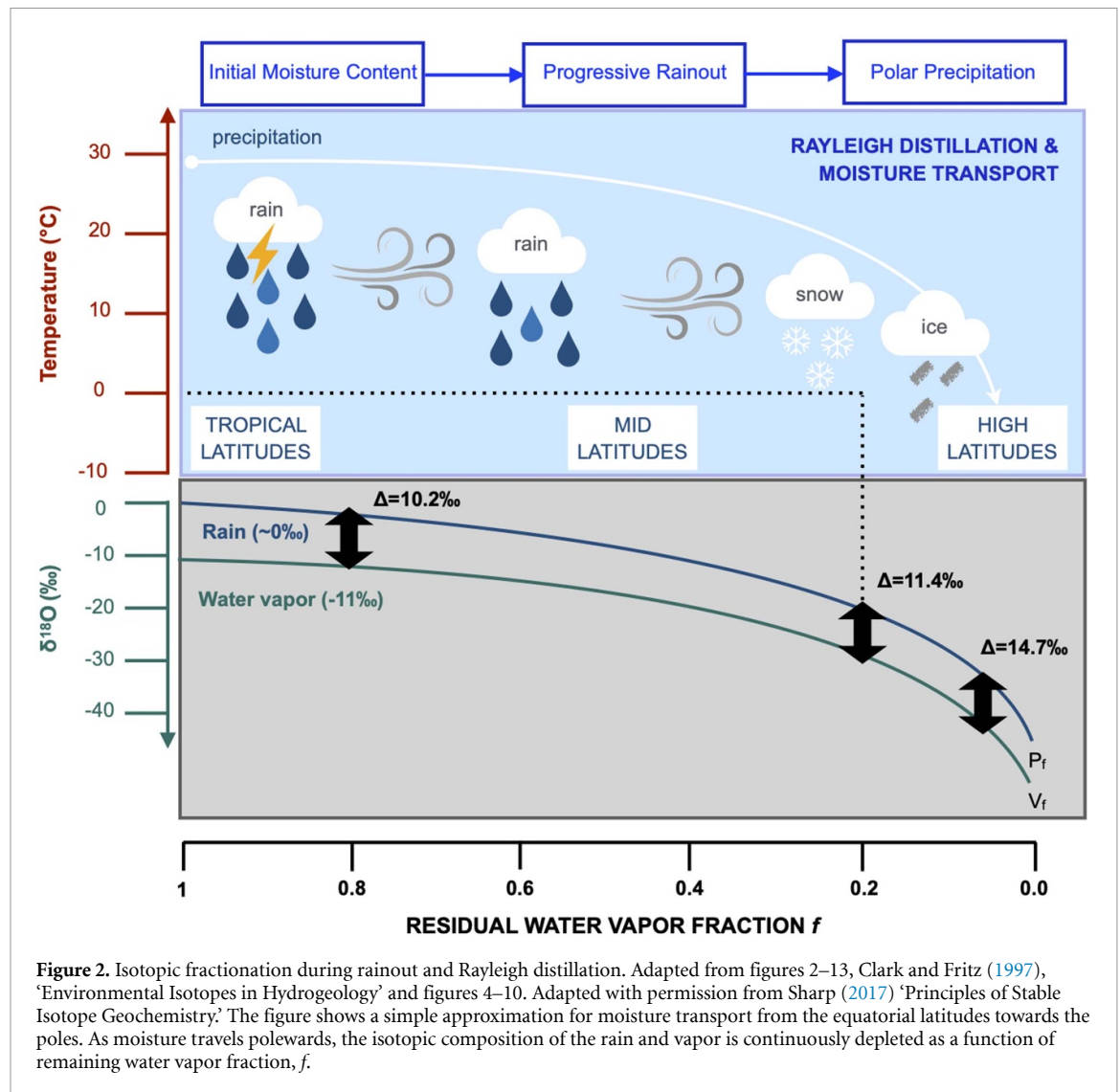


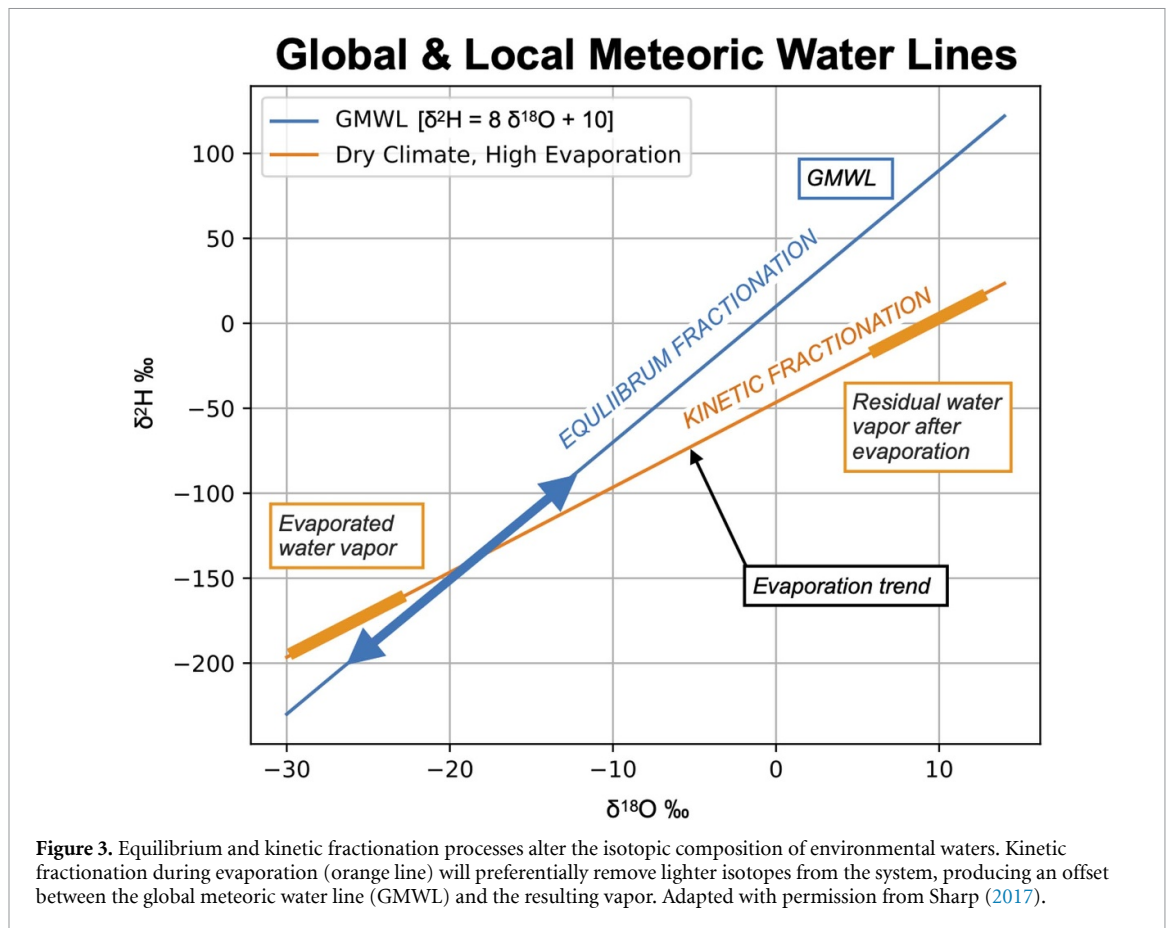
Figure 2. Isotopic fractionation during rainout and Rayleigh distillation. Adapted from figures 2–13, Clark and Fritz (1997), ‘Environmental Isotopes in Hydrogeology’ and figures 4–10. Adapted with permission from Sharp (2017) ‘Principles of Stable Isotope Geochemistry.’ The figure shows a simple approximation for moisture transport from the equatorial latitudes towards the poles. As moisture travels polewards, the isotopic composition of the rain and vapor is continuously depleted as a function of remaining water vapor fraction, f .

Here, R_0 is the initial molar ratio between the heavy and light isotopes, R_t is that ratio at a later time (t), $(1-f)$ is the fraction of initial moisture that has precipitated (and thus left the system), and α (α) is the isotopic equilibrium fractionation factor during condensation, which equals the isotopic ratio of the condensate (which is lost) over that of the water vapor. This fractionation factor increases as temperature decreases, meaning that the isotopes are more heavily fractionated during condensation at colder temperatures:

$$\alpha_{(l-v)} = \frac{R_{LIQUID}}{R_{VAPOR}} \tag{3}$$

where R_{LIQUID} is the ratio of $^{18}\text{O}/^{16}\text{O}$ (or $^2\text{H}/^1\text{H}$) for the liquid, and R_{VAPOR} is the ratio of $(^{18}\text{O}/^{16}\text{O})$ for the vapor. Values for equilibrium fractionation factors have been determined empirically for each isotope ratio and depend on whether the phase change involves liquid or ice (e.g. Majoube 1971).

As a model for the atmosphere, Rayleigh distillation makes several overly simplistic assumptions—namely, that condensation immediately precipitates and is thus removed from the system, and that the mixing of air masses is negligible. Nevertheless, it provides a useful conceptual framework for the behavior of isotope ratios in water vapor and precipitation (figure 2). Although α depends on temperature, it tends to vary temporally in any given location by only a few percent. The dominant driver of isotopic change in water vapor is the amount of condensation and rainout $(1-f)$ that occurs as an air parcel is transported. Thus, as vapor condenses while moving from the tropical oceans to higher latitudes, or from marine to continental locations, the δ values of the vapor—and the subsequent precipitation that forms from that vapor—decrease. Though temperature has little direct effect on isotope ratios, its indirect effect is still important: it modifies the atmosphere’s capacity to hold moisture and the resulting efficiency of precipitation



in transferring (or cycling) water between the atmosphere and Earth's surface. It is because of the strong dependence of these two factors on global temperature, and the covariance between temperature and the general circulation, that water isotope variations can help us map out changes in characteristic moisture transport pathways—and, consequently, moisture source regions—as global climate warms or cools.

