Isoscapes: Spatial Pattern in Isotopic Biogeochemistry

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Key Words

hydrology, ecology, forensic science, GIS, stable isotopes, climate change

Abstract

Isotope ratios of actively cycled elements vary as a function of the biogeochemical processes in which they participate and the conditions under which those processes occur. The resultant spatiotemporal distribution of isotopes in environmental materials can be predicted using models of isotope-fractionating processes and data describing environmental conditions across space and time, and it has been termed an isoscape, or isotopic landscape. Analysis of isoscapes and comparison of isoscape predictions with observational data have been used to test biogeochemical models, calculate aerially integrated biogeochemical fluxes based on isotope mass balance, and determine spatial connectivity in biogeochemical, ecological, and anthropological systems. Isoscape models of varying quality are available for stable H, C, N, and O isotopes in a range of Earth surface systems, but significant opportunities exist to refine our understanding of biogeochemical cycles and our ability to predict isoscapes through the development of more mechanistic and more comprehensive isoscape models.

INTRODUCTION

Earth scientists have long recognized and capitalized on natural, spatial variability in the isotopic composition of environmental materials. The early documentation of isotopic variation among continental freshwaters from different locations (Dansgaard 1954) was a keystone finding that supported the development of theory describing processes of H and O isotope fractionation in the water cycle (Craig & Gordon 1965) and established a widely used method of paleotemperature reconstruction (Dansgaard 1954). Quantification of geologically controlled variation in the Sr isotopic composition of runoff from different river basins (Palmer & Edmond 1989) paved the way for quantitative models of the oceanic Sr cycle and enabled subsequent work on the reconstruction of tectonic histories from marine Sr archives (Richter et al. 1992). After experimental work and advances in theory demonstrated environmentally controlled variation in the C isotope discrimination during photosynthesis (Farquhar et al. 1989), global-scale modeling of ecosystem δ^{13}C values helped to refine global C budgets based on C isotope ratios (Lloyd & Farquhar 1994, Suits et al. 2005).

Such work has taken advantage of the fact that varying environmental conditions—climatological, geological, biological, and hydrological—across landscapes exert effects on isotopic abundance. Over time, data documenting both elements of this relationship, the environment forcing factors and isotopic results, have grown substantially. For many systems it is now possible to develop, implement, test, and apply predictive models that estimate the local isotopic composition of environmental materials as a function of observed local and/or extralocal environmental variables. In 2005, the term isoscapes (isotopic landscapes) emerged to describe maps of isotopic variation produced by iteratively applying these models across regions of space using gridded environmental data sets, and isoscapes are now widely used in many research communities. One common use of isoscapes is as a source of estimated isotopic values at unmonitored sites, which can be an important implementation for both local- and global-scale studies if the isoscape is based on a robust and well-studied model. Isoscapes are also powerful tools for probing the models that produce them, and they play an equally important role in identifying and characterizing spatially distributed Earth systems processes based on their isotopic expression.

This review attempts to synthesize the current state of the rapidly developing, cross-disciplinary spectrum of research involving isoscapes. I begin by introducing aspects of the theoretical context, methodology, and technology that underlie the prediction and use of isoscapes. I then present a noncomprehensive review of isotopic pattern in Earth systems, emphasizing relatively large-scale patterns in the stable isotopes of hydrogen, carbon, nitrogen, and oxygen that emerge from processes within the atmosphere, hydrosphere, and biosphere, and discuss applications that have capitalized on these patterns. I conclude with some thoughts on the relevance of isoscapes and spatial analysis of isotope data to Earth systems science and productive trajectories for the continuation of this work.

CAUSES AND REPRESENTATION OF ISOTOPIC PATTERNS

This review focuses on isotopic ratios of a limited number of biologically reactive elements that cycle actively within Earth surface systems. Important and useful spatial isotopic variability exists for other isotopes and systems not discussed here, including ^{14}C, δ^{36}S, and ^{87}Sr/^{86}Sr (Bowen & West 2008; see also reviews in West et al. 2010). For any isotopic system, physical or chemical transformations produce a product pool with an isotopic composition that is a function of the isotopic composition of the starting pool(s) modified by fractionation (see Isotope Notation and Fractionation sidebar). Processes that involve a complete and/or unidirectional

ISOTOPE NOTATION AND FRACTIONATION

Isotopic values are expressed as δ values: $\delta = (R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}$, where R is the abundance ratio of the heavy and light isotopes (e.g., $^{2}H/^{1}H$) and δ is commonly reported in units of parts per thousand (‰). A chemical or physical process that unevenly partitions the isotopes of an element between reactant and product pools causes isotopic fractionation, expressed as $\alpha_{A-B} = R_A/R_B$. The magnitude of fractionation can be expressed on the δ scale through the logarithmic transformation $10^3\ln(\alpha_{A-B})$, and this value is often approximated as the value ε or Δ, where $\varepsilon_{A-B} = (\alpha_{A-B} - 1)10^3$ and $\Delta_{A-B} = \delta_A - \delta_B$. Mathematical operations involving δ, ε, and Δ values are approximate with respect to true isotope ratios and are increasingly inaccurate over larger ranges of δ values. Many isoscape applications and models use so-called δ math without great compromise, but it is important to be aware of the potential for inaccuracy, particularly in cases involving the use or derivation of mechanistic parameters such as fractionation factors (rather than statistical quantities). Further background is provided by Sessions & Hayes (2005), Fry (2006), and Sharp (2007).

transformation of the mixture to a single product pool (e.g., transport by advection, mixing) produce no fractionation, and therefore the isotopic composition of the product pool is equal either to that of the starting pool (if only one) or to a linear mixture of the starting pool compositions (if more than one). All other processes involving multiple product pools or multidirectional processes (e.g., transport by diffusion, incomplete reactions, reactions with branch points) have the potential to fractionate. Fractionation in most systems is mass dependent, meaning that the magnitude of the fractionation scales approximately with the relative mass difference between the isotopes involved (e.g., fractionation in the system $^{87}Sr/^{86}Sr$ is small relative to that in the system $^{2}H/^{1}H$).

Isoscape models typically deal with transformations that involve a complex of fractionating and nonfractionating processes. H isotope ratios of water in plant leaves, for example, reflect nonfractionating uptake of source water from one or more pools of soil or groundwater and the subsequent fractionating loss of water from leaves through evaporation (Roden & Ehleringer 1999). Within such a system, a number of factors can cause isotopic variation of the products produced at different locations and times, for example, (*a*) the isotopic composition of soil or groundwater, (*b*) the mixture of soil and groundwater taken up by plants, (*c*) the physical conditions, such as ambient humidity and leaf boundary-layer thickness, that contribute to determining fractionation during evaporation, (*d*) the physiological conditions, such as regulation of stomatal conductance and differences in leaf vein structure among plant types, that contribute to determining fractionation during evaporation, and (*e*) the isotopic composition of water vapor in the atmosphere. Large bodies of work have focused on developing and testing isotopic models for systems such as plant leaf water, and in general the process of adapting these models for use in predicting isoscapes simply involves work to enable iterative application of the model across a large number of locations (grid cells) within a region of interest (domain). This may include the following:

- Parameterizing the model for grid-based calculations. Models developed to take advantage of detailed, site-specific information may not be readily applicable over large spatial scales. To enable use for the prediction of isotopic values over large regions, models may need to be simplified, generalized, or reparameterized to be consistent with available data sources. In some cases this involves developing and statistically calibrating derived parameterizations, such as with the use of geostatistical methods as a surrogate for explicit representation of processes that involve transport between grid cells (see Geostatistics sidebar).

GEOSTATISTICS

Geostatistics is a branch of statistics that deals with relationships among spatially distributed data. The basic premise behind geostatistical models is that of spatial autocorrelation: If a spatial process (e.g., atmospheric transport) influences values of a variable (e.g., atmospheric water vapor δ^2H values), then values from nearby locations will tend to be more similar than those from locations that are widely separated in space. Geostatistical methods represent a geographic translation of regression analysis, wherein geographic location is taken to be an independent predictor variable for a quantity of interest. In geostatistics, the relationship between spatial proximity and independent variable value is represented by the sample semivariance

$$\gamma(h) = \frac{1}{2n}\sum_{i=1}^{n}[Z(xi) - Z(xi+h)]^2,$$

where h is the distance between a pair of locations, n is the number of location pairs in the data set separated by h, and $Z(x)$ is the independent variable value at a location. Analogous to simple linear regression analysis, geostatistical analysis can be used both to identify and characterize relationships between the independent and dependent variables and to predict values of the independent variable based on these relationships. Further background is provided by Cressie (1993).

- Identifying data sources. To apply the model across the domain, all model parameters and boundary conditions must be available for every grid cell within the domain. The rapid growth and wide availability of gridded environmental data sets have, in many cases, made this component of the work relatively easy, but they have also led to the availability of multiple, distinct data sets for many variables of interest (e.g., basic climate parameters), and decisions must often be made among these. In addition, most gridded data products, with the exception of some satellite-based products based on direct, regularly spaced measurements, are themselves model based, and careful documentation of data sources and consideration of their potential inaccuracies are important. Lastly, most isoscape models will require other isoscapes as inputs to describe the model source terms, and again documentation and consideration of errors are warranted.
- Preparing and executing grid-based calculations. Once the model and data sources are in hand, modern commercial and open-source geographic information systems (GIS) software packages make data processing and calculation steps relatively accessible to most users. Prior to use, the data sets must be read into the GIS along with their spatial attributes (e.g., geographic boundaries, map projection, grid cell size) and transformed, using standard tools available in most GIS software, so that all data sets share common spatial attributes. Model calculations can either be conducted by hand as a series of discrete steps, or the user can write a script that executes the necessary sequence of operations. Some software programs, such as the widely used commercial package ArcGIS, now provide graphical interfaces for developing complex workflows without specialized knowledge of scripting languages, making the implementation of many models a drag-and-drop process (**Figure 1**).

Many of these operations involve mundane tasks that are nonetheless time consuming and may require familiarity with the specific data formats and software, restricting the participation of researchers who could otherwise be involved in the development and analysis of isoscapes. One solution to this challenge is the development of web-based cyberinfrastructure that supports the seamless implementation of spatially explicit isotope models by automating data access and conversion tasks. Such a platform is currently under development by the U.S. National

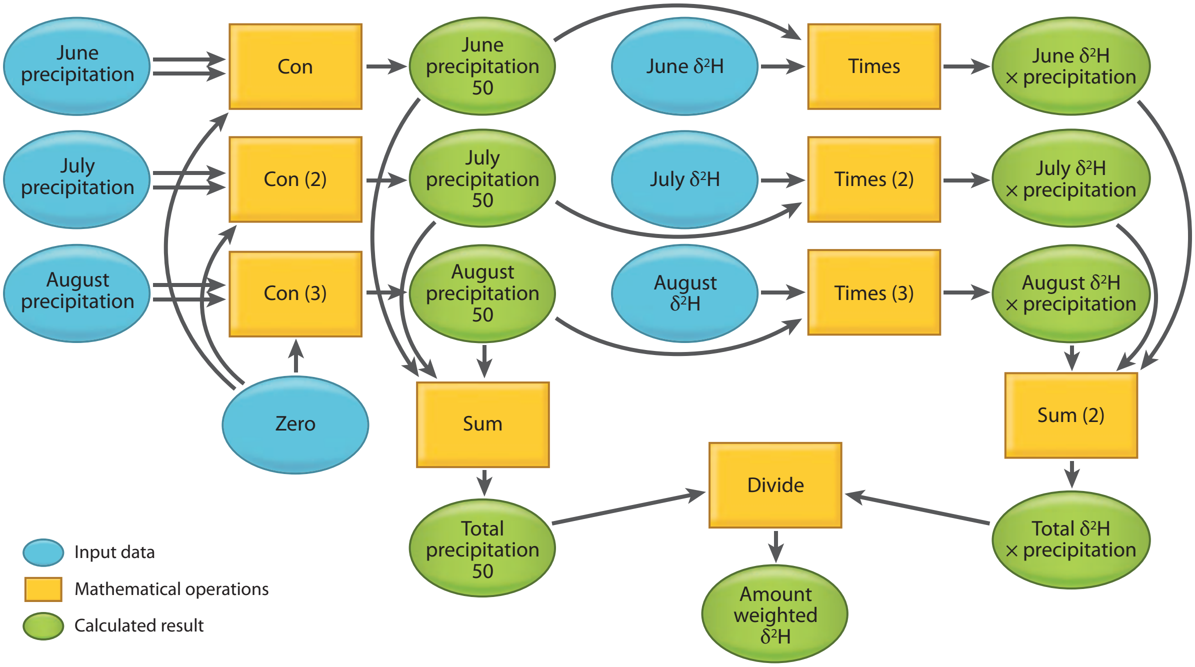

Figure 1

ArcGIS ModelBuilder workflow that creates a raster map of precipitation-amount weighted precipitation δ^2H values for summer months in which the precipitation amount is greater than 50 mm. Input data include maps of monthly precipitation amount and precipitation isotopic composition, plus a map of zero values used as a mask. Mathematical operations include masking monthly precipitation-amount values less than 50 mm (Con functions), weighting monthly δ^2H values by precipitation amount (Times functions), summing weighted δ^2H and precipitation-amount values (Sum functions), and dividing these values (Divide function). Once the user has specified the mathematical operations and data sets to be used in the workflow, the GIS software determines the necessary order of operations and conducts all calculations iteratively for each map grid cell. The workflow can be saved and reused, for example, with different input data sets.

