

## Palaeoclimate interpretation of stable isotope data from lake sediment archives

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## Abstract

The isotope composition of authigenic and biogenic carbonates and diatom silica are commonly used as palaeoclimate proxies from lake sediments. This article reviews the controls on the isotope composition of lacustrine skeletal and non skeletal deposits and illustrates how stable isotope studies contribute to an understanding of changes in temperature, precipitation patterns, evaporation and the carbon cycle. It highlights the differences in the palaeoclimate potential of a wide range of lakes ranging from open to closed lake basins. A large number of the case histories, but not all, are drawn from studies of temperate lakes from Europe.

Large closed lake systems, in the tropics and elsewhere, lose water predominantly through evaporation, and contain sediments with variable and generally high  $\delta^{18}\text{O}$  values. Fluctuations in the isotope composition of authigenic or biogenic minerals are mainly a function of long term changes in the precipitation/evaporation ratio. In contrast small open lakes which have a degree of through-flow typically contain sediments with  $\delta^{18}\text{O}$  values that vary by no more than a few ‰. These variations are generally ascribed to variations in temperature or the isotope composition of precipitation ( $\delta p$ ), from which either an annual or seasonally specific signal can be gained. These types of lakes are common in Northern Europe and at high altitudes. The interpretation of isotope data from a lacustrine succession requires a knowledge of the local processes that might control and modify the signal. Their effects need to be quantified, and a robust calibration using the modern lake system is necessary to establish the relationship between the measured signal, the isotopic composition of the host waters, and climate.

Keywords: Palaeoclimate, stable isotopes, carbon isotopes, oxygen isotopes, carbonate, diatom, lake sediments, lakes

## 1. Introduction

Stable isotope geochemistry has been used as an indicator of palaeoclimate since the work of McCrea (1950) and Urey et al (1951) highlighted the potential for oxygen isotope compositions to be used for palaeotemperature reconstruction. The technique has been applied to marine and non-marine sediments and fossils. In lacustrine environments stratigraphic changes in  $\delta^{18}\text{O}$  values are commonly attributed to changes in temperature or precipitation/evaporation ratio; whereas those of carbon and nitrogen are used to demonstrate (often climatically-induced) changes in carbon, nutrient cycling and productivity within the lake and its catchment.

A perennial problem in the quantitative interpretation of geochemical proxies for climate is that the systems are essentially underdetermined: in other words the variables that can be measured in the sediments (generally  $\delta^{18}\text{O}$  in carbonates and biogenic silica,  $\delta^{13}\text{C}$  in carbonates and organics) are influenced by a wide range of interlinked environmental processes and not a single factor. For example, a change in temperature will produce a shift in the equilibrium oxygen isotope composition of carbonate forming in a lake. However, the same temperature change will affect the isotope composition of the rainfall and may also affect rates of evaporation, both in the lake and in the catchment. All these factors will influence the isotope composition of the lacustrine carbonates and silicates. In general, therefore, it is impossible to measure the isotope composition of carbonates and silicates and translate the values into absolute or even relative temperature variation without making some very significant assumptions.

This review seeks to highlight the environmental factors that influence the isotope composition of lacustrine carbonates and silicates and the assumptions that need to be made in using isotope variation to indicate past changes in climate. We highlight the need to calibrate isotope records from lake sediments using studies of the isotope systematics of the modern lake system. Such studies can often ensure that records can be interpreted with a much higher level of confidence. We then use a number of case studies from Late Quaternary successions to illustrate how isotope geochemistry has been used to demonstrate the variability in climates over the last few thousand years.

## 2. Oxygen isotope composition of lacustrine minerals

Palaeoclimatic studies commonly use stratigraphic changes in the oxygen isotope compositions of lacustrine carbonates or silicates. The composition of either biogenic (skeletal), or authigenic (endogenic) mineral precipitates can be used to infer changes in either (a) temperature or (b) the oxygen isotopic composition of lake water. These may be an important proxy for climate change where the isotopes reflect changes in the source of water to the lake.

Figure 1 indicates the factors that can influence the isotope composition of a lacustrine carbonate precipitate ( $\delta^{18}\text{O}_{\text{carb}}$ ). An almost identical diagram could be drawn for the oxygen isotope composition of silicates. For equilibrium mineral precipitation, the isotopic composition is predictable by thermodynamics. In this case the oxygen isotope composition of the mineral is controlled only by the temperature and by the isotope composition of the lake water from which the mineral precipitated. In principle, if it can be shown that a particular type of carbonate or silicate forms in

isotope equilibrium, fractionation equations (often known as palaeotemperature equations) can be used to estimate past temperatures and their changes (see section 2.2 below). The interpretation of oxygen isotope compositions, in practice however, is complicated because both temperatures and water compositions can be affected by changes in climate.

Knowledge of the factors that may have influenced the isotope composition of the lake water ( $\delta^{18}\text{O}_{\text{water}}$  on Figure 1) is obviously vital to the interpretation of the  $\delta^{18}\text{O}_{\text{carb}}$  signal. Section 2.1 reviews the processes that influence lake water composition and highlights the need to understand the basic hydrology (assuming this is essentially unchanging) of any lake that is to be sampled for palaeoclimate reconstruction.

Disequilibrium effects (Figure 1) (commonly known as 'vital' effects in the case of biogenic carbonates) include a variety of rate effects and micro-environment induced changes that cause the mineral to have an isotope composition that is different from that predicted purely by thermodynamics (section 2.3). Disequilibrium processes can, however, be quite systematic so carbonates such as ostracod shells, which appear to demonstrate species-specific vital effects (Holmes and Chivas 2002), are not precluded from palaeoclimatic studies as long as the offset is demonstrably independent of temperature or the factors that influence the offset from equilibrium are known. This is usually achieved by calibration studies to investigate the precise systematics of isotopic fractionation, for example for the formation of shells of a particular species of ostracod.

In the following sections we will review the importance of each of the main factors highlighted on Figure 1.

### *2.1 Lake water oxygen isotope composition – the importance of lake (palaeo) hydrology*

The oxygen isotope composition of water in hydrologically open lakes ( $\delta^{18}\text{O}_{\text{water}}$  on Figure 1) will dominantly reflect the isotopic composition of the precipitation, both rain and snowfall, received by the lake ( $\delta^{18}\text{O}_{\text{precipitation}}$  or  $\delta p$ ). An extended account of the controls on the isotope composition in precipitation is beyond the scope of this paper (see Clark and Fritz 1997) but many studies have shown that the oxygen isotope composition of mean annual precipitation varies globally and the covariation in  $\delta p$  and  $\delta D$  defines a global meteoric water line (Craig, 1961 and Figure 2a). Outside the tropics, where 'amount' effects (relating to intense precipitation events) are common,  $\delta p$  varies systematically with mean annual temperature (Clark and Fritz 1997; <http://isohis.iaea.org/GNIP>), it thus broadly correlates with latitude and altitude of a site (Bowen and Wilkinson, 2002; and refs therein). The global relationship between changes in  $\delta p$  with temperature ( $d\delta p/dT \sim 0.2$  to  $0.7\text{‰}/^{\circ}\text{C}$ ) is sometimes referred to as the 'Dansgaard relationship' after the seminal early compilation of meteoric water values (Dansgaard, 1964).

In many lacustrine environments it is not safe to assume that either the modern, or past  $\delta^{18}\text{O}_{\text{lakewater}}$ , reflects that of mean annual precipitation. The residence time of water in the lake and modification of water compositions by catchment and lake processes are particularly important to consider, as evaporation will affect the water composition. The size of a lake in comparison to its catchment is important because the isotope composition of rain and snowfall are very variable on short time scales: a lake therefore needs to be big enough and well enough mixed for its isotope

composition to 'average out' the short term variation and reflect mean annual precipitation. The greatest degree of variation in the isotope composition of rainfall occurs on the time scale of hours to days (Darling, this volume). Within individual storm events,  $\delta^{18}\text{O}$  can vary by many ‰ but this is unlikely to have any significance for the sediment record – except, perhaps for the isotopic composition of some species of organisms such as gastropods and ostracods which can inhabit the most ephemeral of puddles. Seasonal variation in precipitation is likely to be much more significant in small, short residence time lakes as these tend to have  $\delta^{18}\text{O}_{\text{water}}$  values which are regularly displaced by later precipitation. At temperate latitudes monthly mean rainfall  $\delta^{18}\text{O}$  values typically have an overall range of between 2-8 ‰, the range increasing with continentality of the site. At such sites winter rainfall has significantly more negative  $\delta^{18}\text{O}$  than its summer equivalent. If a lake is very small in relation to its catchment (with residence times of < 1 year) winter rainfall will be physically displaced by summer rainfall and thus  $\delta^{18}\text{O}_{\text{water}}$  will be influenced by seasonal variation. The precise isotope composition of lake water at any time will depend on the amount of rain in the different seasons and the degree of mixing of winter and summer rainfall. Even in lakes with relatively long overall residence times if the waters become stratified, as often happens in summer, surface waters may have isotope compositions that reflect summer rainfall rather than mean annual precipitation.

Evaporation has a major influence on the isotope composition of any standing body of water (Figure 2a). Closed (terminal) lakes, particularly those in arid regions, where water loss is mainly through evaporation, have waters with variable and elevated oxygen isotope composition. Measured  $\delta^{18}\text{O}$  (and  $\delta\text{D}$ ) values are always higher than those of ambient precipitation as the lighter isotopes of  $^{16}\text{O}$  and ( $^1\text{H}$ ) are preferentially lost to evaporation (see Figure 2a). Isotope records from the sediments in such lakes show large swings in composition as the ratio of the amount of precipitation to evaporation (P/E) change with climate (see section 5). In extreme circumstances evaporation in soil zones and from the surface of a lake can lead to significantly elevated  $\delta^{18}\text{O}_{\text{water}}$  values. Any interpretation of the isotope records from a lake must take into account the hydrology of the lake and likely changes in hydrology that may have occurred in the past.

In modelling isotopic hydrological balance in lakes, studies have tended to concentrate on understanding the modern lake water systems by measuring some components in order to estimate the less easily measured parts. For example studies estimating evaporation using stable isotopes in northern Canada (e.g. Gibson in press). More recently there have been studies which model  $\delta^{18}\text{O}$  variation in authigenic carbonates precipitated in closed basin lakes. For example the HIBAL (hydrologic-isotopic-balance) model of Benson and Paillet (2002) is able to simulate the  $\delta^{18}\text{O}$  response to step, periodic and abrupt changes in fluid inputs for various lakes in the US. However this model, as with all models, requires modern climate information to eliminate part of the uncertainty implicit in the hydrological modelling.

Table 1 demonstrates the significance of changes in the size of lakes and changes from open to closed hydrology. Where catchment effects and changes in P/E can be ruled out, and temperature changes can be constrained (using independent criteria) it may be possible to use the

isotope composition of carbonates and silicates as a proxy for changes in meteoric water compositions. The importance of  $\delta p$  as climatic variable in its own right is highlighted in section 3.

## 2.2 Temperature – and the use of 'palaeotemperature equations'

Equilibrium isotope fractionation is related directly to the thermodynamics of the mineral precipitation reaction. The increase in vibrational, and other, energy associated with increased temperature leads to decrease in isotope fractionation between the water and the mineral that precipitates from it. For equilibrium carbonates, for example, the mineral isotope composition decreases by about 0.24‰ for each 1°C increase in temperature (Craig, 1965) whereas for diatom silica empirical data suggest changes between –0.2 to –0.5‰/°C (Brandriss, 1998; Shemesh et al. 2001).

A number of studies have attempted to determine the empirical relationship between temperature, the oxygen isotope composition of different carbonate minerals and the composition of the water from which they formed. Many so-called palaeotemperature equations utilise the empirical relationship of Epstein et al (1953) which was famously turned into a palaeotemperature equation by Craig (1965). This data set was based on a collection of shells of marine organisms from around the world. The shells included both calcite and aragonite and the temperature of formation of the individual shells was, in many cases, assumed from regional climate data. More recent attempts to determine fractionation behaviour for inorganic and biogenic calcites (Grossman and Ku, 1986; Kim and O'Neil, 1997) involving careful laboratory experiments have yielded more precise equilibrium relationships which have gradients that are, perhaps surprisingly, very similar to the original mixed-mineralogy data.

There are a number of palaeotemperature equations for the equilibrium precipitation of carbonates from solution. Many workers use a version of the 'Craig' equation such as that proposed by Anderson and Arthur (1983):

$$T^{\circ}\text{C} = 16.0 - 4.14(\delta\text{c} - \delta\text{w}) + 0.13(\delta\text{c} - \delta\text{w})^2$$

In this equation  $\delta\text{c}$  is  $\delta^{18}\text{O}$  of the carbonate compared to the PDB international standard and  $\delta\text{w}$  is  $\delta^{18}\text{O}$  of the water compared to the SMOW international standard.