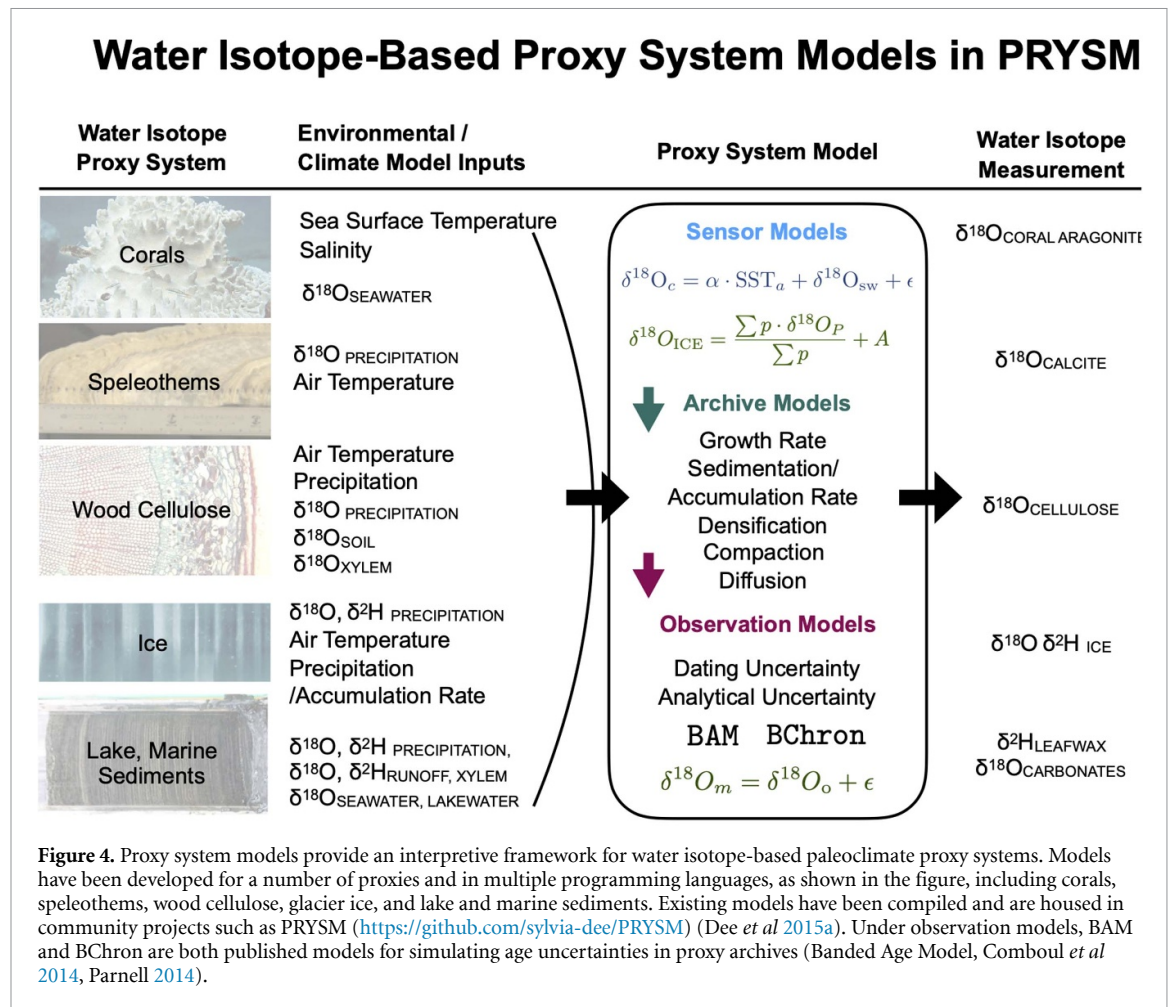
While mass-dependent fractionation occurs in a state of thermodynamic equilibrium, nonequilibrium fractionation also partitions isotopes through different phases of the water cycle (figure 3). This nonequilibrium, or *kinetic* fractionation is due to the lower diffusivities of the heavier isotopologues (as diffusivities also depend on mass) and manifests strongly during evaporation from oceans, lakes, and other surface water bodies, as well as during rain re-evaporation. In the case of evaporation, lower diffusivities cause the heavier isotopologues to be even less likely to enter the gas phase than equilibrium fractionation would predict. A similar effect occurs under strong supersaturation, such as in mixed-phase cloud conditions. There, however, kinetic fractionation works to oppose, rather than enhance, the partitioning caused by equilibrium fractionation.

Since ^2H diffuses more readily than ^{18}O , kinetic fractionation also influences the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ relationship, as quantified by the deuterium- or *d*-excess, which has been traditionally defined as:

$$d_{\text{excess}} = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}. \quad (4)$$

In precipitation, *d*-excess is often expected to be close to 10‰ (Craig 1961, Gat 2005). This value represents the average nonequilibrium effects of seawater evaporation globally. However, *d*-excess can vary by tens of permil regionally depending on the temperature, relative humidity, and other climatic conditions where the moisture first evaporated. Because condensation tends to occur much closer to equilibrium conditions than evaporation, *d*-excess is often considered a tracer of moisture source changes (e.g. Johnsen et al 1989, Ciais et al 1995, Pfahl and Sodemann 2013, Chen et al 2020). Recently, new logarithmic definitions of *d*-excess have become popular, because they reduce the *d*-excess dependence on temperature, making the parameter a better pseudo-conserved tracer of moisture origin during transport (Kopec et al 2016, Dütsch et al 2019).

The controls on water isotope ratios in the ocean, lakes, and other freshwater bodies are similar to those described above for the atmosphere. Evaporation preferentially removes isotopically light water, causing the remaining liquid reservoir to become isotopically heavier, or more 'enriched', while freshwater inputs from



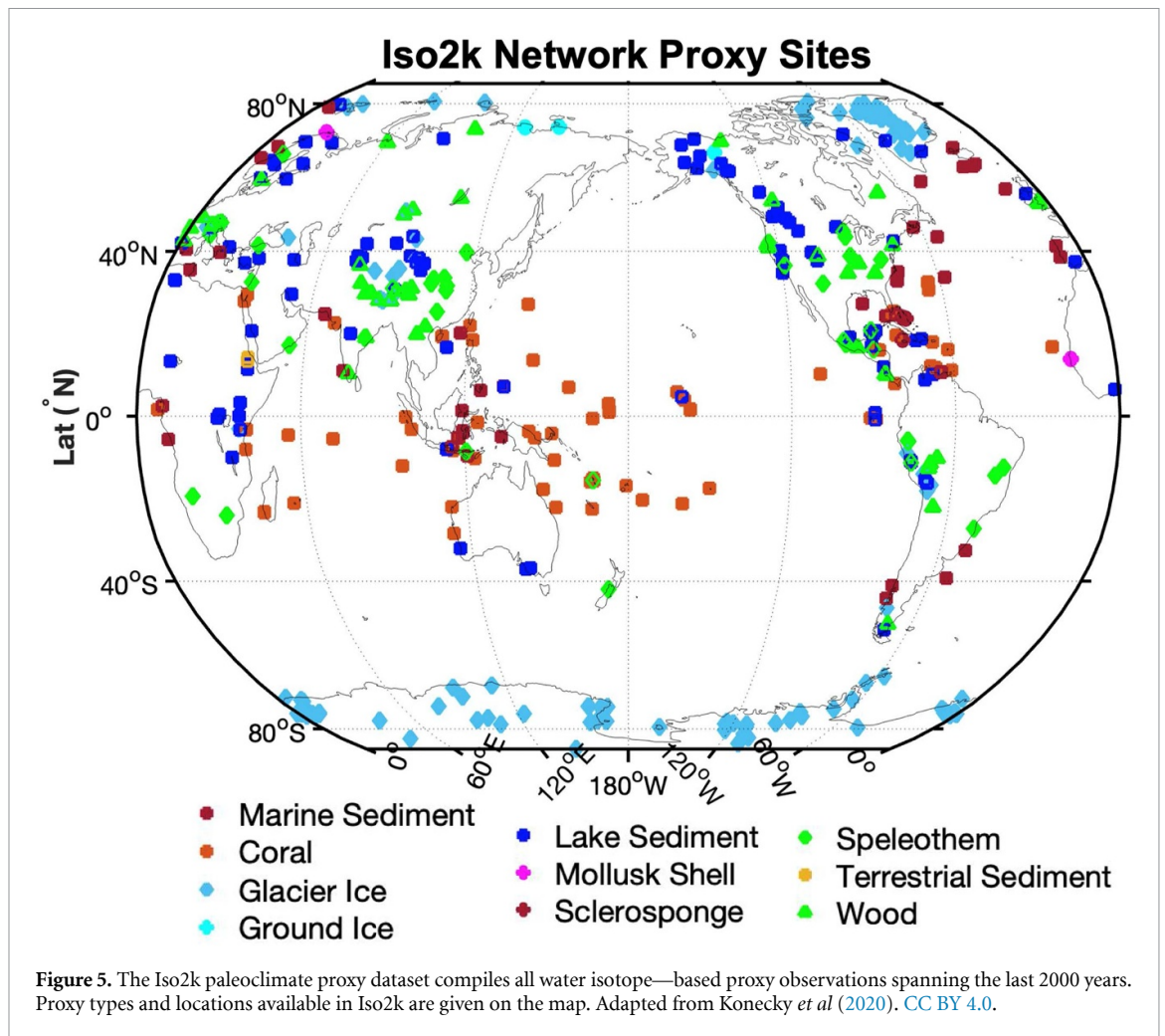
precipitation or river runoff cause the water bodies to become isotopically lighter or more ‘depleted.’ In most oceanic regions, the seawater isotope ratio is thus strongly correlated with sea surface salinity. Other factors influencing regional seawater isotope ratios include upwelling and currents, which advect the isotopic signatures of evaporation and freshwater inputs from one location to another.

A variety of geological archives like coral skeletons, cave deposits, and the carbonate shells and cellular material of organisms preserved in lake and ocean sediments incorporate the isotopic composition of surrounding water into their structure, preserving information on water isotopes in precipitation, seawater, and lake water over timescales ranging from hundreds to millions of years (as discussed in section 3). Additional fractionation takes place during the incorporation of isotopic information into the archive in ways that are specific to the biophysical processes operating within each archive. Extracting the original climate signal from the signals retrieved from the paleoclimate archive is not a trivial process and requires several layers of interpretation. Proxy system models (PSMs, Evans et al 2013) account for all transformations between climate variations and proxy observations, and are now widely used in the interpretation of water isotope-based paleoclimate records (Dee et al 2015a). Among other things, they help disentangle how isotopic compositions in meteoric and ocean waters are altered by post-depositional processes. A schematic summarizing how PSMs work and available models for water isotope-based systems is given in figure 4.

