

1. ISOTOPES IN WATER

W. GEORGE DARLING (wgd@bgs.ac.uk)
British Geological Survey
Wallingford OX10 8BB, UK

ADRIAN H. BATH (abath@intellisci.co.uk)
Intellisci Ltd.
Loughborough LE12 6SZ, UK

JOHN J. GIBSON (john.gibson@ec.gc.ca)
National Water Research Institute
University of Victoria
Victoria V8W 2Y2, Canada

KAZIMIERZ ROZANSKI (rozanski@novell.ftj.agh.edu.pl)
Faculty of Physics and Applied Computer Science
AGH University of Science and Technology
30-059 Krakow, Poland

Key words: Stable isotopes, water cycle, carbon cycle, precipitation, surface waters, groundwater, isotope mass balance, proxies.

Introduction

Scope of this chapter

The study of isotopic proxies has two different though related basic aims: an understanding of the way in which the water cycle is linked to alterations in climate, and how the carbon cycle has responded to these changes. This necessarily requires the study of oxygen, hydrogen and carbon stable isotope ratios. Water plays a vital role in the growth or formation of all proxies whether animal, vegetable or mineral; while water molecules consist of oxygen and hydrogen isotopes alone, they are also a solvent for several different forms of carbon. There are of course stable isotopes of other elements encountered in dissolved form, for example boron, chlorine, nitrogen and sulphur, but none of these has yet achieved more than a niche role in the study of proxies. This chapter therefore concentrates exclusively on the well-established trio of O, H and C. Note that the dating of water by carbon-14 or other radio-isotope methods is not included as direct dating of proxies provides much higher resolution. Water dating and allied information is extensively reviewed in books by Clark and Fritz (1997) and Cook and Herczeg (1999).



Three main reservoirs of water may contribute to the isotopic compositions of proxy indicators: surface waters, soil and unsaturated (vadose) zone moisture, and groundwater. One important aim of studying proxy indicators is to arrive back at the isotopic composition of the antecedent rainfall during the period of growth. While the ways in which the proxies may isotopically fractionate the oxygen and hydrogen in their reservoir water during growth or formation are considered in the following chapters in this volume, it would at least be helpful to establish the typical extent to which the isotopic composition of rainfall may be modified in the three reservoirs at the present day. The largely physical nature of these fractionation effects may vary under different climatic regimes, so the hydrological parts of this chapter will consider the available evidence from a range of climate types worldwide.

Characterising the evolution of the carbon isotope content of waters prior to proxy formation is perhaps a greater challenge, involving as it does both organically and inorganically mediated interactions between water, rock and gases. The almost infinite variety of environmental settings makes it much more difficult to be prescriptive with carbon than with oxygen and hydrogen, but nevertheless we consider it worthwhile to establish the “ground rules” for dissolved carbon. Some of the individual fractionation processes are as climate-dependent as for oxygen and hydrogen isotope ratios, so climatic differences will be considered, albeit in rather less detail than for O and H.

The development of stable isotope hydrology

Research on the technical aspects of O, H and C stable isotope measurement began in the early 1950s (e.g., Epstein and Mayeda (1953); Friedman (1953); Craig (1953)), but widespread hydrological usage concentrating on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ did not arrive until the 1970s. Although studies carried out during the 1960s on rainfall by Craig (1961) and Dansgaard (1964) paved the way for thinking about isotopes in the water cycle, attention was to a large extent diverted by tritium (^3H) in the wake of the atmospheric thermonuclear testing of the 1963–65 period. However, as interest in ^3H gradually waned, the usefulness of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ began to be appreciated once more, leading to the widespread development of stable isotope laboratories during the 1970s and early 1980s.

It was early realised that isotope methods were not restricted to the study of water and ice, but could also be applied to steam (e.g., Giggenbach (1971)). Furthermore, it became apparent that isotopes could be instructively applied to ‘hidden’ forms of water — for example soil moisture (e.g., Zimmerman et al. (1967)), water of crystallisation (e.g., Sofer (1978)) and fluid inclusions (e.g., Roedder (1984)).

It also became apparent that groundwaters from the confined parts of aquifers were often isotopically depleted relative to modern waters. During the 1970s, the development of routine methods for measuring radiocarbon (^{14}C) in groundwaters led to a more quantitative understanding of the magnitude and timing of climate change away from polar regions.

Over the last few decades the proliferation of laboratories routinely using O and H isotopes to understand the water cycle, present and past, means that a fair degree of maturity has been reached. While there remains much data to be collected to fill various

gaps in knowledge, the subject area is understood well enough (e.g., Clark and Fritz (1997)) to constrain the interpretation of proxy data.

The involvement of C isotopes in hydrology and environmental studies has been more cryptic. While it was known as early as the 1930s that there were differences in $^{13}\text{C}/^{12}\text{C}$ between organic and inorganic mineral carbon (Nier and Gulbransen 1939), research in the 1950s and 60s was focused on the use of $\delta^{13}\text{C}$ for correcting radiocarbon ages of groundwaters for ‘dilution’ by inorganic carbonate that is dead to radiocarbon (e.g., Vogel and Ehhalt (1963); Pearson and Hanshaw (1970)) and on the study of reaction mechanisms for carbon in plants, for example the C_3 and C_4 photosynthetic pathways (Bender 1968; Deines 1980). Early work on carbonates centred around the use of $\delta^{18}\text{O}$ rather than $\delta^{13}\text{C}$, and it was not until the mid-1960s that much attention started to be paid to carbon in freshwater fauna and lake deposits (e.g., Keith and Weber (1964); Stuiver (1970)). Likewise, speleothems were initially valued more for their $\delta^{18}\text{O}$ and dating potential (summarised in Schwarcz (1986)) and it was only since the work of Hendy (1971) that the significance of variations in $\delta^{13}\text{C}$ has led to it being more routinely measured and interpreted. The carbon in travertine-type deposits and other potential freshwater proxies may have derived from a multiplicity of sources so that their $\delta^{13}\text{C}$ composition often reveals more about mode of formation than palaeoenvironment (Turi 1986). Nevertheless, interest is developing in the interpretation of carbon isotopes in freshwater tufas and allied cyanobacterial deposits (e.g., Pazdur et al. (1988); Andrews et al. (1993)).

The water and carbon cycles

Figure 1 depicts the global water (or hydrological) cycle. While the concept of the water cycle may be simple in essence — water evaporates from the sea, falls as rain over land, and eventually returns to the sea mainly via river and groundwater discharge — there are a number of complicating factors, at least where stable isotopes are concerned. Much of the focus of this chapter lies in considering how these factors affect the more active parts of the water cycle. The physical processes governing the isotopic composition of precipitation are a natural starting point. Following on from this is a consideration of the transformation of precipitation into the basic ‘terrestrial reservoirs’ of soil-zone moisture, groundwater, and surface waters. Processes such as seasonal freeze-thaw, plant transpiration and soil evaporation can each cause isotopic changes, but perhaps of most significance is evaporation from surface waters. Lake sediments are an important archive for climate change, and it is therefore vital to understand as far as possible the often complex isotopic relationship between individual lakes and regional precipitation. Accordingly this chapter considers isotope mass-balance modelling in some detail.

The situation with regard to carbon is more complicated, because the C cycle cannot be summarised in a simple climate-related manner. While C stable isotopes are crucial to palaeo-environmental reconstruction, as other chapters in this volume demonstrate (McCarroll and Loader; Hedges et al.; Leng et al.; McDermott et al. all this volume), their incorporation in proxies is affected by many factors, including hydrology, that may be more or less related to climate. For instance, the mass budgets and isotopic compositions of carbon in land animal diet and plant photosynthetic pathways are not

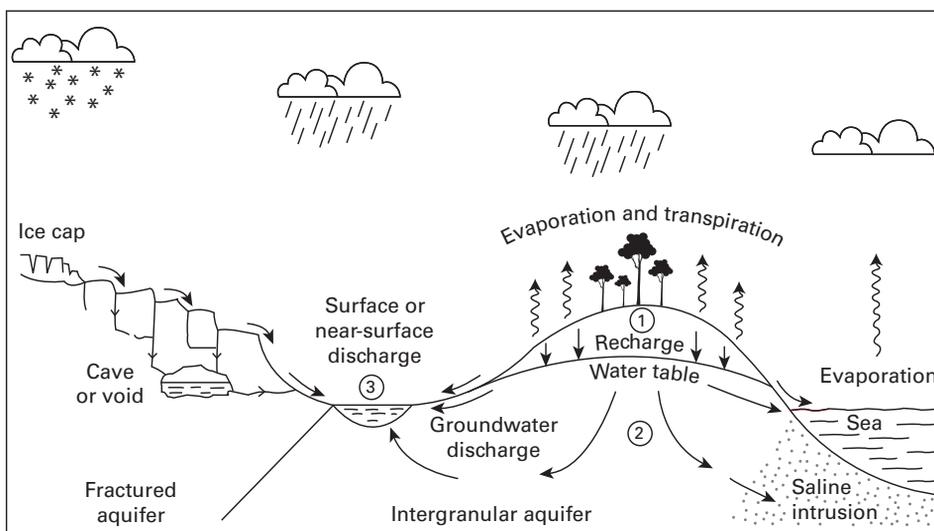


Figure 1. Schematic of the global water cycle. Evaporation of seawater leads to cloud formation with progressive rainout as temperature decreases. The moisture will eventually return to the ocean mainly via surface runoff or subsurface discharge, though it may be delayed by recycling via evaporation from lakes or transpiration from vegetation. Also shown on the figure are the three ‘terrestrial reservoirs’ of water that are of importance to proxy formation: 1 – soil and unsaturated zone moisture, 2 – groundwater, 3 – surface waters.

controlled simply by the carbon contents of environmental waters. However, many proxies growing in aquatic environments will have carbon isotope compositions that can be related back in various ways to the original water signal.

The underlying aim of this chapter is to demonstrate that changes associated with the water cycle have implications for understanding the climatic information recorded by the O, H and C stable isotope compositions of proxies. Constraints on the isotopic approach are discussed in the final section of the chapter.

Oxygen and hydrogen stable isotopes in precipitation

The global atmosphere provides a dynamic link between the major reservoirs of water on Earth (cf. discussion above). Atmospheric water vapour is the primary vehicle through which this link is accomplished. The mass of water vapour in the contemporary atmosphere is estimated to be around 1.3×10^{16} kg, of which about 85% is located in the lower troposphere, below the altitude of 5 km. The amount of water stored in the atmosphere as water vapour is negligible when compared with the world’s oceans or continental ice sheets, the corresponding mass ratios being approximately 10^{-5} and 4×10^{-4} , respectively (Berner and Berner 1987). The atmosphere is only partially saturated with water, with the globally averaged relative humidity of the lower troposphere below the planetary boundary level being around 85%. This lack of saturation stems from the existing thermal structure and large-scale circulation patterns of the troposphere.

Distribution of water vapour in the lower atmosphere is highly inhomogeneous. It is controlled by existing thermal gradients imposing phase changes (evaporation-condensation-freezing, sublimation-resublimation), as well as by the distribution of major water sources on the Earth's surface. In the stratosphere, photochemical reactions such as oxidation of methane constitute the principal mechanism controlling spatial distribution of water vapour. Expressed as a mixing ratio (kg H₂O per kg of dry air), water vapour content decreases from approximately 10⁻³ in the lower troposphere close to the planetary boundary level, to around 3×10⁻⁶ in the lower stratosphere and then increases again to approximately 10⁻⁴ at the altitude of 30 km. Close to the Earth's surface, it varies between approximately 1.5×10⁻² over tropical oceans to 5×10⁻³ over dry regions in the interior of continents and less than 10⁻³ over ice sheets at high latitudes.

The reservoir of atmospheric water vapour is highly dynamic, quickly responding to changes of external conditions such as the flux of solar energy reaching the Earth's surface and/or changes of temperature lapse rate in the troposphere. The mean turnover time is a useful quantity characterising dynamic behaviour of water vapour in the global atmosphere. It is defined as the ratio of the total mass of water in the atmosphere to the flux of water leaving the atmospheric reservoir as precipitation, and is equal to around 10 days.

Although being a trace constituent of the global atmosphere, atmospheric moisture plays a crucial role in the global ecosystem behaviour. Firstly, it is the most important greenhouse gas, responsible for approximately 60% of the natural greenhouse effect. Secondly, atmospheric moisture serves as an important regulator of heat fluxes in the atmosphere, reducing thermal gradients between low and high latitudes. Thirdly, atmospheric water vapour serves as the primary source material from which precipitation is formed.

Isotopic composition of atmospheric water vapour

Interest in the isotopic composition of atmospheric water vapour goes back to the beginning of isotope hydrology. In the early 1960s Craig and Gordon (1965) measured the isotopic composition of atmospheric water vapour over the North Pacific. During the years 1966–67 and 1971–73, Ehhalt (1974) obtained a number of vertical profiles of the ²H content in tropospheric water vapour up to the tropopause region over several locations in the continental USA. In Europe, the ²H and ¹⁸O content in tropospheric water vapour up to an altitude of 5 km was measured during 1967 and 1968 (Taylor 1972). These two sets of measurements remain to date the major source of information about the vertical distribution of ²H and ¹⁸O in water vapour in the lower troposphere, the region where most precipitation is formed.

A common feature observed was a gradual depletion in heavy isotopes with increasing altitude up to the tropopause region, with a reversed trend detected within the stratosphere. The generalised vertical profile of δ²H in atmospheric water vapour is shown in Figure 2. The ²H content decreases gradually with altitude from a δ²H value of -150 ± 50‰ close to the surface to -650 ± 30‰ in the tropopause region, then increases up to -500 ± 50‰ at about 40 km altitude (Rozanski and Sonntag 1982; Johnson et al. 2001). Changes of δ¹⁸O with altitude reveal similar characteristics.

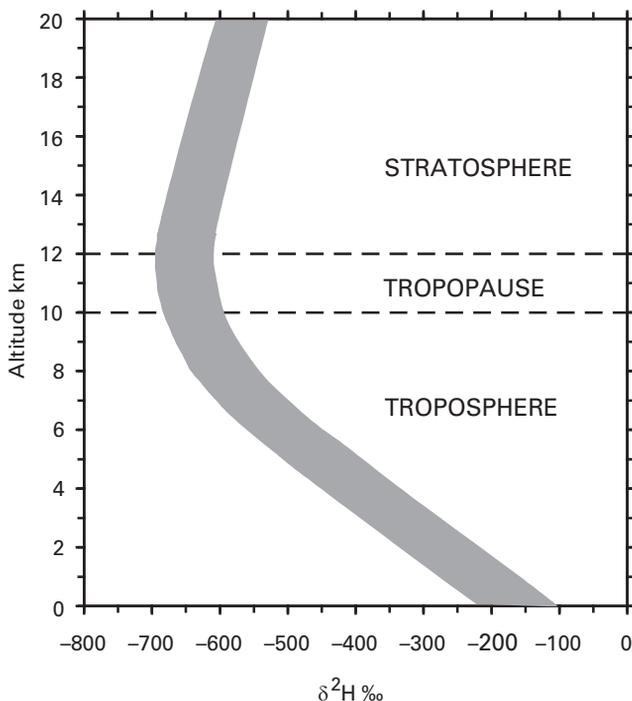


Figure 2. Schematic representation of the vertical distribution of deuterium content in atmospheric water vapour in the troposphere and the lower stratosphere.

The observed distribution of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ with altitude is currently explained as a consequence of the following processes: (i) isotope fractionation (both equilibrium and kinetic), associated with gradual condensation of atmospheric water vapour during cloud formation and subsequent rainout processes, leading to preferential removal of heavy isotopes from the reservoir of atmospheric moisture; (ii) turbulent mixing of different air masses containing water vapour with contrasting isotope compositions; (iii) addition of isotopically heavy moisture, originating in the evapotranspiration process; (iv) lofting (upward advection) and subsequent evaporation of ice crystals; and (v) oxidation of methane. The first two processes are thought to be major mechanisms controlling vertical distribution of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ throughout the troposphere. Transpired moisture modifies the isotopic composition of atmospheric water vapour close to the Earth's surface (Jacob and Sonntag 1991; Bariac et al. 1991). Lofting of ice crystals across the tropopause region was suggested as an important phenomenon influencing ^2H and ^{18}O content in the lowermost stratosphere (Keith 2000). Photochemical oxidation of methane in the middle and upper stratosphere is responsible for the observed increase of water vapour content with altitude as well as the gradual increase of ^2H and ^{18}O content in this region (Johnson et al. 2001).

Systematic studies aimed at characterising the isotopic composition of near-ground water vapour on a regional scale were launched in the early 1980s in Europe. The

isotopic composition of daily composite samples of atmospheric moisture was monitored by a network of several stations across the European continent between 1980 and 1984 (Schoch-Fischer et al. 1984). One site (Heidelberg, Germany) has continued to do this up to the present day (Jacob and Sonntag 1991; Agemar 2001) and has accumulated a unique, high-resolution record of the ^{18}O and ^2H content of atmospheric water vapour spanning more than two decades. During the 1990s the isotopic composition of atmospheric moisture near the ground was further investigated, although these studies were usually local in character and limited in time. The past several years have seen a renaissance of interest in isotopic studies of near-ground atmospheric moisture, stimulated mostly by the need for better understanding of the isotopic signatures of precipitation and the links between the water and carbon cycles within the soil-plant-atmosphere domain.

Most observations of the isotopic composition of atmospheric water vapour carried out to date have been performed at ground level, with moisture being sampled within the planetary boundary layer. Very large short-term variability of the isotopic composition of near-ground water vapour has been detected; day-to-day variations of ^2H and ^{18}O content recorded at mid-latitude continental sites are often of the same magnitude as seasonal changes, and are tightly linked to weather changes, reflecting the passage of air masses with different rainout histories. This variability is particularly pronounced during the winter months. The isotopic composition of atmospheric water vapour recorded near the ground during the summer months reflects a significant contribution of transpired moisture, with the isotopic signature reflecting the mixture of summer and winter precipitation. This has a damping effect on the short-term isotope variability induced by synoptic changes during summer.

Isotopic composition of precipitation

Clearly the reservoir of atmospheric water vapour constitutes the primary source material from which precipitation is formed. The available data suggest that the isotopic composition of monthly precipitation, which is the basic type of data being collected worldwide, properly reflects the mean isotopic status of the atmospheric water vapour reservoir within the planetary boundary layer during these time intervals. Whilst this holds for moderate climates, it may not be the case under semi-arid and arid conditions. In contrast to the limited number of observations relating to the isotopic composition of atmospheric water vapour, a sizeable amount of data on the isotopic composition of precipitation is now available. Over more than four decades precipitation samples have been measured through various research projects and monitoring networks at temporal scales ranging from single minutes (fraction of individual rain event) to monthly composite samples. Among the various initiatives to characterise the isotopic variability in precipitation at global and regional scales, the Global Network for Isotopes in Precipitation (GNIP), jointly operated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO), is by far the largest undertaking (<http://isohis.iaea.org>). The network was launched in 1960 with the primary aim of providing basic information about the isotopic composition of precipitation on the global scale.

Figure 3 summarises the major processes and mechanisms controlling the isotopic composition of atmospheric water vapour and precipitation in the troposphere. They

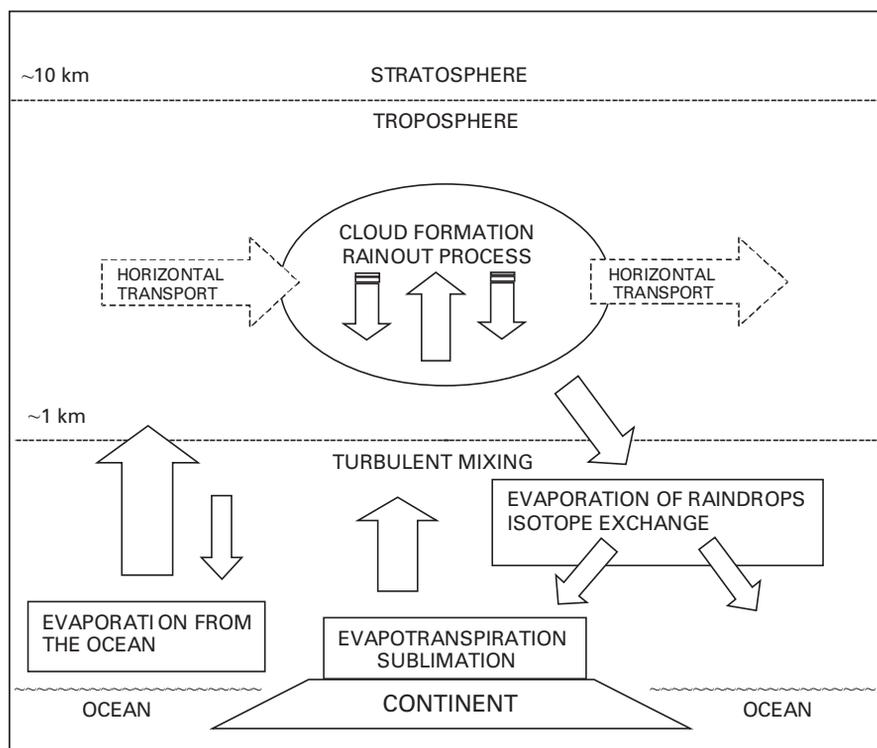


Figure 3. Schematic representation of the processes controlling the isotopic composition of atmospheric water vapour and precipitation.

constitute a physical basis for understanding the observed spatial and temporal variability of heavy isotope ratios in monthly precipitation to which the majority of available data are related.

The first step in the chain of processes depicted in Figure 3 is evaporation from the ocean. Isotopic effects associated with this process are quantified in the framework of a mechanistic model proposed by Craig and Gordon in 1965 (cf. the mass balance modelling section of this chapter). The major controlling parameters are: isotopic composition of the ocean surface, sea-surface temperature, relative humidity of the atmosphere, and wind regime. Water vapour leaving the surface of the ocean is isotopically depleted in comparison with oceanic water.

Marine moisture is transported, both vertically and horizontally, until saturation conditions are reached and cloud formation starts. Partial condensation of water vapour associated with this transport and cloud formation leads to further isotopic depletion of the vapour, even without moisture loss via rainout, since the heavy water molecules $^1\text{H}^2\text{H}^{16}\text{O}$ and $^1\text{H}^1\text{H}^{18}\text{O}$ are preferentially converted into water droplets or ice crystals. In-cloud processes may involve fast advective upward transport with entrainment of moist air from below, phase changes with formation of rain drops and/or snow/hail particles, isotopic exchange between liquid and gaseous phases in the cloud, kinetic isotope

effects during snow formation, removal of precipitation elements at the cloud base and dissipation of dry air with isotopically depleted moisture at cloud tops.

The isotopic composition of rainfall collected at the ground surface appears to be close to isotopic equilibrium with near-ground water vapour. This results from the fact that raindrops leaving the cloud base continuously re-equilibrate isotopically with the surrounding moisture on their way to the surface, the degree of this re-equilibration being controlled by the size of the raindrops, the actual height of the cloud base and the relative humidity of the atmosphere beneath the cloud. Solid precipitation (snow, hail) is usually more depleted in heavy isotopes, reflecting equilibrium conditions at much lower in-cloud temperatures. At sufficiently low condensation temperatures, the isotopic composition of snow is influenced by an additional kinetic effect, linked to supersaturation conditions around the forming snow flakes (Jouzel and Merlivat 1984).

The first comprehensive review of isotopic data gathered by the GNIP network, carried out by Dansgaard (1964), resulted in the formulation of a number of empirical relationships between the observed isotopic composition of monthly precipitation and environmental parameters, such as surface air temperature, amount of precipitation, latitude, altitude, or distance from the coast. Subsequent reviews of the GNIP database (Yurtsever and Gat 1981; Rozanski et al. 1993) have largely confirmed the early findings of Dansgaard. It has become apparent that these empirical relationships, often called 'effects', can be viewed as a measure of the average degree of rainout of moist air masses transported from the major vapour source regions (mainly intertropical ocean) to the site of precipitation.

Spatial variability in the isotopic composition of precipitation

The spatial variability in the isotopic composition of precipitation is shown on global maps of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ on continents presented in Figure 4. The maps have been constructed using the GNIP database as well as other available data and drawn using multivariate interpolation techniques (Bowen and Wilkinson 2002; Bowen and Revenaugh 2003; <http://es.ucsc.edu/~gbowen/Isomaps.html>).

The gradual depletion in the ^2H and ^{18}O content of precipitation from the tropics towards mid- and high-latitudes, seen in Figure 4, can be understood as a result of the progressive removal of water from the moist air masses being transported from the tropical areas towards the poles. Typical $\delta^{18}\text{O}$ values in coastal areas of Antarctica are around -15 to -20‰ and close to the South Pole they reach about -50‰ (Ciais et al. 1995). Very negative $\delta^{18}\text{O}$ values of around -20 to -26‰ are also found in the northern part of Canada and in eastern Siberia (IAEA 2002; Kurita et al. 2004). The highest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are observed in eastern tropical Africa and the Arabian Peninsula.

Precipitation on oceanic islands and coastal, low-elevation continental areas in the intertropical regions shows $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values close to those of the ocean (typical $\delta^{18}\text{O}$ values are from -2 to -4‰) (Figure 4). These values usually represent the first portion of condensate from undisturbed marine moisture. More negative δ -values are found in equatorial Southeast Asia and the West Pacific, where high precipitation rates may locally lead to a relatively high degree of rainout of the given air mass induced by displacement of the Intertropical Convergence Zone (Rozanski and Araguas-Araguas 1995; Araguas-Araguas et al. 1998).

