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Water isotope systematics: improving our palaeoclimate interpretations

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The stable isotopes of oxygen and hydrogen, measured in a variety of archives, are widely used proxies in Quaternary Science. Understanding the processes that control $\delta^{18}\text{O}$ in atmospheric water in particular have long been a focus of research (e.g. Shackleton and Opdyke, 1973; Talbot, 1990; Leng, 2006). Both the dynamics of water isotope cycling and the appropriate interpretation of geological water-isotope proxy time series remain subjects of active research and debate. It is clear that achieving a complete understanding of the isotope systematics for any given archive type, and ideally each individual archive, is vital if these palaeo-data are to be used to their full potential, including comparison with climate model experiments of the past. Combining information from modern monitoring and process studies, climate models, and proxy data is crucial for improving our statistical constraints on reconstructions of past climate variability.

As climate models increasingly incorporate stable water isotope physics, this common language should aid quantitative comparisons between proxy data and climate model output. Water-isotope paleoclimate data provide crucial metrics for validating GCMs, whereas GCMs provide a tool for exploring the climate variability dominating signals in the proxy data. Several of the studies in this set of papers highlight how collaborations between paleoclimate experimentalists and modellers may serve to expand the usefulness of paleoclimate data for climate prediction in future work.

This collection of papers follows the session on *Water Isotope Systematics* held at the 2013 AGU Fall Meeting in San Francisco. Papers in that session, the breadth of which are represented here, discussed such issues as; understanding sub-GNIP scale (Global Network for Isotopes in Precipitation, [IAEA/WMO, 2006]) variability in isotopes in precipitation from different regions, detailed examination of the transfer of isotope signals from precipitation to geological archives, and the implications of advances in understanding in these areas for the interpretation of palaeo records and proxy data – climate model comparison.

Here, we briefly review these areas of research, and discuss challenges for the water isotope community in improving our ability to partition climate vs. auxiliary signals in paleoclimate data.

Isotopes in precipitation and surface water

Understanding water isotopes in proxies and models begins with their measurement in atmospheric vapour and water, ongoing now for over five decades, through established monitoring networks, individual research projects, and remote sensing, at temporal scales ranging from seconds to monthly composites (Darling et al., 2006). From the proxy perspective, however, with the exception of ice cores, the water isotopes incorporated within archives are rarely derived directly from precipitation. Rather, terrestrial isotope archives, such as lake sediments, speleothems and trees, incorporate surface and near-surface waters that may or may not have the same relationships to climate as atmospheric vapour and precipitation. This complication is addressed by Gibson et al., Jones et al., Anderson et al., and Murkowska et al. in this volume. However, for all archives, the understanding of local-to-regional climate controls on precipitation isotope compositions, needed to evaluate isotope proxy records, typically comes from either a few, distant, long-term network stations, or from short-term local measurements if financial and logistical constraints allow (*e.g.*, Bailey et al., 2015; Berkelhammer et al., 2011; Ersek et al., 2012; Klein et al., 2015; Liu et al., 2014). Thus, in terms of monitoring water isotopes in space and time, there is presently notable interest in the proxy community focused on (1) developing strategic precipitation and surface water monitoring approaches to observe isotope systematics between climate, local-to-regional precipitation, and individual proxy archive locations and (2) how to apply monitoring measurements and to appropriately develop proxy calibrations with space-for-time or time-for-space relationships, with appreciation for relative strengths and limitations.

Three studies in this special issue address monitoring of precipitation and surface water and assess implications for paleoclimatic interpretations. Sanchez-Murillo et al. (this issue) investigate the commonly applied tropical “amount” effect on precipitation isotope ratios identified from GNIP measurement over multi-annual time scales, known to substantially weaken at shorter time scales. They present isotope measurements of daily Costa Rican precipitation for 2013 from three strategic locations to more precisely identify regional climate controls on rainfall $\delta^{18}\text{O}$. Similarly, Klein et al. (this issue) interpret the McCall glacier ice core record from Northern Alaska based on 254 event-based precipitation samples obtained nearby over an 18-year period. Utilizing the temporal climate-isotope relationships identified from a fixed location, they apply a local $\delta^{18}\text{O}$ -T coefficient to the ~65 year long ice core record, with consideration for vapour source and circulation changes. Finally, Anderson et al. (this issue) present a new long-term monitoring network in North America of isotopes in Rocky Mountain snowpack with ~20 years of integrated snowpack measurements at 57 locations. The temporal and spatial measurements provide the first opportunity for comparisons between mid-latitude snowpack isotope composition and climate variability. New insights are utilized to re-evaluate previously presented Holocene isotope records with snowpack dominated water sources.

Each of these studies illustrates the potential for local to regional monitoring to inform interpretations of proxy records. For example, analyses of daily-scale Costa Rican precipitation and meteorological data provide a more dynamically-based understanding of

variations that occur over the seasonal cycle. The dominant controls on precipitation and cave drip water, including vapour origin and transport, surface humidity, and lifted condensation levels have important implications for speleothem isotope time series in the region, which can be sampled at annual to sub-annual resolution (e.g., Lachniet et al., 2007). The event-scale precipitation data from northern Alaska (Toolik Lake), the first long-term measurements in the region, indicates a $\delta^{18}\text{O}$ -T coefficient of 0.36‰ per °C, considerably lower than the range of spatial and temporal GNIP based estimates for this latitude (0.7 to 0.9‰ per °C). Further analyses of the ice core suggests the significance of additional influences, including changes in source vapor related to sea-ice extent and decadal-scale North Pacific atmospheric circulation patterns. Lastly, the Rocky Mountain snowpack network also indicated a low spatial $\delta^{18}\text{O}$ -T relationship of 0.4‰ per °C (similarly to northern Alaska), characterized by significant spatial heterogeneity. Temporal $\delta^{18}\text{O}$ -T relationships varied through time from 0.23 to 0.63‰ per °C. Drier/warmer years had a tendency to have no statistically significant correlation at all that suggests the significance of post-depositional effects.