2.2. Recent advances in recovering water isotope information from the past, present, and future

2.2.1. Advances in reconstructing the past

Many paleoclimate reconstructions have been published with varying levels of metadata descriptions, and interpreting results has often required specialist knowledge of the environmental drivers of individual proxy archives. New global paleoclimate networks are closing this usability gap in the existing suite of paleoclimate reconstructions. Water isotope-based paleoclimate databases include Iso2k (figure 5), which includes all proxy types and provides comprehensive metadata allowing efficient proxy intercomparison (Konecky et al 2020). Proxy-specific databases such as SISAL (speleothems) (Atsawaranunt et al 2018) and CoralHydro2k (corals) (Walter et al 2022) allow for investigation of climate changes through a proxy-specific lens. Such databases are well-suited for evaluating hydroclimate processes through time and space by facilitating



large-scale syntheses, model-data intercomparison, and paleoclimate data assimilation (Paleo-DA). Indeed, the newly launched Past Global Changes (PAGES) Phase 4 effort is focused on reconstructing hydroclimate variability over the Common Era using these and other hydroclimate databases. Recent efforts to improve and develop new PSMs (e.g. Evans *et al* 2013, Dee *et al* 2015a, 2018b, Konecky *et al* 2019, Malevich *et al* 2019) further complement the development of these databases, allowing the climate information contained in the records to be more explicitly resolved.

2.2.2. Advances in monitoring the present

Rapid advances in stable water isotope measurement technology have positioned us to evaluate water cycle processes controlling climate variability in greater detail, and to refine interpretations of paleoclimate data. In addition, the establishment of large water isotope databases have positioned water isotopes to contribute significantly to our understanding of internal climate variability and forced change. Galewsky *et al* (2016) reviewed recent advances with respect to the measurement of water vapor. These include advances in remote sensing of water vapor isotopologues from space that have supported the development of multi-year to multi-decadal gridded datasets, providing important context for understanding spatial variability in hydrologic processes and atmosphere's water balance (Galewsky *et al* 2016, Shi *et al* 2022, Bailey *et al* 2017, Tuinenburg *et al* 2015, Lacour *et al* 2018, Risi *et al* 2012a, Risi *et al* 2012, etc). They also include the widespread adoption of cavity-ringdown spectroscopy and off-axis integrated cavity output spectroscopy instruments, which have high throughput and are designed to measure both water vapor and liquid water samples (Gupta *et al* 2009). These analyzers have several advantages over traditional mass spectrometry techniques. They are field-deployable, which has supported the recent proliferation of *in-situ* land-based, ship, and aircraft measurements of vapor stable isotope values to investigate water cycle processes (Galewsky *et al* 2016, Bailey *et al* 2022). They also facilitate high-resolution measurements of isotope ratios in ice cores (e.g. at sub-annual resolution, Jones *et al* 2018) when paired with continuous flow melt systems, creating opportunities to investigate climate variability at even finer resolution.

Large databases of modern isotopic observations are ushering in a new era of global water cycle investigations, enabling new developments in process-oriented studies across large geographic areas, more robust validations of isotope-enabled model simulations, and improved reconstructions of past climate. Several observational databases have paved the way, including the WISER water isotopes database, which includes river water and precipitation data from the foundational Global Network of Isotopes in Precipitation (GNIP) program, and the Goddard Institute of Space Studies (GISSs) Global Seawater $\delta^{18}\text{O}$ database (Rozanski *et al* 1993, Schmidt 1999, LeGrande and Schmidt 2006). A large number of new water isotope observational datasets have since been produced, which have been incorporated into numerous databases, including the Water Isotopes Database (Putman and Bowen 2019), which is merging with IsoBank (Pauli *et al* 2015, 2017), the Stable Water Vapor Isotope Database (Wei *et al* 2019), the CISE-L'OCEAN Seawater Isotope Database (Reverdin *et al* 2022) and the PAGES CoralHydro2k Seawater Isotope Database (expected in 2023, DeLong *et al* 2022). In addition, the EarthChem geochemical data repository has recently been expanded to facilitate the archival of seawater isotope datasets with standardized metadata, and allows researchers to obtain DOIs for submitted seawater isotope records (DeLong *et al* 2022). For a more detailed review of current observational isotope databases we refer the reader to (Bowen *et al* 2019).

2.2.3. Advances in modeling the future

Water isotope modeling efforts have expanded at a similarly rapid pace, reflecting the growing valuation of isotopic tracers for improving climate model physics, chemistry, and biology and their unique contributions to improving paleoclimate reconstructions from proxy records. Isotope-enabled models now include not just atmosphere-only and fully-coupled GCMs, but also regional-scale models (Sturm *et al* 2005, Pfahl *et al* 2012, Stevenson *et al* 2015, Yoshimura and Kanamitsu 2010), cloud-resolving models, and large-eddy simulations (Blossey *et al* 2010, Moore 2016, Smith *et al* 2006, Lee *et al* 2012, Torri 2022; see Box 2, Bailey *et al* 2021). Higher resolution models are an important tool for process-level studies and can be used to (dynamically) down-scale GCM results to aid in the interpretation of paleoclimate proxies collected at specific locations. In some cases, high-resolution models are necessary to simulate smaller-scale atmospheric phenomena such as the mesoscale organization of convection, shown to influence isotope ratios in some proxy archives (Maupin *et al* 2021). Finally, water isotope enabled simulations are poised to generate significant understanding of future anthropogenic changes to the global hydrological cycle and atmospheric circulation. Incorporation of stable water isotope tracers in simulations spanning the 21st century, for example, could elucidate the Walker Circulation's response to tropical Pacific warming (e.g. Dee *et al* 2018a), changes in moisture supply to atmospheric river events (Nusbaumer and Noone 2018), shed light on how climate change affects low-cloud and vertical mixing feedbacks in climate models (e.g. Hu *et al* 2022), and help quantify changes in moisture transport length scales across the mid-latitudes and Arctic (Singh *et al* 2016b, Bailey *et al* 2019).

2.2.4. Water isotopes as a tool to merge data spanning the past, present, and future

Given these recent developments in our ability to measure isotope ratios across space and time, the integration of water isotopes in models of various resolution and complexity, and improved access to both modern and paleoclimate records through continued reconstruction efforts and improved archival practices, this is an opportune moment for the scientific community to take advantage of the full potential of water isotope tracers to tackle both long-standing questions and emerging grand challenges central to understanding and predicting climate change.

3. Climate variability through a water isotope lens

Water isotopes have profoundly informed our understanding of climate variability in both the recent and distant past, providing a means to detect external climate forcing and distinguish it from internal variability. New insights into climate system dynamics have also emerged as the amount of past and modern water isotope observations has increased and data-model intercomparisons have become more sophisticated. In this section, we review the latest advances in our understanding of climate variability and change that have been facilitated by both modern water isotope data and water isotope-based paleoclimate records, from timescales ranging from orbital to seasonal. In particular, these data have led to:

- Improved understanding of climate variability on a range of timescales and its connection to changes in the large-scale circulation of the atmosphere and ocean
- Greater insight into how climate responds to major external forcings, including orbital, volcanic, and anthropogenic forcings
- Better understanding of the dynamics underlying these climate variations and their associated global teleconnection patterns

We present our discussion of past climate variability by timescale purely for ease of organization. Note that essentially all proxy systems span and/or are measured across multiple timescales (e.g. ice cores are measured and capture climate changes at sub-annual to decadal and longer intervals, depending on accumulation rates). Thus, readers should be aware that the assignment of various paleoclimate proxy systems to one timescale is not a comprehensive representation of the literature and climatic understanding retrieved from each proxy type.

3.1. Orbital to centennial timescales: abrupt climate change and monsoon dynamics

Records of stable oxygen and hydrogen isotope values from ice cores, marine sediments, and speleothems have provided much of our understanding of orbital- to centennial-scale variability in the climate system. Because of the long, continuous nature of these proxy records, they provide a means to identify internally and externally driven modes of climate variability on a wide range of timescales. Their interpretations have substantially evolved and become more nuanced over time. In particular, informed by studies based on model and modern *in-situ* monitoring data, these isotopic records are able to provide crucial information on elements of large-scale oceanic and atmospheric circulation and global hydrologic change.

3.1.1. Ice cores

Ice cores constitute our most direct archive of past precipitation, modified by post-deposition processes. Long polar ice core $\delta^{18}\text{O}$ and $\delta^2\text{H}$ records from Greenland and Antarctica—spanning thousands to hundreds of thousands of years—have provided foundational constraints on the timing of glacial and interglacial cycles and their orbital pacing (see review by Brook and Buizert (2018)). They have provided key insights into the temporal relationships between greenhouse-gas forcing and temperature (e.g. Knutti et al 2004, EPICA Community members 2006). And, they are one of several water isotope proxies that have helped characterize periods of abrupt climate change, including Dansgaard–Oeschger (DO) events—characterized by a rapid warming of the Northern Hemisphere, followed by gradual cooling—and Heinrich events, or cooling events in which large freshwater inputs into the North Atlantic from melting ice sheets alter the density-driven thermohaline circulation of the ocean (Grootes et al 1993, EPICA Community members 2004, Jouzel and Masson-Delmotte 2007, Landais et al 2018).

Ice core stable isotope records have been viewed traditionally as a local paleothermometer, since isotopic fractionation is sensitive to the temperature at last saturation—in this case, the temperature of condensation near the ice accumulation region. While this interpretation is not exact, data assimilation analyses, theoretical modeling, and GCM experiments suggest that it is a useful concept (Jouzel et al 1997, Masson-Delmotte et al 2008, Noone 2008, Steiger et al 2017, Brook and Buizert 2018).

Continued research, leveraging modern observations and isotope-enabled simulations, has created a more nuanced understanding of isotopes as indicators of past shifts in moisture source and moisture cycling. Recent analyses of ice core records from West Antarctica, for instance, have used isotopic information to elucidate the coupled atmosphere-ocean response to DO events. Using the distinct phasing of $\delta^{18}\text{O}$ records from Greenland and $\delta^{18}\text{O}$ and d -excess records from Antarctica, these critical records have demonstrated that DO events are characterized by a rapid equatorward shift in the moisture source for Antarctic precipitation. These shifts occur as the atmospheric circulation responds to Northern Hemisphere warming and the Intertropical Convergence Zone migrates north (Markle et al 2017). The fast dynamic response of the atmosphere is followed by a slower warming, driven by Southern Hemisphere sea surface temperatures, that lags by about 200 years. Other studies have suggested a role for Southern Ocean temperatures in influencing the strength of the Atlantic Meridional Overturning Circulation, or AMOC, and thus the duration of DO warm periods (Buizert and Schmittner 2015). Isotopic data thus elucidate the distinct yet linked timescales over which the atmosphere and ocean respond to and influence abrupt climate changes.