On the basis of new experimental data, Kim and O'Neil (1997) propose the following equilibrium fractionation relationship for calcite:

$$1000 \ln \alpha_{(\text{calcite-water})} = 18.03(10^3 T^{-1}) - 32.42$$

Here T is the temperature in Kelvin (i.e. °C + 273.18) and  $\alpha$  is the fractionation between mineral and water  $(^{18}\text{O}/^{16}\text{O})_{\text{calcite}} / (^{18}\text{O}/^{16}\text{O})_{\text{water}}$

In practice whilst water values are reported with respect to SMOW, calcite values are commonly reported with respect to the PDB carbonate standard. Using the relationship between calcite values

on the SMOW and PDB scales (Friedman and O'Neil 1977, Coplen et al 1983) and the approximation that:

$$1000 \ln \alpha_{(\text{calcite-water})} \sim = \delta^{18}\text{O}_{\text{calcite (SMOW)}} - \delta^{18}\text{O}_{\text{water (SMOW)}}$$

We have re-expressed the Kim and O'Neil relationship in a potentially more convenient form:

$$T^{\circ}\text{C} = 13.8 - 4.58(\delta\text{c}-\delta\text{w}) + 0.08(\delta\text{c}-\delta\text{w})^2$$

using the same notation as above.

We recommend adoption of this relationship as a measure of equilibrium although it must be noted that 'palaeotemperatures' calculated using it will be lower than those calculated using the Craig equation or its derivatives.

The above equations use the SMOW and PDB protocol but for all practical purposes these are essentially the same as using 'VSMOW' and 'VPDB' which has been adopted by many laboratories to signify that the data has been standardised in line with international protocols (Coplen 1994).

Aragonite and magnesian calcites precipitated at equilibrium generally have  $\delta^{18}\text{O}$  values that are higher than that for low magnesium calcites. Aragonite  $\delta^{18}\text{O}$  values are typically around +0.6 ‰ higher than equivalent calcite (Grossman, 1982; Abell and Williams, 1989). Magnesium calcites typically have  $\delta^{18}\text{O}$  values that are elevated by 0.06‰/mol%  $\text{MgCO}_3$  (Tarutani et al., 1969). For both aragonite and high magnesium calcite the offset from the calcite value appears to be independent of temperature (cf. Figure 1 in Kim and O'Neil, 1997).

In lake studies it is often assumed, but not proven, that carbonates and silicates formed in isotope equilibrium, but many studies lack the detailed investigation of contemporaneous materials to prove this (see section 2.3). Ideally any palaeoclimate study of sediments or fossils from a lacustrine sequence should include a study of the contemporary lake water and the modern mineral precipitates. The presence of a systematic relationship between temperature, water isotope composition and mineral composition for the modern lake enables quantitative interpretation of the sediment record. It is particularly useful to know when and where the carbonate precipitates in the modern environment. This may tell us whether the sediment record reflects summer or year round conditions.

#### *Temperature interpretation*

Assuming that equilibrium precipitation has occurred, the interpretation of oxygen isotope data in terms of palaeotemperatures requires an understanding of two processes that have opposing effects on the composition of a carbonate or silicate precipitate. At intermediate and high latitudes the oxygen isotope composition of mean annual precipitation correlates directly with change in temperature with a gradient of approximately +0.6‰/°C (Dansgaard 1964). Opposing this effect from

being transferred directly into the sediment record the equilibrium isotope fractionation between carbonate and water has a gradient of around  $-0.24\text{‰}/^{\circ}\text{C}$ . For many lake records the carbonate response to temperature will be dominated by the change in the isotope composition of precipitation and effectively 'damped' by the opposing effect of mineral-water fractionation. In this case the measured carbonate values will covary with temperature – with an increase of  $\sim 0.36\text{‰}/^{\circ}\text{C}$ . Eicher and Siegenthaler (1976) were amongst the first to use this relationship in the interpretation of a lacustrine record and the approach has been followed by many others. This is reasonable for the palaeoclimatic interpretation of many lakes but it implicitly assumes that  $\delta p/dT$  always changes according to the Dansgaard relationship. Several recent studies and our own unpublished data suggest that under some circumstances there are non-linear responses in the meteoric water cycle (see below).

### *2.3 Disequilibrium ('vital') and microenvironmental effects*

It has long been known that many carbonates do not precipitate in equilibrium with their environments. Disequilibrium effects (often called 'vital effects' in biogenic materials) have been attributed to:

- Rates of precipitation i.e. non reversible kinetic fractionation which occur in authigenic and biogenic precipitation.
- pH effects – speciation control (currently thought to be important in ostracod  $\delta^{18}\text{O}$  vital effects).
- Incorporation of metabolic fluids (particularly thought to affect  $\delta^{13}\text{C}$  in marine carbonate secreting organisms).
- Growth in microenvironments not typical of the water body as a whole (this is sometimes referred to as a vital offset – but in fact the organism may precipitate the shell in equilibrium with the microenvironment in which it lives, see section 5).

#### *Disequilibrium – authigenic carbonates*

Many palaeoclimatic studies of lake sediments rely on the analysis of bulk carbonate sediment – or fine fraction carbonate. Unless it can be shown that the bulk sediment is dominantly from a single source (i.e. authigenic) the analysis of bulk carbonate is to be avoided as it may contain variable proportions of biogenic and authigenic phases with very different compositions. In such cases stratigraphic changes in the isotopic composition may have more to do with changes in the relative abundance of components than it has to do with climate or other environmental changes. Fine fraction carbonate (authigenic carbonate) is often thought to be directly precipitated within the surface water of the lake and its production is often closely associated with the photosynthesis of either macroscopic plants or algae but it cannot be assumed to have precipitated in isotopic equilibrium. The precise mechanism of authigenic (and also skeletal) carbonate precipitation in association with photosynthesis remains problematical. Several workers highlight the importance of photosynthesis in carbonate precipitation, macrophytes, algae and cyanobacteria are all thought to be important by controlling the carbonate saturation state. They also provide nucleation sites for

carbonate precipitation where the degree of over-saturation is not high enough to support spontaneous precipitation.

Many palaeoclimatic studies have, often tacitly, assumed that authigenic carbonate formed in isotopic equilibrium but few studies have demonstrated that this has occurred. For example, data from Hawes Water (Figure 3), a small oligotrophic hard-water lake in NW England demonstrate that carbonate currently forms in the surface waters of the lake close to isotopic equilibrium with summer temperatures and water compositions but with an apparent offset of less than 1‰. Teranes et al. (1999) demonstrated a similar picture for carbonate precipitation in Baldeggersee in Switzerland with minor disequilibrium precipitation associated with seasonally rapid carbonate precipitation. In lakes where rates of mineral precipitation are particularly high however the carbonate may have  $\delta^{18}\text{O}$  values 2-3‰ below those expected for equilibrium (Fronval et al, 1995).

McConnaughey and Whelan (1997) highlight the general 'chicken and egg' dilemma for the precipitation of carbonates associated with photosynthesis – does photosynthesis elevate carbonate ion activity and cause calcification or does calcification counteract  $\text{CO}_2$  depletion and thus promote photosynthesis? The surfaces and individual cells of many plants and algae are characterised by discrete acidic and alkaline areas. McConnaughey and Whelan (1997) propose that the calcification of the freshwater alga *Chara*, and indeed the calcification of many organisms, occurs within the cells of the organism and is advantageous to the host in that it generates protons that promote nutrient and bicarbonate uptake and thus promote further photosynthesis. Their 'trans' calcification model is used to explain the strong kinetic (vital) depletions of  $^{18}\text{O}$  and  $^{13}\text{C}$  in many biological carbonates including those of common fresh water algae such as *Chara* (Hammarlund et al 1997).

#### *Vital effects – biogenic carbonates*

Vital effects are most commonly documented in  $\delta^{18}\text{O}$  composition of ostracod shells. Holmes and Chivas (2002) have tabulated the vital offsets (compared to equilibrium calcite) for a number of ostracod taxa. Almost all freshwater ostracods seem to exert a small positive (+0.3 to +2.5‰) vital effect on the oxygen isotopic composition - ie ostracod valve calcite is slightly enriched in comparison to equilibrium precipitates (eg Xia et al, 1997; von Grafenstein et al, 1999a; Holmes and Chivas, 2002). Recent research has suggested that the offset can be attributed to differences in internal pH and rate of calcification within the organism (Keatings et al 2002). In any case ostracod 'vital' effects appear to be systematic and species-specific. The offsets appear to be consistent across a range of temperatures but relatively few studies have attempted to test this.

The  $\delta^{13}\text{C}$  values of ostracod shells are generally thought to be similar to those of contemporaneous authigenic calcite (Keatings et al 2002), as any vital effects are offset by variations in the isotopic composition of the total dissolved inorganic carbon (TDIC) on the micro-scale (cf von Grafenstein et al 1999a).

### **3. Lake sediments as an archive for $\delta p$**

As outlined above, the oxygen isotope composition of modern global precipitation (mean annual  $\delta^{18}\text{O}_{\text{precipitation}}$  – or  $\delta p$ ) varies with latitude and altitude. In detail  $\delta p$  values are a function of the isotope

composition of the moisture source (generally the ocean), air-mass trajectory and the condensation temperature of the rain or snow. The basic physics of the processes controlling  $\delta p$  are relatively well understood and it has been incorporated as an output variable in several numerical climate models (e.g. Hoffmann et al., 2000). During episodes of climate change  $\delta p$  at a particular site will commonly change, and most significantly changes may be independent of changes in temperature.

If the  $\delta p$  signal from a lake-sediment record can be resolved from the local hydrological and temperature effects that affect the isotope composition of lake water and thus the composition of the mineral precipitates, it can provide an independent monitor of changes in meteorology during episodes of climate change and, independently, be used to test the performance of climate models. There is no reason to assume that past  $\delta p$  at a site will have a direct relationship to local temperature change. For example, distant changes in the temperature or isotope composition of the seawater undergoing evaporation or changes in the long-distance trajectory of air-masses may both affect  $\delta p$  in the absence of temperature change at the lake site. A number of recent studies have demonstrated significant short-term deviation from the Dansgaard relationship in the sediment records and have highlighted important shifts in the Holocene climate system (Edwards et al 1996; Teranes and McKenzie 2001; Hammarlund et al. 2002). Isotope studies of lake sediments that attempt to interpret oxygen isotope records solely in terms of temperature change at the site potentially ignore the possible effects of changes in  $\delta p$  that are related to more distant climatic processes (e.g. Figure 4).

The oxygen isotope composition of sedimentary (authigenic and biogenic) lacustrine carbonates or silicates have the potential to be used as a proxy for  $\delta p$  but extreme care must be taken before this interpretation is made. Specifically, it is necessary to know the relationship between the oxygen isotopic composition of lake water and  $\delta p$ . In lakes where evaporation effects are significant or where the residence times are too short for the lake water be representative of mean precipitation the isotope composition of the lake water does not change with  $\delta p$  (*see above*).

In deep lakes where the isotope composition of the lake water can be demonstrated to reflect mean annual precipitation, it has been demonstrated that a  $\delta p$  signal can be determined by the analysis of biogenic calcite from the shells of benthic ostracods which live below the thermocline and are thus not affected by seasonal shifts in temperature or evaporation. A high-resolution  $\delta p$  record from Ammersee, southern Germany (von Grafenstein et al. 1996), parallels that from the Greenland ice-core records but also identifies significant quantitative differences in the records that are attributed to both changes in the source of the water, in the North Atlantic, and changes related to changes in storm tracks across north western Europe (Figure 5).

To gain a fuller understanding of past climate, and test climate models, it will become increasingly necessary to derive global and regional maps of  $\delta p$ . Suitable deep lakes are rare so techniques are required derive reliable  $\delta p$  records from other archives. Sediments and fossils from small lakes or formed in the surface waters of large lakes may be useful in this respect but quantitative records of changes in lake-water composition, and by inference  $\delta p$ , may only be possible where certain conditions apply. For instance, calibration studies of carbonate precipitation

are essential to determine the relationships between contemporary  $\delta^{18}\text{O}_{\text{carbonates}}$ ,  $\delta\text{p}$ ,  $\delta^{18}\text{O}_{\text{lakewater}}$ , and temperature. Where carbonates can be shown to precipitate in equilibrium or with a known vital offset the sediment isotope record can be deconvolved in terms of  $\delta\text{p}$  using independent biological or elemental palaeotemperature proxies. Mg/Ca ratios may provide an indicator of temperature change but major uncertainties in partitioning, particularly in very low Mg lake waters may lead to considerable uncertainty in temperature determination (Figure 2 in Holmes and Chivas 2002). Numerical transfer functions based on modern populations (beetles, chironomids or pollen), and extended into the past using the nearest living relative approach, have potential precision of  $\sim 1^\circ\text{C}$  thus enabling calculations of past water composition to within  $\sim 0.3\text{‰}$ . However, care must be taken as each proxy and temperature reconstruction has its own problems. For example when reconstructing temperature from pollen-based reconstruction, vegetation recovery after a major climate shift often lags behind  $\delta\text{p}$  changes, the amount of lag can be hundreds (e.g. Figure 6) to thousands of years (Eastwood et al, in press). Faunal reconstructions, in general, often face environmental variable problems. For example in some circumstances the distribution and abundance of chironomid assemblages may be influenced by pH, total phosphorus, dissolved oxygen and lake depth, more strongly than temperature, and this may compromise the reliability of chironomid-inferred temperature reconstruction (Brooks, in press).