Science Foundation–funded Isoscape Mapping, Analysis and Prediction (**http://isomap.org**) project, which will ultimately support web-based modeling and analysis capabilities for many of the isotope systems discussed here.

HYDROGEN AND OXYGEN: WATER ISOTOPES

Water in the Oceans and Atmosphere

Isotope ratios of hydrogen and oxygen in water vary widely and systematically primarily because of isotope effects associated with evaporation and condensation. Vapor phase water is depleted in the heavy isotopes ^{2}H and ^{18}O relative to the liquid from which it is derived. As a result, patterns of isotopic variability in the surface ocean largely mimic those of salinity, being higher in regions of net evaporation and lower in regions where there is significant dilution by runoff, and this relationship has been used to model the surface distribution of δ^{18}O values for the global ocean (**Figure 2**; LeGrande & Schmidt 2006). The δ^{18}O/salinity pattern is modulated by systematic differences in the isotopic composition of runoff for different regions (see below), and the lowest surface-water δ^{18}O values are found in and around the Arctic Ocean, which receives abundant, low-δ^{18}O river runoff and glacial meltwater. The highest surface-water isotope ratios occur in the

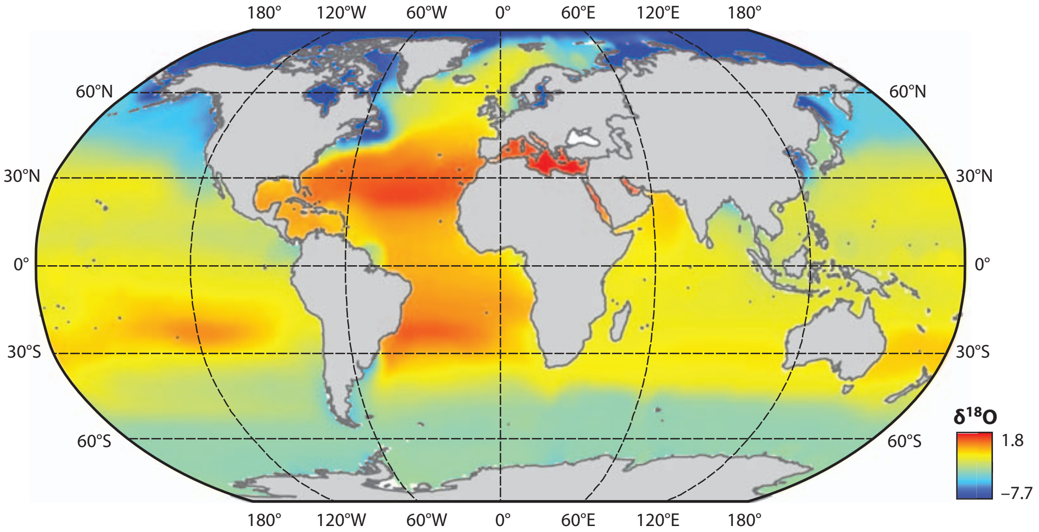

Figure 2

Global isoscape for O isotopes in surface seawater. This isoscape is based on the extrapolation of $\delta^{18}O$/salinity and $\delta^{18}O$/phosphate relationships from a compilation of surface-water sample data (Schmidt et al. 1999). Figure modified from LeGrande & Schmidt (2006).

Mediterranean and Red Seas and the Persian Gulf, restricted waterways in regions characterized by high evaporation rates. Isotope ratios of central Atlantic surface waters are higher than those of Pacific surface waters, mimicking the salinity gradient between these basins, with as much as a 1‰ difference across the Isthmus of Panama. Overall, however, the magnitude of spatial variation in ocean surface-water isotopic composition is small (less than 20%) relative to that in meteoric freshwaters.

Spatial variation in δ^2H and $\delta^{18}O$ values of meteoric precipitation has been documented by the International Atomic Energy Agency's Global Network of Isotopes in Precipitation for more than 40 years (Rozanski et al. 1993). This variation results predominantly from the progressive loss of moisture from air masses as precipitation, which preferentially removes ^2H and ^{18}O and leaves the residual vapor, and any subsequent precipitation formed from it, depleted in these isotopes. Because patterns of precipitation δ^2H and $\delta^{18}O$ values are determined by dynamic, nonlocal processes associated with the atmospheric circulation and water cycle, the only true process-based models that have been applied to map isotope distributions at continental to global scales are atmospheric general circulation models (e.g., Joussaume et al. 1984, Sturm et al. 2005). The water isotope distributions produced by these models allow powerful tests of model physics and, in particular, have been useful in revisiting the interpretation of water isotope proxy data through the investigation of changes in isotope distributions under alternative modeled climate states (Noone & Sturm 2010). In general, these products have not been rigorously tested against observational data sets or distributed and used outside the climate modeling community.

Because rainout is the primary mechanism driving the isotope patterns, many studies have also developed precipitation isoscapes based on statistical or geostatistical models using independent variables that are correlated with the process of rainout and, therefore, precipitation δ^2H and $\delta^{18}O$ patterns (reviewed in Bowen 2010). A range of parameterizations using globally available gridded climate and physiographic data has been explored for regional and global applications (**Table 1**), with most models explaining 60% or more of the spatial isotopic

Table 1 Published statistical models for mean annual precipitation water isotope ratios

Isotope	Region	Model[a]	R^2	Comments	Source
δ^{18}O	Global	$0.587(MAT) - 0.00993(MAT)^2 + 1.152(P) - 0.339(P)^2 - 0.054(E)^{-2} - 13.3$	0.72	Recalculated by Bowen (2010)	Farquhar et al. 1993
δ^{18}O	Global	$0.1805(L) - 0.0051(L)^2 - 0.002(E) - 5.2$	0.76		Bowen & Wilkinson 2002
δ^2H	Global	$0.562(L) - 0.0338(L)^2 - 0.0136(E) + \theta$	0.58	Recalculated by Bowen (2010)	Bowen & Revenaugh 2003
δ^{18}O	Global	$0.0780(L) - 0.00428(L)^2 - 0.00194(E) + \theta$	0.61	Recalculated by Bowen (2010)	Bowen & Revenaugh 2003
δ^{18}O	United States	$0.108(L) - 0.0057(L)^2 - 0.0029(E) - 1.7$	0.79		Dutton et al. 2005
δ^2H	Mediterranean	$-6.2(L) + 0.05(L)^2 - 0.015(E) + 133$	0.70	Gridded data used for independent variables	Lykoudis & Argiriou 2007
δ^{18}O	Mediterranean	$-0.93(L) + 0.008(L)^2 - 0.0017(E) + 17.4$	0.61		Lykoudis & Argiriou 2007
δ^2H	Global	$-51.2 \exp[-0.040(CQT)] - 5.1$	0.79		van der Veer et al. 2009
δ^{18}O	Global	$-5.9 \exp[-0.041(CQT) - 2.4]$	0.79		van der Veer et al. 2009

[a] Abbreviations: CQT, average temperature during the coldest quarter; E, elevation (m); L, absolute value of latitude (°); MAT, mean annual temperature (°C); P, annual precipitation amount (m); θ, interpolated residual term.

variation in terms of independent predictor variables such as temperature, latitude, and altitude. When coupled with geostatistical methods, these regression models are able to predict precipitation isotope ratios globally at unmonitored sites with an average error of <10‰ for δ^2H and <1.2‰ for δ^{18}O (Bowen & Revenaugh 2003). Recent work has shown that cold season temperatures may be the strongest predictor of annually averaged precipitation isotope ratios, suggesting that seasonal extremes play an important role in controlling the time-averaged spatial patterns (van der Veer et al. 2009).

One outcome of this work is the estimation of the precipitation isotopic lapse rate ($\Delta\delta/\Delta$elevation) through calibration of models incorporating Earth surface elevation as a predictor variable. The lapse rate is an important value for isotope-based paleoclimate and paleoelevation studies (Rowley & Garzione 2007), and precipitation isoscape models allow it to be deconvolved from regional and global data sets through multiple regression and/or the extraction of spatial autocorrelation within the data set. Most models have used a linear approximation of this relationship and derive values similar to −2‰ δ^{18}O km^{-1}, which is consistent with the predictions of thermodynamically based models for orographically lifted air parcels within 5–6 km of sea level. Documentation of regional variation in this parameter would be important as a constraint on alternative models for the isotopic lapse rate (Galewsky 2009). Thus far, the only such suggestion from the analysis of isoscapes is based on the stepwise regression of data from the contiguous United States, giving a value of −2.9‰ km^{-1} (Dutton et al. 2005), which is intriguing but may be confounded by autocorrelation between elevation and other variables, such as atmospheric circulation patterns across this region.