As demonstrated by these authors in particular, local-to-regional monitoring at a proxy location provides important evidence for location-specific physical processes, providing additional insight towards the ultimate paleoclimatic interpretation.

Modelling water isotopes and the climate

This special issue additionally highlights the utility of water isotope-enabled GCMs for the enhanced interpretation of proxy data. Using water isotope-enabled GCMs constitutes a point of common comparison with water isotope based climate archives and provides a basis for dynamical interpretations of the paleoclimatic data. In particular, modelling water isotopes in the atmosphere provides insights in the hydrological cycle including circulation changes, temperature, precipitation, condensation, evaporation and vapour source (Sturm et al., 2010; Dee et al., 2014).

Stable water isotope physics have been added to a number of GCMs to-date, including but not limited to: the National Center for Atmospheric Research Community Atmosphere Model (CAM2) [Lee et al., 2007], European Centre/Hamburg (ECHAM4) [Hoffmann et al., 1998], Goddard Institute for Space Studies (GISS) [Schmidt et al., 2007], Hadley Center Coupled Model 3 (HadCM3) [Tindall et al., 2009], iLOVECLIM [Roche, 2013], IsoGSM [Yoshimura et al., 2008], Laboratoire de Météorologie Dynamique Zoom 4 (LMDZ4) [Risi et al., 2010], Model for Interdisciplinary Research on Climate (MIROC) [Kurita et al., 2011], Global Environmental and Ecological Simulation of Interactive Systems 3 (GENESIS3) [Mathieu et al., 2002], Melbourne University General Circulation Model (MUGCM) [Noone and Simmonds, 2002], SPEEDY-IER (Simplified Parameterizations, Primitive Equation Dynamics with Isotope-Enabled Reconstructions) [Dee et al., 2014], and UVic ESCM [Brennan et al., 2012]. Many of these isotope-enabled models have been compared by the Stable Water Isotope Intercomparison Group projects (SWING and SWING2) (<http://www.giss.nasa.gov/staff/gschmidt/SWING2.html>), [Conroy et al., 2013], and share the common capability of tracking changes in the hydrological cycle as they manifest in water isotope signals.

Explicitly embedding water isotope tracers within the physics of a GCM serves to check the reliability of proxy-environment relationships, and helps highlight potential uncertainties. In this issue, Holloway et al. illustrate the usefulness of the isotope-enabled Hadley Center Model (HadCM3) to examine the stationarity of the relationship between oxygen isotope ratios in seawater to sea surface salinity ($\delta^{18}\text{O}_{\text{sw-SSS}}$) on longer timescales. The isotope enabled modelling framework allows for the identification of uncertainties such as freshwater budget, circulation, and sea ice dynamics, and the impacts of such uncertainties on the stability of this widely-used $\delta^{18}\text{O}_{\text{sw-SSS}}$ slope for paleoceanographic studies. Further, the authors identify that paleosalinity reconstructions may be more robust within specific regions, and identify these regions explicitly using the coupled isotope-enabled model. Their work importantly suggests that further constraint is needed when using the $\delta^{18}\text{O}_{\text{sw-SSS}}$ gradient for reconstruction purposes.

Similarly, Holmes et al. (this issue) illustrate the utility of isotope-enabled GCMs for enhanced interpretability of proxy archives. The authors employ HadCM3 to explore oxygen isotope variability in three lakes in western Ireland across the 8.2 ka ('early Holocene cooling') event. The study uses an ensemble of nine transient simulations centred on boundary conditions appropriate for 9000 yr BP with a freshwater melt push mimicking the draining of Lake Agassiz (Tindall and Valdes, 2011). Comparing the timing and magnitude of the isotopic excursions observed in the three Atlantic margin lakes to HadCM3 simulations of precipitation isotopes allows the authors to explore potential dynamical drivers of the observed cooling in Northern Europe. The study finds that all of the ensemble members show effective moisture (lower evaporation coupled with reduced precipitation) linked to a decrease in $\delta^{18}\text{O}$ of precipitation over the study area, and thus provide a climatic interpretation for the lake $\delta^{18}\text{O}$ records, as supported and confirmed by model experiments.

These studies illustrate the usefulness of isotope-enabled GCMs for providing additional dynamical constraints on paleoclimatic data interpretation. Water isotopes are a critical addition, facilitating direct comparison between model and archive by providing a common language linking the two.

Modelling the Archive

Proxy system models (PSMs) are increasingly being discussed (e.g. Evans et al., 2013) and developed as a means for quantitatively understanding the filtering of the climate signal or other environmental variables by natural archives. As discussed above in relation to monitoring, isotope-climate 'transfer functions' are complex and regression-based techniques for comparing proxy data sets and instrumental climate data are not always appropriate, as they can misconstrue the sensitivity of a system to individual climate parameters (e.g. Jones et al., 2005).

PSMs construct a suitable mathematical filter of climate and local hydrology, based on the type of archive and its geomorphological setting (a surficially closed lake compared to one with surface inflows and outflows for example) and the specifics of an individual site. In contrast to transfer functions based on regression methods, such proxy system models avoid assumptions related to the effects of nonstationarity (e.g. the archive has had the same sensitivity to climate or environmental change at all times through the geological record under investigation) and the linearity of the proxy response to climate forcing.

In this volume, the modelling of lakes in particular (Gibson et al., this volume; Jones et al., this volume; Feng et al., this volume) and caves (Markowska et al., this volume) is discussed, but PSMs for water isotopes in corals, tree ring cellulose, ice cores, foraminifera are also being used or are in-development. Published forward models for these and other proxy types are reviewed in Evans et al., (2013) and Dee et al., (2015).