#### 4. Carbon isotope ratios

Inorganic carbon isotope ratios mainly from  $\text{HCO}_3^-$  ( $\sim$ Total Dissolved Inorganic Carbon) in lake waters are useful as tracers of environmentally determined processes which are often related to climate change. Carbon isotopes are fractionated during various carbon-cycle transitions and ultimately get incorporated into authigenic and biogenic carbonates. The bicarbonate is derived from interaction of groundwaters with rocks and soils in the catchment. During the precipitation of carbonate in lake waters there is a relatively small temperature effect (e.g.  $0.0355^\circ\text{C}^{-1}$ ) and only a small carbon isotope fractionation between the TDIC and solid phase (Romanek et al 1992). For example, at  $16^\circ\text{C}$  (typical mid latitude temperate summer) the  $\delta^{13}\text{C}$  of calcite is  $1\text{‰}$  more positive than the corresponding  $\delta^{13}\text{C}$  of the TDIC. Thus the  $\delta^{13}\text{C}$  of the mineral phase can provide information on the past  $\delta^{13}\text{C}$  of the TDIC within the lake. In general there are three predominant processes that control the inorganic carbon isotope composition of the TDIC: the isotope composition of inflowing waters,  $\text{CO}_2$  exchange between atmosphere and lake water, and photosynthesis/respiration of aquatic plants within the lake (Figures 2b and 7).

##### *Isotope composition of inflowing waters*

Ground waters and river waters in general have  $\delta^{13}\text{C}_{\text{TDIC}}$  values that are typically low; values for calcite precipitates between  $-10$  to  $-15\text{‰}$  have been reported from Northern Europe (Andrews et al. 1993, 1997). A significant proportion of the carbon comes from plant respiration and production of  $\text{CO}_2$  in the soils. Terrestrially derived C3 organic matter has mean  $\delta^{13}\text{C}$  between  $-20$  and  $-32\text{‰}$  (average  $-27\text{‰}$ ). Values higher than this for plants (up to  $-16\text{‰}$ ) do occur but are generally restricted to salt marsh plants and arid zone grasses (C4 taxa) which have  $\delta^{13}\text{C}$  between  $-17$  to  $-9\text{‰}$ .

Isotopically light  $\text{CO}_2$  liberated by decay of terrestrial organic matter in the soil enters the soil waters and shallow groundwaters. At pH values of ~7 to 10  $\text{HCO}_3^-$  is the dominant carbon species.  $\text{HCO}_3^-$  in equilibrium with  $\text{CO}_2$  gas has  $\delta^{13}\text{C}$  values ~10‰ higher than  $\text{CO}_2$  (Romanek et al., 1992), so  $\text{HCO}_3^-$  derived solely from soil  $\text{CO}_2$  with  $\delta^{13}\text{C}$  of between -32 and -20 ‰ should have  $\delta^{13}\text{C}$  values of ~ -22 to -10 ‰, i.e. within the range of measured groundwater.

Soil development can have a large effect on the over all TDIC budget, for example the change from pioneer herb communities to boreal forests development in the early Holocene in northern Sweden, resulted in soil development and an increase in the supply of  $^{13}\text{C}$ -depleted  $\text{CO}_2$  to the groundwater recharging the lake. This process can cause decreasing  $\delta^{13}\text{C}$  in the TDIC (Hammarlund et al, 1997).

Much higher  $\delta^{13}\text{C}$  (around -3 to +3 ‰) in groundwaters can occur in karstic regions where a proportion of the carbon atoms come from dissolution of catchment limestones (Andrews et al 1997). For example, calcites from a small, spring-fed open lake in southern Turkey (Lake Pinarbasi) with a limestone catchment has mean  $\delta^{13}\text{C}_{\text{calcite}}$  of +2.0 ‰ indicating that the  $\delta^{13}\text{C}$  of the TDIC in the inflowing water was around +1 ‰ (Leng et al 1999b).

#### *CO<sub>2</sub> exchange between atmosphere and water TDIC*

Many lakes precipitate carbonates which have high  $\delta^{13}\text{C}$ , covariant with high  $\delta^{18}\text{O}$  (Figure 2b). In hydrologically closed lakes, especially in a non-karstic catchments, the high values are likely to reflect different degrees of equilibration of the TDIC with atmospheric  $\text{CO}_2$  and preferential evaporative loss of the  $^{16}\text{O}$ . Experimental data show that this processes will tend towards equilibrium (Uzdowski and Hoefs 1990). Under isotopic equilibrium with atmospheric  $\text{CO}_2$ , which normally has  $\delta^{13}\text{C}$  values of c. -8 ‰, lake water  $\delta^{13}\text{C}$  would have a value between +1 to +3 ‰ (Figure 7). There are many large closed basin lakes, especially in the arid zones, where both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are both high (generally positive) and co-vary. These include low latitude lakes such as Bosumtwi (Talbot and Kelts 1986), Malawi (Ricketts and Johnson 1996), and Turkana (Ricketts and Anderson 1998), but also high-latitude small lakes in the Arctic, for example lakes along the ice sheet edge in western Greenland (Anderson and Leng, this volume). In these examples  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  show a close correlation. This correlation is often used to estimate the degree of hydrological "closure" of a lake through time (Talbot 1990) although it has been recognised that this interpretation is generally only true for lakes that have attained hydrological closure over extended time frames (Drummond et al 1995; Li and Ku 1997).

#### *Photosynthesis/respiration within the lake water*

In lakes the TDIC pool is often changed by biological productivity within the lake, mainly by preferential take up of  $^{12}\text{C}$  by aquatic plants during photosynthesis. During periods of enhanced productivity, or in lakes with a large biomass, the carbon pool in the water becomes depleted in  $^{12}\text{C}$  and consequently has a higher  $\delta^{13}\text{C}_{\text{TDIC}}$ . Changes in plant photosynthesis and respiration can be seasonal, for example at Malham Tarn (NW England, UK) it has been proposed that photosynthesis

by the calcareous algae *Chara* during the summer causes the remaining TDIC to be enriched in  $^{13}\text{C}$  (Coletta et al 2001). Summer stratification in the water column in response to photosynthesis and organic production in the surface waters occurs in many lakes and leads to significant differences in the carbon isotopic composition of the total dissolved organic carbon which will be reflected in the carbon isotopic composition of carbonates precipitated at different depths in the water column (e.g. Figure 8). Another example is Lake Greifen, NE Switzerland (McKenzie 1985, McKenzie and Hollander 1993) where mixing of the water column and very low photosynthesis in the winter and early spring causes the  $\delta^{13}\text{C}_{\text{TDIC}}$  in the water column to remain relatively homogenous. In the late spring and early summer temperature increase and lake water overturn brings a supply of nutrients to the surface and causes phytoplankton blooms. These phytoplankton preferentially utilise the  $^{12}\text{C}$  and so there is a significant increase in the  $\delta^{13}\text{C}$  value of the TDIC in the surface waters, peaking around -7.5 ‰, while the bottom water TDIC drops to around -13 ‰ due to respiration of the sinking organic matter. In highly organic shallow lakes, organic matter oxidation can lead to very low  $\delta^{13}\text{C}_{\text{TDIC}}$  due to the localised availability of  $^{12}\text{C}$ . In Gölhisar, a shallow lake in SW Turkey,  $\delta^{13}\text{C}$  in calcite from an organic rich marginal core have values dropping to -19‰ (Eastwood et al. in press).

Stratification within a lake's water column can also become permanent. This can cause a large change in  $\delta^{13}\text{C}$  value of carbonates precipitating from the lake water. In western Greenland for example (Anderson and Leng, this volume), the preservation of laminated sediments is interpreted as the onset of permanent anoxic hypolimnetic waters. Before stratification the lakes were well mixed and high values for  $\delta^{13}\text{C}$  in authigenic calcite are interpreted as due to exchange with atmospheric  $\text{CO}_2$  during arid periods. When lake levels are high, the  $\delta^{13}\text{C}$  values are low suggesting more TDIC from soil respiration. However the onset of permanent anoxic bottom waters slowed the rate of organic matter oxidation. Stratification effectively reduced the oxidation of organic matter causing higher  $\delta^{13}\text{C}_{\text{TDIC}}$ .

## **5. Interpretation of oxygen isotopes from different components within lake sediments**

### *Authigenic carbonate*

Authigenic carbonates are commonly precipitated by photosynthetic utilisation of  $\text{CO}_2$  and resultant calcium carbonate supersaturation in the water column. Many palaeoclimatic studies have, often tacitly, assumed that fine-fraction carbonate formed in isotopic equilibrium (see section 2.3). In most temperate and high-latitude regions authigenic carbonates are precipitated mainly in the summer months during periods of maximum phytoplankton productivity (Leng et al. 1999b, Teranes and McKenzie 2001). In mid-latitude and tropical lakes, phytoplankton growth may occur throughout the year although other mechanisms may also cause continuous carbonate precipitation e.g. the Dead Sea aragonite (Niemi et al. 1997). More commonly in the tropics carbonate precipitation is related to phytoplankton blooms associated with annual lake-water mixing and nutrient availability (cf. Lamb, H.F. et al. 2002).

The advantage of using authigenic carbonate for palaeoclimatic work is that it provides an integrated climate signal for the whole sample which may be 1, 10 or even 100 years, depending on sedimentation rate. However, there are some potential problems. It can be difficult to distinguish

between authigenic and allogenic (detritus derived from the terrestrial environment) carbonates, especially in karstic regions, so there is always the possibility of contamination of the isotope signal from a washed-in component. Allogenic input is generally only associated with lakes with riverine or stream input. However, the influx of detrital carbonates into a lake can be used to identify climate change such as the Younger Dryas because of the generally much higher  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values from detrital clastics (especially if they are limestones of marine origin) (cf. Hammarlund and Buchardt 1996). In addition, there are several carbonate minerals that could precipitate out in a lake and each mineral has its own mineral-water fractionation (see above). In freshwater systems calcite ( $\text{CaCO}_3$ ) usually forms but with increasing evaporation other forms occur such as aragonite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) can occur as in Lake Bosumtwi (Talbot and Kelts 1986). As described above aragonite  $\delta^{18}\text{O}$  is about 0.6 ‰ more positive than calcite formed under the same conditions, while dolomite is c. 3 ‰ more positive (Land 1980). Physically separating different carbonate minerals is not easy, although there is some suggestion that by limiting reaction times dolomite dissolution can generally be excluded (eg. Al-Asam et al. 1990), although this depends critically on grain size.

Authigenic calcite is probably the most common mineral used for isotope analysis in lake sediments. In general, studies fall into two types: either closed lakes that tend to be more common at the low altitudes; or open high altitude lakes. There are however, a whole range in lake types and different water residence times, from hundreds of years in some large lakes, to open lakes which essentially allow a continuous through-flow of water (Table 1). Large closed lake systems tend to lose water predominantly through evaporation, and have enriched  $\delta^{18}\text{O}_{\text{lakewater}}$  values. Fluctuations in the isotope composition of authigenic carbonate (which can have amplitudes of >10 ‰) are mainly a function of long term changes in the precipitation/evaporation ratio. These types of lakes are often classified as salt lakes and have abundant authigenic carbonate, and there are many examples. They are particularly common at lower latitudes (Li and Ku 1997) especially in the tropics (Ricketts and Johnson 1996, Holmes et al. 1997, Ricketts and Anderson 1998, Lamb, A.L. et al. 2000) (Figure 9) and the Mediterranean (Frogley et al. 1999, Leng et al. 1999b, Reed et al. 1999, Roberts et al. 2001, Eastwood et al in press) although are also known from the Polar regions (Noon et al. 2003, Anderson and Leng, this volume).

