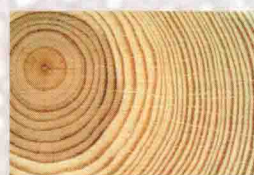


Isotopes in Palaeoenvironmental Research

Volume 10

Edited by
Melanie J. Leng



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Isotopes in Palaeoenvironmental Research

Developments in Paleoenvironmental Research

VOLUME 10

PREFACE

This volume is intended to show how stable isotopes can be applied to understanding the palaeoenvironment. There are chapters on the interpretation of isotopes in water, tree rings, bones and teeth, lake sediments, speleothems and marine sediments. Crucial to the understanding of the environmental signal contained within the isotope composition of different materials is to gain more information about how rainfall isotope compositions are determined by climate. Chapter 1 (Darling et al.) describes O, H and C stable isotope compositions in the modern day water and aqueous carbon cycles to provide a framework for the interpretation of these isotopes in the past. The chapter on the water cycle divides naturally into a number of sections. The starting point, precipitation, is especially important because it is the precursor 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 chapter describes the three reservoirs of water sustaining all terrestrial proxies; soil and vadose zone moisture, groundwater, and surface waters. In each reservoir isotope effects intervene to modify to a greater or lesser extent the isotope signature of antecedent precipitation; groundwaters are least affected and surface waters the most. Since lake sediments are an important archive of the palaeoenvironment, the continuing development of isotope mass-balance modelling techniques is playing a role of considerable importance in interpreting isotope records from lake sediments (see also Leng et al., Chapter 4). The carbon cycle is far more complex than the water cycle, and is mentioned in various guises in all the other chapters. However, carbon is still of use, especially where the various carbon sources can be constrained and can be linked to the overall geochemical conceptual model.

Trees provide a good archive of recent and earlier Holocene climate and environmental change (McCarroll and Loader, Chapter 2). Trees have the advantage of being widespread and can produce a near continuous archive of environmental information. The water isotopes provide two separate signals; the isotope composition of the source water and evaporation from leaves. The former is only a proxy for the isotope composition of precipitation if the trees are accessing relatively young and unmixed water. In other trees evaporative enrichment may be the predominant signal in the tree rings and this is controlled largely by air humidity. Carbon isotopes can complement the water data, notably in dry environments, where the main signals are air humidity and soil moisture content, and in moist environments where photosynthetic rate dominates and the signals are summer temperature and solar radiation.

Perhaps one of the most significant advances in tree ring research is the development of on-line techniques which allow the analyses of increased numbers of tree rings, and these are reviewed. The ability to analyse smaller samples enables individual trees to provide data, while combining the results from several trees allows the quantification of variability, at different temporal frequencies, and thus allows statistically defined confidence limits to be placed around mean values. This way temporal frequencies, including the low-frequency, long-term changes that are so difficult to capture using more traditional methods, are able to be investigated.

The third chapter deals with the isotope composition of bone and teeth (Hedges et al.) which are dominated by biological and ecological controls. This is even true for such isotopes as strontium that are adventitiously taken up according to local geology, and so potentially record animal movements within their ecological setting. However, there is a need to understand the biological features in the subject of study (such as food web structure) in order to get back to environmental information which cannot be done using isotopes alone. One of the problems with using bones as an environmental archive is the sporadic and acontextual deposition of bone, rarely enabling its data to be directly integrated with complementary data from the same site, apart from on a general scale. However, bone and teeth contain many different isotope signals which can be very sensitive - the non-linear change in C3/C4 plant abundance (and therefore with $\delta^{13}\text{C}$ in the bone collagen of herbivorous grazers) with local climate for example. Overall this chapter provides the background to understanding how isotope changes in bone and teeth are caused, and shown how these changes may be understood, though not always, in terms of environmental effects.

Chapter 4 on lakes (Leng et al.) demonstrates that the oxygen, carbon, nitrogen and hydrogen isotope composition of lacustrine sedimentary materials can yield a wide range of useful palaeoclimate information, although a full interpretation of isotope data from lake sediments requires a detailed knowledge of the processes that control and modify the signal. For example, Chapter 1 describes the various factors that can change the isotope composition of precipitation, which is an important consideration in palaeolimnology. Processes that can affect the isotope composition of lacustrine sedimentary materials must be largely determined for an individual lake system, although typical responses are often assumed. Oxygen isotopes are the main isotopes used in palaeolimnology and can be obtained from a large range of inorganic and organic materials. However, even within the most established materials the interpretation is not easy. For example, a change in temperature will produce a shift in the equilibrium oxygen isotope composition of carbonate forming in lake water, but will also affect the isotope composition of the rainfall and rates of evaporation. Recent research has shown that this might be resolved by the analysis of the oxygen isotope composition of lacustrine organic materials, for example aquatic cellulose, which is thought to have $\delta^{18}\text{O}$ values that are independent of water temperature.

Other palaeoenvironmental information can be achieved from organic materials in lakes (Chapter 4) from their carbon and nitrogen ratios, although they will also contain information on productivity and changes in nutrient supply.

Chapter 5 describes the stable isotope composition of speleothems (McDermott et al.). Despite the generally acknowledged lack of precise isotope equilibrium between cave drip-waters and their carbonate precipitates, speleothems are usually deposited sufficiently close to isotope equilibrium to retain useful information about climate-driven changes in the isotope composition of meteoric water that falls on a cave site. As with all archives the quantitative interpretation of stable isotope shifts in speleothems is seldom straightforward, and a detailed knowledge of the meteorological variables that control these archives in the modern cave system is essential to provide a sound interpretation of past climates (see Chapter 1). Where possible, present-day monitoring studies of cave drip waters are essential to understand fully the site-specific relationships between speleothem $\delta^{18}\text{O}$ and meteorological variables at the surface.