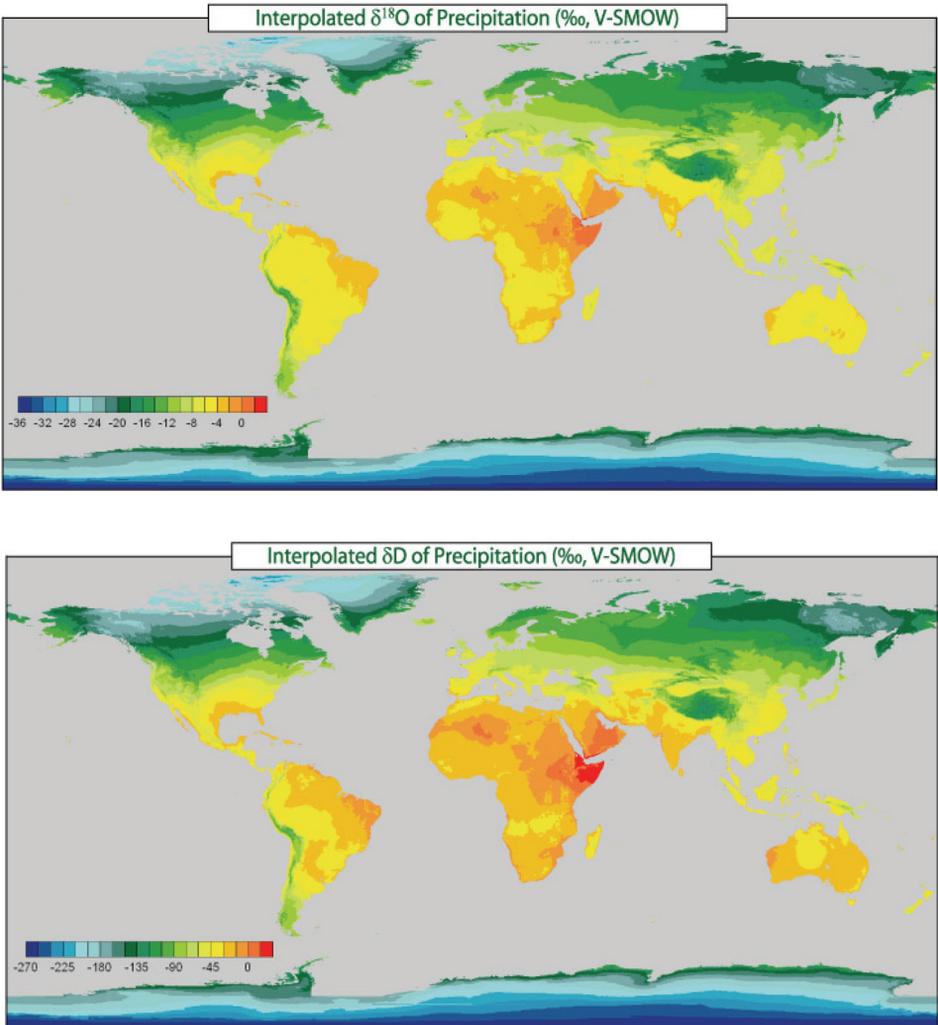


Figure 4. The global maps of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation on continents, constructed using the GNIP database as well as other available data and drawn using multivariate interpolation techniques (<http://es.ucsc.edu/~gbowen/Isomaps.html>).

The lowering of temperature with increasing elevation in mountainous regions usually leads to enhanced condensation and therefore to a progressive depletion in the heavy isotopes of precipitation with altitude, known as the ‘altitude effect’. Such an effect is well seen in Figure 4, along the Andes in South America and on the Tibetan Plateau. The vertical isotope gradients in precipitation vary between -0.15 and -0.50% per 100 m for ^{18}O and -1 to -4% per 100 m for ^2H (e.g., Siegenthaler and Oeschger (1980); Holdsworth et al. (1991)).

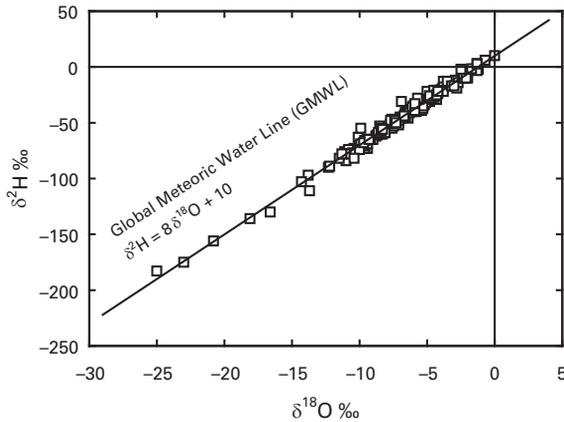


Figure 5. The relationship between long-term annual means of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation, derived for stations of the GNIP network.

The ‘amount effect’ is a well-known feature in oceanic islands and in coastal areas of the tropical regions, where seasonal variations of temperature are minimal. It manifests itself as an apparent correlation between the heavy isotope composition and the amount of rainfall. It can be understood, at least partially, as a consequence of the extent of the rainout process of deep convective clouds producing rainfall in these regions. Prominent examples of this effect can be found in Southeast Asia and intertropical islands in the Pacific (Rozanski et al. 1993; Araguas-Araguas et al. 1998).

In mid-latitudes, a progressive depletion of precipitation in heavy isotopes with increasing distance from the coast has been observed. It is interpreted as a consequence of the gradual rainout of the air masses entering the continents (Salati et al. 1979; Sonntag et al. 1983; Rozanski et al. 1993). The continental gradient in ^{18}O content observed in present-day European precipitation is around -2‰ $\delta^{18}\text{O}$ per 1000 km (Rozanski et al. 1982; Rozanski et al. 1993). A substantially lower isotope gradient has been found in the Amazon Basin in South America. It has been attributed to intense recycling of moisture within the basin by evapotranspiration (Salati et al. 1979; Gat and Matsui 1991).

The $\delta^2\text{H} - \delta^{18}\text{O}$ relationship

It is apparent from the isotopic maps shown in Figure 4 that the ^2H and ^{18}O contents of precipitation are closely correlated. This close relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ is observed on both regional and global scales. Craig (1961), in his survey of the ^2H and ^{18}O contents of fresh waters world-wide, suggested the best fit line of his data points:

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \quad (1)$$

be termed the ‘Global Meteoric Water Line’ (GMWL, also sometimes known simply as the Meteoric Water Line, MWL, or the World Meteoric Line, WML). This relationship is illustrated by Figure 5 which shows the long-term annual mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation collected at the stations belonging to the GNIP network.

The global $\delta^2\text{H}-\delta^{18}\text{O}$ relationship is well understood. It has been demonstrated that the intercept of the GMWL is controlled mainly by parameters of the evaporation process in major source areas for atmospheric moisture (the subtropical oceans), whereas the slope is determined, in the first instance, by the ratio of equilibrium isotope enrichments for ^2H and ^{18}O respectively (Dansgaard 1964; Merlivat and Jouzel 1979).

Significant deviations from this global relationship are observed (Rozanski et al. 1993). Deviations from the GMWL are found on a seasonal basis in many regions, mainly due to enhanced partial evaporation of raindrops below the cloud base during summer months and/or seasonally varying conditions in the source area(s) for the vapour. These effects are responsible for Local Meteoric Water Lines (LMWL) with slopes lower than 8, constructed using monthly isotope data. The LMWLs may also differ substantially from GMWL in cases where the atmospheric circulation regime of the given area varies seasonally, bringing moisture to the precipitation site from two or more different sources which may differ in both absolute $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and the 'deuterium excess' value d , which is defined as (Dansgaard 1964):

$$d = \delta^2\text{H} - 8\delta^{18}\text{O} \quad (2)$$

Slopes of LMWLs larger than 8 are found in areas where the air masses responsible for the relatively enriched δ -values in rainfall are characterised by high d -values and the isotopically depleted rains are below the GMWL (IAEA 1992).

Temporal variability in the isotopic composition of precipitation

Numerous studies have demonstrated or inferred that the isotopic composition of precipitation may vary on wide temporal scales, ranging from single minutes to hundreds of thousands of years. Isotopic studies of single rain events have revealed that in-storm variations can be relatively large, reaching in some cases 10 to 12‰ in $\delta^{18}\text{O}$ (e.g., Ambach et al. (1975); Rindsberger et al. (1990)). The general conclusion of these studies is that the isotopic composition of precipitation sample(s), representing the given rainfall event in whole or part, depends strongly on the meteorological history of the air and specific conditions in which the precipitation is produced, as well as the isotopic composition of moist air through which it falls. Precipitation samples collected on a per-event basis reveal a strong linkage between their isotopic signature and the storm's track, structure and evolution (e.g., Gedzelmann and Lawrence (1990); Smith (1992)).

Regular seasonal variations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation are observed at mid- and high latitudes where seasonal variations of temperature are well developed. These seasonal changes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ may result from the interplay of several factors: (i) seasonal changes of the temperature at the precipitation sites leading to substantial changes of the total precipitable water in the atmosphere with season, when compared to the source areas; (ii) seasonal changes in the evapotranspiration flux on the continents, amplifying seasonal differences in total precipitable water; (iii) seasonal changes of prevailing circulation patterns changing the origin of moisture. In the tropical regions, where changes in air temperature are minimal, the seasonality in the ^2H and ^{18}O content of precipitation may have its origin in seasonal displacement of the Intertropical Convergence Zone (ITCZ) which controls the movement of moist air masses and induces

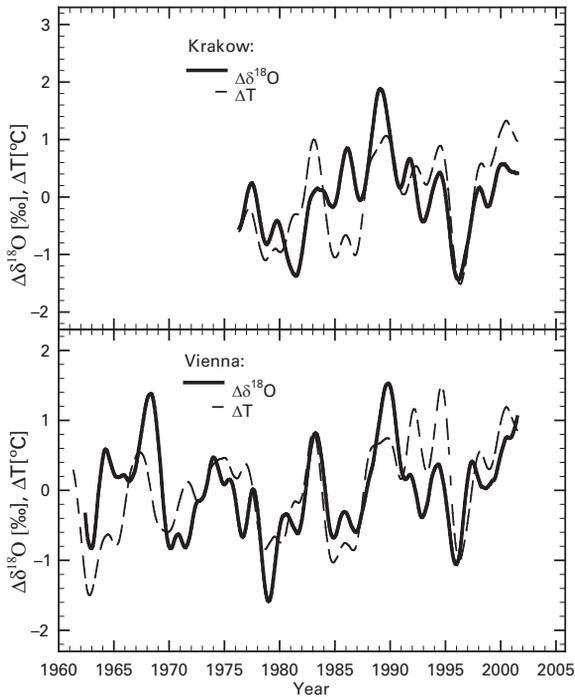


Figure 6. The relationship between long-term trend curves of $\delta^{18}\text{O}$ and surface air temperature for two stations in central Europe (Vienna and Krakow), with the seasonal variation component removed (see text for details of this). With a value of approximately 2.5‰, the long-term amplitude in $\delta^{18}\text{O}$ is only about one-third of the seasonal variation for both stations. The degree of correlation between the stations suggests regional variations in climate. Based on GNIP data.

rainy period(s) at a particular site. In many cases, for the given amount of rainfall and almost constant monthly temperature, large differences in the isotopic composition of precipitation have been reported, depending on the season. This has been attributed to the differing origins of the moisture that produces precipitation over the course of a year.

Apart from well-established seasonal variations, the isotopic signature of precipitation also exhibits some changes on longer timescales. The available instrumental record of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation is still relatively short, reaching several decades for a few sites only. Analysis of these records reveals that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ fluctuate also on a decadal timescale, although amplitudes of these changes are significantly smaller than those observed for shorter timescales. Figure 6 is an illustration of this variability. The trend curves of $\Delta\delta^{18}\text{O}$ and ΔT shown have been derived for two continental sites in central Europe (Vienna and Krakow) from the available time series of monthly $\delta^{18}\text{O}$ and surface temperature data. First, the seasonal component was removed by calculating a 12-month running average of $\delta^{18}\text{O}$ and temperature. Then, the differences $\Delta\delta^{18}\text{O}$ and ΔT were calculated for both stations by subtracting the running average curves from the

long-term annual means. Finally, the resulting curves were smoothed by again applying a 12-month running average. As Figure 6 shows, peak-to-peak amplitude of long-term changes of $\delta^{18}\text{O}$ is similar at both sites, reaching approximately 2.5‰. This may be compared with the seasonal changes of $\delta^{18}\text{O}$ at those stations of the order of 7–8‰. The long-term fluctuations of $\delta^{18}\text{O}$ at both stations are well correlated ($r^2 = 0.52$) suggesting that the observed variations are of regional character.

On longer timescales, for which direct measurements are not available, information about past variability of isotopic composition of precipitation can only be obtained from environmental archives where such variations are preserved. The most straightforward information is provided by ice cores drilled in large ice sheets as well as in continental glaciers. Records of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation reaching back to the last glaciation are now available for several low-latitude continental glaciers (Thompson 2001). In the case of the Greenland ice sheet the information on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of precipitation goes back to the last interglacial (ca. 240 ka BP), while in the case of Antarctic ice sheet it has recently been extended back to 740 ka BP (Johnsen et al. 2001; EPICA community members 2004). The amplitude of glacial/interglacial changes in the isotopic composition of past precipitation, recorded in ice sheets, is of the order of 6–7‰ in $\delta^{18}\text{O}$. For low-altitude continental regions this change is usually significantly smaller (up to 2–3‰), recorded in archives such as groundwater (e.g., Darling (2004); Edmunds et al. (2004)) or carbonate deposits (e.g., McDermott et al. (this volume)). In certain circumstances such archives may provide information about the isotopic composition of precipitation on even longer timescales, going beyond the Quaternary.

Links between climatic parameters and isotopic composition of precipitation

Stable isotope ratios of oxygen and hydrogen in water have long been considered powerful tools in palaeoclimatology. The attractiveness of these tools stems from the fact that strong apparent links exist between some climatically-relevant meteorological parameters, such as surface air temperature or amount of rainfall, and the distribution patterns of ^2H and ^{18}O in precipitation observed for present-day climatic conditions. Based on this link, numerous attempts have been made to reconstruct past climatic changes from records of the isotopic composition of ancient precipitation preserved, often via proxies, in various environmental archives (glacier ice, sediments, groundwater, organic matter, and others). However, quantitative reconstruction of past climatic changes from isotopic records preserved in continental archives requires that the isotope palaeothermometer or isotope palaeopluviometer be adequately calibrated for the timescales of interest.

Most important for palaeoclimatic reconstructions is an apparent link between the isotopic composition of precipitation and surface air temperature (e.g., Fricke and O'Neil (1999)). Dansgaard (1964) presented the empirical relationship between the annual mean values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of precipitation and local surface air temperature, derived from the data gathered during the first three years of operation of the GNIP network. The relationship was developed for mid- and high northern latitude coastal stations and is characterised by the isotope–temperature coefficient equal to 0.69‰ per °C for $\delta^{18}\text{O}$ and 5.6‰ per °C for $\delta^2\text{H}$ (Rozanski et al. 1993). Although this relationship was frequently used in the past for isotope-aided palaeoclimatic reconstructions, for the wide range of

climates and timescales involved, doubts have often arisen as to whether spatial relations between the isotopic composition of precipitation and climatic variables, derived from present-day conditions, can be used with confidence to interpret isotopic records of past precipitation preserved in various environmental archives.

The available instrumental records of the ^{18}O and ^2H content of precipitation permit the link between the stable isotope signature of precipitation waters and surface air temperature ($\delta\text{-T}$) to be considered in three different ways:

i) A spatial relationship between the long-term (annual) averages of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) of precipitation and surface air temperature for different stations. The slope of spatial relationship for $\delta^{18}\text{O}$ varies from about 0.8–0.9‰ per $^{\circ}\text{C}$ for high latitude areas to virtually zero for tropical regions, where a strong correlation between $\delta^{18}\text{O}$ ($\delta^2\text{H}$) and the amount of precipitation is usually observed. For the European continent this slope is equal to 0.58‰ per $^{\circ}\text{C}$ (Rozanski et al. 1992).

ii) A temporal relationship between short-term (seasonal) changes of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) of precipitation and surface air temperature for a single station or a group of stations in a given region. For mid-latitude stations of the GNIP network (40°N to 60°N) this relationship has a slope of 0.32‰ per $^{\circ}\text{C}$ for $\delta^{18}\text{O}$ (Rozanski et al. 1993). For tropical regions this slope is close to zero or even negative (the monsoon-type climate). It has been argued that the $\delta\text{-T}$ coefficients derived from seasonal cycles of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) and temperature for mid- and high-latitude regions might be useful for palaeoclimatic applications because they sample a wide range of different ‘climates’ (e.g., Siegenthaler and Oeschger (1980); van Ommen and Morgan (1997)).

iii) A temporal relationship between long-term (interannual) changes of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) and temperature for a fixed location or a region. Analysis of long-term trends of $\delta^{18}\text{O}$ and temperature at a number of European stations resulted in an average $\delta^{18}\text{O}\text{-T}$ coefficient of $0.63 \pm 0.04\text{‰ per }^{\circ}\text{C}$ (Rozanski et al. 1992). For the trend curves shown in Figure 6 the resulting $\delta^{18}\text{O}\text{-T}$ slopes are equal to 0.60 and 0.58‰ per $^{\circ}\text{C}$, for the Vienna and Krakow stations respectively. Validity of the $\delta^{18}\text{O}\text{-T}$ coefficient derived from precipitation records has been confirmed for the last 200 years through study of the $\delta^{18}\text{O}$ of ostracodes preserved in the sediments of Ammersee Lake in Germany (von Grafenstein et al. 1996).

The $\delta\text{-T}$ coefficients based on interannual changes in $\delta^{18}\text{O}$ ($\delta^2\text{H}$) and surface air temperature are probably the most relevant as far as palaeoclimatic applications of stable isotopes are concerned, as they reflect the long-term linkage between the isotopic composition of precipitation and climate for a given area. However, the numerical values of these coefficients have been derived from relatively short instrumental records (several decades) and the question arises to what extent they are valid for longer periods, including major climatic shifts. Moreover, they most probably vary from region to region (Rozanski et al. 1993).

Proper assessment of the temporal changes of long-term $\delta\text{-T}$ coefficients is a vital problem for calibration of the isotope palaeothermometer (Jouzel 1999; Jouzel et al. 2000). Several processes have been identified which may lead to long-term changes of this relationship over time on a given area: (i) changes in the source region of moisture (e.g., Boyle (1997)); (ii) global or regional changes of the isotopic composition of the ocean (e.g., Shackleton (1987); Werner et al. (2000a)); (iii) changes of atmospheric circulation

patterns shifting the sources and routes of air masses precipitating over the given site (Charles et al. 1994); (iv) changes in seasonality of precipitation (Werner et al. 2000b).

Some insight into temporal variations in the δ - T relationship which occur on timescales exceeding instrumental records has been gained through studies of ice cores. The $\delta^{18}\text{O}$ time series available for ice cores drilled in central Greenland has been compared with the measured borehole temperatures. This comparison in the case of the GRIP ice core yielded $\delta^{18}\text{O}$ - T gradients of around 0.6‰ per °C for the Holocene and only 0.23‰ per °C for the last glacial transition (Johnsen et al. 1995). Somewhat different values were obtained for the GISP2 ice core: from 0.25 to 0.46‰ per °C for the Holocene (the higher values being for recent centuries) and 0.33‰ per °C for the last glacial transition (Cuffey et al. 1995). It has been argued that, unlike for Greenland, present-day spatial isotope gradients can be used as a surrogate of the temporal gradients to interpret glacial-interglacial isotopic changes at sites such as Vostok and Dome C in central Antarctica (Jouzel et al. 2003).

Long-term changes of temporal δ - T relationships can be addressed also through studies of groundwater systems. While the isotopic composition of groundwater yields information about the isotopic composition of past precipitation, the concentration of noble gases provides information about recharge temperature which is directly linked to the mean surface air temperature of the given area (e.g., Bath et al. (1979); Andrews and Lee (1979)). Although there are some issues regarding the dispersion of isotopic signals in groundwater (e.g., Stute and Schlosser (2000)), the groundwater archives allow the assessment of variability in the stable isotope composition of precipitation as a function of temperature from the perspective of major climatic changes during the last glacial-interglacial cycle.

The link between the isotopic composition of precipitation and changes in climate on timescales exceeding direct observations can also be addressed by General Circulation Models (GCMs). They can be employed to simulate isotopic water cycles ($^1\text{H}^2\text{H}^{16}\text{O}$, $^1\text{H}^1\text{H}^{18}\text{O}$) on different spatial and temporal scales, including periods of major climatic shifts (e.g., Jouzel et al. (1991, 1994); Hoffmann et al. (1998)). The simulated changes in the global or regional isotope fields in precipitation can be compared with predicted changes of climate (temperature). The GCM approach is being continuously refined and has been applied successfully in a number of studies aimed at better understanding of the isotopic records preserved in continental archives. However, the available GCMs still lack adequate resolution and computing power to provide continuous reconstructions of changes in isotopic water cycles across timescales addressed in the framework of palaeoclimatic reconstructions.

Outlook

It is apparent from the above discussion that the calibration of isotope palaeothermometers for terrestrial environments remains to be fully achieved. It appears that long-term δ - T gradients derived from analysis of instrumental records of the isotopic composition of precipitation and temperature can be used, with care, to interpret isotopic records preserved in environmental archives located at mid- and high latitudes, under a Holocene climate. In the absence of sufficiently long instrumental records, spatial relationships derived

for a given area can be used as a first-order surrogate for temporal isotope gradients. However, this approach may not be generally valid when the interpreted isotope records cover periods of major climatic shifts, such as the last deglaciation period.

From precipitation to terrestrial water

The purpose of this section is to cover the fate of O and H isotopes in water in the three terrestrial reservoirs described in connection with Figure 1 (with the exception of lakes, which are considered in detail in the next section of this chapter). The necessity for looking at transformation effects on isotopes is clear from the previous section on precipitation, where it was shown that an alteration of 1‰ in $\delta^{18}\text{O}$ can under certain conditions represent a temperature change of as much as 3°C, a significant amount in palaeoclimatic terms.

Processes affecting infiltration

It is necessary for the discussion that follows to distinguish between infiltration (water which enters the soil) and recharge (water which eventually reaches the water table of an aquifer) as they are not usually synonymous, owing to the processes described below.

Soil physics

Under temperate climatic conditions, soil moisture is at a saturated state in winter but not in summer, leading to the concept of ‘soil moisture deficit’ (SMD). Where there is an SMD, rainfall may be absorbed at the soil surface but is unable to move down against pore pressure, and is therefore liable to be removed by evaporation or transpiration. Allied to this is the concept of the ‘zero flux plane’ (ZFP), the notional division between water percolating downwards and water in liquid or vapour form travelling upwards. When the SMD is fully satisfied, the ZFP will be at ground surface. In contrast, towards the end of a dry summer the ZFP could be some meters below the surface.

Moisture in the layers of soil above the ZFP is most prone to isotopic effects because of vaporisation. Under temperate climates it may be difficult to use stable isotope ratios to distinguish evaporative enrichment from transient storage of individual rainfall events in the upper soil layers, though where both O and H isotope data are available the position of the data on a δ -plot may provide a resolution. It is also worth bearing in mind that different soil-water collection methods in the unsaturated zone may be sampling “relatively more and less mobile components of soil water that may have different histories and pathways” (Landon et al. 1999).

Effects of vegetation cover

Even before infiltration can take place, interception by leaves can lead to a certain amount of re-evaporation and hence isotopic fractionation (the ‘canopy effect’: Gat and Tzur (1967); DeWalle and Swistock (1994)). Re-evaporation is not the only effect of trees; branches and trunks can be very effective at conducting rainfall as ‘stem flow’ via root channels to the underlying unsaturated zone without a prolonged residence in the shallow soil zone where evaporation could affect it (Dawson 1993). While it is likely that much

of this infiltration will be recycled by transpiration from the tree itself, the moisture may subsequently be re-distributed in the soil by 'siphoning' (Smith et al. 1999), possibly leading to complex isotopic changes in the soil moisture profile (Adar et al. 1995).

Although it may vary with the type of precipitation from event to event, the magnitude of canopy interception effects rarely seems to be extreme. The amount of evaporative enrichment in throughfall, where directly measured, appears remarkably consistent under different climatic conditions: 0.3‰ in $\delta^{18}\text{O}$ for pine forest in southern Sweden (Saxena 1986) and Pennsylvania (DeWalle and Swistock 1994), 0.5‰ in $\delta^{18}\text{O}$ for chestnut, oak and cork in the south of France (Pichon et al. 1996), and of the same order for tropical montane rainforest in Ecuador (Goller et al. 2005).

Indirectly-measured effects inferred from soil water measurements are of the same order. Brodersen et al. (2000) showed that trees in the Black Forest cause enrichments of just under 0.4‰ in $\delta^{18}\text{O}$, irrespective of whether they are coniferous or deciduous, while Darling (2004) reported a case where 'ventilation' (position of a tree at the forest edge) apparently contributed to a 5‰ increase in $\delta^2\text{H}$ compared to soil moisture elsewhere in a wood in southern England, equivalent to perhaps 0.7‰ in $\delta^{18}\text{O}$.

A corollary of the isotopically-enriching vegetation canopy effect is that tree or scrub clearance should introduce a corresponding isotope depletion in soil moisture compositions. This was found to be the case in semi-arid South Australia, where Allison et al. (1985) measured soil profiles beneath dunes with and without native vegetation. Midwood et al. (1993) noted a similar effect in southern Texas, but occurring in reverse order as grassland was replaced by thorn woodland.

All forms of vegetation, whether plants or trees, must of course transpire to survive. The balance of evidence suggests that under normal growth conditions the process of transpiration is to a great extent non-fractionating (Zimmerman et al. 1967; Allison et al. 1984), so it might be thought to be of little importance in terms of isotopic modification of the infiltration which will become recharge. However, where rainfall has a strong seasonal variation in isotopic composition, transpiration might be subtracting a component of potential recharge. This would result in a divergence between the composition of recharge and transpiration water, neither of which will be fully representative of bulk rainfall. This needs to be considered in the interpretation of isotopic proxies such as $\delta^2\text{H}$ in tree rings (Epstein et al. 1976; White et al. 1985), and $\delta^{18}\text{O}$ in leaves (Iacumin and Longinelli 2002).

Evaporation from the soil

In arid or semi-arid conditions vegetation may be sufficiently sparse that interception and transpiration are only very minor facets of the water balance. However, evaporation from the soil surface layers then emerges as an important process in the isotopic modification of any rainfall which manages to infiltrate (e.g., Dincer et al. (1974)). Obviously, the warmer and drier the climate the more evaporation, and therefore fractionation, will occur. The depth to which soil moisture is significantly affected is rarely more than 1–2 m below ground level (Barnes and Allison 1988), but within that range can give rise to extreme evaporative enrichment. These enrichments will usually show some seasonal changes as a result of the moisture balance. Figure 7 shows an example of this from sequential soil profiles taken in the Negev desert of Israel (Sonntag et al. 1985).

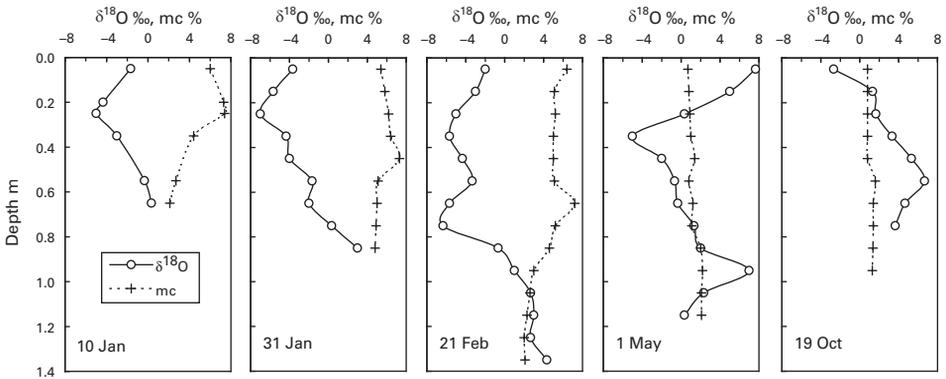


Figure 7. Sequential soil profiles of $\delta^{18}\text{O}$ and soil moisture content (mc) taken in the Negev desert of Israel. The profiles in January and February show infiltration from relatively-depleted winter rainfall moving downwards in the profile. By early summer, evaporation is driving the residual moisture towards isotopic enrichment. By the autumn, infiltration is beginning again. Data from Sonntag et al. (1985).