In contrast high-altitude lakes which have a degree of throughflow typically have oxygen isotope compositions that vary down-core by no more than a few ‰. These variations are generally ascribed to variations in temperature or  $\delta p$  and, as described above, this is an effect on both the isotopic composition of precipitation and the fractionation during carbonate/diatom precipitation. The lake water is generally similar to mean weighted annual precipitation. These types of lakes are common in Northern Europe and at high altitudes where the  $\delta^{18}\text{O}$  values of authigenic carbonate preserve a record of changing isotopic composition of precipitation. In lakes where there is a limited catchment area and short water residence time, it has been assumed that carbonate precipitation occurs at approximately the same time during the annual cycle when the range of the surface-water temperatures is about the same each year. Variations in the  $\delta^{18}\text{O}$  of the carbonate are

then related directly to past changes in the isotopic composition of mean annual precipitation (McKenzie and Hollander 1993).

It must be noted, however, that authigenic calcites can show down-core variations in isotope ratios which may not be climatically influenced. For example, variations in amount and composition of lake water input may be due to catchment change such as occurs after deposition of tephra or deforestation. Effects that are unrelated to climate variation, have been demonstrated as a cause of large changes in authigenic calcites in East Africa (Lamb, A.L. et al 2002) and MesoAmerica (Rosenmeier et al 2002).

### *Biogenic materials*

The use of oxygen and carbon isotopes as environmental tracers can also be used in biogenic materials. However, knowledge of growth period, habitat etc. are essential in interpreting this type of data. Carbonate studies tend to be restricted to ostracod and snail shell carbonates although green algae, such as *Chara* (Coletta et al. 2001) and molluscan glochidia (the larval shells of bivalves) (Griffiths et al. 2002) also have potential. Outlined below are the advantages and disadvantages associated with the various types of biogenic materials, with some examples of where they have been successfully used.

Ostracod shells – advantages include the multiple moults that ostracods undergo to reach the adult stage (analysis of individual shells from the sample period can give an indication of seasonal variation within the lake), the short duration of calcification after each moult, the shell surface morphology (which can be used as an indication of preservation), the relative ease with which they can be isolated from the bulk sediment. The disadvantages include any vital effects (see section 2.3), and the potential for ostracods to be washed in to lakes from rivers/streams and may have calcified their shells in an environment other than where they are found. Ostracods grow their shells seasonally so a good knowledge of species ecology, especially of habitat preferences and moult stages, is required because individuals reach the adult stage over a period of time and thus a random selection of individual shells will span an unknown period (Heaton et al. 1995). In lakes that have large seasonal variation in temperature or lake water  $\delta^{18}\text{O}$ , single or small numbers of shells may only represent water conditions during a part of the seasonal variation so this type of data can be difficult to interpret (Lamb, H.F. et al. 1999, Bridgewater et al. 1999).

Ostracod shells are relatively small, normally weighing only a few micrograms. Techniques that are commonly used for ostracod isotope analysis normally require a minimum of a few micrograms of  $\text{CaCO}_3$ , so some very small species such as *Cypria ophthalmica* which are ubiquitous but weigh much less than this (H. I. Griffiths personal communication) cannot be analysed as individuals. Taking only a small number of shells from a seasonally changing lake obviously has the potential of producing ambiguous data unless a statistically significant population is used. However, ostracod calcite has been used successfully for climate reconstruction (eg. Holmes, 1996, Holmes et al. 1997, Frogley et al. 1999, Ricketts et al 2001).

To use  $\delta^{18}\text{O}_{\text{ostracod}}$  in a quantitative, rather than qualitative way depends on, amongst other things, knowledge of the isotope fractionation between ostracod calcite and water. All

calibration studies of  $^{18}\text{O}/^{16}\text{O}_{\text{ostracod-water}}$  fractionation have shown that ostracods precipitate their shell calcite out of equilibrium with lake waters, the vital effects described earlier. In laboratory cultures, Xia et al. (1997) found that the calcite valves of *Candona rawsoni* had  $\delta^{18}\text{O}$  values higher than expected for equilibrium, and that the amount of offset from equilibrium differed under different culture conditions. In monitoring studies of lakes in southern Germany, von Grafenstein et al. (1999a) recorded  $\delta^{18}\text{O}_{\text{ostracod}}$  values higher than expected for equilibrium, with different offsets for different taxa. Using the delta differences they were able to show that the oxygen isotope composition of Ammersee lake water is mainly controlled by the isotopic composition of local precipitation, which is empirically linked to air temperature and  $\delta p$  (see Figure 5).

Mollusc shells - the isotopic composition of fossil fresh-water mollusc shells is generally utilised less often relative to other forms of carbonate. Both bivalves and gastropods are widespread in Quaternary lacustrine deposits although may not occur continually, and are often composed of thermodynamically unstable aragonite, which can convert to calcite and effectively “reset” the isotope signal. However, it is generally thought that the oxygen and carbon stable isotope values of snail-shell carbonate ( $\delta^{18}\text{O}_{\text{snail}}$ ,  $\delta^{13}\text{C}_{\text{snail}}$ ) reflect the isotopic composition of lake-water (Fritz and Poplawski 1974, Leng et al. 1999a). Although the only robust calibration of fractionation between water and the freshwater mollusc *Lymnaea peregra* showed that there is a fractionation of isotopes in synthetic and biogenic aragonite for molluscs in general, there is no vital effect that is specific to individual genera (White et al 1999). Some studies have raised concerns with inter-species fractionation differences (e.g. Abell and Williams 1989), although records have been published using multiple species where variation has been considered insignificant (Gasse et al. 1987, Abell and Hoelzmann 2000). Some of these records use only one or two individual shells from a stratigraphic level (e.g. Bonadonna and Leone 1995, Zanchetta et al. 1999) although others have shown considerable ranges, albeit from unspecified numbers of shells, from individual sample levels (Abell and Hoelzmann 2000). From Gölhisar in southern Turkey, Jones, M.D. et al. (2002) demonstrated that analysis of individual shells provides a range in data that is related to both seasonal and annual changes in the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the lake-water, since samples from lake-sediment cores represent a number of years, dependent on sedimentation rates. This study also shows that co-existing species yield different  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values, probably due to habitat differences, water source and food supplies within the same lake. If multi-species records are necessary, due to the nature of the fossil mollusc record, overlapping species should be chosen to allow comparison of the species through time.

Some of the larger species of freshwater snails form carbonate in a regular manner over a fixed and relatively short period. These are important in providing the possibility for achieving continuous, inter-seasonal information about the changing isotopic composition of the lake-water. In this regard, the gastropod *Melanooides tuberculata* has great potential. This snail is widespread in modern (Abell 1985) and Quaternary deposits throughout Africa and Asia and is ubiquitous in both fresh and highly evaporated lakes. In one study of whole-shells and incremental growth, Leng et al. (1999a) analysed both modern and fossil *Melanooides* from two lakes in the Ethiopian Rift Valley.  $\delta^{18}\text{O}$  values in the modern shells show that the snail carbonate precipitates in equilibrium with

modern waters.  $\delta^{18}\text{O}$  values in fossil shells show changes over the lifetime of the organism associated with enhanced monsoonal conditions in the early Holocene (Figure 10).

Some snail shells have isotope compositions that are almost never representative of the lake environment as a whole. Individual genera might have very different life styles and mobile individuals can inhabit microenvironments with different water sources and food supplies that may affect the isotopic composition of the shells. Warrington (1990) investigated isotopic fractionation in a number of different groups of freshwater and terrestrial snails and found that whilst purely sub-aquatic, gill-bearing species formed shells close to isotopic equilibrium those capable of breathing air had very variable isotope compositions that could only reflect very local changes in microenvironment.

*Biogenic silica* - is deposited by a variety of aquatic organisms including diatoms and sponges. It is especially useful in acidic lakes with no authigenic or biogenic carbonates. The oxygen isotope composition of biogenic silica is potentially useful in palaeoclimate studies, because it is often found in greatest abundance in high-altitude, open (low residence time), freshwater systems where the isotopic composition of the lake-water is the same as the composition of meteoric water. Biogenic silica has been used as a proxy for temperature change in many studies (Rietti-Shati et al. 1998, Rosqvist et al. 1999, Leng et al. 2001, Jones et al, this volume), although the temperature dependence of oxygen isotope fractionation between diatom silica and water is still controversial. The fractionation has been estimated previously from analyses of diatoms from marine and freshwater sediments, coupled with estimates of the temperatures and isotopic compositions of coexisting waters during silica formation (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987, Matheney and Knauth 1989). Realistic fractionations vary somewhat because data from calibration studies are limited, and based on bulk samples (Labeyrie and Juillet 1982, Wang and Yeh 1985, Juillet-Leclerc and Labeyrie 1987, Shemesh et al. 1995). Published estimates of the average temperature dependence for typical ocean temperatures range from -0.2 to -0.5 ‰/°C (Juillet-Leclerc and Labeyrie 1987; Shemesh et al. 1992) and these estimates are often used in lake-based studies although little may be known about the effect of the changing  $\delta^{18}\text{O}_{\text{water}}$  which is important in lakes. This was partially addressed by analysis of diatoms cultured in the laboratory (Brandriss et al. 1998), which showed a diatom-temperature coefficient of -0.2 ‰/°C. Further questions have been raised by Schmidt et al. (1997), who analysed the oxygen isotope composition of diatom frustules collected live from the oceans. They found no regular correlation between temperature and the oxygen isotope fractionation between diatom silica and water. These results led to the hypothesis that the temperature-dependent oxygen isotope fractionation preserved in biogenic opaline sediments may have been established during diagenesis rather than acquired during growth.

Certain diatom records have been shown to be sensitive to other aspects of climate, such as amount or source of precipitation. For example abrupt shifts of up to 18 ‰ in  $\delta^{18}\text{O}_{\text{diatom silica}}$  have been found in a 14 ka-long record from two alpine lakes on Mount Kenya (Barker et al. 2001), which can not be entirely temperature related given the current knowledge of the diatom-temperature fractionation (Figure 11). Instead the variations have been interpreted as a moisture balance effect related to changes in Indian Ocean sea surface temperatures through the Holocene.

Episodes of heavy convective precipitation in the  $\delta^{18}\text{O}_{\text{diatom}}$  record correlate with enhanced alkenone-based sea surface temperature estimates. In a study in Northern Scandinavia, oxygen isotope ratios in diatoms have been linked with changes in source of precipitation (Shemesh et al. 2001). Lake waters in the region have undergone limited evaporation so the stratigraphic  $\delta^{18}\text{O}_{\text{diatom}}$  record is primarily controlled by changes in the summer isotopic composition of the lake water. The overall 3.5 ‰ decrease in  $\delta^{18}\text{O}_{\text{diatom}}$  since the early Holocene is interpreted as an increase in the influence of the Arctic polar continental air mass which has a much lower oxygen isotopic composition.

*Organic matter* - studies of organic material in lake sediments have demonstrated that the carbon isotope ratio can vary considerably (Figure 7). There are many reported processes that control this variation. The most predominant are the effects associated with different sources of organic material and their different photosynthetic pathways and productivity (Ariztegui et al. 1996). Different sources of organic material may have different  $\delta^{13}\text{C}$  values (eg. Meyers and Lallier-Verges 1999), but there is considerable overlap in the  $\delta^{13}\text{C}$  of various plants (Figure 5), so carbon/nitrogen (C/N) ratio analysis of the same material can help to define the source of the organic matter (Silliman et al. 1996), for example to help distinguish between algal and higher plant carbon sources. C/N values between <10-12 are common for lacustrine algae, values between 10 and 20 for submergent and floating aquatic macrophytes or a mixed source, and values >20 for emergent macrophytes and terrestrial plants (1995, see Lamb et al, this volume). Where there is a limited source of terrestrial carbon, the  $\delta^{13}\text{C}$  of organic carbon can be a reliable proxy for palaeoproductivity, which may be due to the response of aquatic plants to increased nutrients via enhanced inwash during wetter periods (Hodell and Schelske 1998, Battarbee et al. 2001).

The oxygen isotope analyses on the fine-grained cellulose fraction of lacustrine organic matter is a relatively new tool for reconstructing past hydrological conditions (eg. Abbott et al. 2000, Anderson et al. 2001, Saucer et al. 2001). Lake-water  $\delta^{18}\text{O}$  histories have been directly inferred from the  $\delta^{18}\text{O}$  of cellulose in sediment cores on the assumption that the isotopic fractionation between cellulose and lake water is unaffected by changes in temperature and plant species. Assuming a lacustrine origin and constant isotopic fractionation between cellulose and lake water, interpretation of  $\delta^{18}\text{O}$  in lake sediment cellulose is reduced to distinguishing between changing source of precipitation or precipitation/evaporation (Wolfe et al 2000, 2003).