Water isotope records have also demonstrated important shifts in the moisture source of Arctic precipitation during DO events (Sime et al 2019). Data from Greenland ice cores, in conjunction with model simulations, for example, show that seasonal precipitation isotope ratios and seasonal precipitation amounts vary independently—a clear example of water isotopes providing additional constraints beyond what basic hydrological variables provide. These findings suggest sea ice loss during DO events increases the proportion of Greenland precipitation that originates from local oceanic evaporation. Moreover, these shifts in evaporative source help establish the positive, albeit heterogeneous, $\delta^{18}\text{O}$ -temperature relationship across Greenland. The importance of evaporative site changes to the hydroclimate state has emerged as a prominent theme in other modeling experiments that include water isotopic tracers, or that ‘tag’ and explicitly track moisture that has evaporated from predefined regions, both for the Arctic and Antarctic (Noone 2004, Singh et al 2016a, 2016b, Nusbaumer and Noone 2018, Siler et al 2021).

In addition to recording abrupt changes in mean climate state and associated mean moisture source patterns, long, high-resolution ice core records have also been used to identify abrupt changes in the

variability of the climate system through spectral analyses (e.g. Jones *et al* 2018, Grisart *et al* 2022). Careful dating of the timing of these changes, matched with other paleoclimate archives (e.g. speleothems), can isolate likely drivers for subsequent evaluation in numerical model experiments. This approach has helped reveal the importance of northern hemisphere ice sheet topography in influencing the zonal position of deep convection in the tropical Pacific, which, in turn, modifies Southern Hemisphere high-latitude stationary eddies via Rossby wave trains (Jones *et al* 2018). Other studies, using multi-proxy syntheses combined with model simulations, reinforce the importance of ice sheet extent in controlling tropical hydroclimate variability (DiNezio and Tierney 2013, DiNezio *et al* 2018, Windler *et al* 2020). DiNezio and Tierney (2013), for instance, argued that resultant variations in sea level and, ultimately, continental shelf exposure during the Last Glacial Maximum (LGM) (~40kyr ago) inhibited moisture convergence and dried the western Pacific Warm Pool. These findings not only indicate that isotopic records provide critical insight into changes in the general circulation, but they also emphasize the importance of accurately representing ice sheet dynamics so that the effects of sea level rise are incorporated accurately into projections of future atmospheric circulation.

Inverse correlations between ice core aerosol concentrations and $\delta^{18}\text{O}$ provides further evidence that ice core isotope records reflect variations in global circulation patterns. Markle *et al* (2018) interpreted this anti-correlation as showing that as atmospheric circulation slows, in response to a weaker meridional temperature gradient, precipitation intensifies globally, effectively scavenging the atmosphere of dust, sea salt, and other particles. The idea that dust accumulation in ice cores is regulated by the global hydrologic cycle, rather than changes in source emissions, represents a major shift in perspective (see Fischer *et al* 2007). However, the sensitivity of Antarctic isotope records to the general circulation is supported by modern observations and modeling studies (Noone 2008), and modern isotopic observations support the covariance between precipitation scavenging and aerosols (Bailey *et al* 2015). Knowledge gained about such covariant processes from ice cores creates valuable opportunities to test the coupling between components of today's Earth system models and how these components respond jointly to change.

3.1.2. Speleothems

Speleothem calcite formation in karst environments provides a wide range of climate information on timescales ranging from decades to hundreds of thousands of years (see review by Lachniet 2009, Cheng *et al* 2016). As groundwater drips into caves, the calcite that precipitates from the dripwater forms the speleothem; its $\delta^{18}\text{O}$ record thus represents a smoothed time series of amount-weighted precipitation isotope ratios from the local region—with less smoothing in wetter environments, where rainwater flushes groundwater reservoirs more frequently (e.g. Moerman *et al* 2014). The environmental conditions of the cave can also affect the calcite $\delta^{18}\text{O}$ but, again, are less important in wetter regions. These and other details are discussed in considerable detail in (Lachniet 2009).

Because of the strong connection to precipitation $\delta^{18}\text{O}$, speleothems formed at low latitudes provide a means to study the dynamics controlling the strength and seasonality of monsoons, their role in global hydroclimate, and their sensitivity to external and internal forcings. Once considered indicators of monsoonal precipitation amount, speleothem $\delta^{18}\text{O}$ records are now frequently interpreted as reflecting variations in atmospheric circulation and its associated impacts on moisture source, moisture transport, and upstream water cycling—with changes in source encompassing both the location and thermodynamic conditions of the evaporation site (e.g. Pausata *et al* 2011, Battisti *et al* 2014, Chen *et al* 2016, Hu *et al* 2019). Multi-proxy syntheses (e.g. DiNezio and Tierney 2013, DiNezio *et al* 2018), modern precipitation collections, and isotopically-enabled modeling experiments (e.g. LeGrande and Schmidt 2009, Chiang *et al* 2015, 2020, Hu *et al* 2019) have greatly enhanced our ability to resolve this more nuanced picture of monsoon dynamics. Indeed, simulations combining isotopic tracers and water tags have even made it possible to distinguish the individual effects of source, transport, and cycling on the South Asian and East Asian Summer Monsoons (SASM, EASM) (Tabor *et al* 2018, Hu *et al* 2019). While earlier papers emphasize the importance of upstream rainout (e.g. Liu *et al* 2014, Cai *et al* 2017), more recent analyses suggest shifts in source location dominate the EASM hydroclimate response (Hu *et al* 2019, Chiang *et al* 2020), providing a useful analogy for thinking about evaporative site changes with anthropogenic warming (see Singh *et al* 2016b). That said, these analyses remind us that hydroclimate variations seldom occur in isolation, especially when they are tightly linked to large-scale circulation changes and global energetics.

Some of the most coherent variability across speleothem records is caused by the wobbling of Earth's axis, or precession, and its impact on summer insolation, which modifies meridional temperature gradients, the position of the ITCZ, and the strength of subtropical highs (Hai *et al* 2012, Battisti *et al* 2014, Liu *et al* 2014). Both the Asian Monsoon and South American Summer Monsoon are stronger when summer insolation is high. However, millennial-scale forcings, such as meltwater pulses associated with Heinrich events and DO events, also imprint strongly on speleothem records (see also section 3.1.1, Hai *et al* 2012, Liu *et al* 2014). Since these events correspond with changes in the AMOC, they provide a useful lens through which to

examine and benchmark simulations of ties between polar change and tropical climate. For example, freshwater inputs into the North Atlantic associated with Heinrich events slow the AMOC, resulting in Northern Hemisphere cooling. This increases the meridional temperature gradient—just like when summer insolation is low—causing the Inter-Tropical Convergence Zone (ITCZ) to contract southward and alter hydroclimate across the tropical belt. The opposite occurs when AMOC strengthens. This coherent tropical response supports the idea of a Global Monsoon governed by seasonal changes in atmospheric circulation on multiple timescales (Hai *et al* 2012, Battisti *et al* 2014, Trenberth *et al* 2006). Moreover, high-resolution records make it possible to precisely identify the timing and duration of tropical hydroclimate shifts relative to high-latitude temperature changes and meltwater pulses over multi-decadal to millennial timescales—for example, linking speleothem records from Borneo (Carolin *et al* 2013) and East Asia (Rhodes *et al* 2015) to Greenland ice core reconstructions.

Despite the importance of high-latitude change in influencing low-latitude climate, speleothems and multi-proxy studies suggest localized tropical changes can also play a significant role in regulating individual monsoon systems (e.g. Cruz *et al* 2009). For example, Liu and Battisti (2015) found that during low summer insolation periods (and Northern Hemisphere cooling), the southward movement of the Atlantic ITCZ is enhanced by the strengthening of the African winter monsoon, which, in turn, is induced by anomalous north African cooling. Similarly, Jian *et al* (2022) argued that upper ocean heat convergence in the Indo-Pacific Warm Pool accompanies surface wind changes during high summer insolation periods. The resulting rise in ocean heat content enhances northward latent heat transport and provides a coupled atmosphere-ocean link between the Asian Monsoon, ENSO, and the Indian Ocean dipole (IOD) (see section 3.2 for more on modes of climate variability).

Recent water isotope work has also revealed a key role for the mid-latitude jet in influencing the Asian Monsoon, particularly its East Asian component (Chiang *et al* 2015, 2020, Zhang *et al* 2018). Like the ITCZ, the jet responds to meridional temperature gradients, and its position influences how westerly winds interact with the Tibetan Plateau, generating stationary eddies downstream. When the temperature gradient is strong (e.g. during low summer insolation or glacial periods), the westerlies tend to remain south of the plateau, blocking low-level southerly flow, which otherwise carries highly cycled, low $\delta^{18}\text{O}$ moisture toward NE China in summer (see Liu *et al* 2014). The mean EASM moisture source change, as does the speed with which the moisture source rotates counterclockwise from the south toward the Pacific, shortening characteristic stages of the monsoon's development. Associated variations in the progression and reach of the main monsoon rainbelt are captured by the geographic diversity of isotopic signals in speleothems and modern Asian precipitation (Liu *et al* 2020). The jet position thus regulates the seasonality of EASM precipitation (Chiang *et al* 2020), providing a unique benchmark for models aiming to simulate seasonal shifts in monsoonal dynamics and even jet position.

3.1.3. Marine sediments

The oxygen isotope composition of the carbonate shells of marine microfauna (principally foraminifera and also coccolithophores) that are preserved in marine sediments provide some of the most foundational records of past climate variations spanning the last ~100 million years (e.g. Zachos *et al* 2001, Westerhold *et al* 2020). These records have been critical in establishing the close coupling between global temperature, ice volume, sea level, and atmospheric greenhouse gas concentrations on glacial/interglacial timescales (Imbrie *et al* 1992, Lisiecki and Raymo 2005). When calcium carbonate is crystallized slowly in water under equilibrium conditions, ^{18}O is slightly concentrated in the carbonate relative to the water. This process is temperature dependent, with the fractionation factor decreasing as temperature increases (Urey 1947). Oxygen isotopes in marine carbonates thus provide a record of past temperature and seawater $\delta^{18}\text{O}$ variations (the latter of which covaries with global ice volume in shells of deep sea-dwelling benthic foraminifera). This relationship has led to the establishment of $\delta^{18}\text{O}$ in marine carbonates as one of the most widely used tools in paleoclimatology.