The profiles in January and February show infiltration from relatively-depleted winter rainfall moving downwards in the profile, with the ZFP not far from the surface. By early summer, however, the dry conditions and increasing temperature mean that the ZFP is moving down, while above it evaporation is driving the residual moisture towards isotopic enrichment. Similar seasonal changes were observed by Liu et al. (1995) in the desert of southern Arizona. There must therefore be a large margin of uncertainty over the bulk isotope input to proxies relying on soil moisture under arid conditions. This appears to apply as much to clay soils as sands, despite their higher moisture contents (e.g., Mathieu and Bariac (1996)).

Some desert areas are zones of groundwater discharge rather than recharge. If the outflow of water is great enough, these will be manifested as lake or wetland oases and the usual surface-water evaporation dynamics will apply (see next section). However, where outflows are low the production of ‘dry’ lakes is common. Cores taken in the lake beds show the same extreme evaporative enrichment in near-surface moisture as found in recharge zones, but below this there is a progressive depletion until the isotopic value of the underlying groundwater is reached (e.g., Allison and Barnes (1985)). Because there is no infiltration from rainfall events, there are no significant seasonal fluctuations in isotope values at any particular level, though seasonal changes in atmospheric humidity etc. may cause some variation in the maximum isotope enrichment.

In cases of both recharge and discharge, soil moisture from the shallowest depths in the soil zone (say <25 mm) may actually show major isotope depletion (Barnes and Allison 1988). The reason for this is that any soil moisture at such depths consists largely of condensed water vapour, which must be depleted to preserve isotope mass balance with the enriched water immediately below from which it originated.

*Aquifer recharge and the rainfall-groundwater isotope balance**Recharge through the unsaturated zone*

It has been shown above that infiltration of rainfall is a process subject to transpiration and evaporation. The combined effect of these factors varies with climate and soil or rock type, but simple water balance methods reveal that typically around 30% of rainfall becomes recharge under humid temperate climates, 10% in Mediterranean climates, and 0–5% under more arid climates (Gleick 2000). The high ‘wastage rate’ suggests there could be profound effects on the isotopic composition of any precipitation surviving to become recharge.

As illustrated above, evaporation has the most dramatic effects on soil-moisture isotope compositions. While this may affect the isotopic composition of the moisture before it is transpired by plants (e.g., Brunel et al. (1997)), it is equally apparent from the low moisture contents involved that this soil water cannot be an important factor in the overall water balance: either the rainfall event was too small to satisfy the SMD, or it was large enough to provide recharge and the isotopically enriched soil moisture is merely the remnant of percolating water. Transpiration has a greater but more insidious role in modifying recharge, in that it may remove part of the annual rainfall before mixing can occur. If the precipitation has a high seasonal variability in isotopic composition (see for example Rozanski et al. (1993)), then there is the possibility of a missing component in the isotopic balance of recharge. This may not necessarily mean summer growing-season rainfall; it depends on the depth from which roots are extracting water. For example, Robertson et al. (2001) found the best correlation for the $\delta^{18}\text{O}$ values of cellulose from oak trees in East Anglia (UK) was with rainfall of the previous December/January period, when vegetation is dormant.

However, despite evaporation and more significantly transpiration, studies have shown that the isotopic modification during the precipitation–recharge process is generally small, within perhaps $\sim 0.5\text{‰}$ in $\delta^{18}\text{O}$ of the bulk rainfall. This is almost irrespective of climate: for example it applies in many parts of North America (Yonge et al. 1985; Clark and Fritz 1997; Kendall and Coplen 2001), across Europe (Bath 1983; Eichinger et al. 1984; Deak et al. 1996; Gehrels et al. 1998; Kortelainen and Karhu 2004), Jordan (Bajjali et al. 1997), India (Krishnamurthy and Bhattacharya 1991), West Africa (Mathieu and Bariac 1996), East Africa (Nkotagu 1996), and Australia (Sharma and Hughes 1985).

Recharge by surface waters

The results of the above studies suggest that it is actually quite difficult to cause much isotopic bias or selection in rainfall-derived recharge. Mass-balance considerations demand a sizeable input of energy to cause the necessary fractionation, but it appears there is simply not enough of this energy (solar or other) available during normal areal infiltration to cause much modification via evapotranspiration, whatever the terrain or climate. Solar energy is however much more available to surface waters, and it is among the more slow-moving of these that the greatest evaporative effects are seen, usually in lakes (see next section). While terminal (endorheic) lakes in discharge areas will normally be the most affected, lakes in recharge areas are not immune and may pass on evidence of their isotopic signatures to the groundwater. In more temperate areas the

effects may persist for only a few km (Krabbenhoft et al. 1994) before they are damped by areal rainfall recharge, but in warmer, more arid areas the effects may be evident for tens of km and involve isotopic enrichments of many permil ($\delta^{18}\text{O}$) or tens of permil ($\delta^2\text{H}$) compared to unmodified groundwater in the vicinity (Darling et al. 1996).

It is of course possible for river as well as lake waters to infiltrate the subsurface, most easily via swallow holes in karstic terrain (Plummer et al. 1998; Perrin et al. 2003), though generally this will cause relatively little isotopic modification to the underlying aquifer. The main exception to this would be rivers flowing through arid areas, which tend to lose water by infiltration in addition to evaporation. Examples include the Colorado (Payne et al. 1979), the Niger (Fontes et al. 1991), and perhaps most-studied, the Nile (Verhagen et al. (1991); Geirnaert and Laeven (1992); see also Figure 8). These effects are seen to good advantage in the Gezira region of Sudan, immediately to the south of the confluence of the Blue and White Niles at Khartoum. The Niles have different isotopic signatures owing to the different geographical origin of their waters, and this enabled Farah et al. (2000) to detect river infiltration up to 12 km from the rivers, with the White Nile being the greater contributor.

However, rivers do not necessarily lose or gain water over any particular reach for the whole of a hydrological year. Seasonal changes in hydraulic gradient mean that groundwaters near a river can show quite large changes in isotopic composition due to reversals in flow direction. This is particularly the case with large rivers having major fluctuations in flow rate due to snowmelt: for example, Navada and Rao (1991) found seasonal changes of up to 2.5‰ in $\delta^{18}\text{O}$ for groundwaters within a few km of the Ganges.

In arid areas it is common to find lenticular aquifers underlying wadis, which are recharged during flood flow. Depending on how long the waters were exposed to the atmosphere, there may be greater or lesser amounts of evaporative modification (Darling et al. 1987; Clark and Fritz 1997). There is also the possibility of evaporation through the unsaturated zone (Aranyosy et al. 1992; Clark and Fritz 1997).

Mixing with seawater

In coastal areas the possibility exists for mixing between fresh and marine waters, with obvious implications for isotopic compositions. Where this is simple mixing of groundwater and seawater, often resulting from intensive groundwater abstraction or eustatic change (Rao et al. 1987; Edmunds et al. 2001), isotope values cannot be more enriched than approximately 0‰, the mean ocean water value for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Often, however, the situation will be more complex as groundwaters, rainfall and seawater variously interact in lagoonal and sabkha settings, with evaporation frequently giving rise to positive isotope values (Gat and Levy 1978; Manzano et al. 2001; Duane et al. 2004).

Layered aquifers and stratification

Depending on geological conditions, it is possible to have two or more aquifer units underlying an area or region, each of which can have a different isotope composition owing to combinations of factors such as differences in mode of recharge, catchment altitude and residence time (e.g., Brown and Taylor (1974); Gonfiantini et al. (1974)).

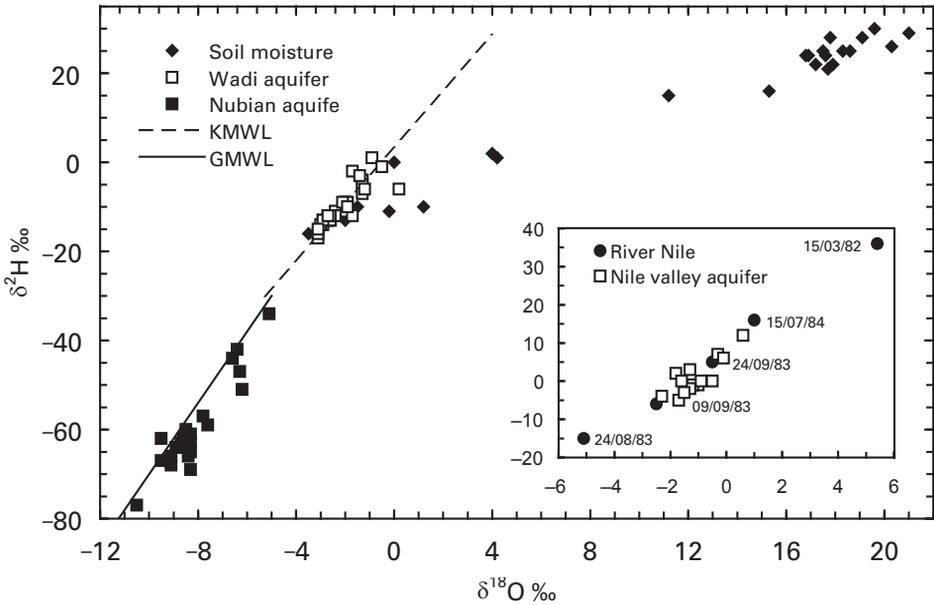


Figure 8. Large contrasts in the O and H stable isotope composition of different reservoirs of water are characteristic of arid regions. This δ -plot, based on a study carried out in the Butana region of northern Sudan, demonstrates the effects of some of the processes outlined elsewhere in this chapter. The observed isotope ranges are large: more than 30‰ in $\delta^{18}\text{O}$ and over 100‰ in $\delta^2\text{H}$. The data in the figure can be considered in terms of the three terrestrial reservoirs between which water is distributed. *Soil moisture* (diamonds) shows extreme enrichment along the slope of ~ 2 typical of soil evaporation. Deeper unsaturated zone moisture is included in this category, and trends back towards the shallow groundwater composition. There can be very little direct rainfall recharge under such an arid climate, and the possibility exists that this trend is due to evaporative discharge driven by the humidity gradient. *Groundwater* (squares) in the main part of the figure divides into two populations: firstly the wadi aquifer, actively being recharged (via occasional flood events) by modern rainfall lying along the Khartoum meteoric water line (KMWL), and secondly the regional aquifer in the underlying Nubian formation, which radiocarbon measurements show was predominantly recharged during early Holocene pluvial episodes, and which tends to conform to the Global Meteoric Water Line (GMWL). For each aquifer there is evidence of isotopic modification. For example, some wells in the wadi aquifer yield water showing signs of evaporation. Whether this occurred before or after recharge is not clear; most sampling points were large-diameter dug wells where in-situ evaporation might have occurred. In the regional aquifer, the less-depleted groundwaters are evidence for mixing between old and modern waters. *Surface water* (circles, inset) is shown in the form of the Nile, sampled seasonally at Shendi. The large range in composition is due to the interplay between the strong evaporation prevailing throughout the year in Sudan, and the depleted water flowing down from the Ethiopian highlands during the annual Blue Nile flood in the late summer. Water from the Nile seeps into the shallow aquifer, where it may mix with locally-recharged groundwater, giving rise to the range of compositions measured. Data from Darling et al. (1987).

Fracturing may then lead to waters from different aquifer units mixing and emerging at the surface in springs with isotopic contents at variance with local meteoric recharge.

Age-related layering within single aquifer units has been recognised in a number of studies (e.g., Edmunds and Smedley (2000); Chen et al. (2004)), and where the age profile spans the Holocene-Pleistocene boundary there is scope for significant isotope gradients: for example, Deak et al. (1993) found a 3‰ change in $\delta^{18}\text{O}$ between the surface and a depth of 160 m in an aquifer in southeast Hungary. Natural spring discharge from such aquifers may represent various degrees of mixing.

Interception of recharge by caves and tunnels

As discussed above, once infiltration has passed through the soil into the unsaturated zone it normally becomes recharge to the underlying aquifer. However, in karstic or fractured-rock areas there is always the possibility that percolating water will find its way into cave systems or artificial excavations, giving rise to speleothem features. These have been used as proxies in two ways: by interpreting the $\delta^{18}\text{O}$ (and $\delta^{13}\text{C}$) in deposited calcite (e.g., Schwarcz (1986)), and by attempting to measure more directly the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the original dripwater via fluid inclusions (e.g., Ayalon et al. (1998)). Both these aspects are covered in detail in McDermott et al. (this volume); the comments here are concerned with the hydrology of the dripwaters.

Two potential difficulties arise with dripwaters. Firstly, there may be seasonal selection of recharge; secondly, the altitude of recharge may not be known with certainty. With regard to the first, karst is not generally as effective as most other lithologies in mixing percolating waters. Seasonal changes or selection effects have been observed in dripwaters of the Villars cave (southwestern France) by Genty et al. (2002), in the B7 cave (western Germany) by Niggemann et al. (2003), and in Reed's Cave (South Dakota, USA) by Serefidin et al. (2004). However, such effects are not inevitable under humid temperate climates: for example, Williams and Fowler (2002) found no evidence for either in a cave at Waitomo in New Zealand.

Warmer, drier conditions might be expected to affect isotope values in dripwaters. The complexities of karst unsaturated zone behaviour in semi-arid terrain have been demonstrated in relation to the much-studied Soreq cave of Israel (e.g., Ayalon et al. (1998); Kaufman et al. (2003)). Two types of infiltration water were identified: fast flow (residence time of weeks) discharging from fractures in the cave roof during heavy rainfall events in the wet season, and slow flow in the form of speleothem dripwater throughout the year (residence time tens of years). Generally the fast-flow waters were enriched 0.3–1.0‰ in $\delta^{18}\text{O}$ compared to the bulk rainfall on the land overlying the cave. Dripwaters tended to vary seasonally by about 1.5‰ in $\delta^{18}\text{O}$, and were themselves slightly enriched relative to the fast-flow waters; the seasonal variation has been preserved despite the lengthy percolation time. There was however little evidence of evaporative enrichment, so different selection processes for the fast and slow waters were proposed. Another Mediterranean locality showed contrasting behaviour: at the Clamouse cave in the south of France, dripwaters showed a remarkable consistency in their isotopic composition over time (Genty et al. 2002), with values similar to modern groundwater in the area (Dever et al. 2001) and to the weighted mean rainfall at the nearest GNIP station (Barcelona), therefore showing no evidence of selection.

Depending on the topography of the overlying land surface, altitude effects may play a part in affecting the interpretation of dripwaters. For example, a comprehensive study of water inflows to tunnels in Alpine crystalline massifs found that $\delta^{18}\text{O}$ values tended to be more negative than expected from the predicted catchment areas (Marechal and Etcheverry 2003). This was attributed to geological structure directing recharge from higher altitudes into the tunnel fracture systems. However, it was also noted that recharge from rivers and lakes might cause local perturbations to the overall pattern. A study on another deep tunnel within granite in the Central Alps concluded that isotopically depleted winter precipitation and glacial meltwaters were important contributors to the local groundwater flow system (Oferdinger et al. 2004).

In some cases speleothem deposits form in caves that are associated with the discharge rather than the recharge end of a groundwater system, for example the Devil's Hole vein calcite deposit in Nevada, USA (Winograd et al. 1992; Quade 2004). In these circumstances, not only is the usual uncertainty over recharge area compounded, but residence time and the possibility of mixing between groundwaters of different provenance also have to be considered.

Fluid inclusions and water of crystallisation

Fluid inclusions have already been referred to above in connection with speleothems. However, many other origins are possible: for example during the formation of evaporites (e.g., Knauth and Roberts (1991)), or in high-temperature hydrothermal systems (e.g., Polyá et al. (2000)). Typically their $\delta^2\text{H}$ and sometimes $\delta^{18}\text{O}$ compositions are used to infer hydrological conditions during periods well beyond the Quaternary, but diagenetic or other complicating factors can lead to rather imprecise conclusions about the composition of contemporaneous meteoric waters.

There tends to be a mineral-dependent fractionation between water of crystallisation and free water, but where the magnitude of this is known it is possible to draw broad conclusions about groundwater fluxes and timing from isotopic measurements of the crystallisation water. Gypsum in particular has been used for this purpose (Halas and Krouse 1982; Bath et al. 1987).

Runoff, discharge and effects on streams and rivers

Consideration of the water cycle diagram shown in Figure 1 reveals several different discharge routes for any precipitation escaping initial evapotranspiration. While some groundwater discharges directly to the sea, water also finds its way into surface watercourses via overland flow or after residence in the subsurface. In practice, overland flow of rainfall is relatively rare, relying as it does on highly impermeable conditions at the ground surface. Under most climatic and geological conditions, a whole continuum of flowpath lengths is likely to contribute to streams and rivers.

From precipitation to river water

It has been mentioned in the second section of this chapter that rainfall can show large variations in its isotopic composition even between individual events, let alone seasonally. Yet infiltration appears to be very effective at mixing what will become

recharge (see above). Therefore only that fraction of rainfall which flows rapidly to a river can conceivably have a much different isotope composition. In practical terms this is not usually important. In the permeable lowland catchments of minor rivers there is little variation in isotopic composition throughout the year (e.g., Lawler (1987); Darling et al. (2003)). Even streams in relatively impermeable, ‘flashy’ upland catchments often fail to show much isotopic response to rainfall, whether under temperate climate (Sklash and Farvolden 1979; McDonnell et al. 1991; Durand et al. 1993) or tropical rainforest conditions (Goller et al. 2005).

Unlike for the more humid climates referred to above, arid-zone runoff can vary considerably in its composition (up to 2‰ $\delta^{18}\text{O}$) on a scale of hours (Adar et al. 1998) to days (Lange et al. 2003) because of the lack of damping in the catchment. However, the general impersistence of this wadi-type flow means that it is not on the whole important in the growth of proxies.

A major factor affecting the isotopic composition of water reaching streams and rivers in regions subject to cold winters is snowmelt. Where there is a significant accumulation of snow during the winter, a pulse of isotopically-depleted water can be detected arriving in the upper parts of catchments during the spring (Sklash and Farvolden 1979; Herrmann and Stichler 1980; Laudon et al. 2004). In smaller river systems, depletions due to the snowmelt pulse are generally within the range 2 to 4‰ in $\delta^{18}\text{O}$ (Bottomley et al. 1986; Schuerch et al. 2003). In larger rivers, depletions are smaller and it can take months for the snowmelt pulse to pass down the river (Mook 1970; Rank et al. 1998) so that proxies may be affected during their growing season (e.g., Ricken et al. (2003)). There are however limits to the propagation of such pulses in recognisable form in continental-scale catchments (e.g., Winston and Criss (2003)).

The effects of evaporation on river and stream waters are difficult to distinguish from seasonal changes, particularly when a number of upstream tributaries are involved. Given that residence time and surface area are important factors in evaporation, its effect on river waters would not be expected to be as profound as on lake waters (see next section). This appears to be the case: for example, after de-convoluting the effects of tributaries, Simpson and Herczeg (1991) calculated that the maximum enrichment of water in the Murray basin (Australia) was about 5‰ in $\delta^2\text{H}$, which would equate to 1‰ in $\delta^{18}\text{O}$ assuming a surface-water evaporation slope of 5. However, they also calculated that irrigation return water contributed an approximately equal enrichment, so anthropogenic factors can have important modifying effects. Where water is delayed in natural or artificial lakes, scope for further isotope enrichment exists: Payne et al. (1979) calculated that damming the Colorado River had resulted in evaporative enrichment of some 2.5‰ in $\delta^{18}\text{O}$. In very large river systems there may be rather complex changes as tributaries fed by snowmelt interact with lowland tributaries subject to evaporation (e.g., Kendall and Coplen (2001); Winston and Criss (2003)). However, large changes in isotope composition are not exclusively caused by snowmelt: strongly seasonal rainfall can have a similar effect, as the example of the Nile shows (Figure 8).

Mixing of river waters

An additional complication in understanding isotopic compositions in major rivers is the mixing – or lack of it – occurring when major tributaries join the main river. Differences

in morphology, flow characteristics etc. mean that the magnitude of incomplete mixing is difficult to predict. In cases that have been investigated, the downstream distance before full mixing ranged from 50 km for the Main-Rhine confluence at Mainz (Fritz 1981), to at least 120 km for the Amazon tributaries Solimoes and Negro at Manaus (Matsui 1976), and 300 km for the Liard-Mackenzie confluence in northern Canada (Krouse and McKay 1971).

Springs

It may seem slightly perverse to include springs towards the end rather than the beginning of a discussion on discharge, but in volumetric terms they are likely to be unimportant contributors to river flow, at least as far as visible manifestations are concerned. (Admittedly there is no simple definition of what constitutes a spring; much river baseflow will be the result of groundwater discharge in the river bed, whether in visible form or not.) It is apparent from evidence discussed earlier in this section that most groundwater is fairly well mixed during percolation through the unsaturated zone and/or during residence in the aquifer, and therefore little variation in spring isotope composition would be expected. The major exceptions are some springs or resurgences found in karstic terrain. These sometimes consist of little more than surface water that has spent only a brief period underground, and therefore tend to show stream-like amplitudes of isotopic variation, typically 1–2‰ in $\delta^{18}\text{O}$ (Flora and Longinelli 1989; Winston and Criss 2004). However, not all karst springs show this amplitude of variation; in particular the higher-volume outlets are often damped by mixing and dilution (Stewart and Downes 1982; Nativ et al. 1999).

In nearly all cases springs will be discharging waters in the age range of a few years to a few thousand years, simply because longer residence times are unlikely to occur in actively circulating flow systems. Such Holocene waters will generally carry the same isotope signatures as present-day recharge. By contrast in the late Pleistocene, beyond 10,000 years before present, the colder climate resulted in groundwaters generally having isotopic signatures depleted by anything from 1 to 10‰ in $\delta^{18}\text{O}$ depending on location (e.g., Darling (2004); Edmunds et al. (2004)). The vast majority of these data come from borehole samples, and not all the aquifers are still being recharged and therefore actively circulating. Nevertheless ‘palaeowater’ springs have been identified, in major aquifer systems like the Nubian Sandstone of North Africa (Sturchio et al. 1996; Sultan et al. 1997) and the Great Artesian Basin of Australia (Mudd 2000; Love et al. 2000).

There are equally rare cases where spring waters contributing to streams and rivers may have been isotopically modified in the subsurface. A prime example would be discharges of thermal water which may be enriched in $\delta^{18}\text{O}$ owing to mineral exchange at high (>150°C) temperatures (the so-called ‘oxygen shift’) after passing through geothermal systems (e.g., Fontes and Zuppi (1976)). Superimposed on this shift may be some evaporative enrichment due to steam separation at the surface (Giggenbach et al. 1983). However, high-temperature springs are not normally important in volumetric terms, often discharging into non-thermal rivers which dilute away any unusual isotopic characteristics. There may however be local effects within those rivers, for example as observed in the Firehole River of Yellowstone National Park (Woodward et al. 2000).

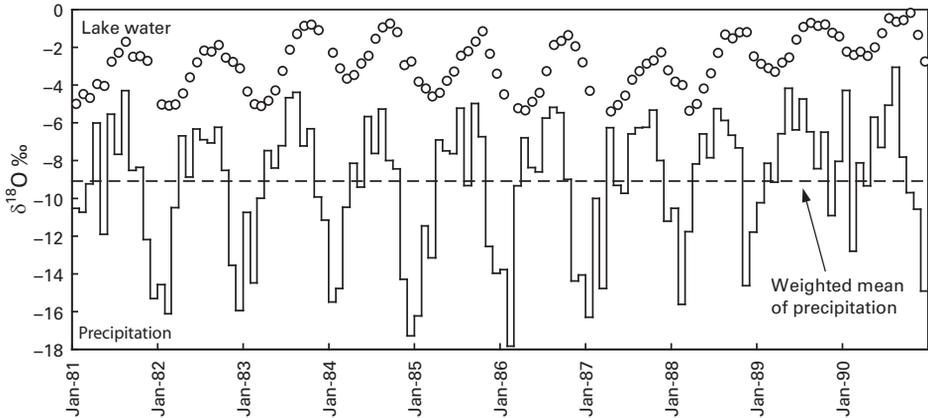


Figure 9. A decade-long record of $\delta^{18}\text{O}$ in the Neusiedlersee, a steppe lake situated on the Pannonian plain in eastern Austria, showing the sizeable displacement between local precipitation and lake water isotope compositions caused by evaporative enrichment. After Rank et al. (1984), with further data courtesy of D. Rank.

Wetlands

No discussion of isotopes in discharge would be complete without a mention of wetlands: these can be important habitats for proxy species (White et al. 2001; Lambs and Berthelot 2002; Menot-Combes et al. 2002). However, it is difficult to be prescriptive about isotopic effects since wetlands vary greatly in their hydrology — indeed not all wetlands are discharge areas. There is often a complex balance between groundwater, river water and rainfall, and stable isotopes can at least be useful in unravelling it (Hunt et al. 1998).

Lake waters and mass balance modelling

There is an almost infinite variety in the form and size of lakes studied for proxy purposes, from upland tarns to the great lakes of tropical Africa and North America. Hydrological context also varies, the balance between volume, surface area and residence time revealing itself as a continuum between simple inflow-outflow systems and true terminal lakes. The most profound isotope effects in lakes are due to the enrichment produced by evaporation. Typically the residual waters lie along a slope of 5 on a δ -plot. The precise gradient of the evaporation slope in a particular area is largely a function of local humidity, while the amount of evaporation determines the amount of displacement along the slope (Gonfiantini 1986).

Lake water compositions may change fairly predictably on a seasonal basis, particularly in temperate or boreal regions, or much less predictably in semi-arid areas subjected to periodic droughts and floods. The magnitude of these changes typically ranges from 1–2‰ in $\delta^{18}\text{O}$ in temperate regions, up to 4–5‰ where snowmelt is involved, and >10‰ for some Mediterranean and tropical lakes. Even at their most depleted, lake waters are often several permil enriched over local bulk rainfall or river inputs (an example is shown in Figure 9).

Lake waters are not always well mixed. Vertical stratification may give rise to isotopic differences (Gonfiantini 1986), though not usually as large as the seasonal changes. Plumes from river inputs may show an isotopic contrast depending on the season.

Evaporation from very saline lakes is actually somewhat inhibited by thermodynamic effects (Gonfiantini 1986). Thus a water body like Lake Asal, a terminal lake well below sea level and mainly fed by seawater, shows rather little isotope enrichment (Fontes et al. 1980). Some lakes may dry out altogether, such as Lake Frome in South Australia (Allison and Barnes 1985).

In general however highly saline, periodic or other 'problem' lakes tend to be avoided for the study of proxies: the isotopic compositions of carbonates, cellulose and diatoms in lake sediments are the most useful to palaeoclimatic reconstructions where they record fluctuations in lake water isotope composition on a regular rather than event basis. Smaller lakes seem to be preferred to large ones (Leng et al. this volume), presumably because hydrological factors are more easily constrained. However, relating the inferred lake water isotope values back to the original rainfall composition is not necessarily straightforward, as earlier discussion suggests. The application of isotope modelling techniques can help to resolve this.