The dominant spatial pattern in annual average precipitation isoscapes is a strong, systematic decrease in isotope ratios with increasing latitude, elevation, and continentality (**Figure 3**). The lowest values are found over Antarctica, and recent data complications from that continent have

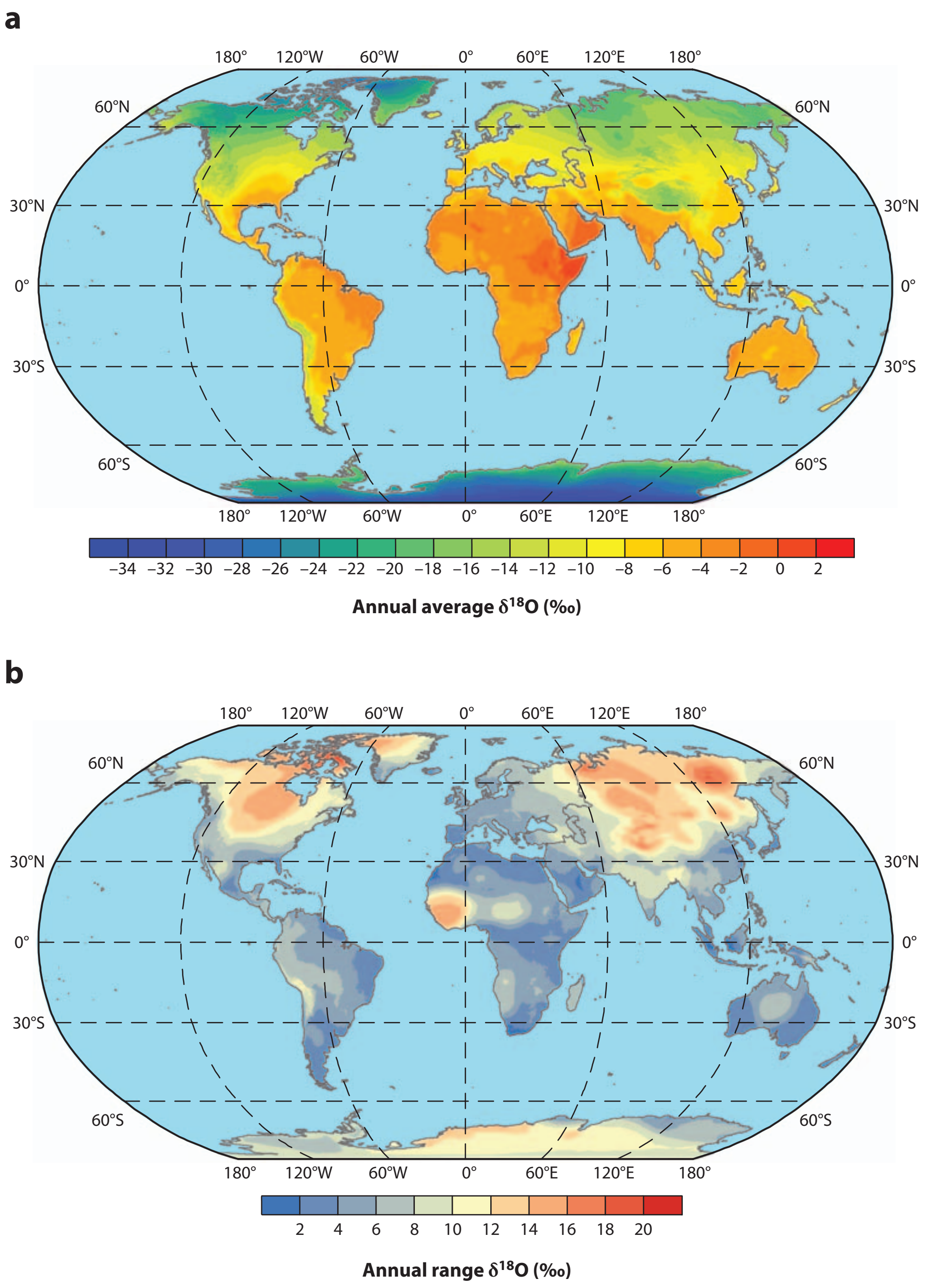

Figure 3

Precipitation δ^{18}O isoscapes. (*a*) Long-term, precipitation-amount weighted annual average δ^{18}O values of precipitation, estimated using data from the Global Network of Isotopes in Precipitation and the literature and the method of Bowen & Revenaugh (2003). (*b*) Intra-annual range of precipitation δ^{18}O values; data from Bowen (2008).

clearly shown that most isoscapes have significantly overestimated central Antarctic precipitation δ^2H and δ^{18}O values (Masson-Delmotte et al. 2008). This may be resolved through the development of regional models (Wang et al. 2009) or the use of alternative climatological variables in global geostatistical models (van der Veer et al. 2009). The highest values are found in the tropics and subtropics, in particular in and around the Horn of Africa. In general, these high values can be attributed to the formation of precipitation from vapor relatively recently evaporated from tropical ocean source regions, in some cases coupled with significant subcloud evaporation (and heavy isotope enrichment) of falling rain drops, but the particular dynamics underlying the very high values found in the Horn of Africa are not fully understood and are worthy of further study. Precipitation isotopic composition also varies seasonally, and the amplitude of this seasonal variation exhibits strong continentality (**Figure 3*b***) and is highest in regions characterized by highly seasonal climate (Bowen 2008).

Meteoric water isoscapes are widely used as inputs to H and O isoscape models for other hydrological and ecological systems (see below), but they are also useful probes of the atmospheric water cycle. One of the primary contributions of isoscapes to our understanding of the atmospheric water cycle is their use in quantifying the recycling (re-evaporation) of meteoric water. An early application of this type involved analyzing the spatial pattern of deuterium excess ($d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$), which serves as a tracer for the re-evaporation of water under strongly subsaturated atmospheric conditions to quantify the magnitude and spatial footprint of water recycled from the North American Great Lakes (Gat et al. 1994). Subsequent work has revisited this approach in other systems and, most recently, capitalized on satellite-based observations of ^{2}H in atmospheric water vapor to identify recycling at unprecedented scales (Worden et al. 2007). Upper-tropospheric vapor δ^2H values extracted from spectral emission lines measured by the Tropospheric Emission Spectrometer across the tropics and mid-latitudes document several surprising patterns, including the tendency for water vapor isotope ratios to be higher over continental regions than over the tropical ocean (**Figure 4**) and for moist air in the tropics to have lower δ^2H values than expected (not shown in the figure). These observations suggest that recycling due to the subcloud evaporation of falling rain droplets and land surface evaporation plays a significant role in the atmospheric

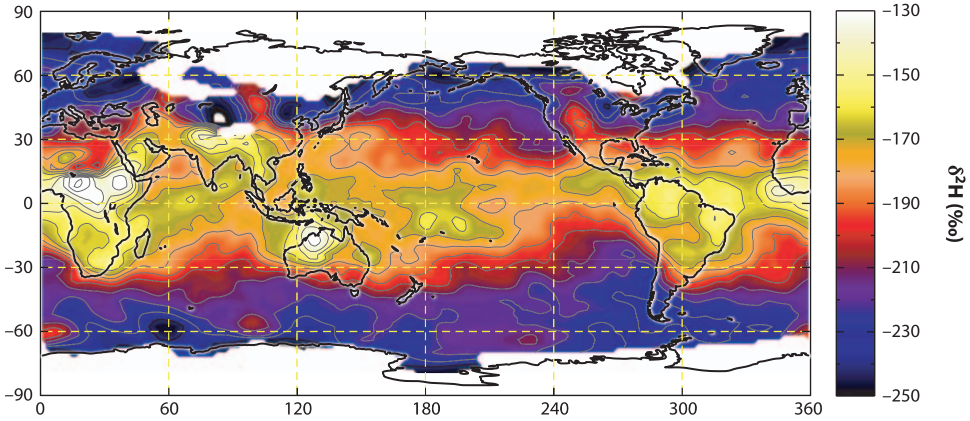

Figure 4

H isoscape for water vapor in the upper troposphere (550 to 800 hPa). Map values were obtained by interpolation of approximately 20,000 observations made between October 2004 and March 2005. Data density is highest over low-latitude oceanic regions. Areas with less than two observations within 1200 km are masked. Figure adapted from Worden et al. (2007) by permission from Macmillan Publishers Ltd: *Nature*.

water cycle of the tropical troposphere, suggesting, for example, that up to 50% of condensation may be re-evaporated within some tropical convective systems.

Water at Earth's Surface

Rivers, lakes, and groundwater derive ultimately from precipitation, and work on isoscapes for these systems confirms that they exhibit patterns similar to those seen for precipitation at the continental scale. Systematically collected river-water isotopic data are sparse, with most work having focused on the database for U.S. river waters assembled by Kendall & Coplen (2001). Those authors and Dutton et al. (2005) each developed statistically based isoscapes for U.S. river waters that document similar latitudinal, altitudinal, and continental patterns of variability (**Figure 5**). These studies, and subsequent work on tap waters by Bowen et al. (2007), also demonstrated two additional controls on U.S. surface-water isoscapes: the transport of low-δ^2H and δ^{18}O waters from high elevations to low-elevation areas, both in natural stream systems and managed waterways and aqueducts, and the enrichment of ^{2}H and ^{18}O in surface waters due to evaporative water loss. These processes have been integrated into a surface hydrology model and used to simulate surface-water isoscapes for the contiguous United States using precipitation isoscapes and climate data as inputs (Fekete et al. 2006). Validation of the resulting isotope fields against Kendall & Coplen's data set suggested that the results were only moderately accurate, likely in part because of the inadequate representation of altitude effects in the precipitation isoscape used as input. Isoscapes produced through this implementation can enable valuable tests of the

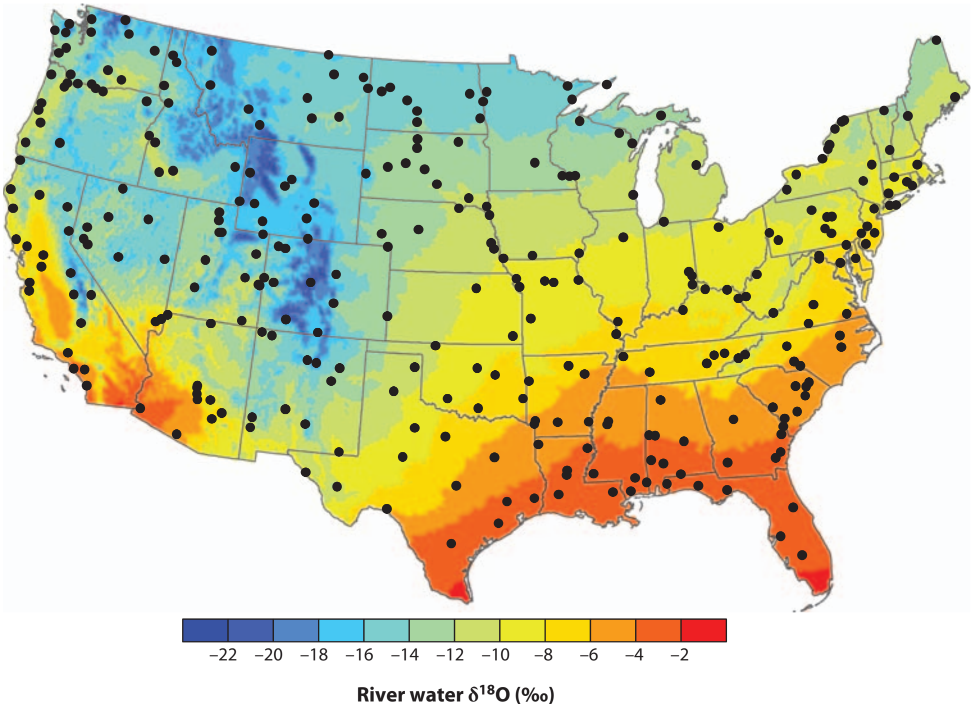

Figure 5

Isoscape for river-water isotopic composition based on the statistical model of Dutton et al. (2005) and river-water monitoring data (*circles*; Kendall & Coplen 2001).

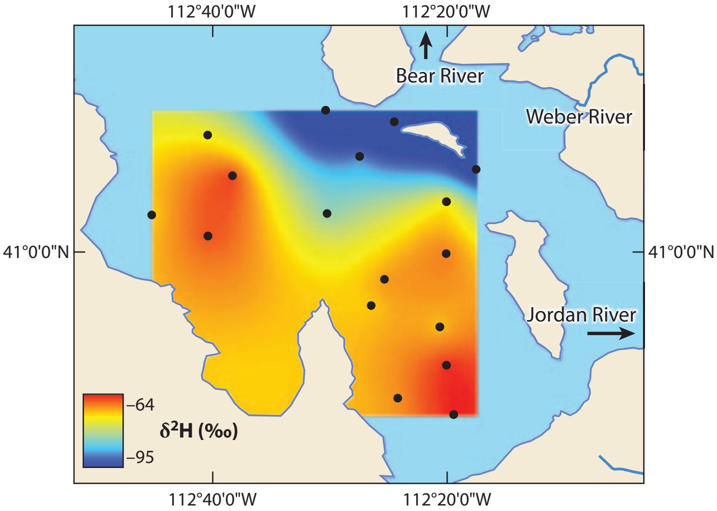

Figure 6

Geostatistical (ordinary kriging) interpolation of the δ^2H values of surface waters from the Great Salt Lake, Utah, for April 2006. A plume of ^{2}H-deleted freshwater can be seen propagating into the northeastern portion of the mapped area, reflecting the mixing of inflow derived from the Bear and Weber River peak spring discharge. Data from Nielson & Bowen (2010) and G.J. Bowen (unpublished).

hydrological model, however, and unlike the statistical models, they explicitly consider the spatial structure and connectivity of river systems, making them a more physically consistent representation of river-water isoscapes.