*Biomarkers* - in recent years, measurement of carbon isotope ratios from individual compounds (biomarkers) within a lake sediment have allowed more detailed analysis of the composition of organic material (see Street-Perrott et al, *this volume*). Both terrestrial and aquatic organic matter sources can be independently assessed and the changing proportion of input from terrestrial, aquatic and algae can be identified (Ficken et al. 1998). In biomarkers from terrestrial plant remains washed into lakes,  $\delta^{13}\text{C}$  values have been shown to exhibit large shifts between glacial and interglacial times associated with shifts from C4 to C3 plants (Huang et al. 1999).

## **6. Multi isotope comparisons**

In many lake sediments there are potentially several types of authigenic components (e.g. calcite, ostracod and snail shells, diatom silica etc) that precipitate during different seasons. There are

studies that combine isotope analysis of carbonate with organic materials, however, these tend to give a comparison of within lake and catchment processes. For example, Lamb et al (this volume) show that changes in the proportion of terrestrial vegetation in Lake Tilo, Ethiopia, is a function of enhanced aridity and lowering of lake levels. By linking the isotope data with pollen records they also demonstrate changing abundance of macrophytes.

Combining isotope analysis of different authigenic minerals offers the possibility of obtaining seasonally specific information. For example where authigenic calcite and diatom silica co-occur they may provide different, yet complementary, oxygen-isotope signatures weighted by different seasonal biological productivities. In most temperate regions planktonic diatom production follows a well-defined seasonal cycle, peaking first in the spring and then in autumn (Reynolds, 1984), although some diatom species can grow from spring to autumn, and species specific blooms also occur during restricted periods (Raubitschek et al., 1999), so a knowledge of species ecology is vital. Oxygen isotope data from diatoms will contain components of different seasonal growth, but bulk analysis will be weighted towards the major growth periods. In contrast authigenic calcite precipitation mainly occurs when nutrient availability, enhanced light regime and warmer temperatures contribute to enhanced algal productivity (Reynolds, 1984). In temperate areas with strong seasonality, biogenic calcite production and its isotopic signature will usually be weighted toward summer conditions. Therefore depending on the period of diatom growth, a comparison of  $\delta^{18}\text{O}_{\text{calcite}}$  and  $\delta^{18}\text{O}_{\text{diatom}}$  may provide information on seasonality (i.e. spring to summer). A comparison of the  $\delta^{18}\text{O}$  of calcite (summer) and diatom silica (predominantly spring) in a small, open groundwater fed lake in Turkey shows differences in the two  $\delta^{18}\text{O}$  curves and confirms diatom silica will not always provide a direct substitute for carbonate based analysis in acid lakes (Figure 12). In this case the strong seasonality probably caused authigenic calcite precipitation to be temporally limited to a few summer months while the diatom silica limited to early spring due to enhanced nutrient supply brought in by the spring thaw of winter snow. Therefore changes in summer temperatures are thought to be recorded by the calcite record, whereas different amounts of snow melt in the spring are thought to influence the diatom record (Leng et al 2001). Isotope comparison between the authigenic calcite and ostracods (*Prionocypris zenkeri*) from this lake show similar curves. Although notable is the large range in both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  from 10 analysis of individual ostracod valves. This is quite surprising since *Prionocypris zenkeri* is thought to reach the adult stage during the autumn (see section 5). Without knowledge of the vital offset it is difficult to interpret the differences in the isotope curves (Leng et al 1999b).

It is possible to get seasonally specific information from biogenic carbonates where details of life cycle and vital off sets are known or can be obtained by undertaking a Recent calibration. For example in a classic study by von Grafenstein et al (1994) from Ammersee in southern Germany oxygen isotope records from the bivalve mollusc *Pisidium* sp. and a mixed ostracod assemblage of various *Candona* species, *Limnocythere santi-patricii*, *Cytherissa lacustris* were able to show high-frequency climate changes during the last deglaciation. The different groups showed different but systematic variation in  $\delta^{18}\text{O}$ . The freshwater bivalve *Pisidium* sp. calcifies its shell in the summer months over several years, and as such it should be influenced by mean

summer temperatures. The ostracod *Candona* sp., reaches the adult stage in the autumn and therefore should represent mean autumn water temperatures. In contrast *Cytherissa lacustris* reproduces throughout the year and lacks a seasonal frequency maximum of adult individuals. If a large number of shells of this species are analysed together this should give an estimate of the mean annual water temperature. The difference between  $\delta^{18}\text{O}$  of *Pisidium* and *Candona* from one sample, corrected for vital effects, provided an estimate of the difference between mean summer and mean autumn water temperatures. The seasonal temperature contrast gained in this way is independent on any change in the  $\delta^{18}\text{O}_{\text{lakewater}}$ , which will be the same for both species. In this way von Grafenstein et al (1994) were able to show a synchronous change in late-glacial climate between Greenland, and the lakes of central Europe.

## **7. Summary**

This review has attempted to demonstrate how the oxygen and carbon isotope composition of lacustrine sedimentary materials can yield a wide range of useful palaeoclimate information. A full interpretation of isotope data from the various components within a lake sediment requires a detailed knowledge of the processes that control and modify the signal, and this must be determined for an individual lake system. Where possible, it is particularly important to carry out a calibration exercise investigating the basic systematics of isotopic variation in the modern lake environment to establish the relationship between the measured signal and the isotopic composition of the host waters. A robust calibration may not be easy; the materials may not occur in the contemporary lake for example or the lake 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 should be based on evidence from both a multi-proxy approach using isotope signals from different materials as well as using other palaeolimnological techniques.

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**Figure 1.** Controls on the oxygen isotope composition of lacustrine carbonates ( $\delta^{18}\text{O}_{\text{carb}}$ ). If carbonate is precipitated in isotopic equilibrium,  $\delta^{18}\text{O}_{\text{carb}}$  depends entirely on temperature and the isotopic composition of the lake water ( $\delta^{18}\text{O}_{\text{water}}$ ). Disequilibrium effects, commonly known as 'vital effects' in biogenic precipitates, caused by local changes in microenvironment or rate of precipitation can induce systematic or non-systematic offsets in the  $\delta^{18}\text{O}_{\text{carb}}$  signal. Interpretation of  $\delta^{18}\text{O}_{\text{carb}}$  signal in terms of temperature depends on a knowledge of the environment and time of year in which a particular type of authigenic or biogenic carbonate forms. For example authigenic carbonates typically form in response to summer photosynthesis in surface waters whereas some benthic ostracods are known to calcify in cold deep waters. Quantitative interpretation similarly demands an understanding of the local controls on the isotopic composition of lake water ( $\delta^{18}\text{O}_{\text{lakewater}}$ ). In lakes with optimum hydrology (size and precipitation/evaporation regime) there is a simple relationship to  $\delta^{18}\text{O}_{\text{precipitation}}$  but in others the water composition is strongly influenced by processes such as evaporation within the catchment and within the lake itself.  $\delta^{18}\text{O}_{\text{precipitation}}$  is increasingly being shown to be an important indicator of climate change: it typically changes with mean annual temperature but non-linear responses to climate change are increasingly being recognised. See text for more discussion of this figure.

**Figure 2.** (a) Major controls on the  $\delta^{18}\text{O}$  v  $\delta\text{D}$  of precipitation and lake waters. The Global Meteoric Water Line (GMWL) is an average of many local or regional meteoric water lines whose slopes and intercepts may differ from the GMWL due to varying climatic and geographic parameters. In general however, warmer, tropical rains have higher  $\delta$  values, while colder, polar precipitation has lower  $\delta$  values. Lake waters plotting on or close to the GMWL are isotopically the same as precipitation, whereas lake waters that plot off the GMWL on a local evaporation line (LEL) have undergone kinetic fractionation. Molecular diffusion from the water to the vapour is a fractionating process due to the fact that the diffusivity of  $^1\text{H}_2^16\text{O}$  in air is greater than  $^2\text{H}^1\text{H}^16\text{O}$  or  $\text{H}_2^{18}\text{O}$ . With evaporation the isotopic composition of the residual water in the lake and the resulting water vapour become progressively more enriched, in both cases the kinetic fractionation of  $^{18}\text{O}$  exceeds that of  $^2\text{H}$ . In general, groundwater-fed open lake waters should have a  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition similar to mean weighted values for precipitation, and fall on a MWL. Evaporating lakes will have  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values which lie on a LEL with a slope determined by local climate (see Clarke and Fritz 1997). (b)  $\delta^{13}\text{C}$  v  $\delta^{18}\text{O}$  of lakewaters. Hydrologically closed lakes often show  $\delta^{18}\text{O}$  v  $\delta^{13}\text{C}_{\text{TDIC}}$  covariance, the high values reflect different degrees of equilibration of the TDIC with atmospheric  $\text{CO}_2$  and preferential evaporative loss of the  $^{16}\text{O}$  respectively. Ground waters and river waters have  $\delta^{13}\text{C}_{\text{TDIC}}$  values that are typically low, values are generally between -10 to -15 ‰ from plant respiration and production of  $\text{CO}_2$  in the catchment soils.

**Figure 3.** Isotopic fractionation (expressed as  $1000\ln\alpha$ ) against temperature for contemporaneous authigenic carbonate precipitates, collected on sediment traps in Hawes Water, NW England. The carbonate in Hawes Water precipitates close to, but with a slight offset from, equilibrium as defined

by the relationships of Friedman and O'Neil (1977) and Kim and O'Neil (1997). Data by courtesy of SF Crowley, Hawes Water Research Group, Department of Earth Sciences, University of Liverpool. (Figure modified from Jones and Marshall 2002).

**Figure 4.** Carbonate based isotope records from Lake Tibetanus, a small open, groundwater fed lake in Northern Sweden show that there are differences in the normal  $\delta^{18}\text{O}$ -temperature relationship which are attributed to changes in oceanography at the source. The transition from relatively moist, maritime conditions in the early Holocene to a much drier climate after 6500 cal. BP is also reflected by major changes in forest coverage and type as recorded in the pollen and macrofossil data. Sed = fine grained sedimentary carbonate (mainly Chara), Pis = *Pisidium* sp. Mollusc aragonite, Can = adult *Candona candida* ostracod calcite. (From Hammarlund et al 2002 with permission from Arnold Publishers).

**Figure 5.** Ammersee *Candona*-mean annual air temperature (MAAT).  $\delta^{18}\text{O}$  values of shells of *Candona* sp. from Ammersee, Germany (upper curve) compared to two times three year backward running means of MAAT from Hohenpießenberg, which lies within the Ammersee catchment (lower curve). Post-1922 ostracod  $\delta^{18}\text{O}$  values have to be corrected for the effects of river regulation: thin line represents uncorrected values. Encircled crosses and diamonds on the upper graph represent uncorrected and corrected values of living *Candona* collected in 1993 (from von Grafenstein et al 1996). Reprinted from: von Grafenstein U, Erlenkeuser H, Muller J, Trimborn P and Alefs J. 1996. A 200 year mid-European air temperature record preserved in lake sediments: an extension of the  $\delta^{18}\text{O}_p$ -air temperature relation into the past. *Geochimica et Cosmochimica Acta*, 60, 4025-4036 with permission from Elsevier.

**Figure 6.** Correlation of late-glacial climate records from Greenland to Europe. Lake isotopic records can provide a coherent picture of climate and enable monitoring of the regional impact of climatic events. Data from the Greenland Ice Core, Hawes Water (a small carbonate lake in NW England)  $\delta^{18}\text{O}$  record from authigenic carbonates (Marshall et al 2002, Jones, R.T. et al 2002), Ammersee benthic ostracods from deepwater lake record from S Germany (von Grafenstein et al 1999b) and a temperature record based on the analysis of Chironomids from southern Scotland (Brooks and Birks, 2001). Note the temporal lags (several hundreds of years) in climate response between pollen and isotope records from Hawes Water. The isotope records are all essentially reflecting changes in the isotope composition of precipitation and local temperature change. Detailed comparison of isotopic data and independent temperature records such as the chironomid record enable calculation of water compositions. (Diagram modified from Jones and Marshall, 2002).

**Figure 7.** Carbon isotope values for the major sources of carbon into lakes and examples of the range of resulting  $\delta^{13}\text{C}_{\text{TDIC}}$ . The  $\delta^{13}\text{C}_{\text{TDIC}}$  is higher (up to ~-3‰) when groundwater flows in an area dominated by C4 plants. Where lake water stratification occurs the TDIC pool may have relatively high  $\delta^{13}\text{C}$  as the onset of permanent anoxic bottom waters slows organic matter oxidation and allows

the preservation of greater amounts of organic material, effectively removing  $^{12}\text{C}$  from the system. In highly organic lakes (especially if a portion of the organic material is derived from the terrestrial environment) oxidation of organic matter leads to lower TDIC as  $^{12}\text{C}$  is liberated.