Isotopic tracing of evaporation losses to the atmosphere

For an evaporating water body, isotopic fractionation occurs at the air–water interface owing to slightly lower vapour pressures and attenuated rates of molecular diffusion in air of $^1\text{H}^1\text{H}^{18}\text{O}$ and $^1\text{H}^2\text{H}^{16}\text{O}$ with respect to the common, light isotope species $^1\text{H}^1\text{H}^{16}\text{O}$. This fractionation typically gives rise to evaporating moisture which is isotopically lighter (depleted in ^{18}O or ^2H) relative to the remaining liquid, an effect which has been exploited to study evaporation by several approaches, including: (i) tracing of evaporate admixtures to the atmosphere based on changes in the isotopic signature of downwind precipitation (e.g., Gat (2000)); (ii) measurement of isotopic gradients in the boundary layer above evaporating surfaces (e.g., Wang and Yakir (2000)); and, (iii) tracing of heavy-isotope buildup which occurs in the residual liquid, i.e., in water bodies (e.g., Gonfiantini (1986); Gat (1995)). The latter approach has by far the most common application owing to the ease with which liquid water can be sampled in the natural environment. In this case, isotope buildup is applied in conjunction with a mass-balance model to account for atmospheric and water balance controls on the isotopic composition of lake water. The high preservation potential of isotopic enrichment signals (mainly $\delta^{18}\text{O}$) contained within inorganic and organic fractions of lake sediments, namely bulk carbonate, molluscs, ostracodes, aquatic cellulose and biogenic silica, has also facilitated palaeohydrological and palaeoclimatic reconstructions using this technique (Talbot 1990; Talbot and Kelts 1990; Edwards 1993; Holmes 1996; Li and Ku 1997; von Grafenstein et al. 1999; Ito 2001; Wolfe et al. 2001; Schwab 2003; Leng et al. this volume). An overview of the fractionation mechanisms and isotopic balance is provided below.

Isotopic fractionation during evaporation is practically described as the product of fractionations occurring by exchange between water molecules in liquid and vapour (in thermodynamic equilibrium), and diffusion of water molecules from the liquid to vapour phase (i.e., kinetic or transport fractionation).

For the case of a water body in thermodynamic equilibrium with the atmosphere, when there is no humidity gradient, the equilibrium fractionation factor (α^*) between liquid and vapour can be represented as:

$$\alpha^*_{\text{liquid-vapour}} = \frac{R_L}{R_V} \quad (3)$$

where R_L and R_V are the ratios of heavy isotope species to the common isotope species in liquid and vapour, respectively where $R = \frac{^{18}\text{O}}{^{16}\text{O}}$ or $\frac{^2\text{H}}{^1\text{H}}$, and $\alpha^* > 1$ such that the rare, heavy isotope species is more abundant in the liquid phase. Isotopic differences between coexisting phases are conventionally discussed in terms of isotope separation factors. In this case the equilibrium isotope separation between liquid and vapour (ε^*) is given by:

$$\varepsilon^* (\text{‰}) = 1000 (\alpha^* - 1) \approx 1000 \ln \alpha^* \approx \delta_L - \delta_V \quad (4)$$

and δ_L and δ_V are the δ -notation equivalents of R_L and R_V respectively.

Numerous laboratory measurements of ε^* have been conducted for oxygen and hydrogen over wide range of temperatures such that their values are reasonably well-constrained for use in water balance studies. Currently, the equilibrium separations are commonly evaluated using the empirical, experimental equations proposed by Horita and Wesolowski (1994):

$$\begin{aligned} \varepsilon^*_{18} \approx 10^3 \cdot \ln \alpha^*(^{18}\text{O}) = & -7.685 + 6.7123 (10^3 / T) \\ & -1.6664 (10^6 / T^2) + 0.35041 (10^9 / T^3) (\text{‰}) \end{aligned} \quad (5)$$

$$\begin{aligned} \varepsilon^*_{2} \approx 10^3 \cdot \ln \alpha^*(^2\text{H}) = & 1158.8 (T^3 / 10^9) - 1620.1 (T^2 / 10^6) \\ & + 794.84 (T / 10^3) - 161.04 + 2.9992 (10^9 / T^3) (\text{‰}) \end{aligned} \quad (6)$$

where T is the air–water interface temperature (K). These equations yield values only slightly different from earlier laboratory experiments, including Majoube (1971) and Bottinga and Craig (1969), in the range of temperatures expected for average evaporation conditions (0 to 35°C). For example, one standard deviation of α^* at 10°C is about 0.2 and 2.0 for oxygen and hydrogen, respectively, which is similar in magnitude to analytical uncertainty. Notably, ε^* values are solely temperature-dependent, and therefore are substantially better-defined than the analogous kinetic isotope separations ε_K (described below).

For the case of evaporation into undersaturated air, the isotopic fractionation typically exceeds equilibrium values due to kinetic effects. The total isotope fractionation α in this case is:

$$\alpha = \alpha^* \alpha_K \quad (7)$$

where α_K is the kinetic fractionation. Alternatively, this can be expressed as total isotope separation given by:

$$\varepsilon = \varepsilon^* + \varepsilon_K \quad (8)$$

where ε_K , the kinetic isotope separation, (and also α_K) are controlled by the evaporation mechanism.

Craig and Gordon (1965) first proposed the use of a 1-D linear resistance model to describe transport of the isotopic species through the boundary layer during constant evaporation, i.e., constant vertical flux with no convergence or divergence in the air column. As summarised in Gat (1996) the model depicts transport of vapour through a series of sublayers, including in order: a saturated sub-layer above the air/water interface, where relative humidity $h = 1$ and the isotopic ratio in the saturated sub-layer according to Equation (3) is $R_V = R_L/\alpha^*$; a boundary layer consisting of a diffusive sublayer and turbulently mixed sublayer in which transport occurs by diffusion and turbulent transfer respectively; and finally, the free-atmosphere where $h = q_A/q_S$, q_A and q_S being the specific humidity in the saturated sublayer and the free atmosphere, respectively. Normally the surface sublayer humidity is assumed to be 1 so that $h = h_A$.

The Craig and Gordon model predicts the net evaporating moisture contribution to the free atmosphere to be:

$$\delta_E(\text{‰}) = \frac{\alpha^{*-1} (\delta_L) - h\delta_A - \varepsilon}{1 - h + \varepsilon_K \cdot 10^{-3}} \quad (9)$$

where δ_E , δ_L , and δ_A are the isotopic compositions of the evaporate, the liquid (assumed to be well-mixed), and the free atmosphere, respectively (Gat 1996).

The kinetic isotope separation depends on both the boundary layer conditions and the humidity deficit according to:

$$\varepsilon_K = \theta C_K (1 - h) \quad (10)$$

where C_K is the kinetic fractionation factor, θ is a mixing/advection index, and $(1-h)$ is the atmospheric humidity deficit. For water balance applications ε_K has often been evaluated with the assumption that $\theta = 1$, using climate or micrometeorological data to define h , and using C_K values from wind tunnel experiments (e.g., Vogt (1976)). Typically C_K is specified to be in the range of 14 to 15‰ for oxygen and 12 to 13‰ for hydrogen, representative of natural open-water bodies under fully-turbulent exchange conditions (Gonfiantini 1986, Araguas-Araguas et al. 2000). While experimental evidence has suggested that C_K can vary depending on the evaporation mechanism, increasing under smooth to static transport conditions, these are not typical of open-water bodies in a continental setting. However, two-fold higher C_K values are typical of evaporation through the unsaturated zone, a process which appears to closely mimic static transport (Allison et al. 1983). The value of ε_K for open water bodies is therefore strongly humidity dependent, varying between 2.9 and 7.2‰ for oxygen and 2.5 and 6.3‰ for hydrogen, over the relative humidity range of between 80 and 50%.

The mixing/advection parameter $\theta = (1-h')/(1-h)$, has been introduced for the special case where the evaporation flux contributes to humidity buildup in the free air, as observed for the atmosphere on the leeward side of large water bodies (see also Gat (1995)). The adjusted humidity h' is the humidity of the atmosphere following the admixture of evaporate. In principle, θ also can be used to describe any situation where humidity and sampling of vapour for isotopic analysis is conducted within the turbulently mixed sublayer, rather than in the free atmosphere. The net impact of humidity buildup from an evaporating water body is to limit the overall fractionation via reduction in ε_K and increase in δ_E , as well as the over-riding influence of reduced evaporation.

Where the concentration of dissolved solids in lake water is sufficient to affect the thermodynamic activity of water, and where ion hydration and crystallisation may lead to isotopic fractionation within the water body, it is necessary to use isotope activity ratios rather than isotopic composition and to normalise the humidity according to the thermodynamic activity of water. In general, activity of water is reduced substantially only at high concentrations of dissolved solids, as in the case of brines: for example the thermodynamic activity of seawater is only 0.98. Salinity effects may therefore be a factor in surface water studies only if using water samples or isotopic proxies from inland seas and sabkhas. Although coupling of the salinity with isotopic changes is a significant complication, use of archives such as brine inclusions in halite have been successfully applied to reconstruct palaeoclimate in high-salinity systems (Horita 1990).

These basic fractionation mechanisms, incorporated within an isotope mass balance context, are useful for prediction and interpretation of the isotopic behaviour of modern water bodies and palaeohydrological archives. An overview follows of isotope mass balance models for simple lake systems.

The isotope mass balance of lake water budgets and processes

For a shallow, well-mixed lake during the ice-free period (Figure 10), the water and isotope balance may be written respectively as:

$$dV/dt = I - Q - E \quad (11)$$

$$\frac{Vd\delta_L + \delta_L dV}{dt} = I\delta_I - Q\delta_Q - E\delta_E \quad (12)$$

where V is the volume of the lake, t is time, dV is the change in volume over time dt , I is instantaneous inflow where $I = I_F + I_G + P$, I_F is surface inflow, I_G is groundwater inflow, and P is precipitation on the lake surface; Q is instantaneous outflow where $Q = Q_R + Q_G$, Q_R is surface outflow and Q_G is the groundwater outflow; E is evaporation; and δ_L , δ_I , δ_Q and δ_E are the isotopic compositions of the lake, inflow, outflow, and evaporative flux respectively (Figure 10a). Note that δ_Q and its subcomponents, δ_R and δ_G will be similar and approximately equal to δ_L in well-mixed lakes.

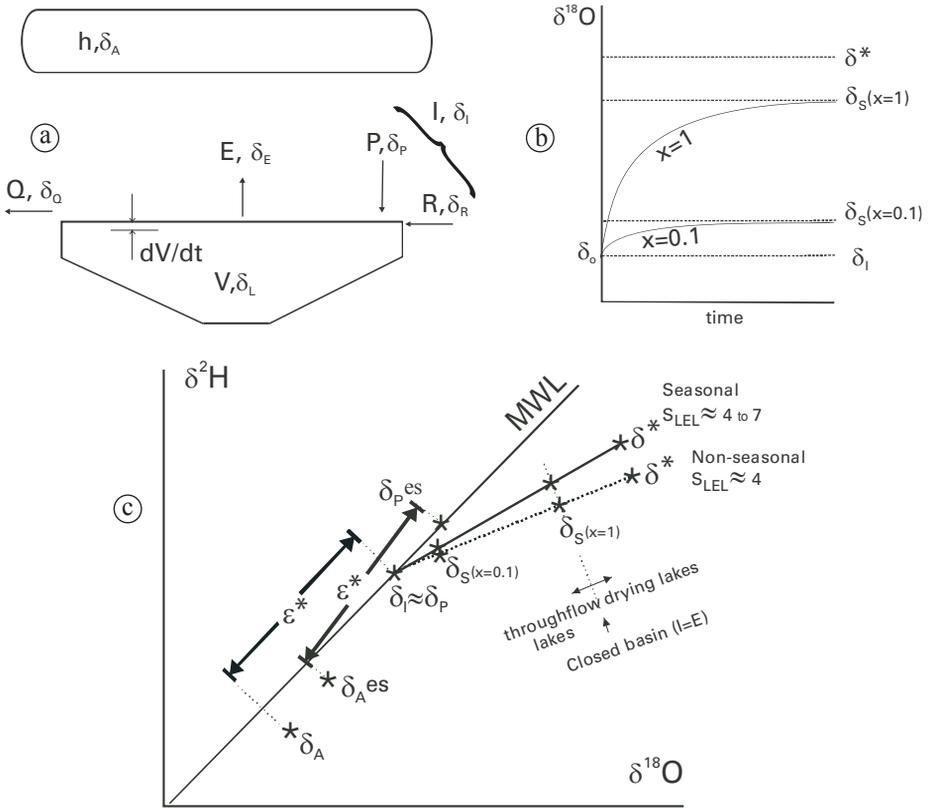


Figure 10. (a) Generalised lake balance schematic showing storage and hydrological fluxes and their isotopic compositions for a simple, well-mixed lake. Note that I is total inflow, P is precipitation, R is surface and subsurface runoff; E is evaporation, Q is the isotopic composition of outflow, V is lake volume, dV/dt is change in lake storage, and h is ambient atmospheric humidity. Note that δ values refer to the isotopic compositions of the respective components. δ_A and δ_L denote the isotopic compositions of ambient atmospheric moisture and lake water, respectively. (b) Time series plot of $\delta^{18}O$ enrichment for two lakes in the same climatic region but with differing values of x (evaporation/inflow). The scenario assumes an initial value for δ_0 that is isotopically depleted, typical of precipitation sources. δ^* is the limiting isotopic enrichment under local atmospheric conditions, δ_S is the steady-state isotope composition. (c) Plot of $\delta^{18}O$ vs δ^2H depicting major controls on isotopic enrichment in lakes. A seasonal and non-seasonal scenario both assume equilibrium between the atmosphere and precipitation. The seasonal scenario is distinct in that isotopic signatures of inflow δ_I and precipitation during the evaporation season (δ_P^{es}) are significantly offset due to the seasonality in evaporation rates, which enhances the slope of the local evaporation lines (S_{LEL}). Other influences that create disequilibrium between inflow and atmosphere could similarly alter the S_{LEL} from around 4. MWL = meteoric water line.

Substitution of the Craig and Gordon model (9) for δ_E into (12) yields:

$$V \frac{d\delta_L}{dt} + \delta_L \frac{dV}{dt} = I\delta_I - Q\delta_Q - \frac{E}{1-h+\epsilon_K \cdot 10^{-3}} (\alpha^{*-1} \delta_L - h\delta_A - \epsilon) \quad (13)$$

which can be further simplified if the lake maintains a near-constant volume ($dV/dt = 0$):

$$\frac{d\delta_L}{dt} = -[(1 + mx)\delta_L - \delta_I - x\delta^*](I/V) \quad (14)$$

where $x = E/I$ is the fraction of lake water lost by evaporation, and $1 - x = Q/I$ is the fraction of water lost to liquid outflows. Here, δ_0 is the initial isotope composition of the reservoir, m is the temporal enrichment slope (Figure 10b; see also Welhan and Fritz (1977); Allison and Leaney (1982)), defined as:

$$m = \frac{h - 10^{-3} \cdot \varepsilon}{1 - h + 10^{-3} \cdot \varepsilon_K} \quad (15)$$

and δ^* is the limiting isotope enrichment (Gat and Levy 1978; Gat 1981) given by:

$$\delta^* = \frac{h\delta_A + \varepsilon}{h - \varepsilon \cdot 10^{-3}} \text{ (‰)} \quad (16)$$

Integration with respect to δ_L , holding all other isotope and water balance parameters constant, yields (Gonfiantini 1986):

$$\delta_L = \delta_S - (\delta_S - \delta_0) \exp[-(1 + mx)(It/V)] \quad (17)$$

where the steady-state isotope composition approached by the reservoir over time is:

$$\delta_S = (\delta_I + mx\delta^*) / (1 + mx) \quad (18)$$

In the case where well-mixed lakes are not subjected to pronounced seasonal shifts in water budget, or when seasonal fluctuations converge on a relatively stable interannual balance point, a lake can be described as attaining long-term isotopic ($\delta_L \approx \delta_S$) and hydrological steady-state (i.e., $dV/dt = 0$). The isotopic composition of inflow, especially for headwater lakes is expected to be close to the isotopic composition of mean annual precipitation δ_p , plotting close to the intersection of the MWL and LEL (Local Evaporation Line) (Figure 10c). In this situation, net displacement of δ_L from the MWL along the LEL is controlled mainly by the fraction of water loss by evaporation:

$$x = \frac{E}{I} = \frac{m(\delta_L - \delta_I)}{(\delta^* - \delta_L)} \quad (19)$$

In the case of small lakes with pronounced isotope changes over one annual cycle, we can define an ‘interannual steady-state’ which may be reached under constant year-to-

year water balance conditions. For interannual steady-state composition in cold climates, rates of evaporation E and inflow I should be defined based on the annual average values, rather than values based upon observations during the thaw season. Archives may selectively record isotopic signatures during summer which can bias the record, typically towards higher evaporation loss, especially in boreal regions.

Volume, residence effects and stratification

Although lake volume does not exert a direct influence on the isotopic composition of lake water in systems which are close to isotopic and hydrological steady state, it does play a role in determining the temporal weighting of the isotopic signals that develop in lake water and in related isotope archives. The temporal footprint of δ_L and hence δ_P is fundamentally dependent on the residence time τ of water in a lake:

$$\tau = \frac{V}{I} \text{ or } x \cdot \frac{V}{E} \text{ (yr)} \quad (20)$$

which suggests that the isotopic composition of long-residence lakes, typically higher-volume lakes, is likely to be weighted over longer time intervals as compared to short-residence lakes, and for this reason display smoother records of changes. Lakes of smaller volume will also tend to be more susceptible to short-term perturbations related to flood-drought cycles and other events. These effects may lead to significant changes in the lake volume which can complicate interpretation of the δ_L record. The rapidity of readjustment of isotopic composition following perturbation events is also dependent on the residence time of isotopes in the lake (see Horita (1990)).

In stratified lakes, or lakes with pronounced horizontal inhomogeneities, it may be necessary to account separately for epilimnion and hypolimnion volumes and exchanges, provided these have distinct isotope compositions. In modern systems, incomplete mixing can be characterised by spatial and temporal sampling to bracket potential errors to any desired level of precision, although this is not always practical. A simple approximation for systems with similar epilimnion and hypolimnion compositions is to use an average value to represent the undifferentiated lake volume. Neglecting stratification can lead to overestimation of the importance of evaporation loss if epilimnion sampling is conducted during dry, stratified periods, and underestimation of evaporation loss if sampling is conducted during wet, stratified periods. From the perspective of palaeohydrological archives, isotopic records obtained from pelagic and benthic organisms, for example, may exhibit differing isotope signatures which may be useful for examining stratification history. On the other hand, use of a single source archive may also lead to systematic bias in the palaeohydrological record. Inflow bypass or short-circuiting of the system may also reduce the effective volume of the lake during wet periods or reduce the effective input in the opposite situation. Incomplete mixing within the lake itself is also a potential source of error when applying the isotope mass-balance approach to large lakes, although such uncertainty may be reduced by using multiple records of isotopic changes in different parts of the lake. While to a large degree these propositions remain

untested, some of the complexities have been considered in theoretical terms by Lewis (1979).

Catchment runoff

One important application of lake isotope balance modelling, as suggested by Gibson et al. (2002), is the tracing of long-term runoff or water yield from the catchment area. Assuming that runoff from the catchment is equal to inflow to the lake minus precipitation on the lake, then the runoff from the drainage basin (Q_{DBA}) can be calculated as:

$$Q_{DBA} = \left\{ \frac{E_L}{x} - PL \right\} \frac{LA}{DBA} \quad (21)$$

where E_L (mm) is the lake evaporation rate, P_L (mm) is the precipitation rate on the lake, and LA/DBA is the ratio of the lake area to the drainage basin area which contributes to the lake. This simplified model assumes a headwater lake setting whereby the isotope enrichment signal is produced entirely by lake evaporation in the water body in question, and not inherited from upstream water sources. In principle, this approach may be useful for examining historical changes in runoff, but this remains to be thoroughly tested. In more complex systems, such as non-headwater lakes or string-of-lakes drainage networks, more detailed models are required to account for multiple sources and feedbacks (see also Gat and Bowser (1991); Gibson and Edwards (2002)). Overall, it is important to note that the $\delta^{18}O$ or δ^2H signals preserved in the palaeohydrological record will depend significantly on both climatic conditions and the hydrology of the lake and watershed. A continuum of settings ranging from climatically-dominated (high throughflow, low x) to hydrologically-dominated (closed basin, $x \approx 1$) is expected based on theoretical considerations, implying differential suitability of lakes for climatic reconstruction (Figure 10c). Note that drying lakes ($x > 1$) where inflow takes place once or sporadically, often will not preserve a long-term continuous sedimentary record and are therefore not expected to be well-suited to regional palaeohydrological reconstructions. Nevertheless, more gradual drying or filling of lakes on climatic timescales (decades and longer) may be represented using volume-variant versions of Equation (13) or step-wise hydrologic steady state models (i.e., Equation (15)).

Practical considerations for modern and palaeoclimate applications

For quantitative isotope balance applications, model parameterisation is normally achieved by using local climate to define humidity and temperature and, in turn, applying standard temperature- and humidity-dependent equations (i.e., Equations (5), (6) and (10)) to estimate the equilibrium and kinetic fractionations under the assumption that exchange during evaporation is fully turbulent and advection is minor. For modern studies, precipitation input is normally defined using the GNIP database, other local precipitation or groundwater database, or indirectly from proxy data or by inferring the input values from the intersection of the local evaporation line and meteoric water line.

The most difficult parameter to measure or estimate is the isotopic composition of atmospheric moisture. The two common approaches for defining δ_A include evaporation-flux-weighting (see Gibson (2002)) and the best-fit approach, whereby δ_A is constrained to fall on a precipitation-vapour tie line in δ -space (see Figure 10c), and to match the slope of the local evaporation line given by:

$$S_{LEL} = (\delta_A - \delta_p + \varepsilon/h)_2 / (\delta_A - \delta_p + \varepsilon/h)_{18} \quad (22)$$

Note that the subscripts 18 and 2 refer to ^{18}O and ^2H , respectively. The latter approach, which explicitly combines the two tracers, has been found to yield similar results to evaporation-flux-weighting for northern Canada, and adequately explains regional trends in the slopes of local evaporation lines (Gibson et al. 2005). Palaeoarchives often do not have sufficient information to explicitly resolve all components of the isotopic balance, but modern analogues have helped to develop more reasonable and realistic scenarios for interpreting past conditions. For example, the application of isotope mass balance to assess regional variations in water balance across the northern treeline in Canada has provided new insight into modern water-balance variability in boreal, tundra and transition areas (Figure 11), as well as better context for understanding the possible range of conditions preserved in palaeoclimatic and palaeohydrological archives.

Dissolved carbon

Unlike oxygen isotopes in water, which represent the solvent itself and therefore have an invariably dominant influence in the oxygen mass balance of an aqueous environmental system, carbon isotopes represent a solute that is (or was) present in relatively minor quantities. Carbon may be present in solutions in two basic forms: inorganic and organic, in which there are many different species and compounds. Isotopic compositions reflect their differing sources and subsequent transformations. Typically, dissolved inorganic carbon (DIC) is present in terrestrial environmental waters (streams, lakes, groundwaters) at concentrations up to 10 millimoles per litre. Dissolved organic carbon (DOC) including dissolved volatiles, principally methane, as well as complex organic molecules, is typically present at concentrations below 1–2 millimoles per litre but may be much higher in certain environments such as peaty lakes and groundwaters. These low budgets of carbon in terrestrial aqueous systems, relative to the dominance of the aqueous oxygen budget, dictate that $^{13}\text{C}/^{12}\text{C}$ is more susceptible to external perturbations at the time of formation or deposition of proxy media. Interpretation of $^{13}\text{C}/^{12}\text{C}$ isotope signals must also consider the possibility of post-depositional exchange that would compromise the validity of climate or environmental information.

This section describes: (i) the $\delta^{13}\text{C}$ compositions of the various inorganic and organic sources of carbon that are in contact with terrestrial waters; (ii) the interactions of these C sources with water and thus the processes that relate the $\delta^{13}\text{C}$ of waters to the $\delta^{13}\text{C}$ of sources; (iii) the $\delta^{13}\text{C}$ compositions of DIC which is the dominant or partial precursor for most of the carbon-bearing proxy media such as carbonates, plant material and biogenic solids; and (iv) the $\delta^{13}\text{C}$ of DOC that may have contributed in various ways to the preserved proxy media.

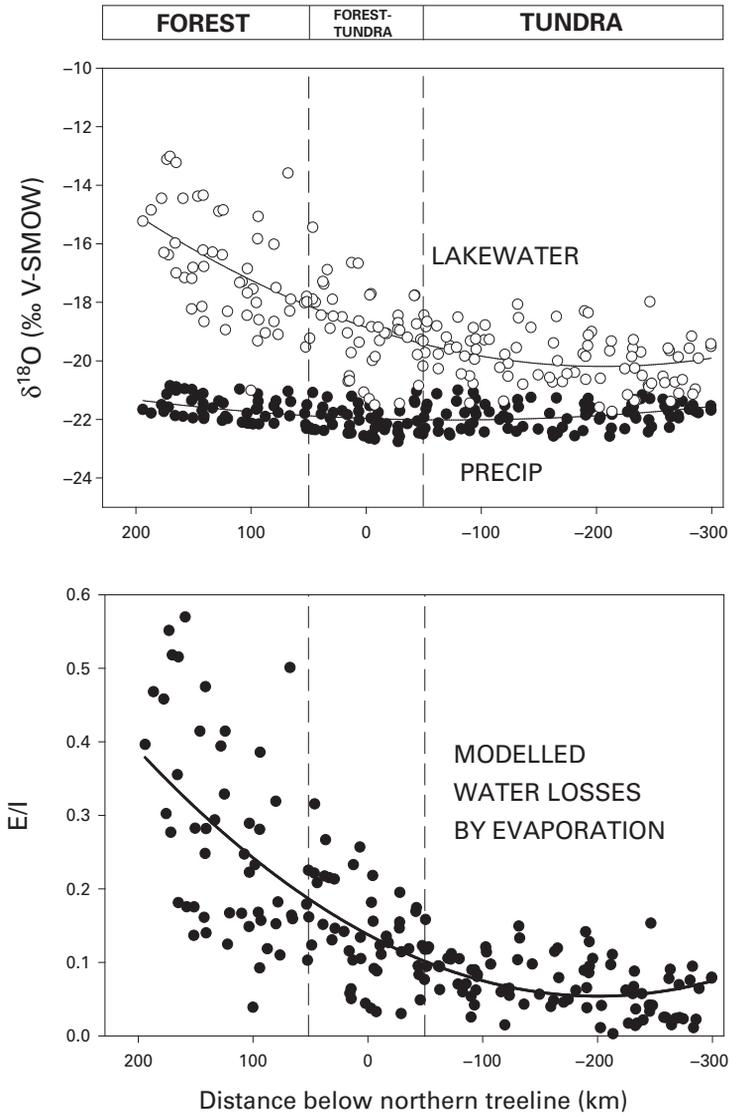


Figure 11. Gradients observed across the northern treeline in central Canada including (a) measured $\delta^{18}\text{O}$ in lake water and interpolated $\delta^{18}\text{O}$ in precipitation based on the Canadian Network for Isotopes in Precipitation database, and (b) modelled watershed losses by evaporation (expressed as evaporation/inflow ratios (E/I %) based on steady state $\delta^{18}\text{O}$ mass balance (Equation 19)). Note that gradients in the isotopic composition of lake water are larger than variations in precipitation which is attributed to higher evaporation losses at lower latitudes. Gibson and Edwards (2002) applied this dataset to quantify the frequency distribution of water budgets in boreal forest, transitional and tundra regions. Evaporative enrichment signals ($\delta_L - \delta_P$) were also used in a subset of lake basins to partition evaporation and transpiration losses.