Hydrological studies have used isoscapes for surface waters and groundwaters both for attribution of water sources and for identification and quantification of isotope fractionating processes. In addition to the large-scale river-water and tap-water studies mentioned above, many studies have used spatial sampling of subsurface aquifers to map recharge sources. One important application has been in mapping the flow of artificial recharge within aquifers for the assessment of groundwater replenishment efforts and contaminant risk (Coplen et al. 1999). Over larger scales, shallow groundwater isotopic compositions have been used to map geographic patterns of water isotope variation in regions without adequate precipitation monitoring data (Wassenaar et al. 2009). Water isotopes are also effective, if less frequently used, hydrological tracers for limnological research and can trace the propagation of inflow as it enters and mixes with lake waters (**Figure 6**).

The quantification of evaporation rates from isotopic measurements of surface waters is particularly useful for understanding water balance and climate change hydrology at catchment to continental scales, and analysis of isoscapes offers one of the few observational methods for obtaining such information. Gibson & Edwards (2002) demonstrated a powerful method for quantifying regional patterns of evaporative loss from ungauged lakes in northern Canada using a simple isotope mass balance model driven by precipitation isoscapes (approximating lake inflow), lake-water isotopic measurements, and estimated isotope ratios of evaporated vapor calculated using climatological data. The results revealed striking changes in the fraction of incident precipitation lost to evaporation across the forest-to-tundra transition and suggest that up to 50% of catchment-integrated precipitation is lost as evaporation within the southern, subarctic forest zone of the study region (**Figure 7**).

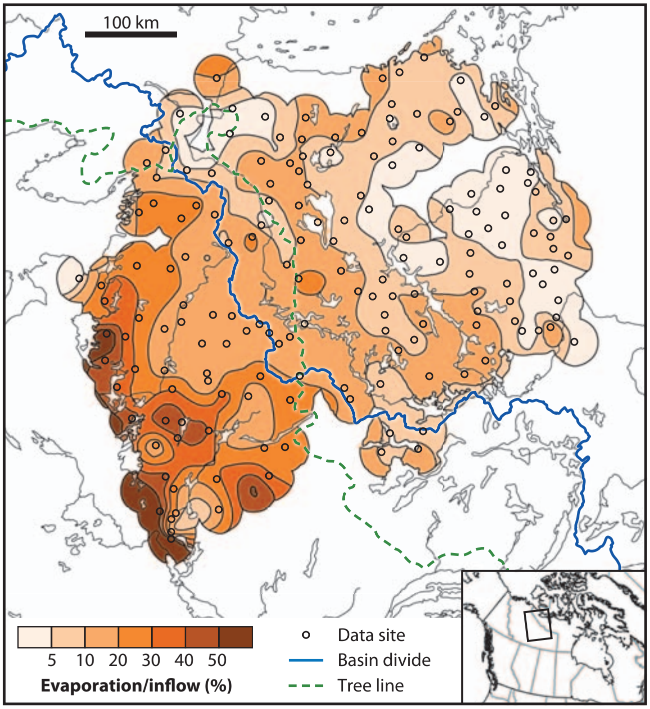

Figure 7

Estimated fraction of lake inflow lost to evaporation in northern Canada (*inset*), as calculated based on isoscapes of lake water and precipitation δ^{18}O. Figure modified from Gibson & Edwards (2002).

Water Isotopes in Plants and Animals

Isotopes of hydrogen and oxygen from water are assimilated in biological tissues with fractionation. For plants, xylem water is typically unfractionated relative to the soil water and groundwater from which it is derived, and it has been employed to map the use of water sources of differing water isotopic composition along environmental gradients, for example, to indicate the preferential use of groundwater over soil or stream water by some trees in arid region riparian zones (Dawson & Ehleringer 1991). Over larger spatial scales, isotopic differences between local water sources tend to become smaller relative to the spatial variation in water δ^2H and δ^{18}O values, and variation in isotopic compositions preserved in stem, leaf, and fruit water, in plant tissues, and in plant-derived products is often driven primarily by spatial source-water isotope ratio variability.

These spatial relationships have been used as a natural experiment to investigate and calibrate tissue/water isotope relationships for the purposes of developing paleoclimate proxies. Lipids produced by land plants have been of particular recent interest. Several studies employing comparisons between measured values of sedimentary lipids and water isoscapes have found linear or nearly linear relationships, suggesting that lipid δ^2H values may be a direct proxy for paleowater H isotopic composition (**Figure 8*a***; Sachse et al. 2004, Hou et al. 2008). Measurements of lipid δ^2H values for well-controlled taxonomic groups, however, have suggested that the relationship between lipid values and those of precipitation source water may be modulated by environmental and physiological processes that influence the degree of evaporation of water in soils and plant leaves (Smith & Freeman 2006). These authors have developed a quantitative model incorporating these effects that accurately reproduces observed lipid δ^2H values

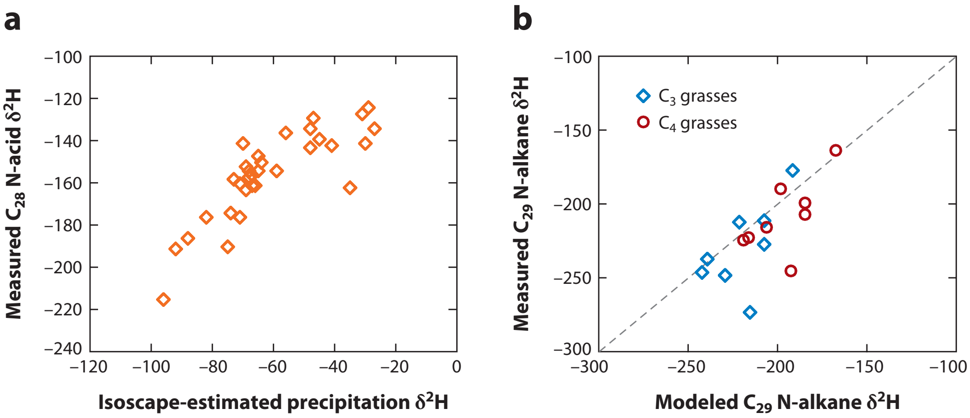

Figure 8

Calibrations of lipid H isotope paleoclimate proxies using precipitation isoscapes (the Online Isotopes in Precipitation Calculator, available at **http://waterisotopes.org**) to approximate source-water isotopic composition. (*a*) Comparison between measured sedimentary lipid δ^2H values and precipitation isoscape δ^2H values. Data from Hou et al. (2008). (*b*) Comparison of measured lipid δ^2H values for specific C_3 and C_4 grasses, with values predicted using a model incorporating isoscape-based precipitation δ^2H values and isotope fractionation due to soil-water and leaf-water evaporation. The dashed line shows a 1:1 relationship. Data from Smith & Freeman (2006).

using isoscape-based source-water estimates and climate data (**Figure 8*b***). Understanding the degree to which these factors are important for the interpretation of lipid paleorecords will require additional work, and one productive approach may be the incorporation of evaporative effects—as well as other taxonomic effects suggested to influence sedimentary lipid δ^2H values (Hou et al. 2008)—in a GIS-based isoscape model to identify hot spots for predicted isotopic response to these variables and to direct further sampling. Once a strong, comprehensive model has been developed, this process can be inverted to allow interpretation of lipid δ^2H measurements as indicators of spatial patterns and/or spatiotemporal variability in ecophysiological processes.

The assimilation of environmental water isotopic signatures in plant tissues is also becoming increasingly important in food and trade regulation. Isotopic values determined by source-water and environmental conditions at the site of plant growth can often be preserved in the water or organic fractions of plant-derived food and commercial products, meaning that the conditions and locations of origin for these products can be constrained based on isotopic measurements. Data on wine water, presumably deriving entirely from the fruit used to produce the wine, from U.S. Pacific coast states demonstrate the potential of this method: Within a collection of 2002 vintage samples, wines from the northern states (Washington and Oregon) were clearly distinguishable from those produced in California based on their $\delta^{18}O$ values (West et al. 2007). A regression model based on these data was used to develop an isoscape for 2002 wine water as a function of precipitation source-water $\delta^{18}O$ values and climate (**Figure 9**), and when applied across the dominant wine-growing regions of these states, it suggests that wines grown in the northern states are unlikely to have $\delta^{18}O$ values greater than 6.0‰, providing a criterion for developing a regulatory monitoring tool. Although this study represents one of the few cases in which isotopic data from plant products have been explicitly modeled within a geographic context, there are a large number of related, emerging applications involving plant- and animal-derived food products that are well suited to this type of analysis (Rossmann 2001).

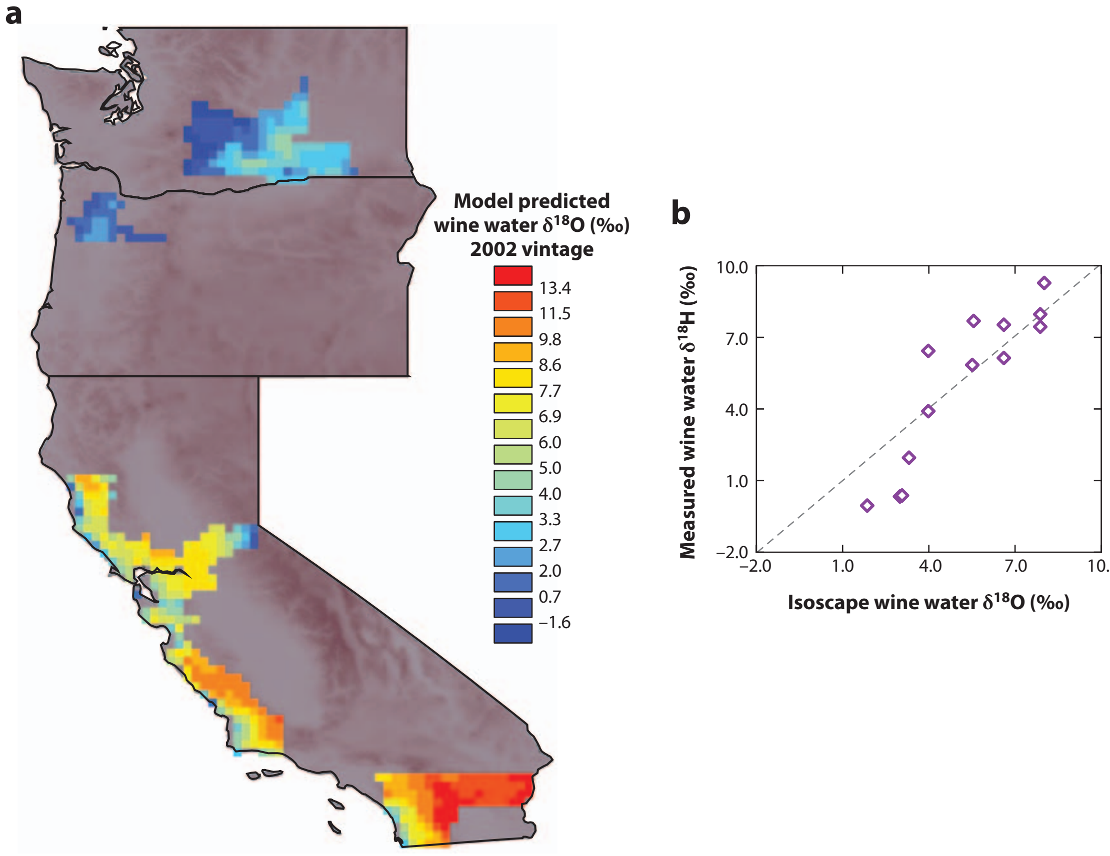

Figure 9

Wine-water isoscape and comparison of isoscape-predicted values with observational data. (*a*) Isoscapes for regional variation in the δ^{18}O values of water in wine produced within several growing regions in California, Oregon, and Washington (*color field, superimposed on shaded relief topography*). Map values were estimated using a regression model relating wine-water values to precipitation δ^{18}O values and climate variables. (*b*) Comparison of map predictions with observed wine-water δ^{18}O values for 2002 Chardonnay. The dashed line shows a 1:1 relationship. Figure modified from West et al. (2007).