Gibson et al. (this volume) present the theoretical basis, illustrated with contemporary lake water data, for improving the parameterization used in lake isotope mass balance models, which form the basis for PSMs of these archives (e.g. Steinmann et al., 2013). The paper describes how the slope of the Local Evaporation Line (LEL) will differ in different regional climatic settings and how the theoretical reasons for this can be accounted for in mass balance models. As well as improving the constraints on PSMs, this approach allows improved understanding of regional climate change from archives where both $\delta^{18}\text{O}$ and δD can be measured, allowing past LELs to be reconstructed. Jones et al. (this volume) also use lake isotope mass balance models, in this case testing them against measured changes of lake water isotope compositions through time. The authors provide mass balance models of two lakes with no surface inflows or outflows constrained by five years of monthly monitoring data of lake water, precipitation, and atmospheric moisture isotope composition, as well as lake level and local climate data. This comprehensive monitoring allows groundwater components of the lake hydrological system to be well constrained, giving rise to the development of isotope mass balance models which can explain up to 74% of the observed variability in lake water isotope composition.

The lake isotope mass balance model used by the above papers use values based on the linear resistance model of Craig and Gordon (1965) for the isotopic composition of evaporating water. Traditionally this has been a difficult value to measure, but more recent advances in technology such as laser isotope systems make this now relatively straightforward, as demonstrated by Feng et al. (this volume), where the authors track the evaporation signal from lakes in Greenland. They show how the isotopic value of the water vapour varies over a given lake and conclude that isotopic compositions of evaporating waters calculated using the Craig and Gordon model may often be too low. Markowska et al. (this volume) also focus on evaporation as it impacts cave hydrology. They show that evaporative processes can dominate the hydrological balance of karst systems, both in terms of the isotopic composition of drip-waters that form speleothem archives, but also in controlling the variability in flow routing that impacts replicability of $\delta^{18}\text{O}$ records from speleothems in the same cave.

All these studies highlight the importance of understanding the hydrological and isotopic mass balance of a given archive system, and begin to quantify known unknowns, or at least known uncertainties, in these systems. Measurement of the isotopic composition of waters, from local precipitation values (as discussed above) through to the archive itself is vital to model individual archives appropriately. Monitoring not only allows improved qualification of palaeoclimatic or palaeoenvironmental inferences drawn from $\delta^{18}\text{O}$ time series, but also, through the development of well parameterised proxy system models, the potential to quantify the environmental or climatic changes required to produce such a change in $\delta^{18}\text{O}$.

Once developed, these PSMs can be used to ‘forward’ model pseudoproxy time series (e.g. Jones et al., this volume), potentially driven by the output from water isotope-enabled GCMs for a full climate-to-proxy experimental platform. Such efforts add greater interpretability and robustness to proxy-data climate-model comparisons, particularly for complex hydrological systems such as lakes, caves and oceans. Work to formalize the design of forward models for water isotope-based proxy systems, and to make them publically available to the community, is now underway (e.g. PRYSM, Dee et al., 2015).

Finally, formally linking GCMs to proxy data via forward modelling affords a much needed platform for uncertainty quantification. Ensemble analyses from isotope-enabled model simulations allow estimates of uncertainty of the climatic influences inferred from proxy data. Modelling the archive from a full-system perspective provides estimates of uncertainty propagation due to, for example, dating uncertainties or poorly constrained system processes such as groundwater storage or bioturbation (Dee et al., 2015).

Interrogating the data

Civilization has moved into the era of ‘big data’, and such data in the Earth sciences are often so large and complex that they are challenging to interpret and/or visualise. It is within this context that this volume includes two papers which seek to interrogate water isotope datasets. ‘Big data’ leads to meta-analyses, the investigation of multiple individual studies to increase their power by increasing the sample size. Horton et al (this volume) compile more than 11,200 paired carbon and oxygen isotope analyses on Quaternary endogenic lake carbonate time series compiled from archived published data. This was combined with modern hydrogen and oxygen isotope analyses of precipitation (7999 samples), river water (3875 samples) and lake water (247 samples) from just one region (western USA). Through a meta analysis of this published data they are able to observe a globally widespread enrichment in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of endogenic lake carbonates which they can attribute to evaporation, with the observation that $\delta^{18}\text{O}$ of lake carbonate is often >10‰ greater than the source water.

The ubiquitous time-series aspect of Quaternary isotope data leads to the need to develop and use appropriate analytical techniques. Fischer (this volume) reviews the use of predictable components analysis (PrCA) to investigate Quaternary time series. Although speleothem oxygen isotope time series archived by the U.S. National Oceanic and Atmospheric Administration (NOAA) World Data Center (WDC), in the Paleoclimatology database are used as an example, the general techniques are applicable to any Quaternary (or other) time series e.g. instrumental temperature series (Fischer, 2015b). The technique contrasts to principal components analysis (PCA), which maximizes the variance in a dataset, but whose components may not necessarily reflect the predictability in time that is actually present. PrCA is a particularly useful technique to explore Quaternary time series data where there may be multiple forcing factors over time, and in the quantification and analysis of signal versus noise in time series data. Code for the techniques highlighted by Fischer (this volume) is freely available in the software package *R* (R core team, 2013).

Challenges Ahead

1 . Challenges in Monitoring the Water

The monitoring of isotopes in precipitation and surface waters exposes the spatial and temporal complexity in the water isotope cycle. This complexity presents challenges for distinguishing a 'most correct' climate signal that is embedded within individual proxy records amongst the multi-variable noise. However, it is also difficult to quantify a spatial resolution and temporal duration over which water needs to be monitored to meet these challenges.