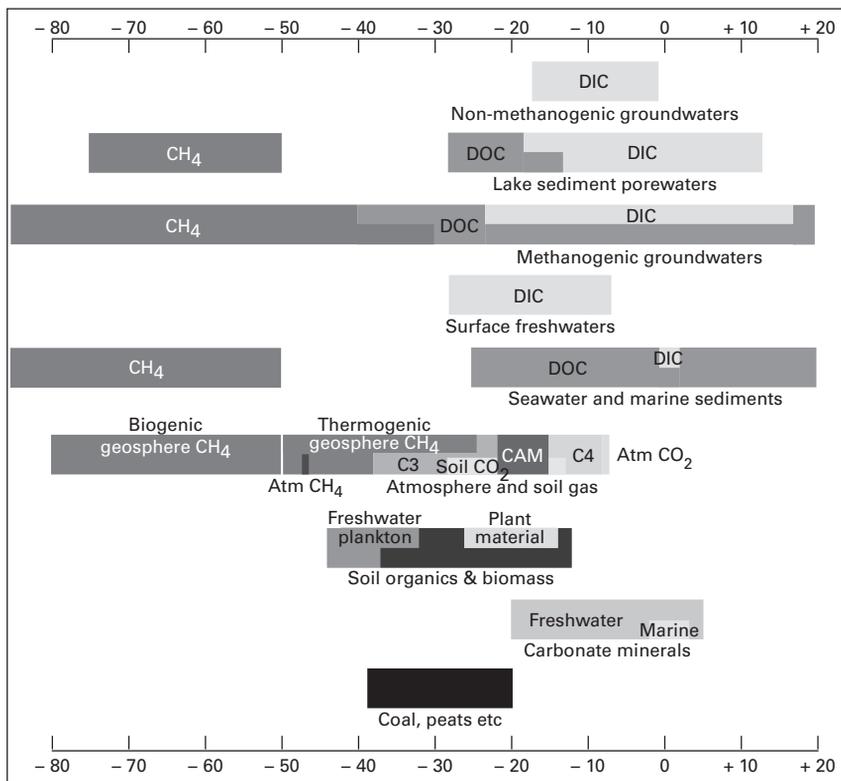


Figure 12. The $\delta^{13}\text{C}$ ranges for dissolved carbon and its sources (scale in permil with respect to VPDB).

Carbon sources in contact with terrestrial waters

A summary of the $\delta^{13}\text{C}$ ranges of potential inorganic and organic carbon sources for DIC and DOC in environmental waters is shown in Figure 12.

Atmospheric carbon: carbon dioxide and methane

Historical abundances of atmospheric carbon dioxide (CO_2) within the last 20 Ma have been lower than modern values: for example around 200 ppmv (parts per million by volume) at the Last Glacial Maximum (LGM) and 280 ppmv in the pre-industrial period (IPCC, 2003). Since the industrial revolution, atmospheric CO_2 has increased to 380 ppmv in 2004 (NOAA data, see <http://www.cmdl.noaa.gov/ccgg/insitu.html>), rising by 20% in the past 50 years. The $\delta^{13}\text{C}$ of atmospheric CO_2 was around -6.7‰ when first measured in the mid-1950s, and had decreased to -7.2‰ in 1979 and -8‰ in 1995 because fossil fuel burning adds isotopically light C (Keeling et al. 1979; 1980; 1995). This historical shift in $\delta^{13}\text{C}$ is correlated with a decrease in atmospheric radiocarbon (^{14}C), also reflecting the addition of fossil C (the 'Suess effect'; Keeling (1979)). Short-term seasonal fluctuations of $\delta^{13}\text{C}$ are superimposed on the long-term anthropogenic

shift due to variations in the rates of CO₂ uptake and release by the biosphere (Keeling et al. 1995).

Methane (CH₄) in the atmosphere has also increased over time, from around 390 ppbv (parts per billion by volume) at the LGM to 650 ppbv in pre-industrial times and 1750 ppbv today (NOAA data, see <http://www.cmdl.noaa.gov/ccgg/insitu.html>). The isotopic composition is around -47‰ (Tyler 1986; Cicerone and Oremland 1988). However the atmospheric abundance is so low that, for dissolved methane to be significant for the content and isotopic composition of carbon in terrestrial waters, there must be an additional dominant terrestrial source of CH₄ such as reductive degradation of organic material.

Carbonate minerals

Carbonate minerals are in many cases the most important contributor, directly or indirectly, to DIC in terrestrial waters. The ¹³C/¹²C ratios of carbonate minerals are determined by their origin and possible post-depositional alteration. However the likely dominance of carbonate-carbon in most environments means that significant alteration of ¹³C/¹²C occurs only in extreme environments or with prolonged exchange.

Marine carbonates have δ¹³C values of ~0‰, with a range from -2 to +3‰ depending on age, depositional environment and mineral phase. Non-marine carbonates have δ¹³C values reflecting closely the isotopic compositions of waters (lake waters, groundwaters, streams) from which they precipitated. They may be biogenic carbonates in lake sediments, diagenetic intergranular or vein carbonates in rock formations, evaporitic deposits in arid playas, speleothems, or tufas in streams in limestone terrains. Typically, δ¹³C values in these environments are in the range -20 to +5‰, though values outside this range are quite possible in special cases representing extremes of, for example, biological, evaporitic, hydrothermal or cryogenic activity in the hydrological environment (e.g., Stiller et al. (1985)). It may be noted that, in addition to carbon origin and temperature, pH of the depositional environment is also a factor in determining the δ¹³C of freshwater carbonates relative to dissolved carbonate in source water because of the pH-dependence of dissolved carbonate speciation and thus of isotopic fractionation (Clark and Fritz 1997).

Organic matter including hydrocarbons

Plant material has δ¹³C values ranging from about -38 to -8‰, dividing into narrower ranges for each of the photosynthetic pathways: -38 to -22‰ for C₃ plants, -15 to -8‰ for C₄ plants, and -30 to -13‰ for CAM plants (Deines 1980; Yeh and Wang 2001). The C₃ pathway ('Calvin cycle') dominates in terrestrial ecosystems, especially in temperate and high-latitude regions and typically produces plant material with δ¹³C values of -27‰. The C₄ pathway ('Hatch-Slack cycle') is prominent in tropical and savannah grasses and typically produces plant material with values of -13‰. The CAM (Crassulacean acid metabolism) cycle occurs mostly in succulents in arid ecosystems and essentially involves diurnal switching between C₃ and C₄ pathways leading to intermediate δ¹³C values.

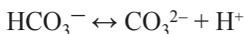
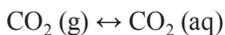
Coals, peats and intermediate deposits have δ¹³C values between -39 and -20‰ which are within the range found in modern-day plant material (see above). Organic material

in non-marine sediments, derived from ancient plant material, also has a similar range of compositions. For example, organic carbon in sediments in a freshwater lake in New York State was measured at $-27 \pm 1\%$ and depth-dependent breakdown of this material by methanogenesis followed by methane oxidation was interpreted to be responsible for variations in the $\delta^{13}\text{C}$ of DIC from -16 to $+6\%$ at different locations in the water and shallow ($<10\text{cm}$) sediment profile (Herczeg 1988). Fossil organic carbon in marine sediments has a narrower range of $\delta^{13}\text{C}$ from -27 to -19% (Hoefs 1973; Deines 1980). Liquid hydrocarbons, i.e., bulk oils, have $\delta^{13}\text{C}$ values in the approximate range -32 to -21% , mostly around -28% (Deines 1980). Volatile hydrocarbons, principally methane, have a wide range of $\delta^{13}\text{C}$ values from -80 to -25% reflecting the diversity of sources and pathways of formation (Deines 1980). Essentially these divide into biogenic methane in shallow geosphere environments and young sediments (-80 to -50% $\delta^{13}\text{C}$) and thermogenic methane associated directly or indirectly with oils or coals at greater depths (-50 to -25% $\delta^{13}\text{C}$) (Schoell 1980; 1984).

Interactions of carbon sources with water

Geochemical reactions and exchanges

Carbon dioxide in a gaseous phase dissolves in water according to Henry's Law partitioning, i.e., $C_{\text{soln}} = K_{\text{H}} P_{\text{CO}_2}$, where K_{H} is the Henry's Law constant and P_{CO_2} is the partial pressure of CO_2 . Dissolved CO_2 then becomes part of the system in which DIC is distributed among pH-dependent species HCO_3^- and CO_3^{2-} :



In general, it can be assumed that chemical exchange between the DIC species is rapid relative to the rate of dissolution and exchange between gaseous and dissolved CO_2 . Exchange between gaseous CO_2 and dissolved CO_2 may be significantly slower, for example at the air-water interface of the ocean, a lake or a stream (e.g., Zhang et al. (1995)). The rate and spatial scale of equilibration may be controlled by rates of advection or diffusion of CO_2 towards the interface and/or across the interface. Thus a perturbed or 'rough' interface may exchange CO_2 more efficiently than a calm, undisturbed interface.

Reaction between the DIC system in solution and solid carbonate phases normally occurs until carbonate dissolution-precipitation equilibrium is achieved, for example with respect to calcite:



The forward reaction, calcite dissolution, is dominated under normal environmental conditions by a reaction involving dissolved carbon dioxide:



whilst the reverse reaction, calcite precipitation, involves loss of CO_2 . The stoichiometry of these reactions in the DIC system is the background for understanding the consequent $^{13}\text{C}/^{12}\text{C}$ fractionations (Deines et al. 1974; Plummer 1977).

Geochemical equilibrium and reaction models calculate DIC speciation and simulate carbon isotope ratios in DIC based on isotopic fractionation and mass balance in relation to mineral dissolution and secondary mineral precipitation (Reardon and Fritz 1978; Wigley et al. 1978; Fontes and Garnier 1979). Although these were aimed primarily at using $\delta^{13}\text{C}$ data to estimate the extent of radiocarbon dilution by ^{14}C -dead, carbonate-derived C, they provide fairly rigorous numerical descriptions of the various pathways for evolution of DIC, taking account of equilibrium or non-equilibrium and open-system or closed-system behaviours. The widely-used geochemical modelling program PHREEQCI uses carbon isotope mass balance as a constraint on inverse modelling of water compositions (Parkhurst and Appelo 1999).

Interactions between water and CH_4 , or other organic C sources, vary from simple dissolution to oxidation to CO_2 . DIC in groundwaters in unconfined aquifers in glacial sediments in Canada has occasional anomalously high $\delta^{13}\text{C}$ values because of a small but significant contribution of CO_2 produced by microbial fermentation of organic material to CH_4 and CO_2 (Fritz et al. 1978; Barker and Fritz 1981). Dissolved CH_4 may have this type of provenance or be the product of microbial reduction of DIC. Higher organic compounds in water are closely related to their parent solid organics and thus are similar in isotopic composition.

Isotopic fractionations

Knowledge of isotopic fractionations is essential for relating $\delta^{13}\text{C}$ in a proxy indicator of palaeoclimate or palaeoenvironment to the precursor carbon source. Values of $\delta^{13}\text{C}$ in DIC or DOC and of a proxy that has grown from these aqueous carbon reservoirs tend to be dominated by the compositions of non-aqueous reservoirs modified by fractionations between them. This happens because aqueous C budgets are generally much lower than those in co-existing solid and/or gaseous phases.

The magnitudes of isotopic fractionations between the various chemical species of dissolved or gaseous carbon are generally determined by carbon bond strengths and phase transformations, so that gaseous or aqueous CO_2 in equilibrium with dissolved carbonate ions gives rise to the greatest fractionation towards light isotope ratios. Solid calcium carbonate is isotopically heavier than dissolved ionic carbonate ions with which it is in equilibrium, though the magnitude of fractionation is much less. Isotopic fractionations between carbon species may be at equilibrium or they may be affected by non-equilibrium kinetic processes. Kinetic effects are more likely in irreversible reactions, for example between solids and dissolved forms, or where microbial intervention occurs.

Figure 13 illustrates the equilibrium fractionations between the primary solid, dissolved and gaseous forms of carbon. Isotopic fractionation between $\text{CO}_2(\text{g})$ and $\text{CO}_2(\text{aq})$ is about -1% , so the $\delta^{13}\text{C}$ value of dissolved CO_2 in equilibrium with atmospheric CO_2 (-8%) is expected to be around -9% . Bicarbonate ion, HCO_3^- , in isotopic equilibrium with dissolved CO_2 at -9% is around $+1$ to $+2\%$ $\delta^{13}\text{C}$. Values of $\delta^{13}\text{C}$ for DIC in surface

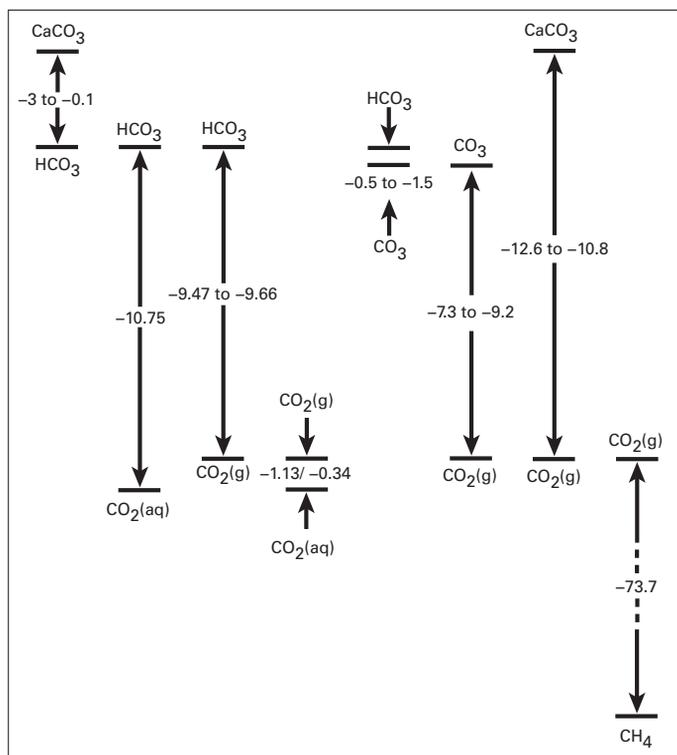


Figure 13. Equilibrium fractionations between the primary solid, dissolved and gaseous forms of carbon, based on data sources as set out in Table 1.

waters are not controlled simply by equilibrium fractionation with atmospheric CO_2 and are usually more negative than these values. There are other sources of DIC in surface waters, such as respiration of soil organic matter and dissolution of carbonates, that are quantitatively of more significance than atmospheric CO_2 .

Precipitation of carbonate minerals from solution may take place rapidly, far from chemical equilibrium, introducing the possibility of isotopic disequilibrium between DIC and precipitated carbonate. The extent to which $^{13}\text{C}/^{12}\text{C}$ fractionation is affected by carbonate precipitation kinetics varies from case to case and between experimental observations and interpretations of natural systems. In some experiments, kinetic fractionation factors decrease as the precipitation rate increases (e.g., Turner (1982)) and in others fractionation is independent of precipitation rate (Romanek et al. 1992; Jimenez-Lopez et al. 2001).

Another possible cause of kinetic isotope fractionation during calcite precipitation is outgassing of CO_2 , though reported deviations from equilibrium fractionation are small in normal hydrological environments. Carbon isotope studies of modern speleothems in Barbados show that most calcite is close to or at isotopic equilibrium with DIC (Mickler et al. 2004). Deviations from equilibrium fractionation are around $\pm 1\%$ $\delta^{13}\text{C}$ and

were attributed to both precipitation kinetics and degassing of CO_2 . Similarly, calcite precipitation from a spring in the French Pyrenees was found to occur with virtually no isotope fractionation (Dandurand et al. 1982). Kinetic fractionations that are even greater than the maximum theoretical values may occur in extreme environments. Outgassing of CO_2 as evaporating waters evolve towards brines in the Dead Sea is associated with non-equilibrium isotope fractionation. Experimental $^{13}\text{C}/^{12}\text{C}$ fractionation between $\text{CO}_2(\text{g})$ and DIC in Dead Sea brine has been measured at -16.2 to -18.2‰ , which is greater than the maximum theoretical kinetic fractionation of -11.2‰ for diffusion-controlled degassing and the fractionation of around -11‰ that is typical for $\text{CO}_2(\text{g})$ -DIC in ocean water (Stiller et al. 1985; Inoue and Sugimura 1985; Zhang et al. 1995; Barkan et al. 2001).

In many natural systems, some or all of the dissolved carbon has entered solution by non-equilibrium processes that involve kinetic isotope fractionations or irreversible stoichiometric dissolution (Dandurand et al. 1982; Usdowski and Hoefs 1986; Clark et al. 1992; Zhang et al. 1995; Skidmore et al. 2004). Simple dissolution of calcium carbonate usually proceeds without any significant isotope fractionation because it is a stoichiometric and irreversible mass transfer from solid to solution. Kinetic fractionation up to -17‰ was found in experimental dissolution of fine-grained carbonate from glacial sediments (Skidmore et al. 2004). The fractionation was found to vary with the water:solids ratio and to decline with increasing contact time.

Complex biogeochemical pathways and microbial transformations can result in substantial fractionations in their contributions to DIC and resulting biomass and/or carbonate deposits. For example, microbial mats that encrust travertine deposits at hot springs in Yellowstone, USA have variable $\delta^{13}\text{C}$ composition of total biomass from -16 to -28‰ . Within this material, specific lipids have $\delta^{13}\text{C}$ values from -12 to -37‰ . The carbon source for all of this material is CO_2 , from the atmosphere (-7 to -8‰) and the geothermal source (-5‰), so large fractionations are occurring during the growth of biomass (Zhang et al. 2004).

Dissolution of minor water-soluble components such as humic and fulvic acids from complex organic sedimentary material is likely to involve little if any isotopic fractionation unless extensive microbiological mediation is involved (Wassenaar et al. 1991). Thus DOC is likely to inherit a $\delta^{13}\text{C}$ composition similar to its parent organic material, i.e., close to -25‰ .

Microbial reduction of inorganic carbon or of higher molecular weight organics to CH_4 produces a large negative fractionation of $^{13}\text{C}/^{12}\text{C}$. Equilibrium fractionation between CH_4 and CO_2 is around -74‰ based on theoretical calculation (Bottinga 1969). Actual fractionation may be larger or smaller for microbial pathways from inorganic or organic sources (Schoell 1980; Deines 1980). Isotopic fractionation during production of CH_4 leaves the source inorganic carbon isotopically enriched which may have a significant effect in the inorganic carbon system depending on the mass balance between product and source compounds (Thorstenson et al. 1979; Barker and Fritz 1981; Aravena and Wassenaar 1993).

Typical $^{13}\text{C}/^{12}\text{C}$ fractionations for environmentally-relevant processes involving inorganic and organic carbon in aqueous, gaseous and solid phases are compiled in Table 1.

Table 1. Compilation of typical $^{13}\text{C}/^{12}\text{C}$ fractionations for environmentally-relevant processes involving inorganic and organic carbon in aqueous, gaseous and solid phases. Fractionation values are tabulated as $\delta^{13}\text{C}$ differences or experimental fractionation factors ϵ , depending on how reported in the data source.

Process	Typical fractionation (‰)	Examples
Precipitation of calcite at neutral pH and in isotopic equilibrium	+3 to +0.1 ($\text{CaCO}_3\text{-HCO}_3$) +2.3 to +1.8 ($\text{CaCO}_3\text{-HCO}_3$, 25°C)	Salomons and Mook 1986; Emrich et al. 1970; Wendt 1971; Turner 1982
Precipitation of calcite at alkaline pH and in isotopic equilibrium	+1.0 \pm 0.2 and +0.94 \pm 0.06 ($\text{CaCO}_3\text{-HCO}_3$, 25°C) +9.0 and +8.9 ($\text{CaCO}_3\text{-CO}_2$, 25°C)	Romanek et al. 1992; Jimenez-Lopez et al. 2001
Precipitation of calcite and aragonite in isotopic equilibrium	-1.4 (calcite-aragonite, 25°C)	Turner 1982
Precipitation of aragonite at alkaline pH and in isotopic equilibrium	+2.7 \pm 0.6 ($\text{CaCO}_3\text{-HCO}_3$, 25°C) +10.6 ($\text{CaCO}_3\text{-CO}_2$, 25°C)	Romanek et al. 1992
Precipitation of siderite at neutral pH and in isotopic equilibrium	+17.5 ($\text{FeCO}_3\text{-CO}_2_{\text{gas}}$) +10 ($\text{FeCO}_3\text{-CO}_2_{\text{gas}}$, 30°C) +7.5,+13.3 to +14.5 (biogenic $\text{FeCO}_3\text{-CO}_2_{\text{gas}}$, 45/30°C)	Golyshev et al. 1981; Carothers et al. 1988; Zhang et al. 2001; Romanek et al. 2003
Precipitation of siderite at alkaline pH and in isotopic equilibrium	+0.5 \pm 0.2 ($\text{FeCO}_3\text{-HCO}_3$, 25°C) +8.5 \pm 0.2 ($\text{FeCO}_3\text{-CO}_2$, 25°C)	Jimenez-Lopez and Romanek 2004
Outgassing/dissolution/exchange of CO_2 in carbonate solution at neutral pH and in isotopic equilibrium	-10.2, -9.4 to -9.7 ($\text{CO}_2_{\text{gas}}\text{-HCO}_3$) +0.3 to +1.1 ($\text{CO}_2_{\text{gas}}\text{-CO}_2_{\text{aq}}$)	Wendt 1968; Emrich et al. 1970; Mook et al. 1974; Friedman and O'Neil 1977; Szarán 1997; Zhang et al 1995; Vogel et al. 1970
Outgassing/exchange of CO_2 from carbonate solution at high pH and in isotopic equilibrium	-7.3 to -9.2 ($\text{CO}_2_{\text{gas}}\text{-CO}_3$) -5.0 \pm 0.2 ($\text{CO}_2_{\text{gas}}\text{-CO}_3$, 25°C)	Deines et al. 1974; Thode et al. 1965; Halas et al. 1997
Diffusive exch. between atmos-pheric CO_2 and DIC in seawater	-11 ($\text{CO}_2_{\text{gas}}\text{-DIC}$)	Zhang et al. 1995
Uptake of CO_2 into hyperalkaline water	\sim -20, -19.5 18°C ($\text{CO}_3\text{-CO}_2_{\text{gas}}$)	Clark et al. 1992; Usdowski and Hoefs 1986

Table 1 continued

Process	Typical fractionation (‰)	Examples
Movement of respired CO ₂ through soil	~+4 (CO ₂ in soil–CO ₂ flux at soil surface)	Cerling et al. 1991; Davidson 1995
Precipitation of calcite with CO ₂ outgassing not in isotopic equilibrium	~0 ± 1 (CaCO ₃ –DIC) +0.3 to +3.4 with decreasing precipitation rate (25°C)	Mickler et al. 2004; Dandurand et al. 1982; Turner 1982
Precipitation of calcite from evaporating brine	–16.2 to –18.2 (CO ₂ gas–DIC)	Stiller et al. 1985; Barkan et al. 2001
Precipitation of CaCO ₃ and outgassing of CO ₂ from freezing seawater	–2 to –20 (C _{lost} –C _{remaining}) (–2 for outgassing + precipitation, –20 for outgassing only)	Papadimitriou et al. 2004
Dissolution of calcite in a non-reversible reaction	~0 (DIC–CaCO ₃)	—
Rapid dissolution of very fine-grained calcite	0 to –17 (DIC–CaCO ₃)	Skidmore et al. 2004
Reduction of CO ₂ to CH ₄ at isotopic equilibrium	–73.7 (CH ₄ –CO ₂)	Bottinga 1969
Biogenic CH ₄ co-existing with DIC in groundwater but not in isotopic equilibrium	–68, –75 (CH ₄ aq–DIC)	Barker and Fritz 1981
Growth of microbial biomass associated with travertine	~–4 to –32 (C _{org} –CO ₂)	Zhang et al. 2004
Dissolution of water-soluble humics from solid organic material	~0 (C _{org diss} –C _{org solid})	Wassenaar et al. 1991

Potential climatic and temporal effects

The potential climatic and temporal influences on the interaction of C sources with water involve several factors: (i) temperature effects on geochemical reactions involving carbon transfers between solid sources and solutions; (ii) direct long-term metabolic pathways, and variations in soil and other surficial compositions in terms of environmental changes such as the ¹³C/¹²C isotope ratio of atmospheric CO₂, variations of types of organic material such as relative proportions of vegetation with C₃ and C₄ balances of organic and inorganic (i.e., carbonate) C sources; (iii) residence times of dissolved C in the available carbon reservoirs with consequences for the extent of isotopic exchange and whether equilibrium has been achieved in exchange reactions having slow kinetics.

The temperature effects on $^{13}\text{C}/^{12}\text{C}$ fractionations between gaseous atmospheric CO_2 , the various DIC species and solid carbonate are rather low compared to the temperature effects that are propagated into the $\delta^{18}\text{O}$ of freshwater carbonates. The temperature coefficients for $\delta^{13}\text{C}$ fractionation between calcite and DIC and between calcite and $\text{CO}_2(\text{g})$ are only $+0.05\text{‰}$ and -0.16‰ per $^\circ\text{C}$ respectively (Bottinga 1968; Salomons and Mook 1986). The temperature coefficient for $\delta^{18}\text{O}$ fractionation between calcite and water is around -0.23‰ per $^\circ\text{C}$ and the temperature-dependent variation of $\delta^{18}\text{O}$ in meteoric water due to atmospheric liquid–vapour fractionation is in the range 0.6 to 0.2‰ per $^\circ\text{C}$ (O’Neil et al. 1969; Rozanski et al. 1993). Therefore the direct sensitivity of $\delta^{13}\text{C}$ as a proxy for environmental temperature is relatively low. Other temporally variable environmental factors in addition to temperature affect isotopic fractionation of $^{13}\text{C}/^{12}\text{C}$, for example pH-dependent speciation of DIC, and thus cause additional uncertainties in temperature dependence.

Groundwaters in karstic and other carbonate aquifer rocks may undergo isotopic exchange between DIC and solid carbonate after the establishment of chemical equilibrium (Smith et al. 1975; Edmunds et al. 1987). It is likely that dissolution and precipitation reactions at a microscopic local scale on the solid–solution interface account for isotopic exchange in chalk which is a fine-grained calcite that retains its micritic structure. Using $\delta^{13}\text{C}$ and ^{14}C activity, the rate of isotopic exchange in a Libyan confined karst aquifer has been estimated to be equivalent to a half-life of 11,000 years (Gonfiantini and Zuppi 2003). Based on this measurement and on surface areas for water–rock exchange, half-lives from 4 ka to 40 ka for ^{13}C exchange in other aquifers were estimated.