The same concept of geographic source determination based on water isotopes has been widely applied to animal tissues in the fields of ecology and anthropology, and it is beginning to be adopted as an investigative tool in forensic science. As tissues are synthesized in animals' bodies, they incorporate hydrogen and oxygen from dietary sources and consumed water, and to the degree that these sources are local in origin and the isotope effects associated with synthesis are constant, the synthesized tissues will vary in isotopic composition among locations and will parallel the pattern of isotopic variation in the sources. A number of studies have demonstrated proof of this concept by measuring the δ^2H value of keratin from feathers of resident birds across wide geographic ranges and showing that it is strongly correlated with precipitation isotope ratios (Chamberlain et al. 1997, Hobson & Wassenaar 1997). If the tissue remains chemically inert following its synthesis (as is the case for keratin) and the relationship between the isotopic compositions of tissue and environmental water source is known, then measurements of tissue isotope ratios can be used to constrain the locations on an environmental water isoscape from which the material might have

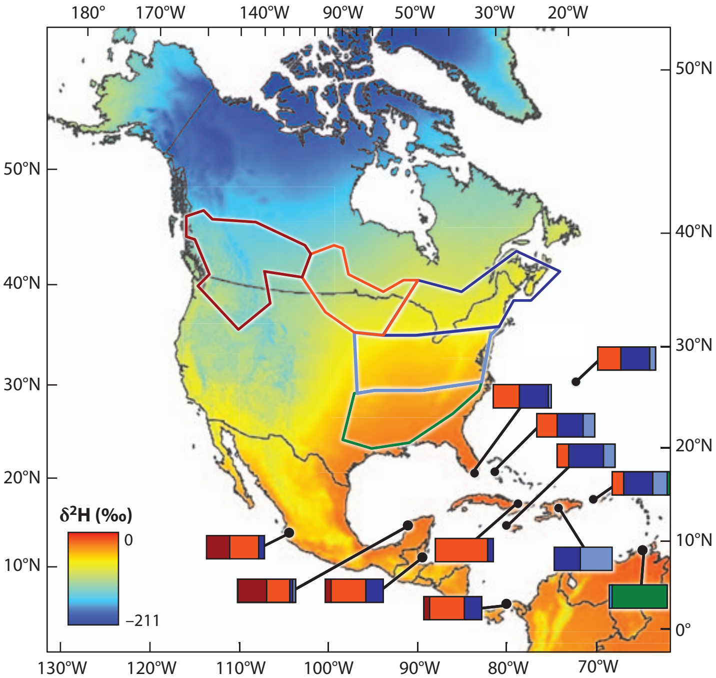

Figure 10

Probabilistic assignment of American Redstart individuals to breeding areas based on the H isotopic composition of feathers grown at breeding sites and collected on the wintering grounds. Horizontal bars show the fraction of individuals collected at each wintering site (*dots*) assigned to each breeding range (*colored polygons*) based on feather isotopic composition and an isoscape predicting compositions of locally grown feathers (*background color field*). This example shows a pattern of chain migration, wherein birds breeding in the northern part of the breeding range, for example, tend to migrate to the northern part of the wintering range. Figure reprinted from Bowen et al. (2009b); data from Norris et al. (2006).

originated. A series of studies have applied this approach to produce unprecedented documentation of the migratory patterns of birds and butterflies (Hobson & Wassenaar 2008), demonstrating patterns of migration and drawing connections between winter and summer habitats (**Figure 10**), with implications for understanding migratory behavior and developing informed strategies for the conservation of migratory animals.

An analogous application has recently emerged for the determination of human travel histories, with applications in anthropology and forensic science. Strong relationships between the H and O isotopic composition of human hair and that of drinking water have been demonstrated through experimental studies (Sharp et al. 2003, O'Brien & Wooller 2007) and geographic surveys (Ehleringer et al. 2008, Bowen et al. 2009a). Synthesis of this data suggests that approximately 30% of hair hydrogen and a slightly larger fraction of hair oxygen are derived from drinking water and should thus incorporate spatial isotopic variation present in drinking-water sources (Ehleringer et al. 2008). A large part of the remaining hydrogen and oxygen is derived from food, however, which is widely transported and often of nonlocal origin in many parts of the modern world. To facilitate interpretation of data from this complex system, Ehleringer et al. (2008) developed a process-based model tracking inputs and fractionation of H and O isotopes within the human body leading to keratin synthesis. This model has tested well against contrasting data sets from twenty-first-century residents of the United States and early to mid-twentieth-century

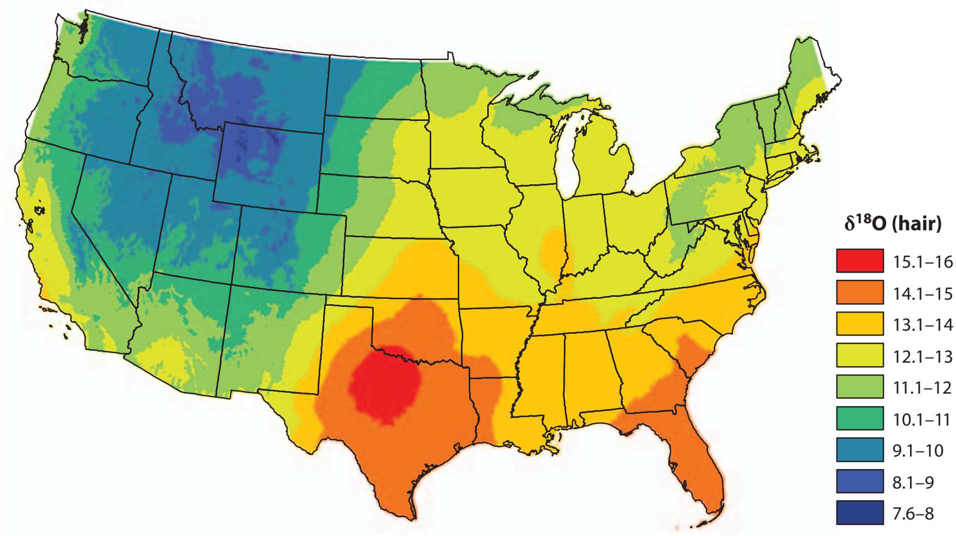

Figure 11

$\delta^{18}O$ isoscape for modern human hair. Map values are estimated based on a modeled isoscape for tap water and a regression model relating observed hair and drinking-water isotope ratios from sample sites in 18 states. Figure reprinted from Ehleringer et al. (2008).

indigenous populations, with the implication that the consumption of a highly spatially homogenized diet has greatly damped the geographic isotopic variation in the body tissues of modern Americans (Ehleringer et al. 2008, Bowen et al. 2009a). The resulting isoscapes for modern American hair, however, still predict strong geographic variability of more than 50‰ for δ^2H and 8.0‰ for $\delta^{18}O$ and suggest the significant power of hair isotope ratios to distinguish residents of or identify travel between many parts of the country (**Figure 11**).

CARBON IN PLANTS, PEOPLE, AND THE ATMOSPHERE

For H and O isoscapes, the fractionating processes of primary importance are evaporation and condensation. For C isotopes, the key process is the fixation of CO_2 by plants, which discriminates against the heavy isotope ^{13}C, giving plant biomass $\delta^{13}C$ values that are low relative to other pools in the C cycle. The magnitude (ε) of this fractionation varies considerably, from approximately 4.4‰ for plants using the C_4 photosynthetic pathway to as much as 27‰ for C_3 plants with low photosynthetic rate and/or high stomatal conductance (Farquhar et al. 1989). This basic distinction related to photosynthetic mechanisms exerts a strong control on large-scale spatial variation in $\delta^{13}C$ values of the biosphere because the geographic distribution of C_4 plants is limited to climates where they either have a competitive advantage over C_3 grasses or are grown as crops (Ehleringer 1978). Theoretical models for C_4 competitiveness and GIS data on crop distributions have been used to generate global and regional isoscapes for plant $\delta^{13}C$ (e.g., Still et al. 2003), which show strongly patterned variation across continental regions with appreciable C_4 plant cover (**Figure 12**). Whereas C isotope discrimination by C_4 plants is relatively constant, C_3 plant discrimination varies by approximately 10‰ owing to the physiological regulation of leaf gas exchange under different environmental conditions. Ecophysiological models incorporating these effects have been used to develop isoscapes reflecting variation in C_3 discrimination in

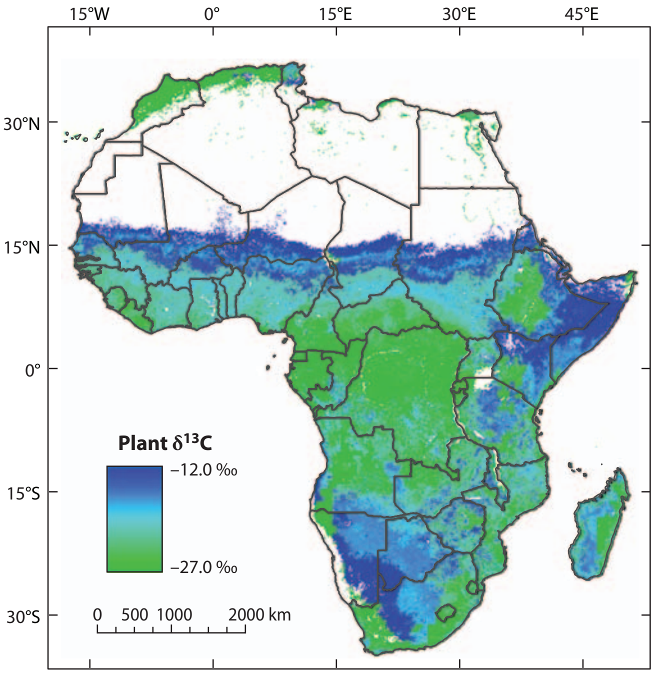

Figure 12

Isoscape for the $\delta^{13}C$ values of African vegetation based on modeled C_3 and C_4 plant and crop distributions. Map values are calculated assuming end-member $\delta^{13}C$ values of −27‰ and −12‰ for C_3 and C_4 vegetation, respectively, and do not account for physiological effects on C_3 photosynthetic isotope discrimination. Figure modified from Still & Powell (2010).

addition to the effects of the photosynthetic pathway (Suits et al. 2005). At plant to stand scales, measurements of C isotope discrimination during photosynthesis have been used as an indicator of gas-exchange physiology, and this approach may be extended to larger scales to enable isoscape-based mapping and monitoring of physiological controls on ecosystem gas exchange in modern systems (Bowling et al. 2002). Similarly, isoscapes for the C isotope ratios of tree rings have been used to map paleoclimatological conditions experienced by plants in the past, with implications for understanding climate teleconnections and past climate impacts on archaeological communities (Leavitt 2007, Aguilera et al. 2009).