For space-for-time substitutions, regressions of GNIP scale monitoring and climate data are readily available and appealing. Akin to the cream rising to the top, if a significant correlation exists with a climate variable amongst disparate and distant environments, then it is likely a dominant control. However, from the perspective of an individual proxy record (as discussed above), the most accurate calibration is achieved by telescoping monitoring efforts down to the regional/local scale of the proxy location, precisely where the broader correlations tend to break down. Smaller spatial scales or high-resolution monitoring in time may provide critical evidence for unique physical processes that better inform paleoclimatic interpretation. As shown by papers in this volume, for some proxy systems it may be adequate to monitor seasonal precipitation- $\delta^{18}\text{O}$ variability at monthly scales from distant locations (e.g., data for input to mass balance models of lakes described by Gibson et al.), whereas for others it is critical to monitor sub-monthly (daily to sub-event scales) in close proximity (e.g., synoptic weather patterns described in Sanchez-Murillo et al., this volume and Good et al., 2014).

The challenge is then to identify the physical processes in the atmosphere that can account for the heterogeneity exhibited by water monitoring studies at different temporal and spatial scales. Such an approach will require the community to embrace the complexity of the water isotope cycle, multiple drivers, and the probability of their varying influence through time. On this point, isotope-enabled modelling tools may prove particularly useful (e.g., Schubert and Jahren, 2015). Different monitoring approaches each add to our understanding of the climate physics underlying precipitation $\delta^{18}\text{O}$ variability and better quantification of the particularly aspects incorporated by individual archives.

2. Challenges in Modeling the Climate

A number of caveats arise through attempts to make direct comparisons between GCM simulations and single-point or small networks of paleoclimate proxy data. First, both GCMs and PSMs introduce specific structural and parametric uncertainties. Evaluating the impacts of structural uncertainties among different GCMs requires comparisons between ensemble analyses from multiple models. Such analyses are limited by the efficiency of existing water-isotope enabled models, which often require extensive computational resources. Structural uncertainties between PSMs can similarly be evaluated by generating multiple realizations of proxy data using common climatic input signals, enabling the user to evaluate uncertainties related to differences in PSMs alone. Within both GCMs and PSMs, parametric or 'process-based' uncertainties, be it poorly constrained representation of atmospheric processes (tunable parameters in convection parameterizations, for example) or proxy system parameters, demand further process, in situ-monitoring, and site-specific studies on local climatic effects or proxy-specific biases (e.g. Moerman et al. 2014, Noone et al., 2014).

Secondly, internal variability precludes an exact replication of climate history at a particular site. This speaks to the difficulties surrounding grid scale and downscaling issues for point-

to-point comparison between paleoclimate data and model simulations. GCM resolution is usually at best 1 degree, which amounts to a distance scale on the order of ~100 km. The spatial resolution of data extracted from a GCM is therefore extremely broad compared to the spatial resolution of proxy data at a single site, which may have high sensitivity to microclimatic effects, for example. Isotope-enabled regional models (e.g. REMO_{ISO}, [Sturm et al., 2005]) may be used to downscale climate fields from a GCM, but at present, few such models exist.

Finally, using paleoclimate data to validate isotope-enabled GCMs is limited by the sparseness of paleoclimate data in time and space. Available paleoclimate records span only very specific time frames, and may differ substantially from GCM output in terms of sampling rate and time series resolution. Efforts to amass statistically - screened databases of paleoclimate data with near-global coverage spanning specific time periods (e.g. PAGES2k, 2013) enhances the utility of paleoclimate data for validating climate models; such efforts can and should be extended for water isotope based records spanning the Holocene.

3. Challenges in modelling the archive: transferability and transparency of PSMs

The use of proxy system models (PSMs) for data-model comparison and advanced proxy interpretation often requires a number of subjective design choices concerning PSM complexity. Such choices may be based on the spatiotemporal scope of each individual study or research question (essentially, the context of PSM use). Published proxy system models generally range from a very simple parameterization applicable globally for a given proxy type to highly-parameterized models calibrated to conditions at a single site, designed to interpret the data for that site only. For example, one can imagine a complex cave karst model calibrated to the climatic conditions at a single cave site (multiple tunable parameters, multiple inputs about site-specific climate and karst conditions) vs. a very simple, idealized groundwater transit-time model which predicts cave drip water values based on model precipitation and $\delta^{18}\text{O}$ of precipitation (few parameters, few inputs).

Complexity choices may also depend on proxy type. For example, ice core models must contain parameterizations for processes such as diffusion and compaction (Dee et al., 2015 and references therein), while coral models might only require a simple bi-variate equation for coral response to temperature (Thompson et al., 2011). These differences stem from the current state of knowledge surrounding proxy system processes, and may ultimately limit efforts to narrow the design of PSMs towards one common parameterization for each proxy type. Forward modelling efforts for lakes and caves in particular often demand site-specific inputs and parameterizations, and can be difficult to transfer for answering questions at a different site.

To perform broader, global analyses using PSMs, one might imagine that a simpler model with fewer tunable parameters is ideal; however, such a model might sacrifice important details describing how the proxy system transduces climate. A balance can be struck using intermediate-complexity models, as described in this text above (Evans et al., 2013), which maximizes the usefulness of PSMs for the greatest number of studies without sacrificing their ability to provide robust scientific insight. Moving forward, our field may consider collaborative efforts working to adopt a more generic, standardized framework for PSM

development 1) at an intermediate-complexity level and 2) in a common programming language, enabling greater transferability and transparency between research groups (e.g. Dee et al., 2015).