Case studies

Selected case studies are summarised here to illustrate the potential complexity of carbon isotope systematics in water–gas–mineral–(organics) systems, especially in surface or near-surface environments.

The $\delta^{13}\text{C}$ composition of DIC in surface waters and shallow groundwaters is influenced variably by input from soil organics and carbonates, and by exchange with atmospheric CO_2 . Input from soil organics and carbonates is dominant in tributaries of the Ottawa River in Canada, where $\delta^{13}\text{C}$ of DIC varies from -8 to -16‰ in lowland carbonate catchments and upland silicate weathering terrains respectively (Telmer and Veizer 1999). This is the case also in the Rhône River in France where $\delta^{13}\text{C}$ of DIC in headwaters and downstream flow varies from -5 to -11‰ and is interpreted as being dominated by carbonate inputs with only minor influence from respiration of soil organics (Aucour et al. 1999). In the upper St Lawrence River in Canada, $\delta^{13}\text{C}$ varies from $+2.2$ to -13.7‰ , with the larger variations towards negative values being associated with the more active carbon cycle of near-shore ecosystems such as are found in creeks and marshes (Barth and Veizer 1999). Smaller catchments with lower flows and situated on non-carbonate rock may have different $\delta^{13}\text{C}$ characteristics. One such catchment in the Vosges mountains, France, has seasonal variations of $\delta^{13}\text{C}$ from -24 to -20‰ in shallow groundwaters that feed stream flow, whereas the stream at the bottom of the catchment has $\delta^{13}\text{C}$ around -12‰ (Amiotte-Suchet et al. 1999). These data show that input of CO_2 from respiration

of soil organics dominates the isotopic composition of DIC in shallow groundwater, whereas isotopic exchange with atmospheric CO₂ has taken over in the stream.

The $\delta^{13}\text{C}$ of DIC in groundwaters in carbonate terrain may indicate carbon origins that are more complex than stoichiometric reaction of soil CO₂ with calcium carbonate. DIC in a karst spring water was found to be derived from the mixing of unsaturated zone and saturated zone water sources (Emblanch et al. 2003). The $\delta^{13}\text{C}$ of each component water was characteristic, the unsaturated zone water being open to exchange with soil CO₂ and the saturated zone water being closed to exchange. This example, though taken from a specific type of karstic groundwater system with a thick unsaturated zone and deep water table, is probably representative of many shallow groundwaters in which seasonal or other temporal fluctuations of recharge and water table location cause variations in the degree of open- or closed-system behaviour with respect to CO₂ and thus variation in $\delta^{13}\text{C}$ of the DIC. Distinct $\delta^{13}\text{C}$ evolutionary pathways for unsaturated zone water according to seasonal hydrological differences have been observed in shallow chalk (Dever et al. 1982). In winter, the soil CO₂ system is isolated from exchange (closed system) with the atmosphere, and consequently soil water evolves its DIC content in isotopic equilibrium with soil CO₂. In contrast, in summer the soil is drier, the CO₂ content is higher, and DIC evolves out of isotopic equilibrium with the soil CO₂ which is exchanging with the atmosphere (open system).

The complexity of reaction pathways by which the $\delta^{13}\text{C}$ of DIC in groundwaters can evolve is illustrated by case studies from many aquifers. A single example serves to illustrate the multiplicity of processes that may be involved in addition to stoichiometric dissolution of carbonate minerals. A geochemical model of the carbon sources and sinks in a confined aquifer in the USA simulated the oxidation of organic matter, reduction of sulphate and the precipitation of calcite (McMahon and Chapelle 1991). The number of alternative models was constrained by consideration of $\delta^{13}\text{C}$ data which suggested that the CO₂ involved in DIC production in the aquifer is dominantly from biogenic fermentation rather than microbial respiration. CO₂ with the $\delta^{13}\text{C}$ signature of microbial fermentation along with organic acids and sulphate is most likely coming from confining beds that contain organics and are also cemented by carbonate. For the present purpose, however, groundwaters in confined aquifers are not of direct relevance unless discharges from them to surface have some influence on the isotopic compositions of potential proxy indicators.

There are rare cases where the $\delta^{13}\text{C}$ of shallow groundwaters feeding springs is totally controlled by dissolution of carbonate by a non-atmospheric source of CO₂. These generally occur in geothermal or tectonically-active areas. For example, CO₂ of deep-seated origin is transmitted through faults into shallow groundwaters in Sichuan, China and dissolves carbonate rock aggressively prior to feeding streams that deposit tufa (Yoshimura et al. 2004). The $\delta^{13}\text{C}$ of DIC in the outflow is a mixture between the isotopic compositions of CO₂ with a value of -3‰ and carbonate rock with +3‰. Further isotope fractionation occurs as CO₂ outgases from the stream water and tufa precipitates.

Evaporation from soils of arid regions causes enrichment of $\delta^{18}\text{O}$ in residual unsaturated zone waters (see Figures 7 and 8); the corresponding effects on $\delta^{13}\text{C}$ in soil waters of evaporation and of short-term and long-term changes in aridity are potentially quite complex. Isotopic compositions of calcrete ('caliche') in a desert area of the USA

indicated that evaporated soil waters develop enriched $\delta^{13}\text{C}$ values (Knauth et al. 2003). This enrichment was tentatively attributed to either fractionation during photosynthetic loss of water from vegetation or to kinetic isotope effects due to direct evaporation. In studying signals of long-term climate change in Bangladesh, Alam et al. (1997) considered $\delta^{13}\text{C}$ enrichment in pedogenic carbonate nodules to indicate that DIC in soil waters had changed over time due to a climate-related decrease in soil CO_2 productivity and a greater input from atmospheric CO_2 .

Implications for proxy growth and interpretation

Dissolved inorganic carbon

There are various sources for DIC: atmospheric, geological (e.g., carbonate minerals) and organic/biogenic. Atmospheric CO_2 , soil CO_2 and DIC itself (e.g., HCO_3^- in lake waters as an indicator of productivity in the C cycle) are the main potential proxies for past climate and other environmental conditions. Therefore any proposed use of $\delta^{13}\text{C}$ in inorganic materials as a proxy for past environmental or climatic conditions should have a conceptual geochemical model that can be tested or otherwise evaluated independently. The contributions of various sources of C and the processes that link them with DIC may be dependent on environmental conditions. For example, temperature and aridity are likely to have affected the balance between the alternative metabolic pathways for C_3 and C_4 vegetation.

Low sensitivity to temperature of $^{13}\text{C}/^{12}\text{C}$ fractionation between the various DIC species and solid phases and the potential complexity of various reaction paths and speciations means that DIC geochemistry introduces large uncertainties into the interpretation of variations of $\delta^{13}\text{C}$ in carbonates as palaeoclimate and palaeoenvironment proxies.

Dissolved organic carbon

The $\delta^{13}\text{C}$ of DOC is potentially useful as a proxy for past climate and environmental conditions where the organics have been immobilised and preserved in solid matrices. Specific organic compounds such as humic and fulvic acids, specific biomarkers, and methane are likely to be of greatest interest, though uncertainties about trapping and preservation and likely very low or zero abundances make these studies somewhat speculative and vulnerable to contamination by anthropogenic carbon sources.

DOC may be derived from parent organic material, for example plant material and soil humus, via intermediate biochemical processes that alter $\delta^{13}\text{C}$ values in unpredictable ways. CO_2 loss during microbial respiration would alter or fractionate $^{13}\text{C}/^{12}\text{C}$, usually to heavier ratios. Dissolved organic carbon may have complex origins including 'dead' fossil organic material that has a geological age much greater than that of the proxy sought.

Methane is unlikely to be preserved as a useful proxy of past environmental conditions in view of its reactivity in oxidising conditions and mobility as a gas phase or as a dissolved gas. However the evidence for CH_4 intervention in past processes, for example anomalously light $\delta^{13}\text{C}$ in carbonate precipitates, is an important indicator of a strongly reducing or anoxic/anaerobic environment in which methanogenic bacteria were viable. Some preliminary geochemical analyses of organics trapped as solutes or as colloids in

speleothem carbonate have been carried out, but stable isotope analyses of the organics have not yet been achieved. Trace organic carbon compounds that are found in old deep groundwaters also have the potential to provide proxy information about environmental conditions at the time of groundwater recharge. However, an origin at the surface and the possibility of mixing with organic compounds from geological sources, for instance fossil hydrocarbons, have to be investigated. Dissolved or colloidal organic carbon is itself now a medium for ^{14}C dating of old groundwaters and has been compared in various studies with ^{14}C dates inferred from co-existing dissolved inorganic carbon, with varying degrees of correlation that are indicative of the complexities of geochemical evolutions of dissolved inorganic and/or organic carbon in the subsurface.

From proxy to climate – constraints on interpretation

In attempting to reconstruct climatic conditions from proxy isotope values, we have to consider the various steps in the following basic chain: proxy→growth water→ground/soil/surface water→precipitation→climate. None is necessarily insurmountable, but the present state of knowledge in some areas may be insufficient to give a confident answer. The complete sequence applies mainly to O and H isotopes; C isotopes effectively bypass the precipitation stage. (It may not always be possible to reconstruct the O and H isotope composition of precipitation either, but from the inferred isotopic signature of soil/surface water we may still be able to draw some conclusions about climate, for example the role of evaporation.)

Proxy to growth water

The first step in the chain lies beyond the scope of this chapter; there are so many different proxies, usually with their own particular fractionation factors for O, H and C isotopes, that it is difficult to discuss in terms of a few universally-applicable caveats. In any case, as Chapters 2 to 5 show (McCarroll and Loader, Hedges et al., Leng et al., McDermott et al., all this volume), the practitioners of the mainstream proxy research areas are well aware of the constraints and difficulties in making this step.

Growth water to ground/soil/surface water

On the assumption that a realistic composition for growth water has been achieved, what are the main constraints to making the next step? Again, there are many proxies, but if we take the main themes covered by Chapters 2 to 5 (tree rings, bones, lake sediments, speleothems), certain caveats are apparent. For trees, different rooting depths make it difficult to know even approximately what section of the year's rainfall infiltration is represented in the rings; the only solution would appear to be control experiments on the nearest modern analogues in terms of species, soil conditions and likely climate regime. For bones it is essential to have a good knowledge of water and food sources for O and C isotopes respectively, though evaporation effects on drinking water sources seem likely to remain a problem area. For lake sediment proxies there is one overriding problem: determining the temperature of proxy growth. As with tree rings, studies of

modern analogues may be the only answer. For speleothems the main difficulty lies with separating seasonal from altitude effects on O and H isotopes, and the only way of doing this convincingly is by monitoring in the cave itself, assuming of course that deposition is still active.

Ground/soil/surface water to precipitation

If the previous steps have been accomplished successfully, the following are now known (where relevant): the isotopic composition of the growth water, depth of rooting in the soil (trees), predominant source of food and water (bones), temperature/season of growth in water (sediments), season and/or ultimate source of recharge (speleothems). These data now have to be linked to hydrology. For soils, how does the soil moisture profile vary seasonally in O and H isotope content? For bones, what is the likely bulk O isotope composition of the drinking water source(s), and bulk C isotope content of diet? (In the case of water, factors such as animal hibernation mean that the annual mean composition of a particular reservoir may not be appropriate.) For lakes, what is the scale of variation in O, H and C isotopes; is it only seasonal, or are there longer-term cycles? How do isotopic compositions relate to temperature and rainfall inputs, and what are the tolerances on lake water composition modelling? For speleothems, how secure is the interpretation of water source: if there is a seasonal isotope variation, does it reflect similar variation in rainfall or is there some selection mechanism?

Precipitation to climate

By this stage the O and H proxy data have been converted to a notional rainfall isotope composition, representing either the annual mean or a known portion of the annual cycle. So far this chapter has focused mainly on present-day processes; the important question now is, to what degree is the present the key to the past? There are two important elements in this: possible changes in the balance between the three terrestrial reservoirs of water referred to earlier, and possible changes to the isotope–temperature (δ -T) relationship.

Regarding the water balance, for earlier Holocene moderate climatic conditions it is reasonable to assume that present-day isotope hydrological relationships remain a good guide, with the proviso that particular climatic regimes with their associated rainfall cycles and carbon productivity may have waxed or waned in area as the various cold or warm periods occurred. Uncertainty over water balance (for example, was there more river runoff and/or isotopic selection of recharge) arises under conditions of widespread glaciation, for which relatively little present-day information exists. Therefore it becomes an issue with regard to proxies of Pleistocene age. It is not necessarily straightforward to disentangle the various factors affecting water balance. An example of this would be the fairly ubiquitous decline in groundwater recharge during the latter part of the last glaciation. Reduced rainfall seems likely to have played a major part: this is supported by (for example) pollen evidence and low speleothem/travertine growth even in non-glaciated areas. A permafrost seal in periglacial areas is a less likely contender since modern permafrost is usually far from totally impermeable. Surface ice cover would appear to preclude recharge altogether, but areas with basal melting might actively

promote it. The best that can be said is that currently there is rather little evidence for major isotope selection effects in high-latitude water balances (see discussion in Darling (2004)).

Assuming such factors can be evaluated to arrive at a notional rainfall isotope composition, how easily can this be converted to a temperature? We have seen earlier in this chapter that δ - T relationships can be viewed in three different ways: a spatial relationship based on long-term annual averages, a temporal relationship based on seasonal variability, and a temporal relationship based on long-term changes in the isotopic signature of rainfall and the temperature. The most appropriate for palaeoclimatic reconstruction is undoubtedly the last of these, but it has hitherto been established with confidence for only few sites/regions. The important question which has to be addressed, particularly when interpreting proxies deposited under different climatic regimes such as glacial climate, is to what extent the δ - T relationship established for present-day climatic conditions is also valid for past climates. One factor which will clearly influence this relationship is the change of the isotopic composition of the global ocean over time. The δ - T is sometimes resolvable by measurement: if groundwater of the right age is available, recharge temperatures can be calculated from noble gas contents, against which isotope values can be compared. However, the dispersion effects in groundwater referred to earlier render this approach less satisfactory during periods of rapid climate change, an important focus of palaeoclimate studies.

The carbon isotope effects of past climatic change are less easily approached in a quantitative way. There are several possible effects: for example the CO_2 productivity of soil tends to drop with temperature, the balance between C_3 and C_4 plants may change, and pluvial episodes may promote the development of peat-type deposits rich in reduced carbon. All these processes carry isotopic implications, as the previous section of this chapter has shown. Nevertheless if the hydrology can be determined from O and H isotopes, this should provide a more secure framework for a C-isotope interpretation of environmental conditions.

Summary

The O, H and C stable isotope compositions of proxies reflect conditions in the water and carbon cycles at the time of formation. To provide a framework for the interpretation of such proxy data now and in the past, isotopic effects in these cycles at the present day need to be understood and characterised.

The water cycle divides naturally into a number of compartments which have been studied in varying detail over the past 40 years since the birth of isotope hydrology. The starting point, precipitation, is especially important because it is the precursor back to which most O and H isotope proxy studies are attempting to relate. While much is understood about the isotope systematics of precipitation, largely owing to the existence of the IAEA-WMO Global Network for Isotopes in Precipitation (GNIP), important questions remain to be answered in relation to the isotope-temperature gradients of past climatic conditions.

The three reservoirs of water sustaining all terrestrial proxies are soil and unsaturated (vadose) zone moisture, groundwater, and surface waters. These can be viewed broadly

as the infiltration, recharge, and discharge stages of the land-based portion of the water cycle. In each case isotopic effects intervene to modify to a greater or lesser extent the stable isotope signature of antecedent precipitation. In general terms these effects vary in severity from low for groundwaters to high for surface waters. Since lake sediments of one type or another form important and accessible archives of the palaeoenvironment, the continuing development of isotope mass-balance modelling techniques is playing a significant role in interpreting the proxy isotope values.

The carbon cycle is far more complex than the water cycle even if, as here, the focus is restricted to dissolved organic and inorganic C. This is because there are several sources of both, in contrast to the single source of water (precipitation). Dissolved carbon stable isotopes are unlikely ever to feature as the 'palaeothermometers' and 'palaeopluviometers' that O and H isotopes are becoming, yet they have great potential in the interpretation of past environmental conditions where the overall geochemical conceptual model can be suitably constrained.

The conversion of proxy data into the stable isotope composition of precursor rainfall or carbon source(s), and by way of this to the characterisation of palaeoclimate and palaeoenvironment, is a multi-step process that has tended to receive most attention at the proxy end. This review shows the need to subject each step to careful scrutiny.

References

- Adar E.M., Gev I., Lipp J., Yakir D., Gat J. and Cohen Y. 1995. Utilization of oxygen-18 and deuterium in stem flow for the identification of transpiration sources: soil water versus groundwater in sand dune terrain. In: *Applied Tracers in Arid Zone Hydrology*, IAHS Publ. No. 232, pp. 329–338.
- Adar E.M., Dodi A., Geyh M., Yair A., Yakirevich A. and Issar A. 1998. Distribution of stable isotopes in arid storms: I. Relation between the distribution of isotopic composition in rainfall and in the consequent runoff. *Hydrogeol. J.* 6:50–65.
- Agemar T. 2001. Temporal variations of $\delta^2\text{H}$, $\delta^{18}\text{O}$ and deuterium excess in atmospheric moisture and improvements in the $\text{CO}_2\text{-H}_2\text{O}$ equilibration technique for the $^{18}\text{O}/^{16}\text{O}$ ratio analysis. PhD thesis, University of Heidelberg, Germany.
- Alam M.S., Keppens E. and Paeppe R. 1997. The use of oxygen and carbon isotope composition of pedogenic carbonates from Pleistocene palaeosols in NW Bangladesh, as palaeoclimatic indicators. *Quaternary Sci. Rev.* 16: 161–168.
- Allison G.B. and Barnes C.J. 1985. Estimation of evaporation from the normally "dry" Lake Frome in South Australia. *J. Hydrol.* 78: 229–242.
- Allison G.B. and Leaney F.W. 1982. Estimation of isotopic exchange parameters, using constant-feed pans. *J. Hydrol.* 55: 151–161.
- Allison G.B., Barnes C.J. and Hughes M.W. 1983. The distribution of deuterium and ^{18}O in dry soils. *J. Hydrol.* 64: 377–397.
- Allison G.B., Barnes C.J., Hughes M.W. and Leaney F.W.J. 1984. Effect of climate and vegetation on oxygen-18 and deuterium profiles in soils. In: *Isotope Hydrology 1983*. IAEA, Vienna, pp. 105–122.
- Allison G.B., Stone W.J. and Hughes M.W. 1985. Recharge in karst and dune elements of a semi-arid landscape as indicated by natural isotopes and chloride. *J. Hydrol.* 76: 1–25.
- Ambach W., Elsasser M., Moser H., Rauert W., Stichler W. and Trimborn P. 1975. Variationen des gehaltes an Deuterium, Sauerstoff-18 und Tritium während einzelner Niederschläge. *Wasser und Leben* 27: 186–192.

- Amiotte-Suchet P., Aubert D., Probst J.L., Gauthier-Lafaye F., Probst A., Andreux F. and Viville D. 1999. $\delta^{13}\text{C}$ pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges Mountains, France). *Chem. Geol.* 159: 129–145.
- Andrews J.N. and Lee D.J. 1979. Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and palaeoclimatic trends. *J. Hydrol.* 41: 233–252.
- Andrews J.E., Riding R. and Dennis P.F. 1993. Stable isotopic composition of Recent freshwater cyanobacterial carbonates from the British Isles: local and regional environmental controls, *Sedimentology* 40: 303–314.
- Araguas-Araguas L., Froehlich K. and Rozanski K. 1998. Stable isotope composition of precipitation over Southeast Asia. *J. Geophys. Res.* 103, D22: 28,721–28,742.
- Araguas-Araguas L., Froehlich K. and Rozanski K. 2000. Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. *Hydrol. Process.* 16: 1341–1355.
- Aranyosy J.F., Filly A., Tandia A.A., Louvat D., Ousmane B., Joseph A. and Fontes J.C. 1992. Estimation des flux d'évaporation diffuse sous couvert sableux en climat hyperaride, Erg de Bilma, Niger. In: *Isotope Techniques in Water Resources Development 1991*. IAEA, Vienna, pp. 309–324.
- Aravena R. and Wassenaar L.I. 1993. Dissolved organic carbon and methane in a regional confined aquifer, southern Ontario, Canada: Carbon isotope evidence for associated subsurface sources. *Appl. Geochem.* 8: 483–493.
- Aucour A.M., Sheppard S.M.F., Guyomar O. and Wattelet J. 1999. Use of ^{13}C to trace origin and cycling of inorganic carbon in the Rhône river system. *Chem. Geol.* 159: 87–105.
- Ayalon A., Bar-Matthews M. and Sass E. 1998. Rainfall-recharge relationships within a karstic terrain in the eastern Mediterranean semi-arid region, Israel: $\delta^{18}\text{O}$ and δD characteristics. *J. Hydrol.* 207: 8–31.
- Bajjali W., Clark I.D. and Fritz P. 1997. The artesian thermal groundwaters of northern Jordan: insights to their recharge history and age. *J. Hydrol.* 192: 355–382.
- Bariac T., Deleens E., Gerbaud A., Andre M. and Mariotti A. 1991. La composition isotopique (^{18}O , ^2H) de la vapeur d'eau transpiree: Etude en conditions asservies. *Geochim. Cosmochim. Ac.* 55: 3391–3402.
- Barkan E., Luz B. and Lazar B. 2001 Dynamics of the carbon dioxide system in the Dead Sea. *Geochim. Cosmochim. Ac.* 65: 355–368.
- Barker J.F. and Fritz P. 1981. The occurrence and origin of methane in some groundwater flow systems. *Can. J. Earth Sci.* 18: 1802–1816.
- Barnes C.J. and Allison G.B. 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *J. Hydrol.* 100: 143–76.
- Barth J.A.C. and Veizer J. 1999. Carbon cycle in St. Lawrence aquatic ecosystems at Cornwall (Ontario), Canada: seasonal and spatial variations. *Chem. Geol.* 159: 107–128.
- Bath A.H. 1983. Stable isotope evidence for palaeo-recharge conditions of groundwater. In: *Palaeoclimates and Palaeowaters: a Collection of Environmental Isotope Studies*. IAEA, Vienna, pp. 169–186.
- Bath A.H., Edmunds W.M. and Andrews J.N. 1979. Palaeoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer, United Kingdom. In: *Isotope Hydrology 1978, Vol II*. IAEA, Vienna, pp. 545–566.
- Bath A.H., Darling W.G., George I.A. and Milodowski A.E. 1987. $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ changes during progressive hydration of a Zechstein anhydrite formation. *Geochim. Cosmochim. Ac.* 51: 3113–3118.
- Bender M.M. 1968. Mass spectrometric studies of carbon-13 variations in corn and other grasses. *Radiocarbon* 10: 468–472.
- Berner E.K. and Berner R.A. 1987. *The Global Water Cycle, Geochemistry and Environment*. Prentice Hall, Inc, 398 pp.
- Bottinga Y. 1968. Calculation of fractionation factors for carbon and oxygen in the system calcite-carbon dioxide-water. *J. Phys. Chem.* 72: 800–808.

- Bottinga Y. 1969. Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-CO₂-graphite-methane hydrogen and water vapour. *Geochim. Cosmochim. Ac.* 33: 49–64.
- Bottinga Y. and Craig H. 1969. Oxygen isotope fractionation between CO₂ and water and the isotopic composition of the marine atmosphere. *Earth Planet. Sc. Lett.* 5: 285–295.
- Bottomley D.J., Craig D. and Johnson L.M. 1986. Oxygen-18 studies of snowmelt runoff in a small Precambrian shield watershed: Implications for streamwater acidification in acid sensitive terrain. *J. Hydrol.* 88: 213–234.
- Bowen G.J. and Wilkinson B. 2002. Spatial distribution of $\delta^{18}\text{O}$ in meteoric precipitation. *Geology* 30: 315–318.
- Bowen G.J. and Revenaugh J. 2003. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* 39: 1299. doi:10.1029/2003WR002086.
- Boyle E.A. 1997. Cool tropical temperature shift the global $\delta^{18}\text{O}$ -T relationship: An explanation for the ice core $\delta^{18}\text{O}$ -borehole thermometry conflict. *Geophys. Res. Lett.* 24: 273–276.
- Brodersen C., Pohl S., Lindenlaub M., Leibendgut C. and von Wilpert K. 2000. Influence of vegetation structure on isotope content of throughfall and soil water. *Hydrol. Process.* 14: 1439–1448.
- Brown L.J. and Taylor C.B. 1974. Geohydrology of the Kaikoura Plain, Marlborough, New Zealand. In: *Isotope Techniques in Groundwater Hydrology*, Vol I. IAEA, Vienna, 169–188.
- Brunel J.P., Walker G.R., Dighton J.C. and Moteny B. 1997. Use of stable isotopes of water to determine the origin of water used by the vegetation and to partition evapotranspiration: A case study from HAPEX-Sahel. *J. Hydrol.* 188-189: 466–481.
- Carothers W.W. Adami L.H. and Rosenbauer R.J. 1988. Experimental oxygen isotope fractionation between siderite-water and phosphoric acid liberated CO₂-siderite. *Geochim. Cosmochim. Ac.* 52: 2445–2450.
- Cerling T.E., Solomon D.K., Quade J. and Bowman J.R. 1991. On the isotopic composition of carbon in soil carbon dioxide. *Geochim. Cosmochim. Ac.* 55: 3403–3405.
- Charles C.D., Rind D., Jouzel J., Koster R.D. and Fairbanks R.G. 1994. Glacial-interglacial changes in moisture sources for Greenland: Influence on the ice core record of climate. *Science* 263: 508–511.
- Chen J., Tang C., Sakura Y., Kondoh A., Yu J., Shimada J. and Tanaka T. 2004. Spatial geochemical and isotopic characteristics associated with groundwater flow in the North China Plain. *Hydrol. Process.* 18: 3133–3146.
- Ciais P., White J.W.C., Jouzel J. and Petit J.R. 1995. The origin of present-day Antarctic precipitation from surface snow deuterium excess data. *J. Geophys. Res.* 100(D9): 18,917–18,927.
- Cicerone R.J. and Oremland R.S. 1988. Biogeochemical aspects of atmospheric methane. *Global Biogeochem. Cy.* 2: 299–327
- Clark I.D. and Fritz P. 1997. *Environmental Isotopes in Hydrogeology*, Lewis Publishers, Boca Raton, 328 pp.
- Clark I.D., Fontes J.C. and Fritz P. 1992. Stable isotope disequilibria in travertine from high pH waters: Laboratory investigations and field observations from Oman. *Geochim. Cosmochim. Ac.* 56: 2041–2050.
- Cook P.G. and Herzeg A.L. 1999. *Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Press, Boston, 529 pp.
- Craig H. 1953. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Ac.* 3: 53–92.
- Craig H. 1961. Isotopic variations in meteoric waters. *Science* 133: 1702–1703.
- Craig H. and Gordon L.I. 1965. Deuterium and oxygen-18 variations in the ocean and marine atmosphere. In Tongiorgi E. (ed.), *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, Pisa: Cons. Naz. Rich. Lab. Geol. Nucl., pp. 9–130.
- Cuffey K.M., Clow G.D., Alley R.B., Stuiver M., Waddington E.D. and Saltus R.W. 1995. Large Arctic temperature change at the Wisconsin-Holocene glacial transition. *Science* 270: 455–458.