C isotope fractionation between diet and most heterotroph body tissues is relatively constant and well constrained (McCutchan et al. 2003). As a result, the large-scale patterns in plant $\delta^{13}C$ that emerge from the geographic distribution of plant types and environmental conditions may be assimilated by consumers, supporting inference about the geographic origin of animals based on $\delta^{13}C$ values of their body tissues. C isotope ratios of human hair provide an interesting example in which the cultural selection of foods coupled with the regional climatic conditions and botanical history of different regions leads to strong and systematic $\delta^{13}C$ variation among different populations of modern humans (**Figure 13**). Both the mean values (reflecting C_3/C_4 dietary intake, climate of food-growing regions, and potentially the consumption of large amounts of marine-derived food) and the range of values (reflecting the degree of dietary variation) vary widely, from Northern European and Chinese residents, who have hair $\delta^{13}C$ values reflecting relatively little C_4 contribution to diet, to residents of Latin America, with median values ∼5‰ higher. Of particular interest, a break in the distribution of values at approximately −18‰ sets apart a subset of

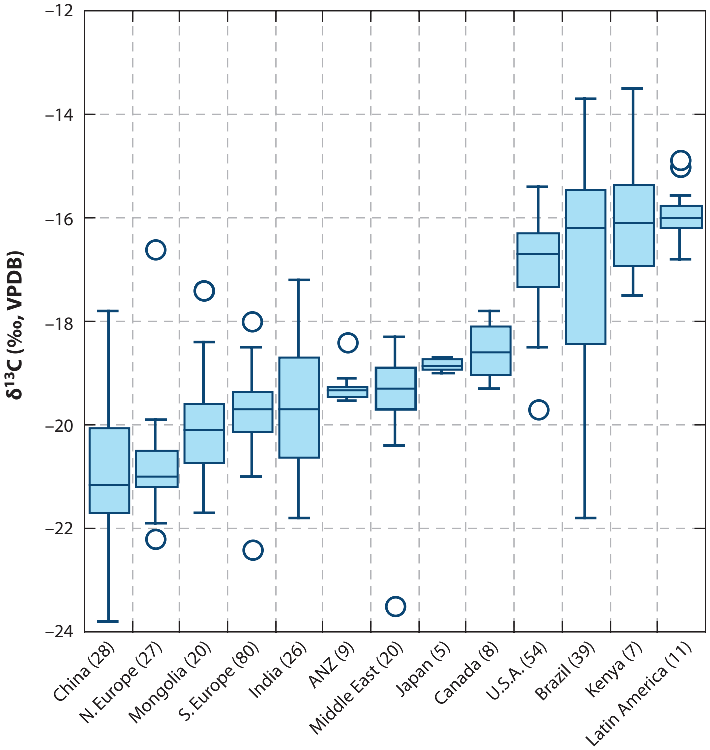

Figure 13

C isotope ratios of modern human hair from 13 countries and regions around the world. Box-and-whisker plots show the median, upper and lower quartiles, and maximum and minimum values, with outlier values shown as circles. The number of individuals sampled in each region is shown in parentheses. Data from Bowen et al. (2009a), Thompson et al. (2010), and J.R. Ehleringer (unpublished). All data are reported relative to the Vienna Pee Dee Belemnite standard (VPDB). ANZ, Australia and New Zealand.

high-C_4 countries and regions, including the United States. Despite perceptions to the contrary (e.g., Pollan 2007), contemporary U.S. residents are not unique in terms of their heavy C isotope composition among modern or ancient humans (**Figure 13**; White & Schwarcz 1989, Bowen et al. 2009a), nor do the hair data suggest more than approximately 50% contribution of C_4-derived carbon to diet [using the mixing model of White & Schwarcz (1989) and fractionation of 2‰ between diet and hair (Yoshinaga et al. 1996)].

Although the patterns of variation in tissue $\delta^{13}C$ values shown in **Figure 13** clearly provide some potential to constrain the geographic origins of a sample, the role of cultural practice and individual behavior in controlling dietary intake, and therefore tissue $\delta^{13}C$, makes it difficult to develop a highly quantified isoscape for human tissue $\delta^{13}C$. C isotope variation within an ocean ecosystem holds more promise in this respect. In the marine system, C isotope ratios are primarily controlled by $\delta^{13}C$ variation in dissolved carbon, which is driven by geographic variation in the export of organic carbon from the surface ocean to depth (Broecker & Peng 1982). This variation is assimilated by phytoplankton and propagates from the base of the food chain, affecting all consumers. Relatively few detailed and well-constrained isoscapes for ocean ecosystem $\delta^{13}C$ values exist, but such products have been developed for specific studies and are of increasing interest for their use in tracking the migration patterns of marine animals (Schell et al. 1998, Graham et al. 2010).

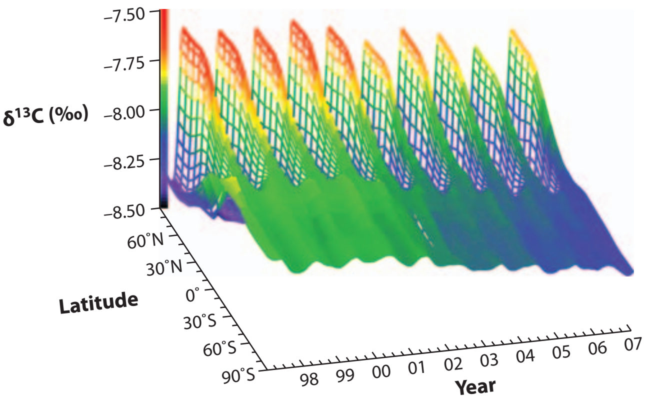

Figure 14

Space/time isoscape for δ^{13}C values of atmospheric CO_2. Map values were interpolated from data from the U.S. National Oceanic and Atmospheric Administration's (NOAA) Global Flask Network (>55 sites). Image courtesy of the Institute of Arctic and Alpine Research, University of Colorado, and NOAA Global Monitoring Division. Figure reprinted from Bowen et al. (2009b).

The magnitude of global photosynthesis and respiration fluxes is significant relative to the mass of CO_2 present in Earth's atmosphere. As a result, the net regional transfer of carbon from the atmosphere to the biosphere during the growing season, and subsequent transfer back to the atmosphere during months when photosynthetic rates are low, has a measurable influence on the δ^{13}C of atmospheric CO_2. This seasonal imbalance of fluxes forces changes in atmospheric CO_2 concentration and isotopic composition at a rate that exceeds the ability of atmospheric circulation to mix and homogenize these values, particularly within the Northern Hemisphere, where high-latitude land areas with highly seasonal climate are expansive. The result is a strong seasonal oscillation of atmospheric $\delta^{13}CO_2$ values of approximately 0.75‰ at high northern latitudes, which can be observed and mapped based on a network of globally distributed atmospheric flask sampling sites (**Figure 14**; Vaughn et al. 2010). Coupled with this seasonal transfer of carbon to/from the atmosphere is the ongoing net transfer of low-δ^{13}C carbon from organic pools to the atmosphere via deforestation and fossil-fuel burning, which is reflected in the space/time isoscape for atmospheric $\delta^{13}CO_2$ as a secular decrease in values. These patterns have been of significant use, in combination with measurements of CO_2 concentrations and other tracers, in understanding and quantifying C fluxes into and out of the atmosphere, for example, in partitioning uptake of anthropogenic CO_2 from the atmosphere into the terrestrial biosphere (with a large fractionation due to photosynthesis) and the oceans (with negligible fractionation) (Ciais et al. 1995, Fung et al. 1997, Battle et al. 2000). In addition, when coupled with process-based models for C isotope fractionation accompanying photosynthesis and respiration, year-to-year variability in the atmospheric isoscapes can be used to identify and improve model simulations of ecophysiological factors, such as responses to climate warming and drought stress, that control the rate of CO_2 uptake by the terrestrial biosphere (Randerson et al. 2002a,b).

NITROGEN IN THE OCEAN, SOILS, AND PLANTS

Unlike the H, O, and C isotope systems discussed above, no single process has been identified as a dominant, global control on geographic δ^{15}N distributions, and as a result work on N isoscapes is relatively less developed. Nonetheless, growing databases of N isotope values for many

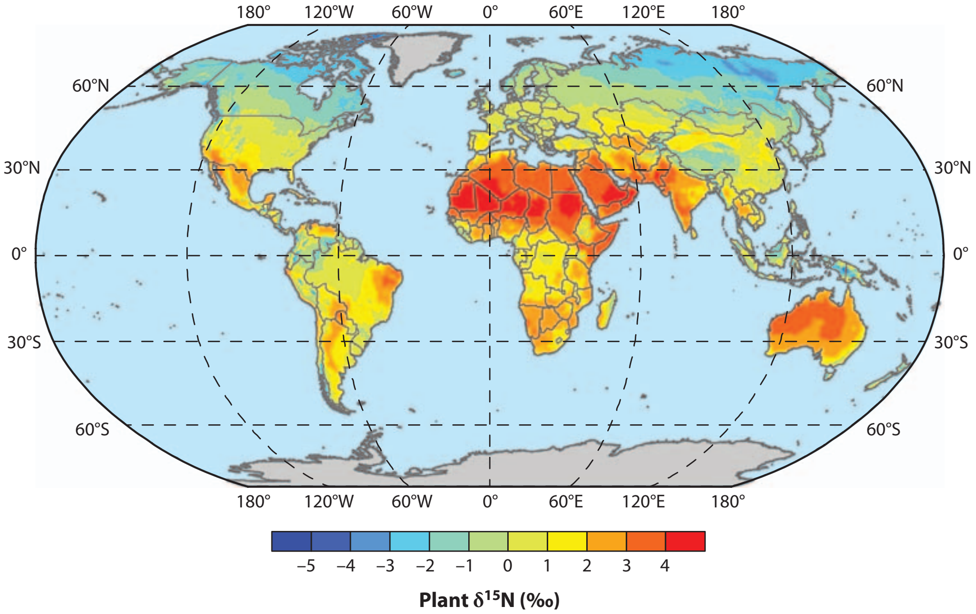

Figure 15

Isoscape of plant foliar δ^{15}N values predicted as a function of mean annual temperature and precipitation amount based on the regression model of Amundson et al. (2003). Although this model captures large-scale patterns of the global isotopic distribution, much of the observed variability in δ^{15}N values (66%) remains unexplained.

systems, coupled with an increased emphasis on identification and interpretation of spatial patterns, have uncovered promising patterns. Within terrestrial ecosystems, soil and plant δ^{15}N values are controlled largely by the rates and types of N losses, which remove ^{15}N-depleted nitrogen, enriching the residual pools in ^{15}N (Pardo & Nadelhoffer 2010). Although the suite of processes through which nitrogen is transformed within and lost from terrestrial ecosystems is complex, global-scale patterns do exist and have been attributed to climatologically driven differences in the openness of the N cycle (rate of N loss relative to pool size) in different environments (**Figure 15**; Amundson et al. 2003). The explanatory power of regression-based models for these patterns is low ($R^2 < 0.35$), however, and at regional and local scales, the dominant controls on N losses and δ^{15}N values can be strongly decoupled from the global trends (Pardo & Nadelhoffer 2010).

Within some terrestrial systems, source effects can strongly influence δ^{15}N values, and N isotopes have been used as tracers of the spatial distribution of N inputs. The δ^{15}N values of atmospheric nitrate deposition and stream nitrate, for example, show strong spatial and temporal patterns that can be linked to point-source emissions (Elliott et al. 2007, Kendall et al. 2010). Other work has used spatial variation in N isotope ratios to assess and quantify transfers of marine nitrogen to terrestrial ecosystems through spawning or human harvesting (Ben-David et al. 1998, Helfield & Naiman 2001, Commisso & Nelson 2006) and atmospheric N_2 fixation (e.g., Vitousek et al. 1989). Although not all of these studies have used isoscape models for data analysis and interpretation, grid-based spatial analysis is increasingly being used to identify source-derived patterns and to quantify the impact of specific N sources on ecosystem patterning and aerially integrated nutrient budgets (e.g., Fox-Dobbs et al. 2010).

N isotope patterns within ocean water are also receiving increased attention for their use as biogeochemical and ecological tracers. Variation in the extent of N utilization within various regions of an ocean leads to strongly patterned variation in the δ^{15}N values of bioavailable nitrogen, and this variation is taken up by primary producers and transferred both to sedimentary organic material and through the food chain (Farrell et al. 1995, Schell et al. 1998, Graham et al. 2010). Within the modern ocean, these patterns have been used to deduce the sources and source conditions contributing to sedimentary organic C burial (Knies et al. 2007) and, in combination with spatial δ^{13}C patterns, to trace the migratory pathways and feeding environments used by marine mammals and fish (Hobson & Schell 1998, Newsome et al. 2007, Graham et al. 2010).