**Figure 8.** Measured oxygen levels, temperature and  $\delta^{13}\text{C}_{\text{TDIC}}$  in the water column at Hawes Water, NW England. Stratification in the water column, which develops during the summer months, in response to photosynthesis and organic production in the surface waters of many lakes leads to significant differences in the carbon isotope composition of the total dissolved organic carbon which will be reflected in the carbon isotopic composition of carbonates precipitated at different depths in the water column. (Data courtesy of the Hawes Water Research Group).

**Figure 9.** The stable isotope composition of authigenic calcites in a core from Lake Tilo, a small crater lake in the Ethiopian Rift Valley, provides a sub-century scale record of lake response to climatic change over the last 8,850  $^{14}\text{C}$  yrs (9,850 cal. yrs). An unusually high range of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values ( $\sim 15\text{‰}$ ) is attributed, in part, to major changes in groundwater flux. Although groundwater influx to the lake was high during the early Holocene its flow rate was relatively stable and thus climatically induced changes to the water budget can be inferred from variations in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  ratios. A major decline in groundwater input from  $\sim 5,500$   $^{14}\text{C}$  yrs BP increased lake water residence time and led to substantial enrichments in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , before the mid Holocene transition to more arid conditions in the region. During the last  $\sim 2,700$   $^{14}\text{C}$  years there has been some diagenetic changes but extremely varied  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are thought to be predominately responding to changes in the range of monsoon strength (redrawn from Lamb, A.L. et al 2000). Data shown reconstructed changes in lake level above standard datum (SD) for the Ziway-Shala lakes in Ethiopia.

**Figure 10.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  incremental growth data ( $\sim 1$  year) along the spiral of the whorl from *Melanoides Tuberculata* from two lakes in the Ethiopian Rift Valley.  $\delta^{18}\text{O}$  values in the modern shells from Lake Awassa are in equilibrium with modern waters, while  $\delta^{18}\text{O}$  values in the early Holocene shell from Lake Tilo indicate shorter-term variability of lake water probably due to enhanced monsoon strength in the early Holocene (modified from Leng et al 1999a).

**Figure 11.** Isotope data from Simba Tarn, Small Hall Tarn, and Hausberg Tarn (Mount Kenya) and a comparison with lake levels in the Ziway-Shala Basin, Ethiopia, derived from  $^{14}\text{C}$  dated shorelines. Abrupt shifts of up to 18 ‰ in diatom silica are thought to represent lake moisture balance. Episodes of heavy convective precipitation dated  $\sim 11.1$ -8.6, 6.7-5.6, 2.9-1.9, and  $<1.3$  thousand years before present, were linked to enhanced soil erosion, neoglacial ice advances, and forest expansion on Mt. Kenya (from Barker et al 2001). Reprinted from Barker, P.A., Street-Perrott, F.A., Leng, M.J., Greenwood, P.B., Swain, D.L., Perrott, R.A., Telford, J. and Ficken, K.J. 2001. A 14 ka

*oxygen isotope record from diatom silica in two alpine tarns on Mt Kenya. Science, 292, 2307-2310, with permission from Elsevier.*

**Figure 12.** Comparing isotope data from authigenic carbonate and diatom silica from a small, hydrologically open, high altitude lake in southern Turkey. Authigenic calcite is thought to precipitate in the summer months, while the diatoms are thought to grow predominately in the spring months. The strong seasonality (spring-summer) of this region allows the materials to capture different climatic conditions. The dating control is relatively poor, but the data seems to show that the warmer interglacial summers in the calcite record correspond to enhanced amounts of snow melt in the spring seen in parts of the diatom record. In the glacial, cooler summer months are associated with arid winters with little snow (modified from Leng et al 2001).

**Table 1.** Features of lakes likely to produce temperature,  $\delta p$  or precipitation/evaporation reconstructions from isotopic composition of primary precipitates within a lake sediment.



<b>Lake-water volume</b>	Very small	Small-medium open lakes	Small-medium closed lakes	Large
<b>Residence time</b>	< 1 year ('open' lake)	$\geq 1$ year	10's years	100's years ('closed' lake)
<b>Predominant forcing</b>	S, T, $\delta P$	T, $\delta P$	P/E	P/E
<b><math>\delta^{18}O</math> ranges through the Holocene</b>	Often -ve values, small range of 1-2‰, possibly large range in ‰ for materials precipitated in different seasons eg. <sup>1</sup> Lake Chuma (Kola Peninsula), <sup>2</sup> Lake Abisko (Sweden)	Often -ve values, small range of 1-2‰ eg. <sup>3</sup> Hawes Water (UK), <sup>4</sup> Lake Ammersee (Germany)	-ve to +ve values, large swings (5 to >10‰) eg. <sup>5</sup> Greenland lakes, <sup>6</sup> Lake Tilo (Ethiopia), <sup>7</sup> Lake Golhisar (Turkey)	+ve values, subdued signal homogenised by buffering of large lake volume eg. <sup>8</sup> Lake Malawi, <sup>9</sup> Lake Turkana (Kenya)

S = seasonality, T = temperature,  $\delta P$  = isotope composition of precipitation, P/E = amount of precipitation relative to evaporation

<sup>1</sup>Jones et al (this volume), <sup>2</sup>Shemesh et al (2002), <sup>3</sup>Marshall et al (2002), <sup>4</sup>von Grafenstein et al (1999), <sup>5</sup>Anderson and Leng (this volume), <sup>6</sup>Lamb et al (2001), <sup>7</sup>Eastwood et al (in press), <sup>8</sup>Ricketts and Johnson (1996), <sup>9</sup>Ricketts and Anderson (1998).