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Notation and standardisation

To prevent repetition regarding notation and standardisation, a short summary is given here. However, fuller descriptions can be found in Bowen (1988), Coleman and Fry (1991), Clarke and Fritz (1997), Hoefs (1997), Criss (1999) and de Groot (2004). Isotope ratios (e.g., $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$) are expressed in terms of delta values (δ), because the isotope ratios are more easily measured as relative differences, rather than absolute values. We refer to the delta value (δ) and this is measured in units of per mille (‰). The δ value is defined as:

$$\delta = (R_{\text{sample}}/R_{\text{standard}}) - 1 \cdot 10^3$$

Where R = the measured ratio of the sample and standard respectively. Since a sample's ratio may be either higher or lower than that of the standard, δ values can be positive or negative. The δ value is dimensionless, so where comparisons are made between samples (e.g., where $\delta_A < \delta_B$) the δ value of A, is said to be 'lower' than that of B (and B 'higher' than A). Where reference is made to absolute ratios A may be said to be 'depleted' in the heavier isotope compared to B (and B 'enriched' compared to A). In the laboratory it is necessary to use 'working standards' with values calibrated against recognised standard materials, thus all values are quoted relative to the latter. For waters (oxygen and hydrogen) and silicates (oxygen) we use VSMOW (Vienna Standard Mean Oceanic Water) an average ocean water, for carbonate and organic material we use VPDB (Vienna Pee Dee Belemnite), for nitrogen the convention is atmospheric nitrogen (described as AIR), for Boron NIST (boric acid SRM 951) and silicon NBS28 (IAEA quartz sand). See discussions in Bowen (1988), Coleman and Fry (1991), Clarke and Fritz (1997), Hoefs (1997), and Criss (1999). The data are presented as per mille (‰) deviations from the relevant international standard (e.g., ‰ VPDB).

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Temporal changes in speleothem $\delta^{13}\text{C}$ can offer considerable potential to reconstruct climate-driven changes in both the nature of vegetation (e.g., C3 vs. C4 type) and the intensity of vegetation above a cave site. One particular requirement in speleothem research is that carbon isotope data should be accompanied, where possible, by appropriate elemental data (e.g., Ca/Mg ratios) in order to evaluate other possible causes for temporal changes in $\delta^{13}\text{C}$. For example, strongly correlated carbon isotope and Mg/Ca ratios may point to a role for partial degassing of cave drip-waters and calcite precipitation in the hydrological flow-path above the cave (so-called 'prior calcite precipitation') that could produce elevated $\delta^{13}\text{C}$ values unrelated to changes in vegetation type or intensity.

One of the distinct advantages of using speleothems, is the ability to use U-series dating. The possibility of using well-dated speleothems records to refine the chronology for the high-latitude ice core records is particularly exciting. In the future it seems likely that data from speleothem fluid inclusions will provide a more robust basis for palaeoclimate interpretations, in particular enabling the relative effects of air temperature and atmospheric circulation changes to be unravelled.

Measurement of oxygen and carbon isotopes in foraminifera have been central to the development and establishment of stable isotopes as one of the most important sets of proxies within palaeoceanography. In Chapter 6, Maslin and Swann, demonstrate how oxygen isotopes records can provide a stratigraphy while enabling the reconstruction of such things as: past global ice volume, ocean temperatures, relative sea level, ocean circulation and structure, surface water salinity, iceberg melting, river discharge, and monsoonal intensity. Carbon isotope records from both carbonate and organic matter found within marine sediments can provide information on the past carbon cycle on a range of time-scales, enabling an insight into past marine productivity, ocean circulation, past surface water, atmospheric CO_2 , storage and exchange of carbon on both the local and global scale. However, the interpretation of carbon isotope records is complicated by different sources of carbon entering the marine environment with an additional number of influences affecting the isotope values of each source. Recent years have witnessed the development of a variety of other isotope proxies, in particular $\delta^{15}\text{N}$ and $\delta^{11}\text{B}$. While these are still not measured routinely, great steps forward have been achieved in our understanding of them, although significant difficulties remain in ensuring robust and accurate interpretations from the generated data. There is potential for both isotopes, however, to provide a more significant insight into past oceanic conditions and palaeo- $p\text{CO}_2$ levels. As such, their use are likely to expand over the next decade as a greater understanding of the marine nitrogen cycle, controls on $\delta^{15}\text{N}$ and the errors associated with $\delta^{11}\text{B}$ based $p\text{CO}_2$ reconstructions are achieved.

Outside foraminiferal isotope based studies, there is great scope to generate isotope data from other biological sources. A current major limitation with foraminifera studies is the void of data from regions depleted in CaCO_3 preservation, particularly in the Southern Ocean and other high latitude regions. Future development and use of $\delta^{18}\text{O}_{(\text{diatom})}$ and $\delta^{30}\text{Si}_{(\text{diatom})}$ alongside $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis of intrinsic organic matter within diatom frustules will ultimately open the gateway for the extension of detailed, isotope based, palaeoceanographic reconstructions to more of the world's oceans.

In summary, all the chapters presented here have several similar messages. Isotopes can be extremely powerful palaeoenvironmental tools. However, as with all archives, it is always desirable to carry out a calibration exercise to investigate the basic systematics

of isotope variation in the modern environment to establish the relationship between the measured signal and the isotope composition of the host. A robust calibration is seldom easy as the materials may not occur in the contemporary environment and the site may be in an isolated geographical region, making a rigorous contemporary study impossible. Where such a calibration is not possible assumptions have to be made, but these should be based on evidence from a multi-proxy approach using isotope signals from different materials or combined with other palaeoenvironmental techniques.

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