The partitioning of trace elements such as Mg into carbonate minerals is also a function of temperature, and Mg/Ca ratios in calcitic foraminifera have been widely applied as a paleotemperature proxy since the mid-1990s (Nuernberg 1995). Paired Mg/Ca and $\delta^{18}\text{O}$ measurements in foraminifera permit the explicit reconstruction of both temperature and seawater $\delta^{18}\text{O}$ variations. In surface-dwelling (planktonic) foraminifera, $\delta^{18}\text{O}$ values are sensitive to surface water fluxes (precipitation and evaporation) and ocean mixing via their impacts on seawater $\delta^{18}\text{O}$. Such paired analyses in planktonic foraminifera are thus a valuable way of assessing past hydroclimate variability and its response to forcing on centennial to orbital timescales (e.g. Lea *et al* 2000, Arbuszewski *et al* 2013, Jacobel *et al* 2016).

Marine sediments also contain organic matter from photosynthesizing organisms that serve as important records of past hydroclimate change. Organic hydrogen preserved in marine sediments serves as a proxy for past hydroclimate changes, as lipid $\delta^2\text{H}$ values derived from photosynthesizing organisms record variations

in $\delta^2\text{H}$ of their environmental waters (since water is the primary hydrogen source of photosynthesizing organisms and their biosynthetic products). The hydrogen isotopic composition of aquatic and terrestrial lipids in marine sediments provide reconstructions of seawater $\delta^2\text{H}$ (e.g. Pahnke *et al* 2007) and precipitation $\delta^2\text{H}$ (Tierney and deMenocal 2013), respectively. Hydroclimate reconstructions derived from the leaf waxes of terrestrial plants have provided a variety of key insights into past hydroclimate variations, including the identification of wet-to-dry transitions in tropical Africa over the past several thousand years the intensity, onset and duration of the green Sahara (Tierney *et al* 2017b) and potential climate forcing of migrations out of Africa \sim 200,000 years ago (Tierney *et al* 2017a). At higher latitudes, leaf wax reconstructions have been used to evaluate forced changes in modes of climate variability like the North American Monsoon during the Pliocene and LGM (Bhattacharya *et al* 2017, 2022) and polar climate variability during the Holocene (Corcoran *et al* 2021).

3.2. Centennial to interannual timescales: modes of climate variability and their teleconnections

On shorter, interannual-to-centennial timescales, water isotope-based records have provided critical information on the behavior of large-scale coupled modes of climate variability. Sources of isotopic information on these timescales include high-resolution (up to seasonal and sub-seasonal) proxy reconstructions using terrestrial and marine archives, as well as direct observations of isotopes in precipitation and seawater. Because of their higher temporal resolution, these isotopic data can be readily compared with results from isotope-enabled simulations of the ocean and atmosphere and other high resolution paleoclimate reconstructions, such as annual temperature reconstructions spanning the last 2000 years.

3.2.1. Lake sediments

On land, lake sediment records are an important source of high resolution (typically decadal to centennial) paleo-hydroclimatic information that spans centuries to millennia. As lakes have a global distribution, from the tropics to the high latitudes, such records provide crucial terrestrial water cycle information when other proxy archives, such as trees and ice, are not available. Hydroclimate reconstructions have been derived from a range of disparate isotope proxies in lake sediments, including the $\delta^2\text{H}$ values of aquatic and terrestrial lipids (Sachse *et al* 2012), the $\delta^{18}\text{O}$ values of authigenic and biogenic carbonates (e.g. Hodell *et al* 1991, Leng and Marshall 2004, Zhang *et al* 2011, Bhattacharya *et al* 2015, Wyman *et al* 2021), the $\delta^{18}\text{O}$ values of the siliceous frustules of diatoms (Dodd and Sharp 2010) and the $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\delta^2\text{H}$ values of gypsum hydration waters (Evans *et al* 2018). The unique combination of robust age control (up to annual resolution when annual sediment laminae, or varves, are present), along with the numerous other physical, geochemical, and biological measurements that typically accompany stable isotope measurements from lake sediments, renders lake sediment isotope records especially valuable as indicators of past climate and environmental change.

Although the temperature dependence of isotope fractionation between lake water and carbonate imparts a temperature signal in lake carbonate isotope values, stable isotope measurements from lake sediments are more commonly interpreted as proxies for the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of lake water (Ito 2001; Leng and Marshall 2004). In turn, these lake water isotope values reflect the balance and isotopic values of inputs into a lake system, namely precipitation, runoff, surface inflow and groundwater inflow, and outputs from the lake system, which include evaporation, runoff, surface outflow and groundwater outflow (Gonfiantini 1986, Gat 1995). If supplied with constraints on these values, isotope mass-balance hydrologic modeling can be used to improve understanding of the climatic signals archived in lake sediment isotope values (Gibson *et al* 2015).

Lakes without surface inflow or outflow, or closed basin lakes, simplify this mass balance, and thus are a frequent focus of paleolake studies (Talbot and Kelts 1990). In these studies, isotope records are frequently interpreted as reflecting precipitation minus lake water evaporation (Leng and Marshall 2004). One recent methodological advance of note used a lake catchment isotope mass balance model to demonstrate the predominance of precipitation in setting lake $\delta^{18}\text{O}$ values in the Pacific Northwest (Steinmann *et al* 2013). Given the extra degree of freedom provided by isotopic data, variability in precipitation isotope values are also often implicated in driving lake water isotope variability (e.g. Richey and Sachs 2016). Additionally, proxy system modeling for lake sediment isotope proxies have also been developed for the community in recent years, for both carbonate $\delta^{18}\text{O}$ and leaf wax $\delta^2\text{H}$ values (Jones *et al* 2018, Dee *et al* 2018b, Konecky *et al* 2019). Such process-based approaches permit more nuanced inquiries into the drivers of lake sediment-based $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values.

Lake sediment isotope records are a temporal ‘bridge’ between longer records of orbital climate variability and shorter proxy archive records that capture seasonal to interannual timescales. The sedimentation rates of most lakes produce records that are decadal to multi-decadally resolved, but interpretations of annual variability are possible, if varves (annual laminae) are present. Recently, stable

isotope records developed from lakes in ‘gold’ locales, sensitive to particular modes of the climate system, as well as networks of stable isotope records have been used to reconstruct the history of large-scale features and modes of the climate system. In the tropics and subtropics, salient examples include interpretations of shifts in ENSO frequency and intensity (Atwood and Sachs 2014, Yamoah *et al* 2016, Rodysill *et al* 2019) the meridional location of the ITCZ (Konecky *et al* 2013, Richey and Sachs 2016), Pacific Walker Circulation strength changes (Konecky *et al* 2013, Wyman *et al* 2021), as well as numerous records of past monsoon circulation variability (e.g. Zhang *et al* 2011, Anderson 2012, Bird *et al* 2011, Dixit *et al* 2014). In the mid-latitudes of the Northern Hemisphere, lake sediment isotope records have provided evidence of drought and pluvials resulting from past multidecadal variability in the Pacific North American (PNA) pattern (Bird *et al* 2017), and the North Atlantic Oscillation (NAO) (Diefendorf *et al* 2006, Auger *et al* 2019, Zhao *et al* 2022a). In the mid to high latitudes of the Southern Hemisphere, lake sediment isotope records have been applied to track westerly wind shifts (Moy *et al* 2008). In sum, lake sediment isotope records provide valuable information on major climate modes over past centuries to millennia that capture the high degree of natural variability inherent in the climate system and water cycle.

3.2.2. Corals

The majority of water isotope-based reconstructions on interannual to multidecadal timescales are derived from the stable isotope measurements of ice cores and coral skeletons, with the latter providing records that cover the last several millennia in tropical locations such as the central equatorial and southwest Pacific (see review by Thompson, 2022). Many coral species precipitate aragonite skeletons, with annual banding similar to tree rings. Variations in sea surface temperature exert a first-order control on the coral aragonite $\delta^{18}\text{O}$, but a secondary and critical control is the ambient seawater $\delta^{18}\text{O}$ during coral growth. The relative balance of temperature and seawater $\delta^{18}\text{O}$ influences on coral records varies widely across tropical ocean basins and depends on the relative magnitudes of sea surface temperature and seawater $\delta^{18}\text{O}$ variability, as well as their covariance, in the location of coral growth (Russon *et al* 2013, Thompson 2022).

Because seawater $\delta^{18}\text{O}$ depends on both surface freshwater fluxes and advection or mixing of oceanic water masses (Stevenson *et al* 2015, 2018, Conroy *et al* 2017, LeGrande and Schmidt 2006), coral records with stronger sensitivity to seawater $\delta^{18}\text{O}$ create opportunities to evaluate past ocean circulation (e.g. Conroy *et al* 2023), much as proxies recording precipitation $\delta^{18}\text{O}$ provide a means to evaluate past atmospheric circulation (LeGrande and Schmidt 2006). Moreover, with seawater $\delta^{18}\text{O}$ and salinity both sensitive to freshwater inputs—and salinity strongly correlated with large-scale changes in evaporation and precipitation (e.g. Durack *et al* 2012)—some coral $\delta^{18}\text{O}$ records are well-suited for evaluating changes in salinity and large-scale atmospheric moisture balance (Reed *et al* 2022, Thompson *et al* 2022). Given the need for improved constraints on regional patterns of both ocean temperature and hydrology, the practice of separating the temperature component of the coral isotope signal from the seawater $\delta^{18}\text{O}$ component, by pairing the coral $\delta^{18}\text{O}$ with Sr/Ca temperature proxies, has become increasingly common (McCulloch *et al* 1994, Walter *et al* 2022).