Table 1

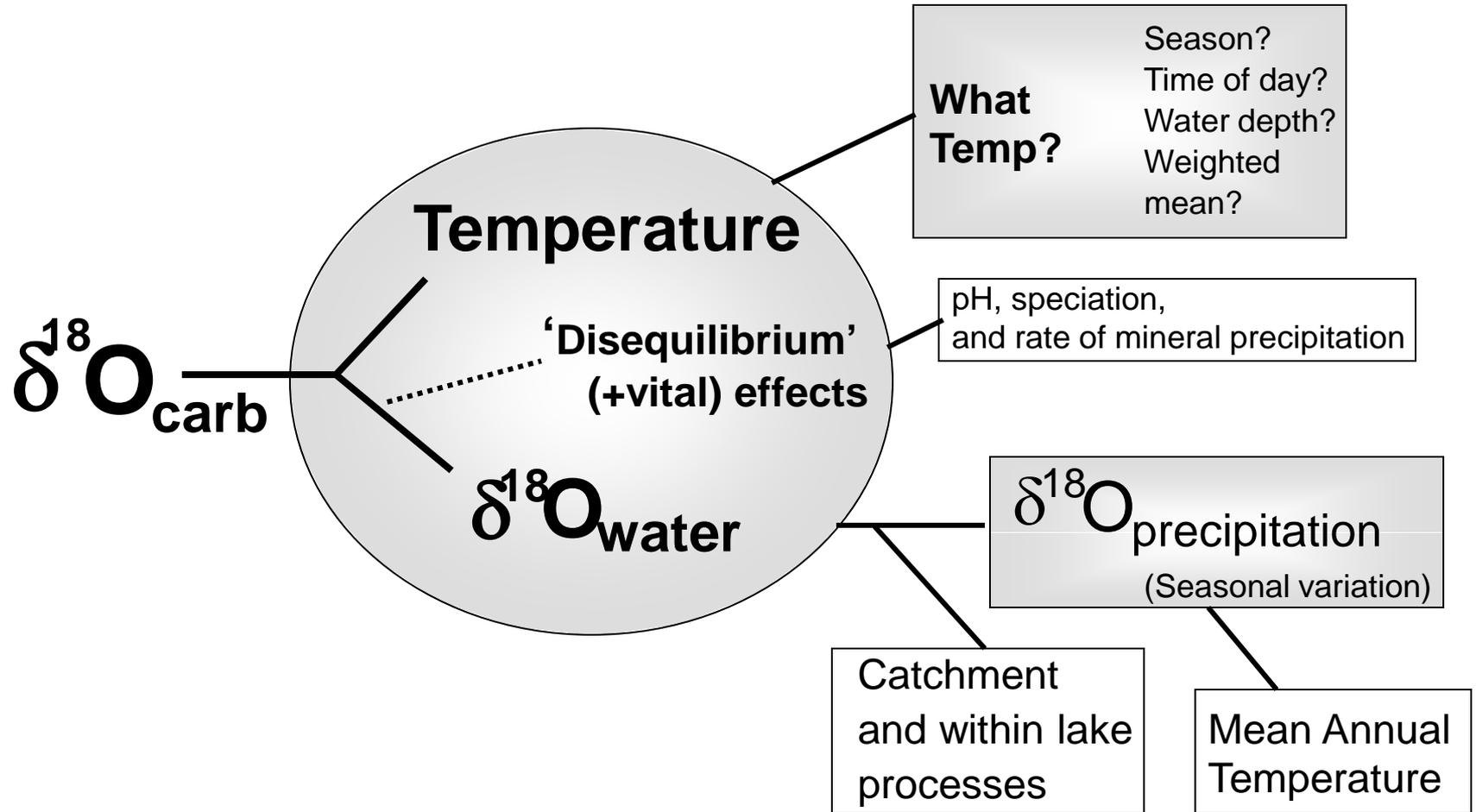


Figure 1

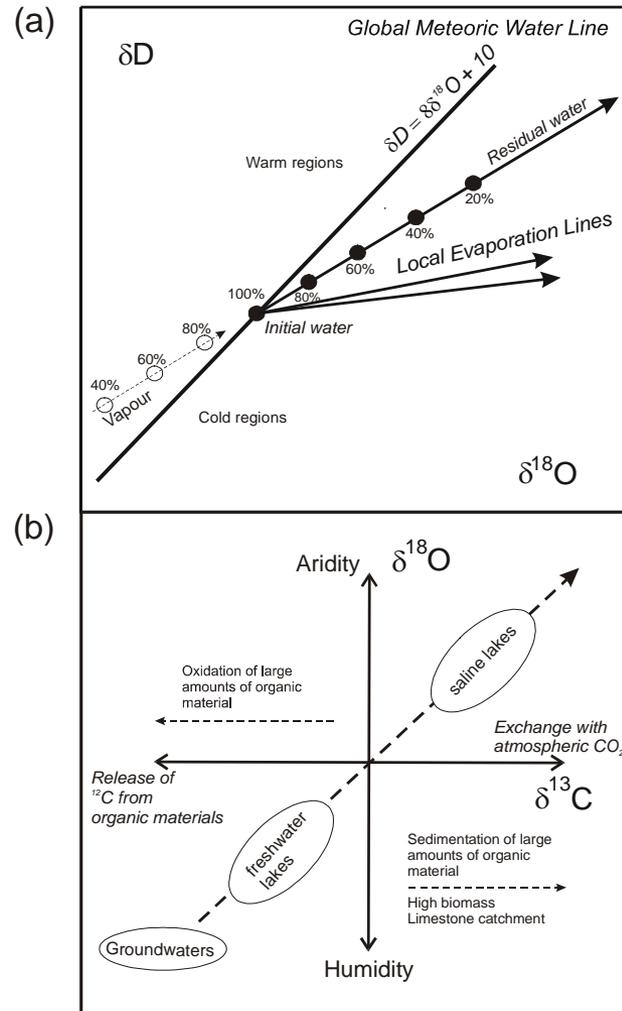


Figure 2

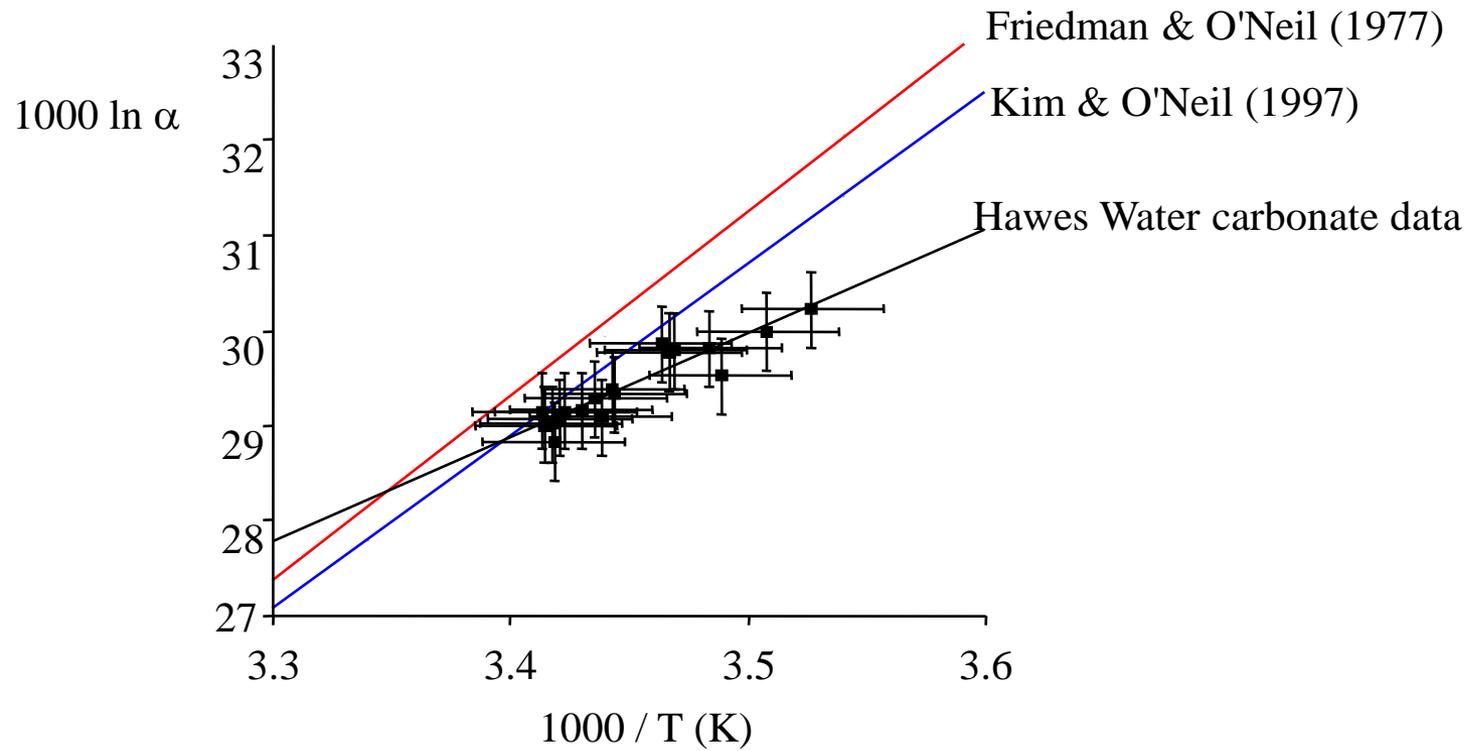


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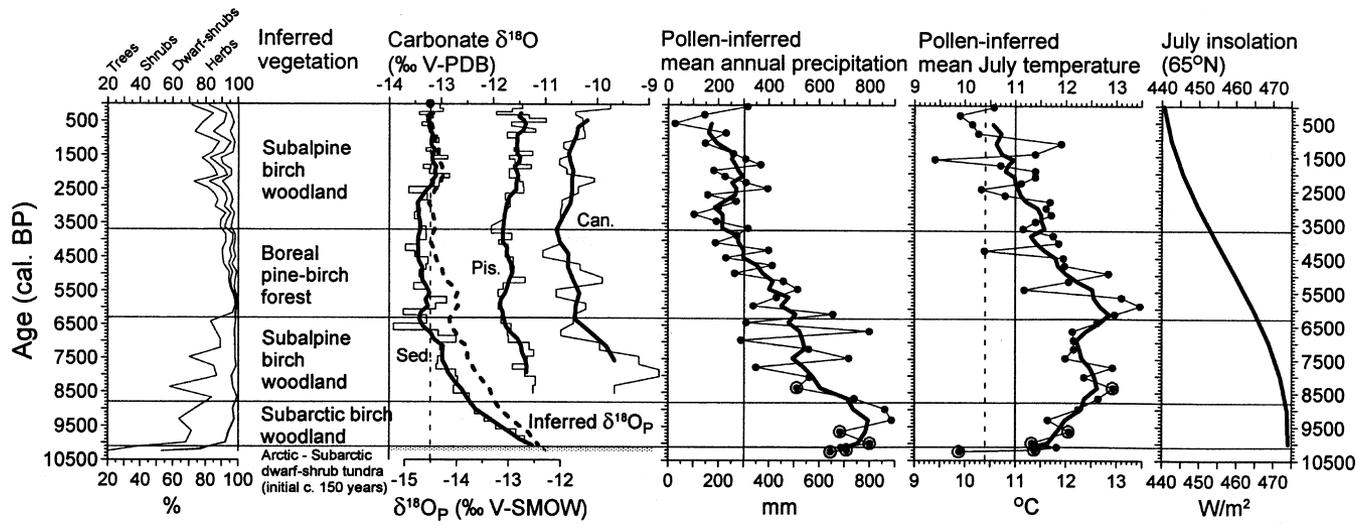


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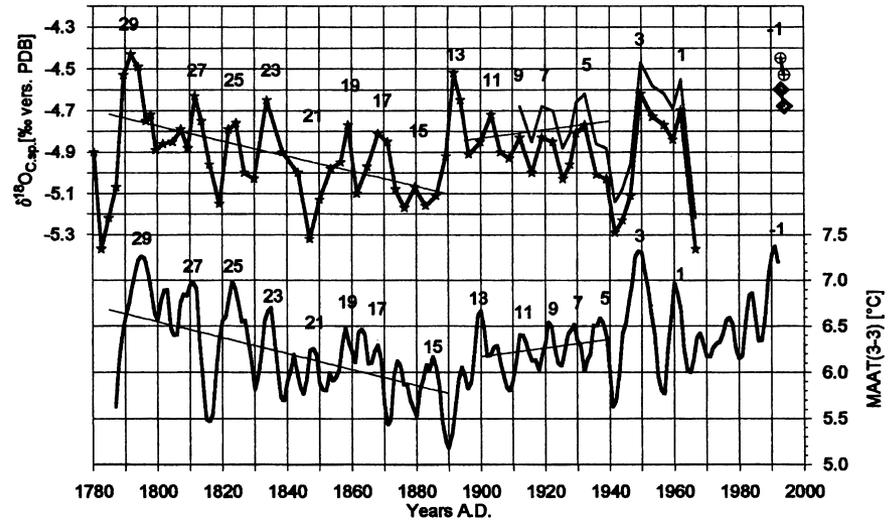


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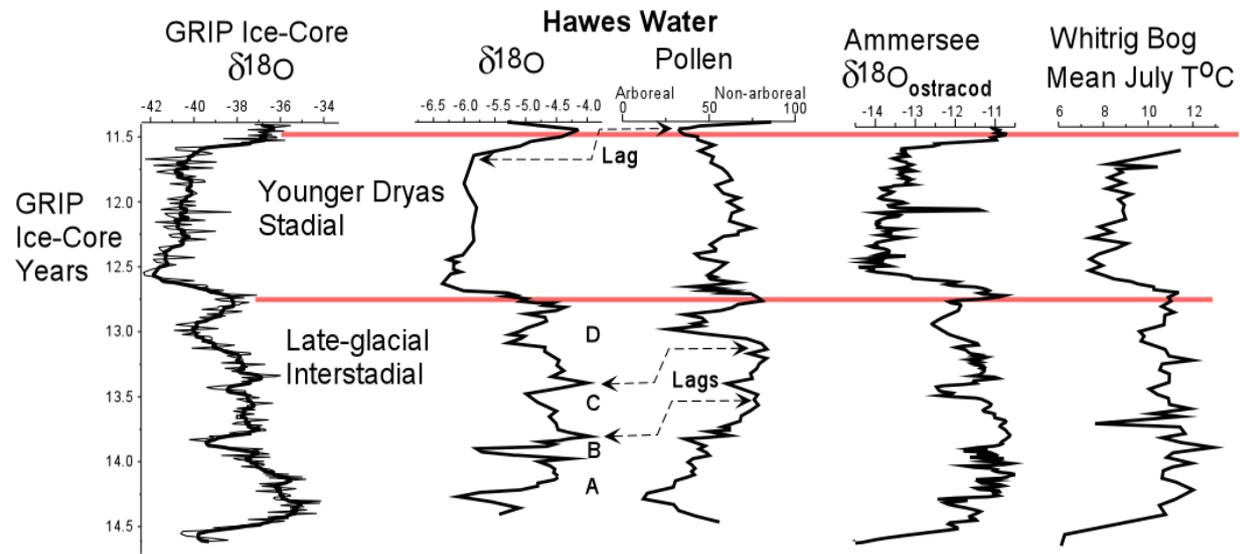