SYNTHESIS AND THE FUTURE OF ISOSCAPES

Spatial patterns have been studied in each of the isotopic systems described above independently of the development of spatially explicit, grid-based, isoscape-type models, but the use of such models has opened up new and timely research opportunities. Isoscape models allow researchers to fill in the gaps in observational data sets, creating spatially continuous predictions of isotopic distributions that are essential for many applications that deal with processes occurring across time and space. Global or regional isotope mass balance calculations for atmospheric CO_2 or catchment-scale calculations of evaporation from water isotopes require spatially distributed estimates of the isotopic composition of inputs and outputs to/from these systems. Studies that seek to identify the origin of animals, products, or biogeochemical species require estimates of the distribution of isotopic tracers in source regions. These applications address the fundamental workings of complex systems across large spatial scales, and the development of isoscapes has provided ways of scaling up the power of isotopes as indicators of sources and processes from studies of phenomena to studies of systems. Presumably, one way to further advance this work is through the continued development and improvement of isoscapes and isoscape models, but is this necessarily so? To what extent can we hope to be able to model and predict spatiotemporal isotopic variation in Earth systems, and is there likely to be significant value in better isoscapes?

The answers to these questions will depend largely on the particular systems and applications considered, and it is possible that for some systems and scales, we may never develop models that predict isotopic compositions with a high degree of accuracy or that teach us much more about the system. Huge gaps exist in the current portfolio of published isoscapes, however, and across a wide range of systems, it is clear that significant opportunities remain both for those who are interested in the processes reflected by spatial isotope distributions and for workers seeking to use isotopes as spatial tracers. Even for highly studied systems, such as precipitation, existing isoscapes are highly generalized (e.g., reflecting climatological rather than meteorological conditions), limiting the ability for researchers to analyze observational data in the context of these products. For other systems, only the most basic exploratory analyses have been conducted. These gaps point to areas of opportunity for advancing our basic understanding of biogeochemical systems and models, ranging from improved understanding of the accuracy of water cycle fluxes in global climate models to the development of a quantitative theory describing the controls on N cycling in terrestrial ecosystems.

Across a wide range of systems, a spectrum of isoscape models has been explored, from highly parameterized statistical models to more physically based process models. Perhaps one of the most universally productive emphases for future work on isoscapes will be the transition away from descriptive models to more comprehensive, mechanistic, process models. The use of mechanistic model parameterizations provides opportunities for researchers to investigate physical, biological, and chemical processes and their representations in models using spatial data sets.

For example, integrating a $\delta^{15}N$ isoscape model using explicit representation of soil N transformation effects with spatially distributed data on soil $\delta^{15}N$ values might lead to an improved understanding of the soil N cycle that would not emerge from attempts to model soil $\delta^{15}N$ values based on empirical correlations with climate variables. For researchers interested in the quality of isoscape-based predictions (e.g., as a basis for testing the origin of a vintage wine), well-validated process models provide powerful opportunities to extrapolate beyond the bounds of existing databases—for example, to develop isoscapes for vintages or grape types for which authentic samples are not available. A number of nontrivial challenges exist, however, among them the lack of an adequate theoretical basis for the development of process-based models for some systems and complications associated with attempting to incorporate nonlocal information in models for fluid transport systems (atmospheric, aqueous) without explicitly modeling the dynamics of these systems.

Perhaps the ultimate endpoint for the development of process-based isoscape models is the implementation of isotope tracers in comprehensive Earth systems models. Because these models integrate chemical reactions, biological processes, and transport dynamics, they offer a coherent means of representing the coupled, spatially distributed responses of these processes to environmental forcing factors and their net effect on spatiotemporal isotope distributions. The tradeoffs associated with this approach are significant, however, and range from the computational requirements associated with dynamical models to reductions in the transparency and accessibility of results derived from models representing complex coupled systems. Moreover, critical work remains to elucidate the component processes within many systems, and as we move toward the use of more comprehensive models to describe and analyze spatial isotopic patterns, a strong focus on spatial modeling of isotope effects within individual systems will need to be retained. Key to this work will be the continued growth in accessibility of spatial data that will allow researchers to capitalize on the natural experiments driven by variation in conditions across space and time. Measured isotope distributions from monitoring networks, Earth observation data sets describing the experimental conditions, and well-documented isoscapes that can be used to describe spatial isotopic variability of elemental sources will each be critical to the continued advancement of spatial isotope modeling, improving our understanding of biogeochemical processes and spatial connectivity within Earth systems.

SUMMARY POINTS

1. Isotopic variation results from geological, environmental, and biological influences on biogeochemical processes. Isoscape models represent the impact of these processes on the spatiotemporal distribution of isotopes in the environment.
2. Isoscapes for hydrogen and oxygen in water reflect water transport and evaporation/condensation and have been used to probe water cycling in the oceans and atmosphere and on land.
3. The $\delta^{2}H$ and $\delta^{18}O$ values of continental water vary widely and exert a strong influence on the isotopic composition of local biological materials. The geographic origin of those materials can be constrained based on their isotopic composition.
4. $\delta^{13}C$ isoscapes primarily reflect isotope effects associated with the uptake and release of carbon from organic material and can be used to study these fluxes as well as the transfer of carbon through food webs.

5. Global-scale N isotopic variation in terrestrial and marine ecosystems is related to climatic controls on N cycle fluxes, but predictive process-based models of these relationships have not been developed.
6. A shift in emphasis from descriptive to mechanistic isoscape models, and ultimately to comprehensive Earth systems models, will lead to improved understanding of Earth systems processes based on the analysis of spatial isotopic distributions and to the development of more accurate isoscapes.

FUTURE ISSUES

1. Can general circulation model simulations provide accurate isoscapes of meteoric water δ^2H and δ^{18}O values, including water in land surface schemes and water in meteorological simulations that are nudged with archival climate data?
2. How are hydrogen and oxygen routed and isotopically fractionated during uptake of hydrogen and oxygen by the biosphere?
3. How important are taxonomic effects relative to large-scale environmental controls in determining spatial and temporal isotopic variation within and among ecosystems?
4. What are the primary, process-level controls on δ^{15}N distributions in terrestrial and marine systems, and can these be used to develop robust N isoscapes for these systems?
5. Can web-based cyberinfrastructure reduce the overhead associated with the use of large geospatial data sets for isoscape modeling and make this approach (and the resulting data products) accessible to a wider range of scientists?

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LITERATURE CITED

Aguilera M, Espinar C, Ferrio JP, Pérez G, Voltas J. 2009. A map of autumn precipitation for the third millennium BP in the Eastern Iberian Peninsula from charcoal carbon isotopes. *J. Geochem. Explor.* 102:157–65

Amundson R, Austin AT, Schuur EAG, Yoo K, Matzek V, et al. 2003. Global patterns of the isotopic composition of soil and plant nitrogen. *Glob. Biogeochem. Cycles* 17:1031

Battle M, Bender ML, Tans PP, White JWC, Ellis JT, et al. 2000. Global carbon sinks and their variability inferred from atmospheric O_2 and $\delta^{13}C$. *Science* 287:2467–70

Ben-David M, Hanley TA, Schell DM. 1998. Fertilization of terrestrial vegetation by spawning Pacific salmon: the role of flooding and predator activity. *Oikos* 83:47–55

Bowen GJ. 2008. Spatial analysis of the intra-annual variation of precipitation isotope ratios and its climatological corollaries. *J. Geophys. Res.* 113:D05113

Bowen GJ. 2010. Statistical and geostatistical mapping of precipitation water isotope ratios. See West et al. 2010, pp. 139–60

Bowen GJ, Ehleringer JR, Chesson LA, Stange E, Cerling TE. 2007. Stable isotope ratios of tap water in the contiguous USA. *Water Resour. Res.* 43:W03419

Bowen GJ, Ehleringer JR, Chesson LA, Thompson AH, Podlesak DW, Cerling TE. 2009a. Dietary and physiological controls on the hydrogen and oxygen isotope ratios of hair from mid-20th century indigenous populations. *Am. J. Phys. Anthropol.* 139:494–504

Bowen GJ, Revenaugh J. 2003. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* 39:1299

Bowen GJ, West JB. 2008. Isotope landscapes for terrestrial migration research. In *Tracking Animal Migration with Stable Isotopes*, ed. KA Hobson, LI Wassenaar, pp. 79–105. Amsterdam: Elsevier

Bowen GJ, West JB, Vaughn BH, Dawson TE, Ehleringer JR, et al. 2009b. Isoscapes to address large-scale Earth science challenges. *Eos* 90:109–10

Bowen GJ, Wilkinson B. 2002. Spatial distribution of $\delta^{18}O$ in meteoric precipitation. *Geology* 30:315–18

Bowling DR, McDowell NG, Bond BJ, Law BE, Ehleringer JR. 2002. ^{13}C content of ecosystem respiration is linked to precipitation and vapor pressure deficit. *Oecologia* 131:113–24

Broecker WS, Peng T-H. 1982. *Tracers in the Sea*. Palisades, NY: Eldigio Press. 690 pp.

Chamberlain CP, Blum JD, Holmes RT, Feng XH, Sherry TW, Graves GR. 1997. The use of isotope tracers for identifying populations of migratory birds. *Oecologia* 109:132–41

Ciais P, Tans PP, Trolier M, White JWC, Francey RJ. 1995. A large northern hemisphere terrestrial CO_2 sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO_2. *Science* 269:1098–102

Commisso RG, Nelson DE. 2006. Modern plant $d^{15}N$ values reflect ancient human activity. *J. Archaeol. Sci.* 33:1167–76

Coplen TB, Herczeg AL, Barnes C. 1999. Isotope engineering: using stable isotopes of the water molecule to solve practical problems. In *Environmental Tracers in Subsurface Hydrology*, ed. PG Cook, AL Herczeg, pp. 79–110. Boston: Kluwer Acad.

Craig H, Gordon LI. 1965. Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In *Proceedings of a Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures*, *Spoleto*, *Italy*, ed. E Tongiorgi, pp. 9–130. Pisa: V Lishi e F

Cressie NAC. 1993. *Statistics for Spatial Data*. New York: Wiley & Sons. 900 pp.