Because of where they grow and their high growth rates, coral isotope records have proven particularly useful for reconstructing the past interannual behavior of tropical climate, including one of the most globally important modes of variability, ENSO (Cobb *et al* 2013). While evidence from long coral reconstructions suggests anthropogenic warming is indeed leaving a mark in coral networks across the western Pacific, western Atlantic, and Indian Oceans (PAGES Oceans2k, Tierney *et al* 2015, Thompson 2022), one especially salient finding is that ENSO variability may be increasing with anthropogenic forcing (Cobb *et al* 2013, Li *et al* 2013, Grothe *et al* 2020, Zhu *et al* 2017)—a finding that is also substantiated by East Antarctic ice core records from the past five centuries (Rahaman *et al* 2019). Corals from the central Pacific suggest that ENSO’s variance over the last 50 years is 25% stronger than it was over the [last millennium (Grothe *et al* 2020). Other high-resolution coral reconstructions studies have provided evidence for multi-decadal changes in ENSO variability over the last millennium (e.g., Lawman *et al* 2020). Millennial analyses of Indian Ocean coral $\delta^{18}\text{O}$ suggest that the IOD has also become more variable and that positive IOD events have become more intense in recent decades (Abram *et al* 2020); broadly speaking, such long records indicate an important coherence between Pacific and Indian Ocean variability.

In addition to revealing changes in ENSO intensity, coral networks have provided insight into the changing ‘flavors’ of El Niño events. Central Pacific El Niños—events which tend to be weaker and centered farther west—are contribute to drought conditions in south Asian monsoon regions (Kumar *et al* 2006), among other important distinctions from their Eastern Pacific counterparts in terms of teleconnection impacts. Analyses of corals over the past four centuries suggest that Central Pacific El Niños may have become more frequent compared to Eastern Pacific El Niños during the 20th century (Freund *et al* 2019). However, Central Pacific El Niños do not appear to have become more intense in the way that Eastern Pacific El Niños have (Freund *et al* 2019, Grothe *et al* 2020). Beyond changes in interannual variability, ensembles of

coral $\delta^{18}\text{O}$ records can also capture longer climate trends, such as 20th century warming and freshening trends in the tropical Pacific (Hitt *et al* 2022).

Finally, while providing long records on tropical hydroclimate change, coral $\delta^{18}\text{O}$ also provides information about ENSO's response to short-term forcings. Dee *et al* (2020), for example, used monthly-resolved coral records from the central Pacific to show that the ENSO response to volcanic forcings appears to be weaker than previously suggested by tree ring-based proxy synthesis products—a finding that stands in direct contrast to many model simulations.

3.2.3. Tree ring cellulose

The cellulose of tree ring wood expands paleoclimate information from tree rings, providing rich water isotope hydrology information with seasonal-to-annual resolution (McCarroll and Loader 2004, Schubert and Hope Jahren 2015). The isotopic composition of the soil and xylem water, evapotranspiration during photosynthesis, and isotopic back-diffusion between the leaf/needle and xylem water all contribute to the final measured $\delta^{18}\text{O}$ signal. Thus, tree ring cellulose oxygen isotopes may commingle variations in precipitation, evaporation, and soil and groundwater processes (Roden and Ehleringer 2000, Roden *et al* 2000, 2002, Anderson *et al* 2002, Barbour *et al* 2002, Evans 2007)

Wood cellulose reconstructions have enabled high-resolution paleoclimate reconstructions in tropical latitudes, where other proxy data at annual resolution are generally sparse. Reconstructions using tree ring width, for example, rely on strong seasonality, which is often absent at low latitudes. By contrast, the oxygen isotope composition in wood cellulose houses information about changes in the $\delta^{18}\text{O}$ of precipitation, capturing changes in wet- and dry-season rainfall and moisture supply. The $\delta^{18}\text{O}$ of wood cellulose has been used to explore hydroclimate and ENSO variability (Boysen *et al* 2014) in the tropical Americas (Anchukaitis *et al* 2008, Anchukaitis and Evans 2010, Rodriguez-Caton *et al* 2022) and in Southeast Asia (Chenxi *et al* 2011, Zhu *et al* 2012). Cellulose reconstructions have also been used to capture high-resolution changes in the Asian Summer Monsoon system (Xu *et al* 2018). These records broadly indicate that stable oxygen isotopes in cellulose are dominated by interannual hydroclimate variability rather than by large global warming trends, and the seasonal resolution of these records accurately captures both wet and dry periods associated with extreme ENSO events and record monsoon years, often tied to both human and ecological perturbations (e.g. Anchukaitis and Evans 2010). Long reconstructions from multiple oxygen isotope chronologies offer evidence for a post-industrial weakening of the Indian Summer Monsoon (Xu *et al* 2018). Given recent advances in extraction methodology (Andreu-Hayles *et al* 2019, Switsur and Waterhouse n.d.2020), oxygen isotopes in tree wood cellulose have proven to be powerful tools for capturing past hydroclimate extremes (e.g. drought, pluvials) on seasonal-to-interannual timescales (Zhao *et al* 2022b, Szejner *et al* 2021, Nagavciuc *et al* 2022).

3.2.4. Ice cores

Ice cores with annual and sub-annual resolution have provided critical context for rates and amplitudes of anthropogenic climate change at high latitudes and polar amplification (as summarized in Jones *et al* 2001, Thompson *et al* 2003, Abram *et al* 2013, and many others). For example, recently, Hörhold *et al* (2023), used water isotopes in ice cores to demonstrate that current temperatures in central Greenland exceed those of any other time in the last millennium.

High resolution ice core data also help elucidate the dynamical conditions that enhance the strength of tropical-polar teleconnections associated with modes of climate variability like ENSO (Patterson *et al* 2005, Schneider *et al* 2012, Crockart *et al* 2021). Indeed, many West Antarctic isotope records are broadly correlated with tropical SSTs on multi-year timescales (Schneider and Steig 2008, Okumura *et al* 2012). During the positive phase of ENSO, mid-latitude eddies, including the polar jet stream, tend to weaken (Xichen *et al* 2021). This reduces vertical mixing and advection of evaporated water from the mid-latitudes and creates stronger moisture dependencies between the tropics and the poles (Noone 2008). Moreover, as tropical deep convection shifts eastward, Rossby wave trains develop, whose downstream high pressure anomalies alter warm air advection near the West Antarctic coast (Okumura *et al* 2012, Jones *et al* 2018, Xichen *et al* 2021). Specifically, it is the zonal position of convection that appears to influence the efficacy with which the waves permeate mid-latitude wind barriers and propagate poleward. These teleconnections highlight the correlations between high polar isotope ratios, high polar temperatures, and weakened global circulation during El Niño events.

Other modes of variability regulate the strength of these correlations. For instance, West Antarctic ice records from the first half of the 20th century show an anomalously large positive shift in isotope ratios associated with the 1939–1942 El Niño, which occurred during a period in which the Southern Oscillation Index (SOI) was in phase with the Southern Annular Mode, or SAM (Schneider and Steig 2008)—the dominant mode of high-latitude circulation variability in the Southern Hemisphere. (Gregory and Noone

2008) argued that even though SOI and SAM have opposing effects on West Antarctic isotope ratios, the two patterns of variability must be positively correlated in order for ENSO teleconnections to reach the poles effectively. Other studies have demonstrated qualitatively similar teleconnection sensitivities to SAM in other Antarctic locations (Fogt and Bromwich 2006, Kino *et al* 2021). Ice core isotopic records thus provide two important opportunities. First, they reinforce the idea that models must accurately simulate tropical climate and its teleconnections in order to predict Antarctic temperature and sea ice changes (Steig *et al* 2013, Holland *et al* 2019). Second, they provide an opportunity to test our understanding of how the strength and position of tropical SSTs influence mid- and high-latitude circulation anomalies and the ability of Rossby wave trains to reach higher latitudes.

Low-latitude ice core isotopic records, such as from the Quelccaya ice cap in Peru (well-known for its strong 19th–20th century anthropogenic trend, Thompson 2000, Thompson *et al* 2003) also record higher $\delta^{18}\text{O}$ values during El Niños (Thompson and Mosley-Thompson 2013, Thompson *et al* 2017). Multi-year snow sampling and modeling efforts have confirmed that these signals are the result of changes in the South American Monsoon, which reduce precipitation over the Amazon and allow a greater proportion of isotopically heavy water to reach the western Amazon and high Andes (Hurley *et al* 2019b).

3.2.5. Modern water isotope observations

As modern water isotope observations—including precipitation samples and remote-sensing retrievals—grow in number, they are becoming increasingly used to evaluate modes of climate variability and their teleconnections. Through the GNIP, precipitation collections extend back to the 1960s in some locations, and remotely sensed $\text{H}^2\text{HO}-\text{H}_2\text{O}$ pairs are available from the early 2000s onward (see Section 2.2.2). These records provide both higher temporal resolution and greater spatial coverage than proxy networks. They also extend our ability to investigate teleconnection patterns to many mid- and high-latitude locations. Examples include the PNA pattern (Birks and Edwards 2009, Liu *et al* 2011, 2013, Liu *et al* 2014); the NAO (Sodemann *et al* 2008), ENSO and the IOD (Sutanto *et al* 2015, Dee *et al* 2018a, Moerman *et al* 2014, Moerman *et al* 2013).

In addition to capturing interannual variations in tropical Pacific dynamics associated with ENSO, water isotopic information has been used to study variations in the strength of the Walker Circulation on decadal timescales (Dee *et al* 2018a, Falster *et al* 2021). Indeed, (Dee *et al* 2018a) used simulations to show that as the Walker Circulation slows, $\delta^2\text{H}$ in the mid-troposphere decreases in the west Pacific (the region of large-scale upward motion) and increases in the east Pacific (the region of large-scale subsidence), capturing the changing vertical mass flux. Falster *et al* 2021 subsequently showed that the changing water vapor signal leaves an imprint on local precipitation isotope ratios, which can be detected across the Pacific basin.

3.3. The common era: internal variability from global proxy compilations

Using water isotope-based proxies to better constrain water cycle processes has not only improved our understanding of large-scale dynamics, teleconnections, and the general circulation; it has also greatly improved temperature reconstructions over the Common Era (PAGES 2k Consortium 2013, PAGES 2k-PMIP3 group 2015, Jungclaus *et al* 2017, Mann 2021). These reconstructions place today's anthropogenically-forced climate & temperature changes within the important context of centuries of inherent variability. Such Paleo-DA reconstructions—which fuse the dynamical information of climate models with annually resolved proxy information spanning the last 2000 years using offline data assimilation (e.g. Steiger *et al* 2014)—has resulted in proxy-constrained products such as the Last Millennium Reanalysis Project (Hakim *et al* 2016) and the Paleo Hydrodynamics Data Assimilation (PHYDA, Steiger *et al* 2018). Both LMR and PHYDA provide gridded multivariate and dynamically consistent climate reconstructions spanning from 1 to 2000 C.E. PHYDA specifically reconstructs global hydroclimate using over 2000 proxies, including hydroclimate-sensitive water isotope records.