- Dandurand J.L., Gout R., Hoefs J., Menschell G., Schott J. and Usdowski E. 1982. Kinetically controlled variations of major components and carbon and oxygen isotopes in a calcite-precipitating spring. *Chem. Geol.* 36: 299–315.
- Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* 16: 436–468.
- Darling W.G. 2004. Hydrological factors in the interpretation of stable isotopic proxy data present and past: a European perspective. *Quaternary Sci. Rev.* 23: 743–770.
- Darling W.G., Gizaw B. and Arusei M.K. 1996. Lake-groundwater relationships and fluid-rock interaction in the East African Rift Valley: Isotopic evidence. *J. Afr. Earth Sci.* 22: 423–431.
- Darling W.G., Bath A.H. and Talbot J.C. 2003. The O and H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrol. Earth Syst. Sc.* 7: 183–195.
- Darling W.G., Edmunds W.M., Kinniburgh D.G. and Kotoub S. 1987. Sources of recharge to the Basal Nubian Sandstone aquifer, Butana Region, Sudan. In: *Isotope Techniques in Water Resources Development*. IAEA, Vienna, pp. 205–224.
- Davidson G.R. 1995. The stable isotopic composition and measurement of carbon in soil CO₂. *Geochim. Cosmochim. Ac.* 59: 2485–2489.
- Dawson T.E. 1993. Water sources of plants as determined from xylem-water isotopic composition: perspectives on plant competition, distribution, and water relations. In: Ehleringer J.R., Hall A.E. and Farquhar G.D. (eds), *Stable Isotopes and Plant Carbon–Water Relations*. Academic Press, San Diego, CA, pp. 465–496.
- Deak J., Deseo E., Bohlke J.K. and Revesz K. 1996. Isotope hydrology studies in the Szigetkoz region, northwest Hungary. In: *Isotopes in Water Resources Management, Vol I*. IAEA, Vienna, pp. 419–432.
- Deak J., Forizs I., Deseo E. and Hertelendi E. 1993. Origin of groundwater and dissolved ammonium in SE Hungary: evaluation by environmental isotopes. In: *Tracers in Hydrology*, IAHS Publ. No. 215, pp. 117–124.
- Deines P. 1980. The isotopic composition of reduced organic carbon. In: Fritz P. and Fontes J.C. (eds), *Handbook of Environmental Isotope Geochemistry, Vol. 1, The Terrestrial Environment*, A. Elsevier, Amsterdam, pp. 329–406.
- Deines P., Langmuir D. and Harmon R.S. 1974. Stable carbon isotope ratios and the existence of a gas phase in the evaluation of carbonate groundwaters. *Geochim. Cosmochim. Ac.* 38: 1147–1164.
- Dever L., Durand R., Fontes J.C. and Vachier P. 1982. Géochimie et teneurs isotopiques des systèmes saisonniers de dissolution de la calcite dans un sol sur craie. *Geochim. Cosmochim. Ac.* 46: 1947–1956.
- Dever L., Travi Y., Barbecot F., Marlin C. and Gibert E. 2001. Evidence for palaeowaters in the coastal aquifers of France. In: Edmunds W.M. and Milne C.J. (eds), *Palaeowaters in Coastal Europe*. Geol. Soc. Lond. Spec. Publ. No. 189, pp. 93–106.
- DeWalle D.R. and Swistock B.R. 1994. Differences in oxygen-18 content of throughfall and rainfall in hardwood and coniferous forests. *Hydrol. Process.* 8: 75–82.
- Dincer T., Al-Mugrin A. and Zimmerman U. 1974. Study of the infiltration and recharge through the sand dunes in arid zones with special reference to the stable isotopes and thermonuclear tritium. *J. Hydrol.* 23:79–109.
- Duane M.J., Al-Zamel A. and Eastoe C.J. 2004. Stable isotope (chlorine, hydrogen and oxygen), geochemical and field evidence for continental fluid flow vectors in the Al-Khiran sabkha. *J. Afr. Earth Sci.* 40: 49–60.
- Durand P., Neal M. and Neal C. 1993. Variations in stable oxygen isotope and solute concentrations in small submediterranean montane streams. *J. Hydrol.* 144: 283–290.
- Edmunds W.M. and Smedley P.L. 2000. Residence time indicators in groundwaters: The East Midlands Triassic Sandstone aquifer. *Appl. Geochem.* 15: 737–752.
- Edmunds W.M., Buckley D.K., Darling W.G., Milne C.J., Smedley P.L. and Williams A.T. 2001. In: Edmunds W.M. and Milne C.J. (eds), *Palaeowaters in Coastal Europe*. Geol. Soc. Lond. Spec. Publ. No. 189, pp. 71–92.

- Edmunds W.M., Cook J.M., Darling W.G., Kinniburgh D.G., Miles D.L., Bath A.H., Morgan-Jones M. and Andrews J.N. 1987. Baseline geochemical conditions in the Chalk aquifer, Berkshire, U.K.: A basis for groundwater quality management. *Appl. Geochem.* 2: 251–274.
- Edmunds W.M., Dodo A., Djoret D., Gasse F., Gaye C.B., Goni I.B., Travi Y., Zouari K. and Zuppi G.M. 2004. Groundwater as an archive of climatic and environmental change: Europe to Africa. In: Battarbee R.W., Gasse F., and Stickley C.E. (eds), *Past Climate Variability through Europe and Africa*. Springer, Dordrecht, pp. 279–306.
- Edwards T.W.D. 1993. Interpreting past climate from stable isotopes in continental organic matter. In: Swart P.K., Lohmann K.C., McKenzie J. and Savin S. (eds), *Climate Change in Continental Isotopic Records*. *Geophys. Monogr.* 78, Am. Geophys. Union, Washington, pp. 333–341.
- Ehhalt D.H. 1974. Vertical profiles of HTO, HDO and H₂O in the troposphere. NCAR Tech. Note, NCAR-TN/STR-100.
- Eichinger L., Rauert W., Stichler W., Bertleff B. and Egger R. 1984. Comparative study of different aquifer types in Central Europe, using environmental isotopes. In: *Isotope Hydrology 1983*. IAEA, Vienna, pp. 271–289.
- Emblanch C., Zuppi G.M., Mundy J., Blavoux B. and Batiot C. 2003. Carbon-13 of TDIC to quantify the role of the unsaturated zone: the example of the Vaucluse karst systems (Southeastern France). *J. Hydrol.* 279: 262–274.
- Emrich K., Ehhalt D.H. and Vogel J.C. 1970. Carbon isotope fractionation during the precipitation of calcium carbonate. *Earth Planet. Sc. Lett.* 8: 363–371.
- EPICA community members. 2004. Eight glacial cycles from an Antarctic ice core. *Nature* 429: 623–628.
- Epstein S. and Mayeda T.K. 1953. Variation of ¹⁸O content of waters from natural sources. *Geochim. Cosmochim. Ac.* 4: 213–224.
- Epstein S., Yapp C.J. and Hall J.H. 1976. The determination of the D/H ratio of non-exchangeable hydrogen in cellulose extracted from aquatic land plants. *Earth Planet. Sc. Lett.* 30: 241–251.
- Farah E.A., Mustafa E.M.A. and Kumai H. 2000. Sources of groundwater recharge at the confluence of the Niles, Sudan. *Environ. Geol.* 39: 667–672.
- Flora O. and Longinelli A. 1989. Stable isotope hydrology of a classical Karst area, Trieste, Italy. In: *Isotope Techniques in the Study of the Hydrology of Fractured and Fissured Rocks*. IAEA, Vienna, pp. 203–213.
- Fontes J.C. and Zuppi G.M. 1976. Isotopes and water chemistry in sulphide-bearing springs of Central Italy. In: *Interpretation of Environmental Isotope and Hydrogeochemical data in Ground Water Hydrology*. IAEA, Vienna, pp. 143–158.
- Fontes J.C. and Garnier J.M. 1979. Determination of the initial ¹⁴C activity of the total dissolved carbon: A review of the existing models and a new approach. *Water Resour. Res.* 15: 399–413.
- Fontes J.C., Pouchan P., Saliege J.F. and Zuppi G.M. 1980. Environmental isotope study of groundwater systems in the Republic of Djibouti. In: *Arid Zone Hydrology*. IAEA, Vienna, pp. 237–262.
- Fontes J.C., Andrews J.N., Edmunds W.M., Guerre A. and Travi Y. 1991. Palaeorecharge by the Niger River (Mali) deduced from groundwater geochemistry. *Water Resour. Res.* 27: 199–214.
- Fricke H.C. and O'Neil J.R. 1999. The correlation between ¹⁸O/¹⁶O ratios of meteoric water and surface air temperature: its use in investigating terrestrial climate change over geologic time. *Earth Planet. Sc. Lett.* 170: 181–196.
- Friedman I. 1953. Deuterium content of natural waters and other substances. *Geochim. Cosmochim. Ac.* 4: 89–103.
- Friedman, I. and O'Neil J.R. 1977. Compilation of stable isotope fractionation factors of geochemical interest. In: Fleischer M. (ed.) *Data of Geochemistry*, U.S. Geological Survey Professional Paper 440-KK, 6th ed., USGS, Reston VA.
- Fritz P. 1981. River waters. In: Gat J.R. and Gonfiantini R (eds), *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*. Technical Reports Series No. 210. IAEA, Vienna, pp. 177–201.

- Fritz P., Reardon E.J., Barker J., Brown R.M., Cherry J.A., Killey R.W.D. and McNaughton D. 1978. The carbon isotope geochemistry of a small groundwater system in northeastern Ontario. *Wat. Resour. Res.* 14: 1059–1067.
- Fritz P., Mozeto A.A. and Reardon E.J. 1985. Practical considerations on carbon isotope studies on soil carbon dioxide. *Chem. Geol. (Isot. Geosci.)* 58: 89–95.
- Gat J.R. 1981. Lakes. In: Gat J.R. and Gonfiantini R. (eds), *Stable Isotope Hydrology — Deuterium and Oxygen-18 in the Water Cycle*. Tech. Rep. Series No. 210, IAEA, Vienna, pp. 203–221.
- Gat J.R. 1995. Stable isotopes of fresh and saline lakes. In: Lerman A., Imboden D. and Gat J.R. (eds), *Physics and Chemistry of Lakes*. Springer-Verlag, New York, pp. 139–166.
- Gat J.R. 1996. Oxygen and hydrogen isotopes in the hydrological cycle. *Annu. Rev. Earth Pl. Sc.* 24: 225–262.
- Gat J.R. 2000. Atmospheric water balance – the isotopic perspective. *Hydrol. Process.* 14: 1357–1369.
- Gat J.R. and Tzur Y. 1967. Modification of the isotopic composition of rainwater by processes which occur before groundwater recharge. In: *Isotopes in Hydrology*. IAEA, Vienna, pp. 49–60.
- Gat J.R. and Levy Y. 1978. Isotope hydrology of inland sabkhas in the Bardawil area, Sinai. *Limnol. Oceanogr.* 23: 841–850.
- Gat J.R. and Bowser C.J. 1991. Heavy isotope enrichment in coupled evaporative systems. In: Taylor H.P., O’Neil J.R. and Kaplan I.R. (eds), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. Spec. Publ. No. 3, The Geochem. Society, San Antonio, Texas, pp. 159–168.
- Gat J.R. and Matsui E. 1991. Atmospheric water balance in the Amazon basin: An isotopic evapotranspiration model. *J. Geophys. Res.* 96(D7): 13,179–13,188.
- Gedzelmann S.D. and Lawrence J.R. 1990. The isotopic composition of precipitation from two extratropical cyclones. *Mon. Weather Rev.* 118: 495–509.
- Gehrels J.C., Peeters J.E.M., de Vries J.J. and Dekkers M. 1998. The mechanism of soil water movement as inferred from ^{18}O stable isotope studies. *Hydrolog. Sci. J.* 43: 579–594.
- Geirnaert W. and Laeven M.P. 1992. Composition and history of ground water in the western Nile Delta. *J. Hydrol.* 138: 169–189.
- Genty D., Baker A., Massulat M., Proctor C., Gilmour M., Poris-Branchu E. and Hamelin B. 2001. Dead carbon in stalagmites: carbonate bedrock paleodissolution vs ageing of soil organic matter. Implications for ^{13}C variations in speleothems. *Geochim. Cosmochim. Ac.* 65: 3443–3457.
- Genty D., Plagnes V., Causse C., Cattani O., Stievenard M., Falourd S., Blamart D., Ouahdi R. and Van-Exter S. 2002. Fossil water in large stalagmite voids as a tool for paleoprecipitation stable isotope composition reconstitution and paleotemperature calculation. *Chem. Geol.* 184: 83–95.
- Gibson J.J. 2002. A new conceptual model for predicting isotope enrichment of lakes in seasonal climates. *International Geosphere Biosphere Programme IGBP PAGES News* 10: 10–11.
- Gibson J.J. and Edwards T.W.D. 2002. Regional surface water balance and evaporation–transpiration partitioning from a stable isotope survey of lakes in northern Canada. *Global Biogeochem. Cy.* 16: 1026. doi:10.1029/2001GB001839.
- Gibson J.J., Prepas E.E. and McEachern P. 2002. Quantitative comparison of lake throughflow, residency, and catchment runoff using stable isotopes: modelling and results from a survey of boreal lakes. *J. Hydrol.* 262: 128–144.
- Gibson J.J., Edwards T.W.D., Birks S.J., St. Amour N.A., Buhay W., McEachern P., Wolfe B.B. and Peters D.L. 2005. Progress in Isotope Tracer Hydrology in Canada. *Hydrol. Process.* 19: 303–327.
- Giggenbach W. 1971. Isotopic composition of waters of the Broadlands geothermal field. *New Zeal. J. Sci.* 14: 959–970.
- Giggenbach W., Gonfiantini R. and Panichi C. 1983. Geothermal systems. In: *Guidebook on Nuclear Techniques in Hydrology*. Tech. Rep. Series No. 91, pp. 359–380.
- Gleick P. 2000. *The World’s Water 2000–2001*. Island Press, Washington D.C., 315 pp.

- Goller R., Wilcke W., Leng M.J., Tobschall H.J., Wagner K., Valarezo C. and Zech W. 2005. Tracing water paths through small catchments under a tropical montane rain forest in south Ecuador by an oxygen isotope approach. *J. Hydrol.* 308: 67–80.
- Golyshev S.I., Padalko N.L. and Pechenkin S.A. 1981. Fractionation of stable oxygen and carbon stable isotopes in carbonate systems. *Geochem. Intl.* 18: 85–99.
- Gonfiantini R. 1986. Environmental isotopes in Lake Studies. In: Fritz P. and Fontes J.C. (eds), *Handbook of Environmental Isotope Geochemistry: Vol 2, The Terrestrial Environment*, B. Elsevier, Amsterdam, pp. 113–168.
- Gonfiantini R. and Zuppi G.M. 2003. Carbon isotopic exchange rate of DIC in karst groundwater. *Chem. Geol.* 197: 319–336.
- Gonfiantini R., Conrad G., Fontes J.C., Sauzay G. and Payne B.R. 1974. Etude isotopique de la nappe du Continental Intercalaire et de ses relations avec les autres nappes du Sahara septentrional. In: *Isotope Techniques in Groundwater Hydrology, Vol. I*. IAEA, Vienna, pp. 227–241.
- Halas S. and Krouse H.R. 1982. Isotopic abundances of water of crystallization of gypsum from the Miocene evaporite formation, Carpathian Foredeep, Poland. *Geochim. Cosmochim. Ac.* 46: 293–296.
- Halas S., Szaran J. and Niezgodna H. 1997. Experimental determination of carbon isotope equilibrium fractionation between dissolved carbonate and carbon dioxide. *Geochim. Cosmochim. Ac.* 61: 2691–2695.
- Hedges R.W.E., Stevens R.E. and Koch P.L. This volume. Isotopes in bones and teeth. In: Leng M.J. (ed.), *Isotopes in Palaeoenvironmental Research*. Springer, Dordrecht, The Netherlands.
- Hendy G. 1971. The isotopic geochemistry of speleothems. *Geochim. Cosmochim. Ac.* 35: 801–824.
- Herczeg A.L. 1988. Early diagenesis of organic matter in lake sediments: a stable carbon isotope study of pore waters. *Chem. Geol. (Isot. Geosci.)* 72: 199–209.
- Herrmann A. and Stichler W. 1980. Groundwater-runoff relationships. *Catena* 7: 251–264.
- Hoefs J. 1973. *Stable Isotope Geochemistry*. Springer-Verlag, Berlin, 140 pp.
- Hoffmann G., Werner M. and Heimann M. 1998. Water isotope module of the ECHAM atmospheric general circulation model: A study on timescales from days to several years. *J. Geophys. Res.* 103(D14): 16,871–16,896.
- Holdsworth G., Fogarasi S. and Krouse H.R. 1991. Variation of the stable isotopes of water with altitude in the Saint Elias Mountains of Canada. *J. Geophys. Res.* 96(D4): 7483–7494.
- Holmes J.A. 1996. Trace-element and stable-isotope geochemistry of non-marine ostracod shells in Quaternary paleoenvironmental reconstruction. *J. Paleolimnol.* 15: 223–235.
- Horita J. 1990. Stable isotope paleoclimatology of brine inclusions in halite: modeling and application to Searles Lake, California. *Geochim. Cosmochim. Ac.* 54: 2059–2073.
- Horita J. and Wesolowski D. 1994. Liquid-vapour fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature. *Geochim. Cosmochim. Ac.* 47: 2314–2326.
- Hunt R.J., Bullen T.D., Krabbenhoft D.P. and Kendall C. 1998. Using stable isotopes of water and strontium to investigate the hydrology of a natural and a constructed wetland. *Ground Water* 36: 434–443.
- Iacumin P. and Longinelli A. 2002. Relationship between $\delta^{18}\text{O}$ values for skeletal apatite from reindeer and foxes and yearly mean $\delta^{18}\text{O}$ values of environmental water. *Earth Planet. Sc. Lett.* 201: 213–219.
- IAEA (International Atomic Energy Agency). 1992. *Statistical treatment of environmental isotope data in precipitation*. 2nd edition. Technical Report Series No. 331. IAEA, Vienna, 784 pp.
- IAEA (International Atomic Energy Agency). 2002. *GNIP Maps and Animations*. IAEA, Vienna, <http://isohis.iaea.org>.
- Inoue H. and Sugimura Y. 1985. Carbon isotopic fractionation during the CO_2 exchange process between air and seawater under equilibrium and kinetic conditions. *Geochim. Cosmochim. Ac.* 49: 2453–2460.

- IPCC (Intergovernmental Panel on Climate Change). 2003. Workshop on Climate Sensitivity, Paris, 2003.
- Ito E. 2001. Application of stable isotope techniques to inorganic and biogenic carbonates. In: Last W.M. and Smol J.P. (eds), *Tracking Environmental Change Using Lake Sediments, Vol. 2: Physical and Chemical Techniques*. Kluwer Academic Publishers, Dordrecht, pp. 351–371.
- Jacob H. and Sonntag C. 1991. An 8-year record of the seasonal variations of ^2H and ^{18}O in atmospheric water vapour and precipitation at Heidelberg, Germany. *Tellus* 43B: 291–300.
- Jimenez-Lopez C. and Romanek C.S. 2004. Precipitation kinetics and carbon isotope partitioning of inorganic siderite at 25°C and 1 atm. *Geochim. Cosmochim. Ac.* 68: 557–571.
- Jimenez-Lopez C., Caballero E., Huertas F.J. and Romanek C.S. 2001. Chemical, mineralogical and isotope behaviour, and phase transformation during the precipitation of calcium carbonate minerals from intermediate ionic solution at 25°C. *Geochim. Cosmochim. Ac.* 65: 3219–3231.
- Johnsen S.J., Dahl-Jensen D., Dansgaard W. and Gundestrup N. 1995. Greenland palaeotemperatures derived from GRIP borehole temperature and ice core isotope profiles. *Tellus* 47B: 624–629.
- Johnsen S.J., Dahl-Jensen D., Gundestrup N., Steffensen J.P., Clausen H.B., Miller H., Masson-Delmotte V., Sveinbjornsdottir A.E. and White J. 2001. Oxygen isotope and palaeotemperature records from six Greenland ice-core stations: Camp Century, Dye-3, GRIP, GISP2, Renland and NorthGRIP. *J. Quaternary Sci.* 16: 299–307.
- Johnson D.G., Jucks K.W., Traub W.A. and Chance K.V. 2001. Isotopic composition of stratospheric water vapour: Measurements and photochemistry. *J. Geophys. Res.* 106D: 12,211–12,217.
- Jouzel J. 1999. Calibrating the isotopic paleothermometer. *Science* 286: 910–911.
- Jouzel J. and Merlivat L. 1984. Deuterium and oxygen-18 in precipitation, modelling of the isotope effect during snow formation. *J. Geophys. Res.* 89D: 11,749–11,757.
- Jouzel J., Koster R.D., Suozzo R.J., Russell G.L., White J.W.C. and Broecker W.S. 1991. Simulations of the HDO and H_2^{18}O atmospheric cycles using the NASA GISS General Circulation Model: Sensitivity experiments for present-day conditions. *J. Geophys. Res.* 96D: 7495–7507.
- Jouzel J., Hoffmann G., Koster R.D. and Masson V. 2000. Water isotopes in precipitation: data/model comparison for present-day and past climates. *Quaternary Sci. Rev.* 19: 363–379.
- Jouzel J., Koster R.D., Suozzo R.J. and Russell G.L. 1994. Stable water isotope behaviour during the last glacial maximum: A general circulation model analysis. *J. Geophys. Res.* 99D: 25,791–25,801.
- Jouzel J., Vimeux F., Caillon N., Delaygue G., Hoffmann G., Masson-Delmotte V. and Parrenin F. 2003. Magnitude of isotope/temperature scaling for interpretation of central Antarctic ice cores. *J. Geophys. Res.* 108D: 4361. doi:10.1029/2002JD002677.
- Kaufman A., Bar-Matthews M., Ayalon A. and Carmi I. 2003. The vadose flow above Soreq Cave, Israel: a tritium study of the cave waters. *J. Hydrol.* 273: 155–163.
- Keeling C.D. 1979. The Suess effect: 13-Carbon – 14-Carbon interrelations. *Environ. International* 2: 229–300.
- Keeling C.D., Mook W.G. and Tans P.P. 1979. Recent trends in the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric carbon dioxide. *Nature* 277: 121–123.
- Keeling C.D., Bacastow R.B. and Tans P.P. 1980. Predicted shift in the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric carbon dioxide. *Geophys. Res. Lett.* 7: 505–508.
- Keeling C.D., Whorf T.P., Wahlen M. and van der Plicht J. 1995. Interannual extremes in the rate of rise and atmosphere carbon dioxide since 1980. *Nature* 375: 666–670.
- Keith D.W. 2000. Stratosphere-troposphere exchange, Inferences from the isotopic composition of water vapour. *J. Geophys. Res.* 105D: 15,167–15,173.
- Keith M.L. and Weber J.N. 1964. Isotopic composition and environmental classification of selected limestones and fossils. *Geochim. Cosmochim. Ac.* 28: 1787–1816.
- Kendall C. and Coplen T.B. 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol. Process.* 15: 1363–1393.
- Knauth L.P. and Roberts S.K. 1991. The hydrogen and oxygen isotope history of the Silurian-Permian hydrosphere as determined by direct measurement of fossil water. In: Taylor H.P.,

- O'Neil J.R. and Kaplan I.R. (eds), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. Spec. Publ. No. 3, The Geochem. Society, San Antonio, Texas, pp. 91–104.
- Knauth L.P., Brilli M. and Klonowski S. 2003. Isotope geochemistry of caliche developed on basalt. *Geochim. Cosmochim. Ac.* 67: 185–195.
- Kortelainen N.M. and Karhu J.A. 2004. Regional and seasonal trends in the oxygen and hydrogen isotope ratios of Finnish groundwaters: a key for mean annual precipitation. *J. Hydrol.* 285: 143–157.
- Krabbenhoft D.P., Bowser C.J. and Kendall C. 1994. Use of O-18 and deuterium to assess the hydrology of groundwater-lake systems. *Advances in Chemistry Series 237*: 67–90.
- Krishnamurthy R.V. and Bhattacharya S.K. 1991. Stable oxygen and hydrogen isotope ratio in shallow ground waters from Northern India and a study of the role of evapotranspiration in the Indian monsoon. In: Taylor H.P., O'Neil J.R. and Kaplan I.R. (eds), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. Spec. Publ. No. 3, The Geochem. Society, San Antonio, Texas, pp. 1–7.
- Krouse H.R. and McKay J.R. 1971. Application of the $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ abundances to the problem of lateral mixing in the Liard/Mackenzie river system, Canada. *Can. J. Earth Sci.* 8: 1107–1115.
- Kurita N., Yoshida N., Inoue, G. and Chayanova E.A. 2004. Modern isotope climatology of Russia: A first assessment. *J. Geophys. Res.*, 109D: D03102. doi:10.1029/2003JD003404.
- Lambs L. and Berthelot M. 2002. Monitoring water from the underground to the tree: first results with a new sap extractor on a riparian woodland. *Plant Soil* 242: 197–207.
- Landon M.K., Delin G.N., Komor S.C. and Regan C.P. 1999. Comparison of the stable-isotopic composition of soil water collected from suction lysimeters, wick samplers, and cores in a sandy unsaturated zone. *J. Hydrol.* 224: 45–54.
- Lange J., Greenbaum N., Husary S., Timmer J., Leibundgut C. and Schick A.P. 2003. Tracers for runoff generation studies in a Mediterranean region: comparison of different scales. *IAHS Publ.* 278: 117–123.
- Laudon H., Seibert J., Kohler S. and Bishop K. 2004. Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen-18 in meltwater, soil water, and runoff. *Water Resour. Res.* 40: W03102. doi:10.1029/2003WR002455.
- Lawler H.A. 1987. Sampling for isotopic responses in surface waters. *Earth Surf. Processes* 12: 551–559.
- Leng M.J., Lamb A.L., Heaton T.H.E., Marshall J.D., Wolfe B.B., Jones M.D., Holmes J.A. and Arrowsmith C. This volume. Isotopes in lake sediments. In: Leng M.J. (ed.), *Isotopes in Palaeoenvironmental Research*. Springer, Dordrecht, The Netherlands.
- Lewis S. 1979. Environmental isotope balance of Lake Kinneret as a tool in evaporation rate estimates. In: *Isotopes in Lake Studies*. IAEA, Vienna, pp. 33–65.
- Li H.C. and Ku T.L. 1997. $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariance as a paleohydrological indicator for closed-basin lakes. *Palaeogeogr. Palaeoecol.* 133: 69–80.
- Liu B., Phillips F., Hoines S., Campbell R. and Sharma P. 1995. Water movement in desert soil traced by hydrogen and oxygen isotopes, chloride, and chlorine-36, southern Arizona. *J. Hydrol.* 168: 91–110.
- Love A.J., Herczeg A.L., Sampson L, Cresswell R.G. and Fifield L.K. 2000. Sources of chloride and implications for ^{36}Cl dating of old groundwater, southwestern Great Artesian Basin, Australia. *Water Resour. Res.* 36: 1561–1574.
- Majoube M. 1971. Fractionnement en oxygene-18 et en deuterium entre l'eau et sa vapeur. *J. Chem. Phys.* 197: 1423–1436.
- Manzano M., Custodio E., Loosli H.H., Cabrera M.C., Riera X. and Custodio J. 2001. Palaeowater in coastal aquifers of Spain. In: Edmunds W.M. and Milne C.J. (eds), *Palaeowaters in Coastal Europe*. *Geol. Soc. Lond. Spec. Publ. No. 189*, pp. 107–138.
- Marechal J.C. and Etcheverry D. 2003. The use of ^3H and ^{18}O tracers to characterize water inflows in Alpine tunnels. *Appl. Geochem.* 18: 339–351.
- Mathieu R. and Bariac T. 1996. An isotopic study (^2H and ^{18}O) on water movements in clayey soils under a semiarid climate. *Water Resour. Res.* 32: 779–789.