Dansgaard W. 1954. The O^{18}-abundance in fresh water. *Geochim. Cosmochim. Acta* 6:241–60

Dawson TE, Ehleringer JR. 1991. Streamside trees that do not use stream water. *Nature* 350:335–37

Dutton A, Wilkinson BH, Welker JM, Bowen GJ, Lohmann KC. 2005. Spatial distribution and seasonal variation in $^{18}O/^{16}O$ of modern precipitation and river water across the conterminous United States. *Hydrol. Process.* 19:4121–46

Ehleringer JR. 1978. Implications of quantum yield differences on the distributions of C_3 and C_4 grasses. *Oecologia* 31:255–67

Ehleringer JR, Bowen GJ, Chesson LA, West AG, Podlesak DW, Cerling TE. 2008. Hydrogen and oxygen isotope ratios in human hair are related to geography. *Proc. Natl. Acad. Sci. USA* 105:2788–93

Elliott EM, Kendall C, Wankel SD, Burns DA, Boyer EW, et al. 2007. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States. *Environ. Sci. Technol.* 41:7661–67

Farquhar GD, Ehleringer JR, Hubick KT. 1989. Carbon isotope discrimination and photosynthesis. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 40:503–37

Farquhar GD, Lloyd J, Taylor JA, Flanagan LB, Syvertsen JP, et al. 1993. Vegetation effects on the isotope composition of oxygen in atmospheric CO_2. *Nature* 363:439–43

Farrell JW, Pederson TF, Calvert SE, Nielsen B. 1995. Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean. *Nature* 377:514–17

Fekete BM, Gibson JJ, Aggarwal P, Vorosmarty CJ. 2006. Application of isotope tracers in continental scale hydrological modeling. *J. Hydrol.* 330:444–56

Fox-Dobbs K, Doak DF, Brody AK, Palmer TM. 2010. Termites create spatial structure and govern ecosystem function by affecting nitrogen fixation in an East African savanna. *Ecology*. In press

Fry B. 2006. *Stable Isotope Ecology*. New York: Springer

Fung I, Field CB, Berry JA, Thompson MV, Randerson JT, et al. 1997. Carbon 13 exchanges between the atmosphere and biosphere. *Glob. Biogeochem. Cycles* 11:507–33

Galewsky J. 2009. Orographic precipitation isotope ratios in stratified atmospheric flows: implications for paleoelevation studies. *Geology* 37:791–94

Gat JR, Bowser CJ, Kendall C. 1994. The contribution of evaporation from the Great Lakes to the continental atmosphere: estimate based on stable isotope data. *Geophys. Res. Lett.* 21:557–60

Gibson JJ, Edwards TWD. 2002. Regional water balance trends and evaporation-transpiration partitioning from a stable isotope survey of lakes in northern Canada. *Glob. Biogeochem. Cycles* 16:1026

Graham BS, Koch PL, Newsome SD, McMahon KW, Aurioles D. 2010. Using isoscapes to trace the movements and foraging behavior of top predators in ocean ecosystems. See West et al. 2010, pp. 299–318

Helfield JM, Naiman RJ. 2001. Effects of salmon-derived nitrogen on riparian forest growth and implications for stream productivity. *Ecology* 82:2403–9

Hobson K, Schell DM. 1998. Stable carbon and nitrogen isotope patterns in baleen from eastern Arctic bowhead whales (*Balaena mysticetus*). *Can. J. Fisheries Aquatic Sci.* 55:2601–7

Hobson KA, Wassenaar LI. 1997. Linking breeding and wintering grounds of neotropical migrant songbirds using stable hydrogen isotopic analysis of feathers. *Oecologia* 109:142–48

Hobson KA, Wassenaar LI, eds. 2008. *Tracking Animal Migration with Stable Isotopes*. Amsterdam: Elsevier. 182 pp.

Hou J, D'Andrea WJ, Huang Y. 2008. Can sedimentary leaf waxes record *D/H* ratios of continental precipitation? Field, model, and experimental assessments. *Geochim. Cosmochim. Acta* 72:3503–17

Joussaume S, Sadourny R, Jouzel J. 1984. A general circulation model of water isotope cycles in the atmosphere. *Nature* 311:24–29

Kendall C, Coplen TB. 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol. Process.* 15:1363–93

Kendall C, Young MB, Silva SR. 2010. Applications of stable isotopes for regional to national-scale water quality and environmental monitoring programs. See West et al. 2010, pp. 89–112

Knies J, Brookes S, Schubert CJ. 2007. Re-assessing the nitrogen signal in continental margin sediments: new insights from the high northern latitudes. *Earth Planet. Sci. Lett.* 253:471–84

Leavitt SW. 2007. Southwestern U.S. drought maps from pinyon tree-ring carbon isotopes. *Eos* 88:39–40

LeGrande AN, Schmidt GA. 2006. Global gridded data set of the oxygen isotopic composition in seawater. *Geophys. Res. Lett.* 33:L12604

Lloyd J, Farquhar GD. 1994. ^{13}C discrimination during CO_2 assimilation by the terrestrial biosphere. *Oecologia* 99:201–15

Lykoudis SP, Argiriou AA. 2007. Gridded data set of the stable isotopic composition of precipitation over the eastern and central Mediterranean. *J. Geophys. Res.* 112:D18107

Masson-Delmotte V, Hou S, Ekaykin A, Jouzel J, Aristarain A, et al. 2008. A review of Antarctic surface snow isotopic composition: observations, atmospheric circulation, and isotopic modeling. *J. Clim.* 21:3359–87

McCutchan JH, Lewis WM, Kendall C, McGrath CC. 2003. Variation in trophic shift for stable isotope ratios of carbon, nitrogen, and sulfur. *Oikos* 102:378–90

Newsome SD, Etnier MA, Gifford-Gonzalez D, Phillips DL, van Tuinen M, et al. 2007. The shifting baseline of northern fur seal ecology in the northeast Pacific Ocean. *Proc. Natl. Acad. Sci. USA* 104:9709–14

Nielson KE, Bowen GJ. 2010. Hydrogen and oxygen in brine shrimp chitin reflect environmental water and dietary isotopic composition. *Geochim. Cosmochim. Acta* 74:1812–22

Noone D, Sturm C. 2010. Comprehensive dynamical models of global and regional water isotope distributions. See West et al. 2010, pp. 195–220

Norris DR, Marra PP, Bowen GJ, Ratcliffe LM, Royale JA, Kyser TK. 2006. Migratory connectivity of a widely distributed songbird, the American Redstart (*Setophaga ruticilla*). *Ornithol. Monogr.* 61:14–28

O'Brien DM, Wooller MJ. 2007. Tracking human travel using stable oxygen and hydrogen isotope analyses of hair and urine. *Rapid Commun. Mass Spectrom.* 21:2422–30

Palmer MR, Edmond JM. 1989. The strontium isotope budget of the modern ocean. *Earth Planet. Sci. Lett.* 92:11–26

Pardo LH, Nadelhoffer KJ. 2010. Using nitrogen isotope ratios to assess terrestrial ecosystems at regional and global scales. See West et al. 2010, pp. 221–50

Pollan M. 2007. *The Omnivore's Dilemma: A Natural History of Four Meals*. New York: Penguin. 464 pp.

Randerson JT, Collatz GJ, Fessenden JE, Munoz AD, Still CJ, et al. 2002a. A possible global covariance between terrestrial gross primary production and ^{13}C discrimination: consequences for the atmospheric ^{13}C budget and its response to ENSO. *Glob. Biogeochem. Cycles* 16:1136

Randerson JT, Still CJ, Ballé JJ, Fung IY, Doney SC, et al. 2002b. Carbon isotope discrimination of arctic and boreal biomes inferred from remote atmospheric measurements and a biosphere-atmosphere model. *Glob. Biogeochem. Cycles* 16:1028

Richter FM, Rowley DB, DePaolo DJ. 1992. Sr isotope evolution of seawater: the role of tectonics. *Earth Planet. Sci. Lett.* 109:11–23

Roden JS, Ehleringer JR. 1999. Observations of hydrogen and oxygen isotopes in leaf water confirm the Craig-Gordon model under wide-ranging environmental conditions. *Plant Physiol.* 120:1165–73

Rossmann A. 2001. Determination of stable isotope ratios in food analysis. *Food Rev. Int.* 17:347–81

Rowley DB, Garzione CN. 2007. Stable isotope-based paleoaltimetry. *Annu. Rev. Earth Planet. Sci.* 35:463–508

Rozanski K, Araguas-Araguas L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In *Climate Change in Continental Isotopic Records*, ed. PK Swart, KC Lohmann, J McKenzie, S Savin, pp. 1–36. Washington, DC: Am. Geophys. Union

Sachse D, Radke J, Gleixner G. 2004. Hydrogen isotope ratios of recent lacustrine sedimentary *n*-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* 68:4877–89

Schell DM, Barnett BA, Vinette KA. 1998. Carbon and nitrogen isotope ratios in zooplankton of the Bering, Chukchi and Beaufort seas. *Mar. Ecol. Prog. Ser.* 162:11–23

Schmidt GA, Bigg GR, Rohling EJ. 1999. *Global seawater oxygen-18 database*. **http://data.giss.nasa.gov/o18data/**

Sessions AL, Hayes JM. 2005. Calculation of hydrogen isotopic fractionations in biogeochemical systems. *Geochim. Cosmochim. Acta* 69:593–97

Sharp Z. 2007. *Stable Isotope Geochemistry*. Upper Saddle River, NJ: Pearson Prentice Hall. 344 pp.

Sharp ZD, Atudorei V, Panarello HO, Fernández J, Douthitt C. 2003. Hydrogen isotope systematics of hair: archeological and forensic applications. *J. Archaeol. Sci.* 30:1709–16

Smith FA, Freeman KH. 2006. Influence of physiology and climate on δD of leaf wax *n*-alkanes from C_3 and C_4 grasses. *Geochim. Cosmochim. Acta* 70:1172–87

Still CJ, Berry JA, Collatz GJ, DeFries RS. 2003. Global distribution of C_3 and C_4 vegetation: carbon cycle implications. *Glob. Biogeochem. Cycles* 17:1006

Still CJ, Powell RL. 2010. Continental-scale distributions of vegetation stable carbon isotope ratios. See West et al. 2010, pp. 179–94

Sturm K, Hoffmann G, Langmann B, Stichler W. 2005. Simulation of δ^{18}O in precipitation by the regional circulation model $\mathrm{REMO_{iso}}$. *Hydrol. Process.* 19:3425–44

Suits NS, Denning AS, Berry JA, Still CJ, Kaduk J, et al. 2005. Simulation of carbon isotope discrimination of the terrestrial biosphere. *Glob. Biogeochem. Cycles* 19:GB1017

Thompson AH, Chesson LA, Podlesak DW, Bowen GJ, Cerling TE, Ehleringer JR. 2010. Stable isotope analysis of modern human hair collected from Asia (China, India, Mongolia, and Pakistan). *Am. J. Phys. Anthropol.* 141:440–51

van der Veer G, Voerkelius S, Lorentz G, Heiss G, Hoogewerff JA. 2009. Spatial interpolation of the deuterium and oxygen-18 composition of global precipitation using temperature as ancillary variable. *J. Geochem. Explor.* 101:175–84

Vaughn BH, Evans CU, White JWC, Still CJ, Masarie KA, Turnbull J. 2010. Global network measurements of atmospheric trace gas isotopes. See West et al. 2010, pp. 3–32

Vitousek PM, Shearer G, Kohl DH. 1989. Foliar ^{15}N natural abundance in Hawaiian rainforest: patterns and possible mechanisms. *Oecologia* 78:383–88

Wang Y, Hou S, Masson-Delmotte V, Jouzel J. 2009. A new spatial distribution map of δ^{18}O in Antarctic surface snow. *Geophys. Res. Lett.* 36:L06501

Wassenaar LI, Van Wilgenburg SL, Larson K, Hobson KA. 2009. A groundwater isoscape (δD, δ^{18}O) for Mexico. *J. Geochem. Explor.* 102:123–36

West JB, Bowen GJ, Dawson TE, Tu KP, eds. 2010. *Isoscapes: Understanding Movement, Pattern, and Process on Earth Through Isotope Mapping*. New York: Springer. 487 pp.

West JB, Ehleringer JR, Cerling TE. 2007. Geography and vintage predicted by a novel GIS model of wine δ^{18}O. *J. Agric. Food Chem.* 55:7075–83

White CD, Schwarcz HP. 1989. Ancient Maya diet: as inferred from isotopic and elemental analysis of human bone. *J. Archaeol. Sci.* 16:451–74

Worden J, Noone D, Bowman K, Beer R, Eldering A, et al. 2007. Importance of rain evaporation and continental convection in the tropical water cycle. *Nature* 445:528–32

Yoshinaga J, Minagawa M, Suzuki T, Ohtsuka R, Kawabe T, et al. 1996. Stable carbon and nitrogen isotopic composition of diet and hair of Gidra-speaking Papuans. *Am. J. Phys. Anthropol.* 100:23–34

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http://waterisotopes.org. Information and data access related to precipitation water isotope ratios.

http://isomap.org. Internet-based isoscape modeling functionality for a range of systems, including precipitation, river and plant water, and carbon isotopes in plants and soils.

http://isoscapes.org. Information and data access related to plant water isoscapes.

http://www.iaea.org/water. Water isotope data from the International Atomic Energy Agency.

http://www.esrl.noaa.gov/gmd/ccgg/iadv. Data and visualization of atmospheric CO_2 isotope ratios.

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