Such reconstructions provide an important benchmark for GCM-simulated internal variability. For instance, recent analyses show that simulations tend to agree with reconstructions on the amplitude of unforced global-mean multidecadal temperature variability; this increases confidence in future projections of climate change on these timescales (PAGES 2k Consortium 2019). Simulations and reconstructions are also in broad agreement for Northern Hemisphere regions, but disagree in the Southern Hemisphere. These discrepancies suggest that models may underestimate internal variability and produce too much regional coherence. Alternatively, they may overestimate the Southern Hemisphere response to external forcing (Goosse 2015, PAGES 2k-PMIP3 group 2015, Abram *et al* 2017, PAGES2k Consortium 2017). New studies are now using global networks of water isotope proxy records (e.g. Iso2k, Konecky *et al* 2020) to provide constraints on global water-cycle changes during the Common Era. These will provide an important check on simulated relationships between global hydrology and global temperature from models (Atwood *et al* 2021). As discussed in section 4, our ability to precisely quantify climate variations in the past helps improve

our ability to predict climate changes in the future and to identify anthropogenically-forced changes as they emerge from the background of climate noise.

3.4. Seasonal to weather timescales: the MJO

Modern precipitation and water vapor isotope observations provide an opportunity to evaluate the dynamical processes regulating higher frequency variability, including seasonal (Wright *et al* 2017, Feng *et al* 2009), intraseasonal (Berkelhammer *et al* 2012, Tuinenburg *et al* 2015, Hurley *et al* 2019a), and synoptic variability (Noone *et al* 2011). In the tropics, the dominant mode of intraseasonal variability is the MJO, which is characterized by the eastward propagation of mesoscale convective systems (MCSs) across the Indian and tropical Pacific Oceans over a period of 30–90 days (Madden and Julian 1994). Understanding this propagation remains a question of critical interest for extended-range weather and climate prediction, since the MJO's convective activity influences the timing and strength of monsoons (e.g. Lorenz and Hartmann 2006, Lavender and Matthews 2009, Grimm 2019), the number and strength of tropical cyclones (e.g. Maloney and Hartmann 2000), and the characteristics of extratropical circulation anomalies and precipitation patterns (e.g. Higgins *et al* 2000, L'Heureux and Wayne Higgins 2008, Riddle *et al* 2013, Lukens *et al* 2017, Lin and Brunet 2018, Barnes *et al* 2019, Franzke *et al* 2019).

The role of moist processes in helping generate and sustain the MJO has long been suspected (Madden and Julian 1994). However, efforts to describe moisture's role theoretically are more recent (Adames and Kim 2016). Isotopic investigations have contributed to our understanding mainly by identifying the moist processes that define the distinct stages of the MJO (Kurita *et al* 2011, Berkelhammer *et al* 2012, Kurita 2013, Tuinenburg *et al* 2015, Conroy *et al* 2016, Hurley *et al* 2019a), thus helping pinpoint the GCM physics critical for MJO simulation.

Studies leveraging tropics-wide isotopic retrievals from satellites consistently identify four stages of distinct moisture regimes (Berkelhammer *et al* 2012, Tuinenburg *et al* 2015, Hurley *et al* 2019a). These stages occupy the four quadrants on a plot of isotope ratio versus specific humidity, indicating that the isotopic observations contribute unique information in the identification of moistening and dehydrating processes (Hurley *et al* 2019a). During the first stage of the MJO lifecycle, large-scale vertical mixing isotopically enriches the lower free troposphere. During the second phase, development of shallow convection moistens the free troposphere and pre-conditions the atmosphere for deep convection. In the third stage, during the height of convective activity, minima in vapor isotope ratios indicate that rain re-evaporation plays a role in sustaining organized convection by maintaining moisture aloft and facilitating cold pool formation. Berkelhammer *et al* 2012 specifically suggested that both moistening by vertical mixing and drying by large-scale circulation may be active during this period. Finally, in the fourth stage, large-scale drying occurs, associated with subsidence and stratiform cloud formation.

To better understand the processes involved at the center of MJO convective activity, (Kurita 2013) developed a simplified model that illustrates how rain evaporation and exchange processes within the stratiform region of an MCS lower the water isotope ratio. Based on his analysis, he postulated that as each MJO MCS develops, it entrains moisture that has been progressively depleted of isotopically heavy water by a preceding storm, producing ever-more depleted precipitation. Rainfall collections from tropical islands during MJO events support this hypothesis (Moerman *et al* 2013, Conroy *et al* 2016). These findings have inspired a new direction of study into the relationship between rainwater isotope ratios and the proportion of stratiform versus convective precipitation (Aggarwal *et al* 2016, Sun *et al* 2019, Chang *et al* 2020). Collectively, these investigations suggest that water isotope ratios are a sensitive metric to the degree of storm organization. Not only does this provide a valuable diagnostic for GCMs, which often parameterize convection, but it also creates an exciting new lens through which to view paleoclimate archives. One recent study has used water isotope data from speleothem records in Texas to argue that storm regimes across the Southern Great Plains became stronger and more organized during glacial to interglacial transitions—a finding that suggests they may also do so with anthropogenic warming (Maupin *et al* 2021).

4. Anthropogenic forcing, detection, and attribution

Water isotope-based proxies and modern measurements both have a critical part to play in helping us understand how human activities are fundamentally changing the climate system and water cycle now and in the future. While proxy archives inform temperature and hydroclimate reconstructions and provide benchmarks for longer paleoclimate simulations, modern measurements allow us to evaluate our confidence in GCM physics, and to refine our interpretation of proxies. Together, these observations are key for testing predictions about which processes control the sensitivity of the climate system to radiative forcing changes, and for detecting anthropogenically-forced changes against the climate system's highly variable background.

4.1. Climate sensitivity

Equilibrium climate sensitivity (ECS) measures a GCM's warming response to a doubling of atmospheric CO₂ and has become a popular and important metric for describing our confidence in future warming projections. Much of today's divergence in ECS estimates stems from uncertainties in the parameterized representation of cloud and precipitation processes (Sherwood *et al* 2020). Water isotope records thus provide some of our most informative constraints on climate sensitivity. One way to evaluate climate sensitivity is to assess whether models are able to reproduce the precipitation and oceanic isotope ratios inferred from proxy records from periods whose greenhouse gas forcing and mean climate states are far different from today's (Sherwood *et al* 2020, Tierney *et al* 2020). For example, (Zhu *et al* 2022) used paleoclimate reconstructions from the LGM to tune the cloud microphysics scheme of the Community Earth System Model (CESM). By removing a cap on cloud ice number and modifying the scheme's timestep in order to make simulations consistent with LGM records, they lowered the model's ECS, proving that current estimates using standard configurations are too high. Similar analyses with CESM have isolated cloud feedbacks as key drivers of high climate sensitivity in simulations of the Eocene (Zhu *et al* 2019). Other studies working with the NASA GISS model have worked to refine climate sensitivity estimates by tuning cloud and convection parameters against water isotope-based reconstructions from time periods like the LGM, mid-Holocene, and pre-industrial (e.g., Ramos *et al* 2022).

In addition to supporting data-model comparisons for periods before the instrumental record, water isotopes can bolster our confidence in simulations of future climate by helping diagnose and address problems in model physics broadly. As a higher order quantity, water isotopes tend to highlight problems with water cycle *processes*, not just the hydroclimate *state*. They can therefore isolate compensating errors that may not be immediately obvious from other variables. For instance, (Risi *et al* 2012) used water vapor isotopic observations to show that excessive vertical diffusivity of moisture contributes to humidity biases in many models. Nusbaumer *et al* (2017) used precipitation isotope ratios to determine that deep convection triggers too frequently in CESM, causing biases in precipitation. Others have similarly used water isotopic information to identify problems with the representation of stratiform precipitation in convection, to detect biases in the Walker circulation, and to characterize the sensitivity of low clouds to mixing processes (Hu *et al* 2018, 2020, 2022). Water isotopes can also provide a means to distinguish between thermodynamic and dynamic drives of climate variability (Dee *et al* 2018a, Bailey 2020, Risi *et al* 2020), helping us understand, for instance, the differences between local moistening of the atmosphere and moisture transport. These studies prove that there is immense potential for continued water isotope data-model comparison across key paleoclimate and modern horizons to help improve models, simulations, and forecasts.

4.2. Detection and time of emergence

While water isotopic information provides an important model diagnostic to evaluate the accuracy and precision of climate changes in the future, it may also help us identify signs of anthropogenically forced climate change over the next few decades. Signs of anthropogenic forcing are already evident when it comes to global-mean temperature (Arias *et al* 2021, Stephen 2021) and regional patterns of soil moisture (Stevenson *et al* 2022); however, the human fingerprint on many hydrologic variables is not always clear. For instance, while early studies reported evidence of increasing precipitation in the deep tropics from satellite observations (Allan *et al* 2010, Zhou *et al* 2011)—as predicted from basic thermodynamic theory (e.g. Held and Soden 2006)—more recent syntheses covering the last decade have argued that precipitation trends are not statistically significant (Allan *et al* 2020). Isotopes may prove especially useful for helping detect signals of change in this case.

Indeed, because water isotope ratios are integrative quantities, they can help 'smooth out' the high level of inherent spatial variability that plagues traditional measurements and obfuscates signals of forced anthropogenic change. Moerman *et al* (2013), for instance, showed that precipitation isotope ratios expressed a regionally coherent pan-tropical climate signal, even in cases when measurements of regional precipitation amount did not. Furthermore, because there is broad coherence between the isotope ratios of water vapor and precipitation (e.g. Bailey *et al* 2017, 2018), isotopic measurements in water vapor should allow us to detect the time of emergence of water cycle changes even in regions where precipitation is scarce.