Figure 6

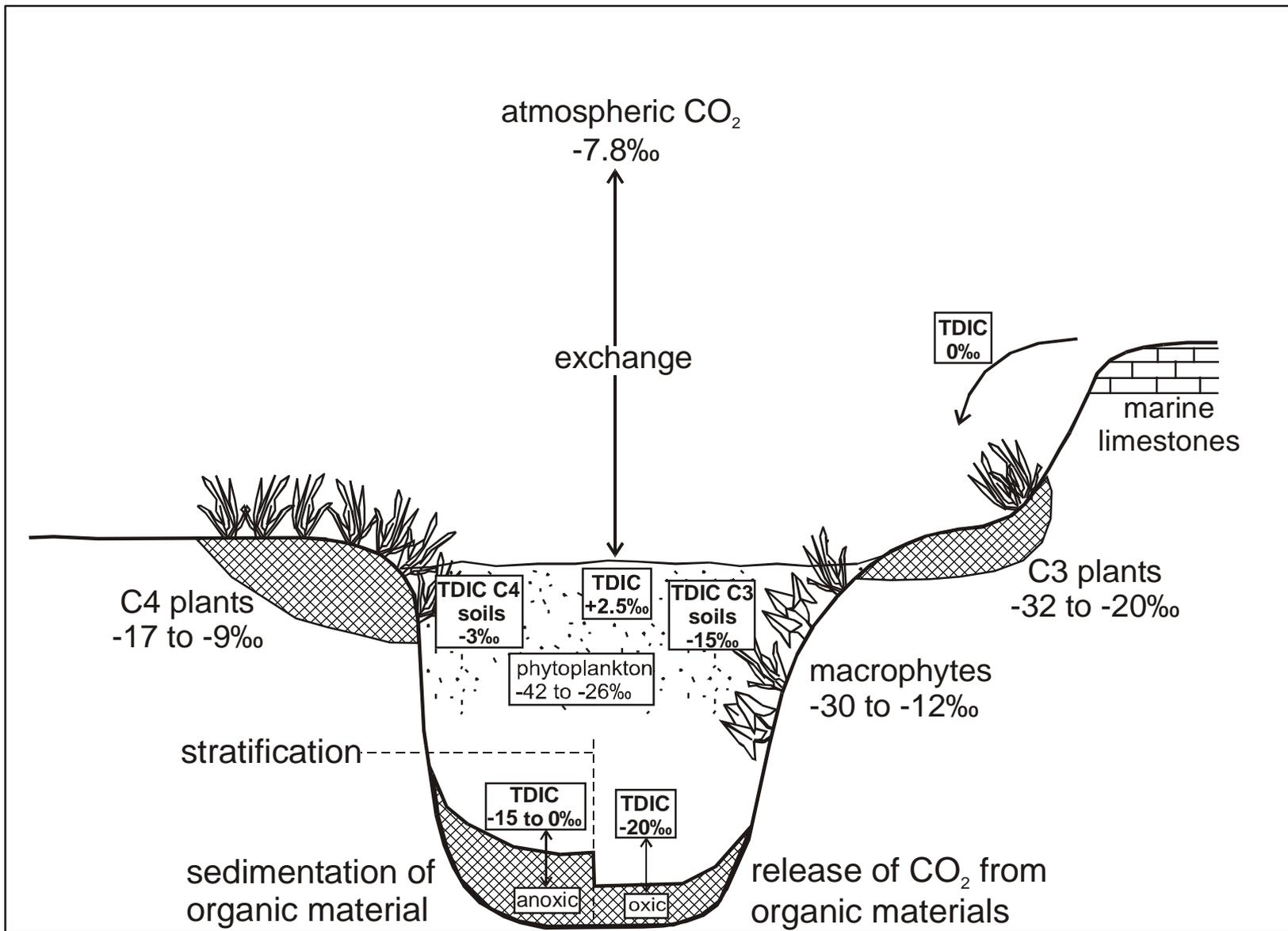


Figure 7

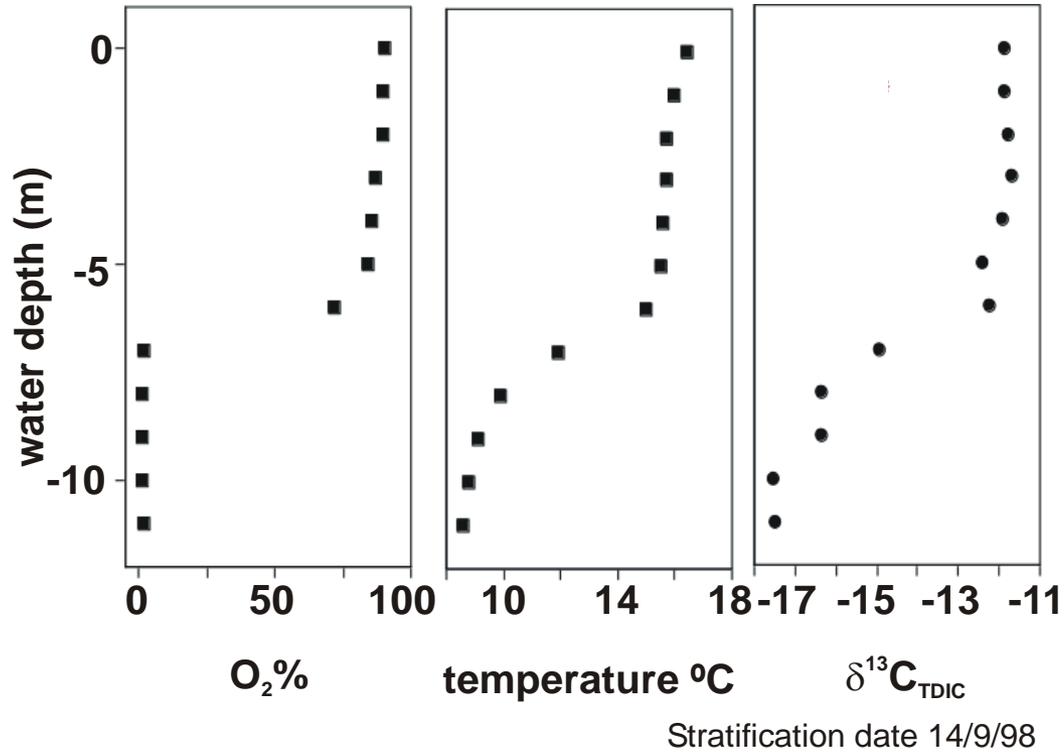


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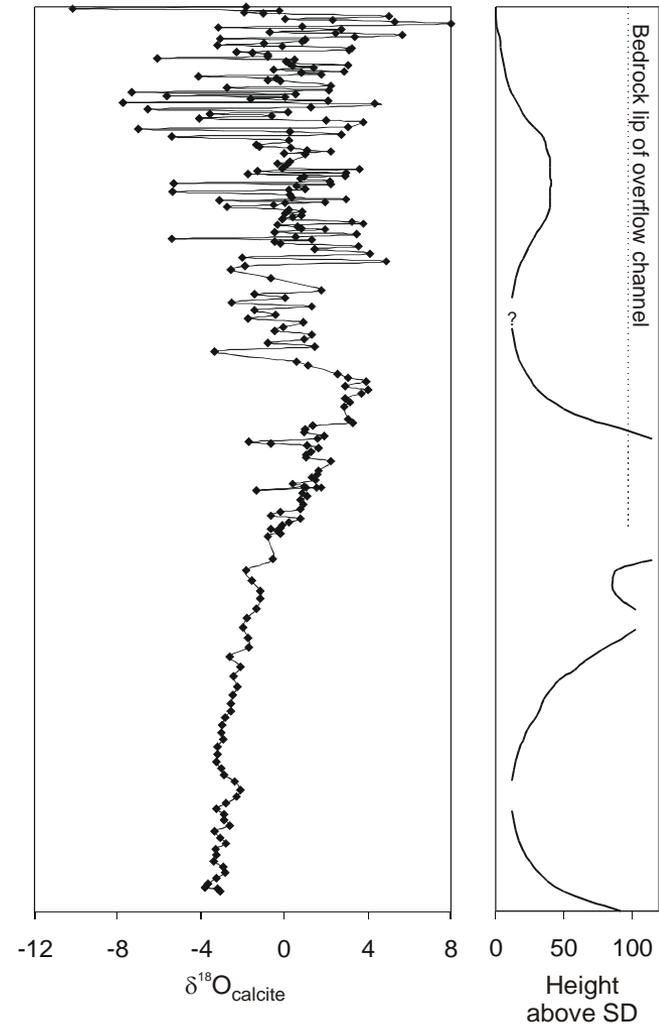


Figure 9

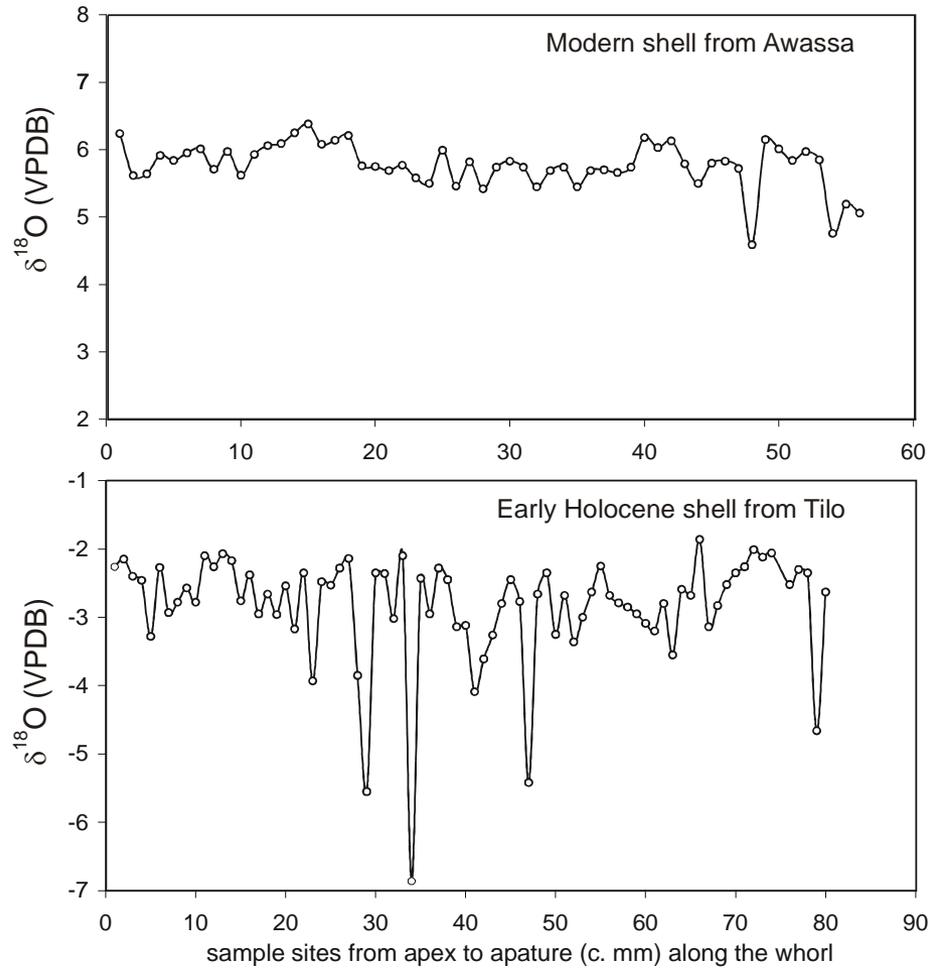


Figure 10

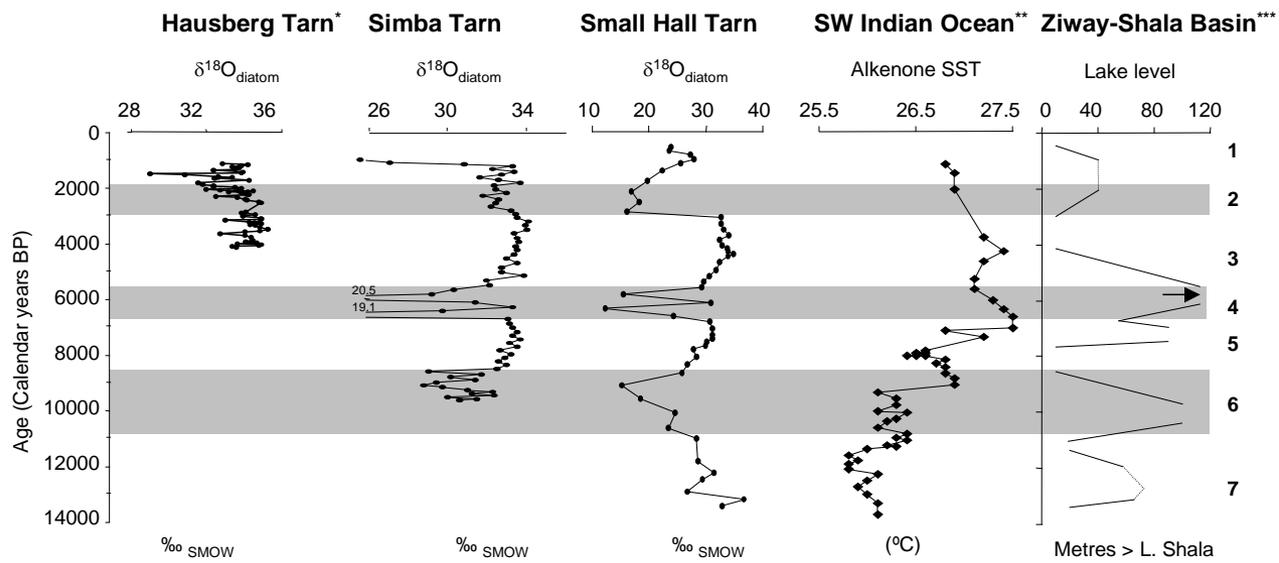


Figure 11

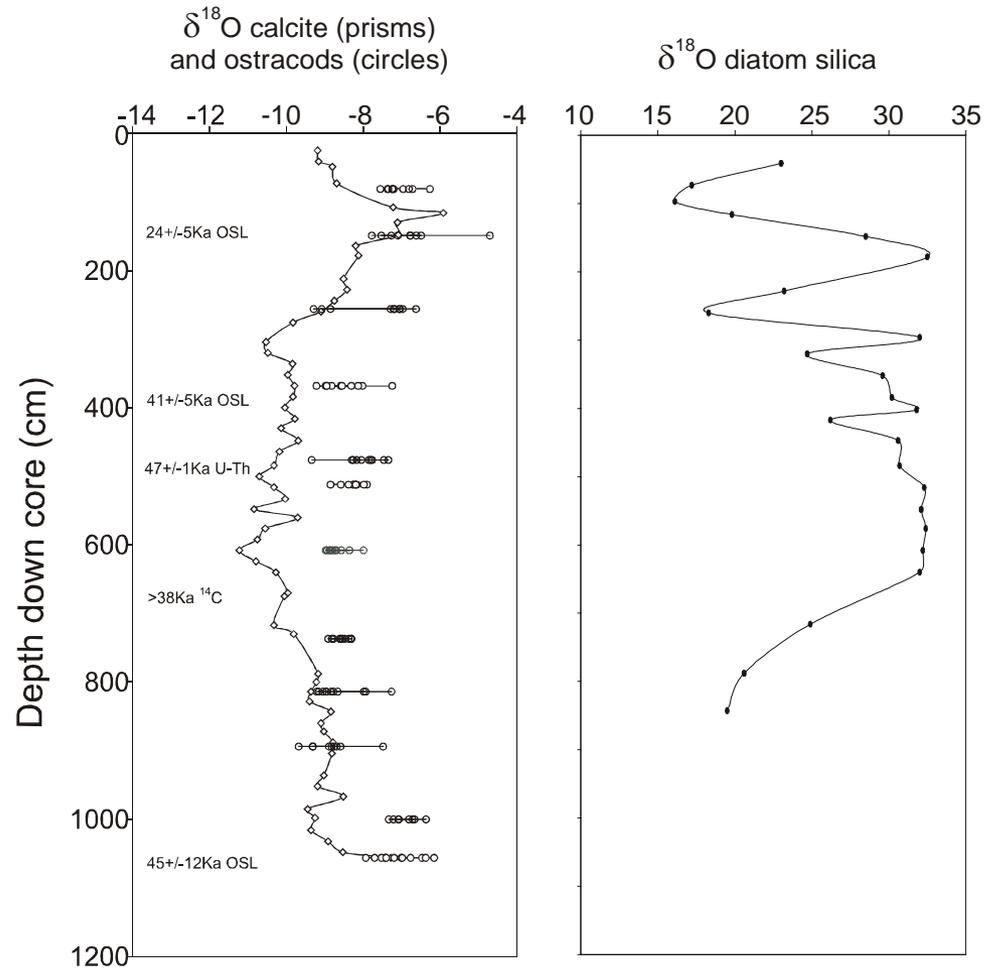


Figure 12