4. Challenges in Managing the Data

Academic research communities are increasingly recognizing the challenges of analysing datasets of increasing size and complexity. These challenges were first recognized in disciplines such as high-energy physics and astronomy, and now more recently in high-throughput genomics and biology (Mattman, 2013; Marz, 2013). Within ecology, it has been argued that large amount of data containing high-value information have been collected but remain 'dark' and unavailable to the larger scientific community (Hampton et al., 2013). Quaternary Science occupies a 'data space', which falls between macro-scale ecology, climatology, and stratigraphy. It requires the synthesis of data-rich time series, which can be both spatially dense and widely geographically distributed and covering long time periods. Further, water isotope research throughput has been revolutionized in recent years through the advent of laser isotope spectroscopic techniques (Lis et al., 2007), and the subsequent widespread adoption of this technique for water isotope analyses (for example, in this volume see Anderson et al. and Markowska et al. for liquid analyses, and Feng et al. for vapour analyses). For liquid water isotope analyses, off-axis and cavity ringdown spectroscopy now permit an order of magnitude greater throughput of water isotope samples compared to conventional isotope ratio mass spectroscopy (IRMS). Continued method development will lead to routine coupling of laser isotope systems to appropriate preparation lines for Quaternary applications such as the analysis of paleo groundwater (David et al., 2015), ice cores (Emanuelsson et al., 2015) and speleothem fluid inclusions (Affolter et al., 2014). This will further increase sample throughput and the size of datasets available to the research community.

Data archiving has been facilitated by initiatives such as the U.S. NOAA-WDC database for Paleoclimatology to be incorporated into the International Council of Scientific Unions (ICSU) World Data System. Founded in 1992, the WDC-Paleoclimatology database now contains 11,000 records, with over 1000 of these containing water isotope data (Bruce Bauer, personal communication). Alongside the above-described advancements in data analysis and retrieval in Quaternary research, we envision conversations and organization within the community regarding the evolution of data management for a growing number of Quaternary water isotope records coupled with the 'big data' space occupied by climate model simulations and satellite retrievals.

Looking Ahead: realizing the full potential of water isotopes in paleoclimate science

This special issue demonstrates the potential for the study of water isotope systematics to continue to improve our interpretations of the paleohydrological cycle, and highlights new research areas using water isotopes to constrain hydroclimate variability. The wide array of water isotope data coming online in both monitoring and palaeo studies will require careful management and archiving to maximize their usefulness to the full community, and to build an even better understanding of the spatiotemporal dynamics of the water isotope cycle (e.g. Liu et al., 2014).

For example, new data enhancing both monitoring and validation for water isotope studies is now available in the form of deuterium measurements in atmospheric vapour from satellite missions such as TES (Worden et al., 2012, Risi et al., 2012) and SCIAMACHY (Frankenberg et al., 2009). Satellite based water isotope measurements are poised to provide invaluable tools for constraining unknowns in atmospheric processes as captured by water isotopes, and for validating isotope-enabled GCMs. The near-global coverage provided by satellite data greatly augments the collection of measurements provided by monitoring programs such as GNIP and GNIR (IAEA, 2006), which are limited in both space and time. These new satellite-based measurements of deuterium in water vapour lend insight into poorly constrained atmospheric processes (such as deep convection) giving rise to large variability in water isotope fields (e.g. Noone, 2012, Hurley et al., 2012, Bailey et al., 2013). These and other studies focusing on the *systematics* of the water isotope cycle add relevance to paleoclimate records by providing new information on dynamical processes controlling water isotope variability in the present. This helps identify the manifestations of, or confounding factors introduced by such atmospheric processes in paleoclimate archives.

Efforts are now underway to amass water isotope data spanning the last 2000 years under the PAGES2k initiative (Iso2k; Konecky & Partin, 2015). Continued contributions to databases such as these, the basis for uniformly formatted, publicly available data will go some way to dealing with the challenges discussed here. Combining water isotope paleoclimate records with isotope enabled GCM output, all validated by monitoring at appropriate scales, will provide exciting opportunities to improve our palaeoclimate interpretations.

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References

Affolter, S., Fleitmann, D., and Leuenberger, M. (2014). New online method for water isotope analysis of speleothem fluid inclusions using laser absorption spectroscopy (WR-CRDS). *Climate of the Past* 10 1291-1304.

Anchukaitis, K. J., M. N. Evans, A. Kaplan, E. A. Vaganov, M. K. Hughes, H. D. Grissino-Mayer, and M. A. Cane (2006), Forward modeling of regional scale tree-ring patterns in the southeastern United States and the recent influence of summer drought, *Geophys. Res. Lett.*, 33, L04705, doi:10.1029/2005GL025050.

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Anderson, W., S. Bernasconi, J. McKenzie, M. Saurer, and F. Schweingruber (2002), *Model evaluation for reconstructing the oxygen isotopic composition in precipitation from tree ring*

cellulose over the last century, *Chem. Geol.*, 182(2-4), 121–137, doi:10.1016/S0009-2541(01)00285-6

Arthern, R. J., D. G. Vaughan, A. M. Rankin, R. Mulvaney, and E. R. Thomas (2010), *In situ measurements of Antarctic snow compaction compared with predictions of models*, *J. Geophys. Res. Earth Surf.*, 115, F03011, doi:10.1029/2009JF001306.

Bader, H. (1954), *Sorges law of densification of snow on high polar glaciers*, *J. Glaciol*, 2(15), 319–323

Bailey, H.L., Kaufman, D.S., Henderson, A.C.G., Leng, M.J. (2015). Synoptic controls on the $\delta^{18}\text{O}$ in precipitation across Beringia. *Geophysical Research Letters*42, doi:10.1002/2015GL063983.

Bailey, A., Toohey, D. and Noone, D. (2013) Characterizing moisture exchange between the Hawaiian convective boundary layer and free troposphere using stable isotopes in water, *Journal of Geophysical Research*, 118, 8208–8221.,

Barbour, M. M., J. S. Roden, G. D. Farquhar, and J. R. Ehleringer (2004), *Expressing leaf water and cellulose oxygen isotope ratios as enrichment above source water reveals evidence of a Pecllet effect*, *Oecologia*, 138(3), 426–435, doi:10.1007/s00442-003-1449-3

Berkelhammer, M., Stott, L., Yoshimura, K. Johnson, K., Sinha, A. (2011). Synoptic and mesoscale controls on the isotopic composition of precipitation in the western United States. *Climate Dynamics* doi 10.1007/s00382-011-1262-3.