- Matsui E., Salati F., Friedman I. and Brinkman W.L.F. 1976. Isotopic hydrology in the Amazonia, 2. Relative discharges of the Negro and Solimoes rivers through ^{18}O concentrations. *Water Resour. Res.* 12: 781–785.
- McCarroll D. and Loader N. This volume. Isotopes in tree rings. In: Leng M.J. (ed.), *Isotopes in Palaeoenvironmental Research*. Springer, Dordrecht, The Netherlands.
- McDermott F., Schwarcz H. and Rowe P.J. This volume. Isotopes in speleothems. In: Leng M.J. (ed.), *Isotopes in Palaeoenvironmental Research*. Springer, Dordrecht, The Netherlands.
- McDonnell J.J., Stewart M.K. and Owens I.F. 1991. Effect of catchment-scale subsurface mixing on stream isotopic response. *Water Resour. Res.* 27: 3065–3073.
- McMahon P.B. and Chapelle F.H. 1991. Geochemistry of dissolved inorganic carbon in a Coastal Plain aquifer. 2. Modeling carbon sources, sinks, and $\delta^{13}\text{C}$ evolution. *J. Hydrol.* 127: 109–135.
- Menot-Combes G., Burns S.J. and Leuenberger M. 2002. Variations of $^{18}\text{O}/^{16}\text{O}$ in plants from temperate peat bogs (Switzerland): implications for paleoclimatic studies. *Earth Planet. Sc. Lett.* 202: 419–434.
- Merlivat L. and Jouzel J. 1979. Global climatic interpretation of the deuterium–oxygen-18 relationship for precipitation. *J. Geophys. Res.* 84: 5029–5033.
- Mickler P.J., Banner J.L., Stern L., Asmerom Y., Edwards R.L. and Ito E. 2004. Stable isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope effects. *Geochim. Cosmochim. Ac.* 68: 4381–4393.
- Midwood A.J., Boutton T.W., Watts S. and Archer S. 1993. Natural abundance of ^2H and ^{18}O in soil moisture, rainfall and plants in a subtropical thorn woodland ecosystem: implications for plant water use. In: *Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and Atmosphere*. IAEA, Vienna, pp. 419–431.
- Mook W.G. 1970. Stable carbon and oxygen isotopes of natural waters in the Netherlands. In: *Isotope Hydrology 1970*. IAEA, Vienna, pp. 163–189.
- Mook W.G., Bommerson J.C. and Staverman W.H. 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sc. Lett.* 22: 169–176.
- Mudd G.M. 2000. Mound Springs of the Great Artesian Basin in South Australia: a case study from Olympic Dam. *Environ. Geol.* 39: 463–476.
- Nativ R., Gunay G., Hotzl H., Reichert B., Solomon D.K. and Tezcan L. 1999. Separation of groundwater-flow components in a karstified aquifer using environmental tracers. *Appl. Geochem.* 14: 1001–1014.
- Navada S.V. and Rao S.M. 1991. Study of Ganga River–groundwater interaction using environmental ^{18}O . *Isotopenpraxis* 27: 380–384.
- Nier A.O. and Gulbransen E.A. 1939. Variations in the relative abundance of the carbon isotopes. *J. Am. Chem. Soc.* 61: 697–698.
- Niggemann S., Mangini A., Richter D.K. and Wurth G. 2003. A paleoclimate record of the last 17,600 years in stalagmites from the B7 cave, Sauerland, Germany. *Quaternary Sci. Rev.* 22: 555–567.
- Nkotagu H.H. 1996. Application of environmental isotopes to groundwater recharge studies in a semi-arid fractured crystalline basement area of Dodoma, Tanzania. *J. Afr. Earth Sci.* 22: 443–457.
- Ofterdinger U.S., Balderer W., Loew S. and Renard P. 2004. Environmental isotopes as indicators for ground water recharge to fractured granite. *Ground Water* 42: 868–879.
- Oremland R.S., Miller L.G. and Whiticar M.J. 1987. Sources and fluxes of natural gases from Mono Lake, California. *Geochim. Cosmochim. Ac.* 51: 2915–2929.
- Papadimitriou S., Kennedy H., Kottner G., Dieckmann G.S. and Thomas D.N. 2004. Experimental evidence for carbonate precipitation and CO_2 degassing during sea ice formation. *Geochim. Cosmochim. Ac.* 68: 1749–1761.
- Parkhurst D.L. and Appelo C.A.J. 1999. User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geol. Surv. Water-Resources Investigations Rep. 99-4259, 310 pp. Code available at: http://www.wbr.cr.usgs.gov/projects/GWC_coupled/phreeqci/index.html.

- Payne B.R., Quijano L. and Latorre C. 1979. Environmental isotopes in a study of the origin of salinity of groundwater in the Mexicali Valley, Mexico. *J. Hydrol.* 41: 201–215.
- Pazdur A., Pazdur M.F., Starkel L. and Szulc J. 1988. Stable isotopes of Holocene calcareous tufa in Southern Poland as paleoclimatic indicators. *Quaternary Res.* 30: 177–189.
- Pearson F.J. and Hanshaw B.B. 1970. Sources of dissolved carbonate species in groundwater and their effects on carbon-14 dating. In: *Isotope Hydrology 1970*. IAEA, Vienna, pp. 271–286.
- Perrin J., Jeannin P.Y. and Zwahlen F. 2003. Epikarst storage in a karst aquifer: a conceptual model based on isotopic data, Milandre test site, Switzerland. *J. Hydrol.* 279: 106–124.
- Pichon A., Travi Y. and Marc V. 1996. Chemical and isotopic variations in throughfall in a Mediterranean context. *Geophys. Res. Lett.* 23: 531–534.
- Plummer L.N. 1977. Defining reactions and mass transfer in part of the Floridan aquifer. *Water Resour. Res.* 13: 801–812.
- Plummer L.N., McConnell J.B., Busenberg E., Drenkard S., Schlosser P. and Michel R.L. 1998. Flow of river water into a karstic limestone aquifer—1. Tracing the young fraction in groundwater mixtures in the Upper Floridan aquifer near Valdosta, Georgia. *Appl. Geochem.* 13: 995–1015.
- Polya D.A., Foxford K.A., Stuart F., Boyce A. and Fallick A.E. 2000. Evolution and paragenetic context of low δD hydrothermal fluids from the Panasqueira W-Sn deposit, Portugal: new evidence from microthermometric, stable isotope, noble gas and halogen analyses of primary fluid inclusions. *Geochim. Cosmochim. Ac.* 64: 3357–3371.
- Quade J. 2004. Isotopic records from ground-water and cave speleothem calcite in North America. *Dev. Quatern. Sci.* 1: 205–220.
- Rank D., Rajner V., Nussbaumer W., Papesch W., Dreher J. and Reitingner J. 1984. Study of the interrelationships between groundwater and lake water at Neusiedlersee, Austria. In: *Isotope Hydrology 1983*. IAEA, Vienna, pp. 67–81.
- Rank D., Adler A., Araguas-Araguas L., Froehlich K., Rozanski K. and Stichler W. 1998. Hydrological parameters and climatic signals derived from long term tritium and stable isotope time series of the river Danube. In: *Isotope Techniques in the Study of Environmental Change*. IAEA, Vienna, pp. 191–207.
- Rao S.M., Jain S.K., Navada S.V., Nair A.R. and Shivana K. 1987. Isotopic studies on sea water intrusion and interpretations between water bodies: some field examples. In: *Isotope Techniques in Water Resources Development*. IAEA, Vienna, pp. 403–425.
- Reardon E.J. and Fritz P. 1978. Computer modelling of groundwater ^{13}C and ^{14}C isotope compositions. *J. Hydrol.* 36: 201–224.
- Ricken W., Steuber T., Freitag H., Hirschfeld M. and Niedenzu B. 2003. Recent and historical discharge of a large European river system — oxygen isotopic composition of river water and skeletal aragonite of Unionidae in the Rhine. *Palaeogeogr. Palaeoecol.* 193: 73–86.
- Rindsberger M., Jaffe S., Rahmain S. and Gat J.R. 1990. Patterns of the isotopic composition of precipitation in time and space: data from the Israeli storm water collection program. *Tellus* 42B: 263–271.
- Robertson I., Waterhouse J.S., Barker A.C., Carter A.H.C. and Switsur V.R. 2001. Oxygen isotope ratios of oak in east England: implications for reconstructing the isotopic composition of precipitation. *Earth Planet. Sc. Lett.* 191: 21–31.
- Roedder E. 1984. Fluid inclusions. *Min. Soc. America. Reviews in Mineralogy* 12, 644 pp.
- Romanek C.S., Grossman E.L. and Morse J.L. 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate. *Geochim. Cosmochim. Ac.* 56: 419–430.
- Romanek C.S., Zhang C.L., Li Y., Horita J., Vali H., Cole D.R. and Phelps T.J. 2003. Carbon and hydrogen isotope fractionations associated with dissimilatory iron-reducing bacteria. *Chem. Geol.* 195: 5–16.
- Rozanski K. and Sonntag C. 1982. Vertical distribution of deuterium in atmospheric water vapour. *Tellus* 34: 135–141.

- Rozanski K. and Araguas-Araguas L. 1995. Spatial and temporal variability of stable isotope composition of precipitation over the South American continent. *Bull. Inst. Fr. Etudes Andines* 23: 379–390.
- Rozanski K., Sonntag C. and Münnich K.O. 1982. Factors controlling stable isotope composition of European precipitation. *Tellus* 34: 142–150.
- Rozanski K., Araguas-Araguas L. and Gonfiantini R. 1992. Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate. *Science* 258: 981–985.
- Rozanski K., Araguas-Araguas L. and Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. *Climate Change in Continental Isotopic Records*. Am. Geophys. Union, Geophys. Monogr. 78: 1–36.
- Salati E., Dall'Olio A., Matsui E. and Gat J.R. 1979. Recycling of water in the Amazon basin: an isotopic study. *Water Resour. Res.* 15: 1250–1258.
- Salomons W. and Mook W.G. 1986. Isotope geochemistry of carbonates in the weathering zone. In: Fritz P. and Fontes J.C. (eds), *Handbook of Environmental Isotope Geochemistry*, Vol. 1, The Terrestrial Environment, A. Elsevier, Amsterdam, pp. 239–270.
- Saxena R.K. 1986. Estimation of canopy reservoir capacity and oxygen-18 fractionation in throughfall in a pine forest. *Nordic Hydrol.* 17: 251–260.
- Schoch-Fischer H., Rozanski K., Jacob H., Sonntag C., Jouzel J., Oestlund G. and Geyh M.A. 1984. Hydrometeorological factors controlling the time variation of D, ^{18}O and ^3H in atmospheric water vapour and precipitation in the northern westwind belt. In: *Isotope Hydrology 1983*, IAEA, Vienna, pp. 3–31.
- Schoell M. 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Ac.* 44: 649–661.
- Schoell M. 1984. Stable isotopes in petroleum research. In Brooks J. and Wete D. (eds), *Advances in Petroleum Geochemistry*, Vol. 1. Academic Press, London, pp. 215–245.
- Schuerch M., Kozel R., Schotterer U. and Tripet J.P. 2003. Observation of isotopes in the water cycle - the Swiss National Network (NISOT). *Environ. Geol.* 45: 1–11.
- Schwalb A. 2003. Lacustrine ostracodes as stable isotope recorders of late-glacial and Holocene environmental dynamics and climate. *J. Paleolimnol.* 29: 265–351.
- Schwarcz H.P. 1986. Geochronology and isotope geochemistry of speleothems. In: Fritz P. and Fontes J.C. (eds), *Handbook of Environmental Isotope Geochemistry: Vol 2, The Terrestrial Environment*, B. Elsevier, Amsterdam, pp. 271–303.
- Serefiddin F., Schwarcz H.P., Ford D.C. and Baldwin S. 2004. Late Pleistocene paleoclimate in the Black Hills of South Dakota from isotope records in speleothems. *Palaeogeogr. Palaeoecol.* 203: 1–17.
- Shackleton N.J. 1987. Oxygen isotopes, ice volume and sea level. *Quaternary Sci. Rev.* 6: 183–190.
- Sharma M.L. and Hughes M.W. 1985. Groundwater recharge estimation using chloride, deuterium and oxygen-18 profiles in the deep coastal sands of Western Australia. *J. Hydrol.* 81: 93–109.
- Siegenthaler U. and Oeschger H. 1980. Correlation of O-18 in precipitation with temperature and altitude. *Nature* 285: 314–317.
- Simpkins W.W. and Parkin T.B. 1993. Hydrogeology and redox geochemistry of CH_4 in a late Wisconsinian till and loess sequence in central Iowa. *Water Resour. Res.* 29: 3643–3657.
- Simpson H.J. and Herczeg A.L. 1991. Stable isotopes as indicators of evaporation in the River Murray, Australia. *Water Resour. Res.* 27: 1925–1935.
- Skidmore M., Sharp M. and Tranter M. 2004. Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: Implications for detection of microbial CO_2 signature using $\delta^{13}\text{C}\text{-DIC}$. *Geochim. Cosmochim. Ac.* 68: 4309–4317.
- Sklash M.G. and Farvolden R.N. 1979. The role of groundwater in storm runoff. *J. Hydrol.* 43: 45–65.

- Smith D.B., Otlet R.L., Downing R.A., Monkhouse R.A. and Pearson F.J. 1975. Stable carbon and oxygen isotope ratios of groundwaters from the Chalk and Lincolnshire Limestone. *Nature* 257: 783–784.
- Smith D.M., Jackson N.A., Roberts J.M. and Ong C.K. 1999. Reverse flow of sap in tree roots and downward siphoning of water by *Grevillae robusta*. *Funct. Ecol.* 13: 256–264.
- Smith R.B. 1992. Deuterium in North Atlantic storm tops. *J. Atm. Sci.* 49: 2041–2057.
- Sofer Z. 1978. Isotopic composition of hydration-water in gypsum. *Geochim. Cosmochim. Ac.* 42: 1141–1149.
- Sonntag C., Christmann D. and Munnich K.O. 1985. Laboratory and field experiments on infiltration and evaporation of soil water by means of deuterium and oxygen-18. In: *Stable and radioactive isotopes in the study of the unsaturated soil zone*, IAEA, Vienna, TECDOC-357, 145–159.
- Sonntag C., Rozanski K., Munnich K.O. and Jacob H. 1983. Variations of deuterium and oxygen-18 in continental precipitation and groundwater and their causes. In: *Street-Perrott F.A., Beran M.A. and Ratcliffe R.G. (eds), Variations in the Global Water Budget*. D. Reidel Publishing Company, pp. 107–124.
- Soulsby C., Malcolm R., Helliwell R.C., Ferrier R.C. and Jenkins A. 2000. Isotope hydrology of the Allt a' Mharcaidh catchment, Cairngorm mountains, Scotland: implications for hydrological pathways and water residence times. *Hydrol. Process.* 14: 747–762.
- Stewart M.K. and Downes C.J. 1982. Isotope hydrology of Waikoropupu Springs, New Zealand. In: *Perry E.C. and Montgomery C.W. (eds), Isotope Studies in Hydrologic Processes*, Northern Illinois University Press, pp. 15–23.
- Stiller M., Rounick J.S. and Shasha S. 1985. Extreme carbon-isotope enrichments in evaporating brines. *Nature* 316: 434–435.
- Stuiver M. 1970. Oxygen and carbon isotope ratios of fresh-water carbonates as climatic indicators: *J. Geophys. Res.* 75: 5247–5257.
- Sturchio N.C., Sultan M., Arehart G.B., Sano Y., Kamar Y.A. and Sayed M. 1996. Composition and origin of thermal waters in the Gulf of Suez area, Egypt. *Appl. Geochem.* 11: 471–479.
- Stute M. and Schlosser P. 2000. Atmospheric noble gases. In: *Cook P.G. and Herczeg A. (eds), Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Publishers, pp. 349–379.
- Sultan M., Sturchio N., Hassan F.A., Hamdan M.A.R., Mahmood A.M., El Alfy Z. and Stein T. 1997. Precipitation source inferred from stable isotopic composition of Pleistocene ground-water and carbonate deposits in the Western Desert of Egypt. *Quaternary Res.* 48: 29–37.
- Szaran J. 1997. Achievement of carbon isotope equilibrium in the system HCO_3^- (solution) – CO_2 (gas). *Chem. Geol.* 142: 79–86.
- Talbot M.R. 1990. A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chem. Geol. (Isot. Geosci.)* 80: 261–279.
- Talbot M.R. and Kelts K. 1990. Palaeolimnological signatures from carbon and oxygen isotopic ratios in carbonates from organic-rich lacustrine sediments. In: *Katz B.J. (ed.), Lacustrine Exploration: Case Studies and Modern Analogues*. Memoir No. 50, Am. Assoc. Petrol. Geol., Tulsa, OK, pp. 99–112.
- Taylor C.B. 1972. The vertical variations of isotopic compositions of tropospheric water vapour over continental Europe and their relations to tropospheric structure. *Inst. Nucl. Sci. Rep. INS-R-107*, Lower Hutt, New Zealand, 44 pp.
- Telmer K. and Veizer J. 1999. Carbon fluxes, pCO_2 and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives. *Chem. Geol.* 159: 61–86.
- Thode H.G., Shima M., Rees C.E. and Krishnamurty K.V. 1965. Carbon-13 isotope effects in systems containing carbon dioxide, bicarbonate, carbonate, and metal ions. *Can. J. Chemistry* 43: 582–595.
- Thompson L.G. 2001. Stable isotopes and their relationships to temperature as recorder in low-latitude ice cores. In: *Gerhard L.C., Harrison W.E. and Hanson B.M. (eds), Geological Perspectives of Global Climate Change*, Studies in Geology No. 47, Am. Assoc. Petrol. Geol., Tulsa, Oklahoma, pp. 99–119.

- Thorstenson D.C., Fisher D.W. and Croft M.G. 1979. The Geochemistry of the Fox Hills-Basal Hill Creek aquifer in southeastern North Dakota and northwestern South Dakota. *Water Resour. Res.* 15: 1479–1498.
- Turi B. 1986. Stable isotope geochemistry of travertines. In: Fritz P. and Fontes J.C. (eds), *Handbook of Environmental Isotope Geochemistry: Vol 2, The Terrestrial Environment*, B. Elsevier, Amsterdam, pp. 207–238.
- Turner J.V. 1982. Kinetic fractionation of carbon-13 during calcium carbonate precipitation. *Geochim. Cosmochim. Ac.* 46: 1183–1191.
- Turner J.V. and Fritz P. 1982. Enriched ^{13}C composition of interstitial waters in sediments of a freshwater lake. *Can. J. Earth Sci.* 20: 616–621.
- Tyler S.C. 1986. Stable carbon isotope ratios in atmospheric methane and some of its sources. *J. Geophys. Res.* 91D: 13,232–13,238.
- Uzdowski E. and Hoefs J. 1986. $^{13}\text{C}/^{12}\text{C}$ partitioning and kinetics of CO_2 absorption by hydroxide buffer solutions. *Earth Planet. Sc. Lett.* 8: 130–134.
- van Ommen T.D. and Morgan V. 1997. Calibrating the ice core paleothermometer using seasonality. *J. Geophys. Res.* 102D: 9351–9357.
- Verhagen B.T., Geyh M.A., Froehlich K. and Wirth K. 1991. Isotope hydrological methods for the quantitative evaluation of groundwater resources in arid and semi-arid areas: Development of a methodology. Rep. Federal Ministry for Economic Cooperation, Bonn, FRG, 164 pp.
- Vogel J.C. and Ehhalt D. 1963. The use of the carbon isotopes in groundwater studies. In: *Radioisotopes in Hydrology*. IAEA, Vienna, pp. 383–395.
- Vogel J.C., Grootes P.M. and Mook W.G. 1970. Isotope fractionation between gaseous and dissolved carbon dioxide. *Z. Phys.* 230: 255–258.
- Vogt H.J. 1976. Isotopentrennung bei der Verdampfung von Wasser. PhD thesis, University of Heidelberg, Germany.
- von Grafenstein U., Erlenkeuser H., Müller J. and Alefs J. 1996. A 200-year mid-European temperature record preserved in lake sediments: an extension of the $\delta^{18}\text{O}_\text{p}$ -air temperature relation into the past. *Geochim. Cosmochim. Ac.* 60: 4025–4036.
- von Grafenstein U., Erlenkeuser H., Brauer A., Jouzel J. and Johnsen S.J. 1999. A Mid-European decadal isotope-climate record from 15,500 to 500 years B.P. *Science* 284: 1654–1657.
- Wang X.F. and Yakir D. 2000. Using stable isotopes of water in evapotranspiration studies. *Hydrol. Process.* 14: 1407–1421.
- Wassenaar L.I., Aravena R., Fritz P. and Barker J.F. 1991. Controls on the transport and carbon isotopic composition of dissolved organic carbon in a shallow groundwater system, Central Ontario, Canada. *Chem. Geol. (Isot. Geosci.)* 87: 39–57.
- Welhan J.A. and Fritz P. 1977. Evaporation pan isotopic behavior as an index of isotopic evaporation conditions. *J. Hydrol.* 41: 682–686.
- Wendt I. 1968. Fractionation of carbon isotopes and its temperature dependence in the system CO_2 -Gas- CO_2 in solution and HCO_3^- - CO_2 in solution. *Earth Planet. Sc. Lett.* 4: 64–68.
- Wendt I. 1971. Carbon and oxygen isotope exchange between HCO_3^- in saline solution and solid CaCO_3 . *Earth Planet. Sc. Lett.* 12: 439–442.
- Werner M., Mikolajewicz U., Hoffmann G. and Heimann M. 2000a. Possible changes of the delta O 18 in precipitation caused by a meltwater event in the North Atlantic. *J. Geophys. Res.*, 105D: 10161–10167.
- Werner M., Mikolajewicz U., Heimann M., and Hoffmann G. 2000b. Borehole versus isotope temperature on Greenland: Seasonality does matter. *Geophys. Res. Lett.* 27: 723–726.
- White J.W.C., Cook E.R., Lawrence J.R. and Broecker W.S. 1985. The D/H ratio of sap in trees: implications for water sources and tree ring D/H ratios. *Geochim. Cosmochim. Ac.* 49, 237–246.
- White T., Gonzalez L., Ludwigson G. and Poulsen C. 2001. Middle Cretaceous greenhouse hydrologic cycle of North America. *Geology* 29: 363–366.
- Wigley T.M.L., Plummer L.N. and Pearson F.J. 1978. Mass transfer and carbon isotope evolution in natural water systems. *Geochim. Cosmochim. Ac.* 42: 1117–1139.

- Williams P.W. and Fowler A. 2002. Relationship between oxygen isotopes in rainfall, cave percolation waters and speleothem calcite at Waitomo, New Zealand. *New Zeal. J. Hydrol.* 41: 53–70.
- Winograd I.J., Coplen T.B., Landwehr J.M., Riggs A.C., Ludwig K.R., Szabo B.J., Kolesar P.T. and Revesz K.M. 1992. Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. *Science* 258: 255–260.
- Winston W.E. and Criss R.E. 2003. Oxygen isotope and geochemical variations in the Missouri River. *Environ. Geol.* 43: 546–556.
- Winston W.E. and Criss R.E. 2004. Dynamic hydrologic and geochemical response in a perennial karst spring, *Water Resour. Res.* 40: W05106. doi:10.1029/2004WR003054.
- Wolfe B.B., Edwards T.W.D., Beuning K.R.M. and Elgood R.J. 2001. Carbon and oxygen isotope analysis of lake sediment cellulose: methods and applications. In: Last W.M. and Smol J.P. (eds), *Tracking Environmental Change Using Lake Sediments, Vol. 2, Physical and Geochemical Methods, Developments in Paleoenvironmental Research*, Kluwer Academic Publishers, Dordrecht, pp. 373–400.
- Woodward D.F., Farag A., Hubert W.A., Goldstein J.N. and Meyer J.S. 2000. Effects of geothermal effluents on rainbow trout and brown trout in the Firehole River, Yellowstone National Park, Wyoming. *Rep. Columbia Environ. Res. Center, USGS*, 124 pp.
- Yeh H.W. and Wang W.M. 2001. Factors affecting the isotopic composition of organic matter. (1) Carbon isotopic composition of terrestrial plant materials. *Proc. Nat. Sci. Council. ROC(B)*, 25: 137–147. <http://nr.stic.gov.tw/ejournal/ProceedingB/v25n3/137-147.pdf>.
- Yonge C.J., Ford D.C., Gray J. and Schwarcz H.P. 1985. Stable isotope studies of cave seepage water. *Chem. Geol.* 58: 97–105.
- Yoshimura K., Liu Z., Cao J., Yuan D., Inokura Y and Noto M. 2004. Deep source CO₂ in natural waters and its role in extensive tufa deposition in the Huanglong Ravines, Sichuan, China. *Chem. Geol.* 205: 141–153.
- Yurtsever Y. and Gat J.R. 1981. Atmospheric waters. In: Gat J.R. and Gonfiantini R. (eds), *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*. Tech. Rep. Series No. 210. IAEA, Vienna, pp. 103–142.
- Zhang C.L., Fouks B.W., Bonheyo G.T., Peacock A.D., White D.C., Huang Y. and Romanek C.S. 2004. Lipid biomarkers and carbon-isotopes of modern travertine deposits (Yellowstone National Park, USA): Implications for biogeochemical dynamics in hot-spring systems. *Geochim. Cosmochim. Ac.* 68: 3157–3169.
- Zhang C.L., Horita J., Cole D.R., Zhou J., Lovley D.R. and Phelps T.J. 2001. Temperature-dependent oxygen and carbon isotope fractionations of biogenic siderite. *Geochim. Cosmochim. Ac.* 65: 2257–2271.
- Zhang J., Quay P.D. and Wilbur D.O. 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO₂. *Geochim. Cosmochim. Ac.* 59: 107–114.
- Zimmerman U., Ehhalt D., Münnich K.O. 1967. Soil-water movement and evapotranspiration: changes in the isotopic composition of the water. In: *Isotopes in Hydrology*. IAEA, Vienna, pp. 567–584.