Modern isotope observations can also be compared with the long paleoclimate record, which provides a critical baseline for statistically quantifying the behavior of water fluxes. This comparison should allow us to identify, with greater confidence, the time at which forced signals emerge beyond the range of natural variability. Additional opportunities include leveraging data assimilation techniques to identify the places where water isotopic changes should most strongly and clearly emerge; this will ensure that observational stations are optimized for detecting the fingerprint of human-caused change (Bailey *et al* 2021).

5. Outlook, opportunities, and recommendations

Water isotopes throughout the Earth system create a common unit that uniquely links paleoclimate reconstructions, modern climate observations and isotope-enabled model simulations (as described in sections 1–3). This common framework—linking the past, present, and future—enhances our understanding of past variability throughout Earth’s history and provides key opportunities for benchmarking climate models by comparing them with observed variables in the same units (figures 1 and 6). Water isotopes also help distinguish drivers of climatic variability over time, informing us about the processes that influence hydroclimate in ways that more traditional variables do not. Because of these characteristics and the integrative nature of isotopic information, there is profound potential for water isotopes to improve estimates of time of emergence and ECS, both from paleoclimate reconstructions and by refining model physics (section 4).

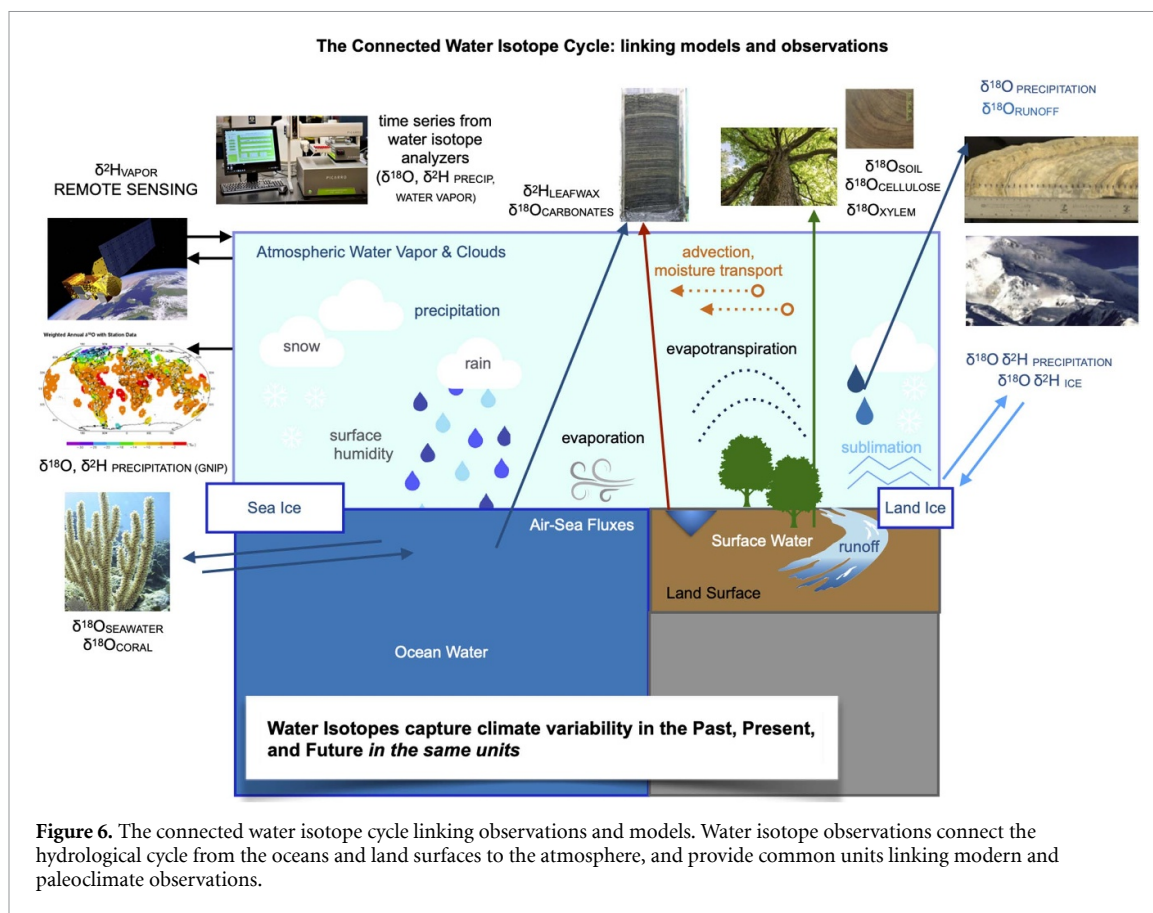
In this review, we have shown how increased observations and greater integration of isotopic tracers in numerical simulations have helped us gain critical insight into climate variability on timescales ranging from hours to millennia. For example, they have helped us:

- elucidate the coupled atmosphere-ocean response to abrupt climate forcings
- identify the factors that influence the strength of tropical monsoons and their seasonality
- investigate the dynamics that define ENSO states and elevate the sensitivity of polar regions to melt through global teleconnections
- define the moist processes that dominate distinct stages of the MJO

We have also seen how long records of isotopic variability allow us to capture changes in both the mean state of the climate system and its variance with greater confidence. This has allowed us to detect increases in variance in both ENSO and the IOD over recent decades. Finally, we have discussed how projecting future climate and identifying near-term changes in the water cycle can significantly benefit from the addition of water isotopic information—on the one hand, because water isotopes smooth inherently noisy signals, and, on the other, because they provide an extra degree of freedom for diagnosing model skill.

Nevertheless, to achieve the full potential of water isotopes as climate variables, additional commitments to modern observations, modern and paleoclimate data syntheses, and isotopically enabled models are necessary. Activities that bridge these scientific tools, including proxy system modeling, data assimilation, isotope data-model comparisons, should also be accelerated. We suggest the following recommendations to achieve these goals.

- *Sustaining Existing Long-term Measurements:* One of the unique qualities of water isotopes is that they provide an incredibly long record of climate variation. Supporting existing stations, networks, and satellite retrievals will help lengthen isotopic records to quantify current and future hydroclimate trends. Sustained *in-situ* monitoring is also critical for clarifying proxy biases, including those driven by seasonality, microclimate, or proxy system effects.
- *Expanding Observations Into New Key Locations:* Many climatically important regions are still severely under-represented in the modern isotopic record, compromising process-oriented studies and model diagnostic evaluations. These include the tropical Pacific and the Global South, as well as most of the free troposphere (where vertically resolved observations are few and far between). Given the enormous influence of tropical Pacific interannual variability and the high sensitivity of polar regions, robust pan-tropical and pan-Arctic networks of water isotope observations would be highly beneficial for evaluating global change. Furthermore, observations that target processes that influence how isotopic signals are transferred from the atmosphere to other reservoirs can help us improve our interpretation of paleoclimate records. Finally, we can use model simulations to identify locations where isotopic signal-to-noise is expected to be higher than that of other hydroclimate variables (e.g. precipitation). Such sites could help quantify the time of emergence of climate changes.
- *Supporting Paleoclimate Data Campaigns and Reconstructions:* New global paleoclimate networks are poised to facilitate advanced interpretation of global climate changes and large-scale shifts in the hydrological cycle. Increasing the number of independent proxy reconstructions from climatically important regions is needed to bolster confidence in PSMs and paleoclimate signals (particularly where geographic variability in isotopic records is complex). Such replication efforts and increased data availability will broaden our use of paleoclimate reconstructions. Of particular need are high-fidelity, high resolution records that provide context for understanding present and future global water cycle changes. Key target periods include time horizons where Earth has seen large changes in external climate forcing, such as the Last Interglacial (~120kyr ago),



LGM (~21kyr ago), Mid-Holocene (6–8kyr), and the Common Era (last 2000 years), including the recent past during.

- *Developing New PSMs:* Continued improvement of PSMs will help us reconstruct past variations in temperature and precipitation with greater accuracy (e.g. Evans *et al* 2013, Dee *et al* 2015a, 2018b, Jones and Dee 2018, Konecky *et al* 2019, Lawman *et al* 2020) and provide important constraints on proxy uncertainties. Coupled with water isotope-enabled models, PSMs provide a full data-model comparison framework that links climate to proxy observation, placing models and observations in the same units. We suggest that development efforts focus on water isotope based proxy systems for which no PSM exists and on adding functionality to published models for corals, speleothems, tree ring cellulose, leaf waxes, ice cores, and lake sedimentary archives (figure 4).
- *Building Big Databases:* Developing and expanding large observational or multi-proxy databases (e.g. IsoBank, Iso2k; figure 5) enhances access to isotopic information and creates new opportunities to investigate large-scale climate features, such as the Global Monsoon and the Walker Circulation, while also providing multiple data points for model-observation comparison. Additional efforts are needed to synthesize and compile modern observations into databases that facilitate comparison with paleoclimate reconstructions and isotope-enabled climate model output.
- *Leveraging Water Isotopes to Refine Model Physics and Tuning; Updating Water Isotope Tracers in Models:* As tracers of water-cycle processes, water isotopes provide an important benchmark and extra degree of freedom for evaluating numerical simulations across timescales. Global atmospheric observations on sub-monthly timescales will prove crucial for forthcoming data-model comparison efforts and model inter-comparison efforts (e.g. Noone and Sturm 2010, Risi *et al* 2012a). While paleoclimate archives and modern in-situ observations are essential for model-data comparisons, gridded satellite measurements of water vapor isotope ratios could also prove especially useful in this regard, as they provide near-global spatial coverage. However, to facilitate this, water isotope physics must be added up front to production runs for IPCC-class GCMs. Usually, water isotope physics are added after the fact, once a model has been locked; we suggest that, because of the utility for data-model comparison and hydrological cycle variability reviewed here, water isotopes must be included throughout the model development process, and require consistent stewardship to ensure continuity between model versions. Yet few modeling centers include water isotopic physics *at all*. More widespread integration of isotopic physics in numerical simulations and stewardship to

ensure continuity between model versions would allow more comprehensive evaluation of inherent climate variability and the representation of moist processes. Just as we have teams that are responsible for land model hydrology, so too should large modeling centers maintain teams responsible for the water isotope physics in all model components.

Given the maturation of isotope measurement and modeling, this is an opportune time to leverage water isotopes to address grand challenges in our understanding of the climate system and to advance our ability to predict climate variations and changes across time scales. We hope this review serves as a catalyst spearheading new water isotope science to address the critical climate challenges we face as a global society in the 21st century.

Data availability statement

No new data were created or analysed in this study.

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