Brennan, C., A. Weaver, M. Eby, and K. Meissner (2012), *Modelling oxygen isotopes in the University of Victoria Earth System Climate Model for pre-industrial and Last Glacial Maximum conditions*, *Atmos. Ocean*, 50, 447–465.

Craig H, Gordon LI. 1965. Deuterium and oxygen-18 in the ocean and marine atmosphere, In Tongiorgi E. (Ed.), *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, Spoleto, Italy, 9-130.

Cuffey, K. M., and E. J. Steig (1998), *Isotopic diffusion in polar firn: Implications for interpretation of seasonal climate parameters in ice-core records, with emphasis on central Greenland*, *J. Glaciol.*, 44(147), 273–284

David, K., Timms, W., and Baker, A. (2015). Direct stable isotope porewater equilibration and identification of groundwater processes in heterogeneous sedimentary rock, *Science of the Total Environment*, 538, 1010 – 1023

Darling, G.W., Bath, A.H., Gibson, J.J., Rozanski, K. (2006). *Isotopes in Water*. In M.J. Leng (ed), *Isotopes in Palaeoenvironmental Research*. Springer, The Netherlands, pp. 1-66.

Dee et al.,(2015), *PRYSM: An open-source framework for PRoxY System Modeling, with applications to oxygen-isotope systems*. *Journal of Advances in Modeling Earth Systems*. DOI: 10.1002/2015MS000447

Dee, S., D. Noone, N. Buenning, J. Emile-Geay, and Y. Zhou (2014b), SPEEDY-IER: A fast atmospheric GCM with water isotope physics, *J. Geophys. Res. Atmos.*, 120, 73–91, doi:10.1002/2014JD022194.

Emanuelsson, B.D., Baisden, W.T., Bertler, N.A.N., Keller, E.D. and Gkinis, V. (2015) High resolution continuous flow analysis setup for water isotopic measurement from ice cores using laser spectroscopy. *Atmos. Meas. Tech.*, 8, 2869-2883.

Ersek, V., Clark, P.U., Mix, A.C., Cheng, J., Edwards, L.R. (2012). Holocene winter climate variability in mid-latitude western North America. *Nature Communications* 3, doi:10.1038/ncomms2222.

Evans, M. N. (2007), Toward forward modeling for paleoclimatic proxy signal calibration: A case study with oxygen isotopic composition of tropical woods, *Geochem. Geophys. Geosyst.*, 8, Q07008, doi:10.1029/2006GC001406

Evans, M.N., Tolwinski-Ward, S.E., Thompson, D.M., Anchukaitis, K.J., 2013. Applications of proxy system modeling in high resolution paleoclimatology. *Quat. Sci. Rev.* 76, 16-28.

Feng, X., Lauder, A.M., Posmentier, E.S., Kopec, B.G., Virginia, R.A. this volume
Evaporation and transport of water isotopologues from Greenland lakes: The lake size effect. *Quat. Sci. Rev.*

Fischer et al 2015a *this volume*

Fischer, M.J., (2015b). Predictable Components in Australian Daily Temperature Data. *J. Climate*, 28, 5969–5984.

Frankenberg, C., et al. (2009), Dynamic processes governing lower-tropospheric HDO/H₂O ratios as observed from space and ground, *Science*, 325, 1374–1377

Gibson, J.J., Birks, S.J., Yi, Y. this volume Stable isotope mass balance of lakes: a contemporary perspective. *Quat. Sci. Rev.*

Gkinis, V., S. Simonsen, S. Buchardt, J. White, and B. Vinther (2014), Water isotope diffusion rates from the NorthGRIP ice core for the last 16,000 years glaciological and paleoclimatic implications, *Earth Planet. Sci. Lett.*, 405, 132–141, doi:10.1016/j.epsl.2014.08.022

Good, S.P., Mallia, D.V., Lin, J.C., Bowen, G.J., 2014. Stable isotope analysis of precipitation samples obtained via crowdsourcing reveals the spatiotemporal evolution of superstorm sandy. *PloS one* 9, e91117.

Hampton, S.E., Strasser, C.A., Tewksbury, J.J., Gram, W.K., Budden, A.E., Batcheller, A.L., Duke, C.S. and Porter, J.H. (2013) Big data and the future of ecology. *Frontiers in Ecology and Environment* 11, 156-162.

Herron, M. M., and C. C. Langway (1980), Firn densification: An empirical model, *J. Glaciol.*, 25, 373–385.

Hoffmann, G., M. Werner, and M. Heimann (1998), Water isotope module of the ECHAM atmospheric general circulation model: A study on timescales from days to several years, *J. Geophys. Res.*, 103, 16,871–16,896.

Holloway et al., this volume

Holmes et al., this volume

Horton et al 2015 *This volume*

Hurley, J.V., Galewsky, J. Worden, J. and Noone, D. (2012) A test of the advection-condensation model for subtropical water vapor using stable isotopologue observations from Mauna Loa Observatory, Hawaii, *Journal of Geophysical Research*, 117, D19118,

IAEA/WMO (2006), Global network of isotopes in precipitation: The GNIP database.

Johnsen, S. J. (1977), Stable isotope homogenization of polar firn and ice, in *Proceedings of the Symposium on Isotopes and Impurities in Snow and Ice*, IAHS–AISH Publ. 118, pp. 210–219, Int. Assoc. of Hydrol. Sci., Gentbrugge, Belgium.

Johnsen, S. J., H. B. Clausen, K. M. Cuffey, G. Hoffmann, J. Schwander, and T. Creyts (2000), Diffusion of stable isotopes in polar firn and ice: The isotope effect in firn diffusion, *Phys. Ice Core Records*, 159, 121–140

Jones, M.D., Cuthbert, M.O., Leng, M.J., McGowan, S., Mariethoz, G., Arrowsmith, C., Sloane, H.J., Humphrey, K.K., Cross, I. this volume. Comparisons of observed and modelled lake $\delta^{18}\text{O}$ variability. *Quat. Sci. Rev.*

Jones, M.D., Leng, M.J., Roberts, C.N., Turkes, M., Moyeed, R., 2005. A coupled calibration and modelling approach to the understanding of dry-land lake oxygen isotope records. *Journal of Paleolimnology* 34, 391-411.

Klein et al. this volume

Klein, E.S., Cherry, J.E., Young, J., Noone, D., Leffler, A.J., Welker, J.M. (2015). Arctic cyclone water vapor isotopes support past sea ice retreat recorded in Greenland ice. *Scientific Reports* 5:10295, doi:10.1038/srep10295.

Konecky, B. and Partin, J. (2015), Iso2k: A community-driven effort to develop a global database of paleo-water isotopes covering the past two millennia, Abstract PP11B-2215 presented at the 2015 AGU Fall Meeting, AGU, San Francisco, CA.
<https://agu.confex.com/agu/fm15/meetingapp.cgi/Paper/59808>

Kurita, N., D. Noone, C. Risi, G. A. Schmidt, H. Yamada, and K. Yoneyama (2011), Intraseasonal isotopic variation associated with the Madden-Julian oscillation, *J. Geophys. Res.*, 116, D24101, doi:10.1029/2010JD015209

Kuttel, M., E. J. Steig, Q. Ding, A. J. Monaghan, and D. S. Battisti (2012), Seasonal climate information preserved in West Antarctic ice core water isotopes: Relationships to temperature, large-scale circulation, and sea ice, *Clim. Dyn.*, 39(7-8), 1841–1857

Lachniet, M., Paterson, W.P., Burnes, S. Asmeron, Y., Polyak, V. 2007. Caribbean and Pacific moisture sources on the isthmus of Panama revealed from stalagmite and surface water d18O gradients. *GRL* 34, L01708.

Lee, J.-E., I. Fung, D. J. DePaolo, and C. C. Henning (2007), Analysis of the global distribution of water isotopes using the NCAR atmospheric general circulation model, *J. Geophys. Res.*, 112, D16306, doi:10.1029/2006JD007657.

Leng, M.J. (Ed.), 2006. *Isotopes in Palaeoenvironmental Research*. Springer.

Li, J., and H. J. Zwally (2011), Modeling of firn compaction for estimating ice-sheet mass change from observed ice-sheet elevation change, *Ann. Glaciol.*, 52(59), 1–7, doi:10.3189/172756411799096321

Lis, G., Wassenaar, L.I., and Hendry, M.J. (2008) High-precision laser spectroscopy D/H and $^{18}\text{O}/^{16}\text{O}$ measurements of microliter natural water samples. *Analytical Chemistry*, 80, 287-293.

Liu, Z., Yoshimura, K., Bowen, G.J., Buening, N.H., Risi, C., Welker, J.M., Yuan, F.S. (2014). Paired oxygen isotope records reveal modern North American atmospheric dynamics during the Holocene. *Nature Communications* 5:3701, doi:10.1038/ncomms4701.

Markowska, M. et al. this volume Semi-arid zone caves...

Marx, V. (2013). Biology: the big challenges of big data. *Nature* 498 255-260

Mathieu, R., D. Pollard, J. E. Cole, J. W. White, R. S. Webb, and S. L. Thompson (2002), Simulation of stable water isotope variations by the GENESIS GCM for modern conditions, 107(D4), 4037, doi:10.1029/2001JD900255.

Mattmann, C.A. (2013) Computing: a vision for data science. *Nature*, 493, 473-475.

Moerman, J. W., K. M. Cobb, J. W. Partin, A. N. Meckler, S. A. Carolin, J. F. Adkins, S. Lejau, J. Malang, B. Clark, and A. A. Tuen (2014), Transformation of ENSO-related rainwater to dripwater variability by vadose water mixing, *Geophys. Res. Lett.*, 41, 7907–7915, doi:10.1002/2014GL061696.

Noone, D., A. Raudzens-Bailey, M. Berkelhammer, C. Cox, K. Steffen, and J. White (2014), A reassessment of Greenland climate history using a proxy system model for accumulation

of the isotope record in snow, Abstract PP34B-07 presented at 2014 AGU Fall Meeting, AGU, San Francisco, Calif.

Noone, D., and C. Sturm (2010), Comprehensive dynamical models of global and regional water isotope distributions, in *Isoscapes*, edited by J. B. West et al., pp. 195–219, Springer, Netherlands.

Noone, D., and I. Simmonds (2002), Annular variations in moisture transport mechanisms and the abundance of $\delta^{18}\text{O}$ in Antarctic snow, *J. Geophys. Res.*, 107(D24), 4742, doi:10.1029/2002JD002262.

Noone, D. (2012), Pairing Measurements of the Water Vapor Isotope Ratio with Humidity to Deduce Atmospheric Moistening and Dehydration in the Tropical Midtroposphere, *Journal of Climate*, 25, 4476–4494,

R Core Team (2013). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria. <http://www.R-project.org/>

PAGES2K Consortium (2013), Continental-scale temperature variability during the past two millennia, *Nature Geosci.*, 6(5), 339–346

Risi, C., S. Bony, F. Vimeux, and J. Jouzel (2010), Water-stable isotopes in the LMDZ4 general circulation model: Model evaluation for present-day and past climates and applications to climatic interpretations of tropical isotopic records, *J. Geophys. Res.*, 115, D12118, doi:10.1029/2009JD013255

Camille, R., Noone, D., Worden, J., Frankenberg, C., Stiller, G., Kiefer, M., Funke, B., Walker, K., Bernath, P., Schneider, M., Wunch, D., Sherlock, V., Deutscher, N., Griffith, D., Wennberg, P.O. (2012) Process-evaluation of tropospheric humidity simulated by general circulation models using water vapor isotopologues: 1. Comparison between models and observations, *JOURNAL OF GEOPHYSICAL RESEARCH*, VOL. 117, D05303,

Roche, D. (2013), $\delta^{18}\text{O}$ water isotope in the iLOVECLIM model (version 1.0)—Part 1: Implementation and verification, *Geosci. Model Dev. Discuss.*, 6, 1467–1494. Rodríguez-Fonseca,

Roden, J. S., and J. R. Ehleringer (1999), Hydrogen and oxygen isotope ratios of tree-ring cellulose for riparian trees grown long-term under hydroponically controlled environments, *Oecologia*, 121(4), 467–477.

Roden, J. S., G. Lin, and J. R. Ehleringer (2000), A mechanistic model for interpretation of hydrogen and oxygen isotope ratios in tree-ring cellulose, *Geochim. Cosmochim. Acta*, 64(1), 21–35.

Roden, J. S., G. Lin, and J. R. Ehleringer (2002), Response to the comment of V.J. Terwilliger on “A mechanistic model for interpretation of hydrogen and oxygen ratios in tree-

ring cellulose”, by J. S. Roden, G. Lin, and J. R. Ehleringer (2000), *Geochim. Cosmochim. Acta*, 66, 733–734.

Sanchez et al., this volume

Schmidt, G. a., Forward modeling of carbonate proxy data from planktonic foraminifera using oxygen isotope tracers in a global ocean model, *Paleoceanography*, 14, 482, 1999.

Schmidt, G. A., A. N. LeGrande, and G. Hoffmann (2007), Water isotope expressions of intrinsic and forced variability in a coupled ocean-atmosphere model, *J. Geophys. Res.*, 112, D10103, doi:10.1029/2006JD007781.

Schubert, B.A. and Jahren, A.H. (2015), Seasonal temperature and precipitation recorded in the intra-annual oxygen isotope pattern of meteoric water and tree-ring cellulose. *Quaternary Science Reviews* 125, 1-14.

Shackleton, N.J., Opdyke, N.D., 1973. Oxygen isotope and palaeomagnetic stratigraphy of Equatorial Pacific core V28-238: Oxygen isotope temperatures and ice volumes on a 105 year and 106 year scale. *Quat. Res.* 3, 39-55.

Steinman, B. A., & Abbott, M. B. 2013. Isotopic and hydrologic responses of small, closed lakes to climate variability: Hydroclimate reconstructions from lake sediment oxygen isotope records and mass balance models. *Geochimica et Cosmochimica Acta*, 105, 342-359.

Stevenson, S., H. V. McGregor, S. J. Phipps, and B. Fox-Kemper (2013), Quantifying errors in coral-based ENSO estimates: Toward improved forward modeling of $\delta^{18}\text{O}$, *Paleoceanography*, 28, doi:10.1002/palo.20059

Sturm, C., Q. Zhang, and D. Noone (2010), An introduction to stable water isotopes in climate models: Benefits of forward proxy modelling for paleoclimatology, *Clim. Past*, 6, 115–129

Sturm, K., Hoffmann, G., Langmann, B., & Stichler, W. (2005). Simulation of $\delta^{18}\text{O}$ in precipitation by the regional circulation model REMOiso. *Hydrological Processes*, 19(17), 3425-3444.

Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chemical Geology: Isotope Geoscience section* 80, 261-279.

Thompson, D. M., T. R. Ault, M. N. Evans, J. E. Cole, and J. Emile-Geay (2011), Comparison of observed and simulated tropical climate trends using a forward model of coral $\delta^{18}\text{O}$, *Geophys. Res. Lett.*, 38, L14706, doi:10.1029/2011GL048224.

Tindall, J. C., P. J. Valdes, and L. C. Sime (2009), Stable water isotopes in HadCM3: Isotopic signature of El Niño Southern Oscillation and the tropical amount effect, *J. Geophys. Res.*, 114, D04111, doi:10.1029/2008JD010825.

Tindall, J., Paul J. Valdes, Modeling the 8.2 ka event using a coupled atmosphere–ocean GCM, *Global and Planetary Change*, Volume 79, Issues 3–4, December 2011, Pages 312–321, ISSN 0921-8181, <http://dx.doi.org/10.1016/j.gloplacha.2011.02.004>. (<http://www.sciencedirect.com/science/article/pii/S0921818111000312>)

Tolwinski-Ward, S. E., M. N. Evans, M. K. Hughes, and K. J. Anchukaitis, An efficient forward model of the climate controls on interannual variation in tree-ring width, *Climate Dynamics*, 36, 2419–2439, 2010.

Vaganov, E., M. Hughes, and A. Shashkin, *Growth Dynamics of Conifer Tree Rings: Images of Past and Future Environments*, vol. 183, ecological ed., Springer-Verlag Berlin Heidelberg 2006, 2006.

Vuille, M., Modeling $\delta^{18}\text{O}$ in precipitation over the tropical Americas: 2. Simulation of the stable isotope signal in Andean ice cores, *Journal of Geophysical Research*, 108, 2003.

Werner, M., and M. Heimann, Modeling interannual variability of water isotopes in Greenland and Antarctica, *Journal of Geophysical Research*, 107, 2002.

Whillans, I., and P. Grootes (1985), Isotopic diffusion in cold snow and firn, *J. Geophys. Res.*, 90, 3910–3918.

Worden, J., S. Kulawik, C. Frankenberg, V. Payne, K. Bowman, K. Cady-Peirara, K. Wecht, J.-E. Lee, and D. Noone, (2012) Profiles of CH₄, HDO, H₂O, and N₂O with improved lower tropospheric vertical resolution from Aura TES radiances, *Atmospheric Measurement Techniques*, 5, 397–411.

Yoshimura, K., M. Kanamitsu, D. Noone, and T. Oki (2008), Historical isotope simulation using reanalysis atmospheric data, *J. Geophys. Res.*, 113, D19108, doi:10.1029/2008JD010074.