5. ISOTOPES IN SPELEOTHEMS

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Introduction

Interest in speleothems (secondary cave carbonates such as stalagmites) as recorders of continental palaeoenvironments has increased markedly during the past decade, reflecting the need to provide reliable palaeoclimatic records from a range of continental settings. This renewed interest has been underpinned by important analytical advances that facilitate the acquisition of well-dated oxygen and carbon isotope data at a high spatial resolution, and by emerging methodologies for the extraction of stable isotope signals from speleothem fluid inclusions. Speleothems (mostly calcite, but occasionally aragonite) are deposited slowly by degassing of meteoric water-fed drips in caves. Most studies utilise stalagmites rather than stalactites or flowstones, because their simple geometry, relatively rapid growth rates and tendency to precipitate close to isotope equilibrium with the cave drip waters facilitates palaeoclimatic reconstruction. The rationale for interpreting oxygen isotopes in speleothems is broadly similar to that for other secondary carbonate archives on the continents such as lake carbonates and tufa, insofar as they reflect (i) the δ^18O of meteoric water (cave drips) and (ii) the temperature dependent water-calcite oxygen isotope fractionation. In common with most continental secondary carbonate deposits, the quantitative, and sometimes even the qualitative interpretation of isotopes in speleothems can be problematic because of the multiplicity of factors that potentially affect the δ^18O of drip waters. Importantly however, speleothems preserve several additional non-isotope climate sensitive signals (e.g., carbonate petrography, annual band thickness, trace element ratios, luminescence and organic molecular signals) the details of which (Frisia et al. 2000; 2002; Baker and Barnes 1998; Fairchild et al. 2001) are beyond the scope of this review, but which contribute greatly to the correct interpretation of isotope-based speleothem records. Carbon isotope variations in speleothems are usually taken to reflect climate-driven palaeovegetation signals, but careful consideration of all possible fractionation effects is essential to avoid misinterpreting these data.

In this chapter we focus on the use of stable (oxygen, hydrogen, carbon) isotopes, with an emphasis on understanding the isotope systematics in the context of karst systems, and on the processes by which isotope signals are transferred from the atmosphere and near-surface environment (e.g., vegetation and shallow soil zone) through the karst system to the speleothem calcite. Key issues are those processes (climatic and non-climatic) that can affect the integrity of the recorded signal and its utility for palaeoclimatic reconstruction. While the emphasis is firmly on isotope systematics and a process-based understanding, a small number of case studies are included to illustrate specific points, and to highlight some of the emerging issues in this rapidly evolving field. Also included are updates on recent methodological developments for the extraction of reliable stable isotope signals from speleothem fluid inclusions and the rationale for their interpretation.

Brief historical perspective

The potential of speleothems as palaeoclimatic recorders was first explored more than thirty-five years ago (Hendy and Wilson 1968; Thompson et al. 1974) and the emphasis
in early studies was on providing palaeotemperature estimates. These pioneering researchers quickly recognised however that, in common with most continental carbonate archives, the recovery of palaeotemperatures from oxygen isotope data is inherently complex. This complexity arises because the $\delta^{18}O$ of speleothem calcite depends not only on the temperature at the time of deposition, but also on the $\delta^{18}O$ of the cave seepage waters, that in turn can reflect a multiplicity of climatic (and sometimes non-climatic) variables (e.g., McDermott 2004). These include temporal changes in the $\delta^{18}O$ of the vapour sources, changes in vapour track trajectories, rainout history and condensation, evaporative enrichment at the surface and in the epikarst zone, variable water transit times in the karst system, complex mixing histories and seasonal changes in the calcite deposition rate. As a consequence of these complexities, and because of the need to provide climate modellers with parameters against which they can test their models, the emphasis has now shifted away from attempting to reconstruct palaeotemperatures towards the provision of well-dated isotope records. The latter can, for example, provide a valuable means to detect and evaluate 'leads' and 'lags' in the climate system and to identify so-called 'teleconnections', because a major strength of speleothem isotope records is their robust chronology (see below). Another emerging application is the provision of data to test 'isotope-enabled' general circulation models (GCMs) that are currently being developed by several climate modelling groups. The latter models can predict secular changes in the $\delta^{18}O$ of precipitation at selected points on the Earth's surface, and the provision of estimates of the hydrogen and oxygen isotopic composition of palaeo-precipitation is a key priority in future research. Speleothems have a valuable role to play in providing such data, and in particular their fluid inclusions are potentially important recorders of the H and O isotope ratios of palaeoprecipitation if, as discussed below, technical problems regarding their extraction and measurement can be overcome.

The cave environment

Caves are a product of karstification whereby relatively soluble rocks such as limestones are dissolved by downward percolating meteoric waters that have interacted with a soil zone containing elevated levels of CO$_2$ (Figure 1). Cave air temperatures remain essentially constant throughout the year in poorly ventilated caves (typically ±1°C), reflecting the high thermal inertia of host rocks. As a consequence, seasonal temperature variations are usually averaged out, and cave air temperatures are similar to the mean annual air temperature of the region above the cave. Cave air is characterised by high relative humidity (typically 95 to 100%) that minimises evaporation of cave drip water. Aside from areas close to cave entrances where lower humidity and air currents permit evaporation, secondary calcite deposition typically occurs by degassing of CO$_2$ from carbonate-saturated drip waters, and not by evaporation of water (Schwarz 1986; Ford and Williams 1989). Details of carbonate equilibria in karst waters have been well documented elsewhere (e.g., Buhmann and Dreybrodt 1985), but a key point is that drip waters degas when they enter a cave, because cave atmospheres usually have lower CO$_2$ levels (0.06–0.6% vol.) compared with the overlying soil gas (0.1–3.5% vol.). Stalagmite growth rates are variable (usually 20–300 µm/year) and are influenced by the mean annual air temperature at the site, drip–water availability and
the calcium concentration of drip waters (Genty et al. 2001; Polyak and Asmeron 2001; Fleitmann et al. 2004), in reasonable agreement with theoretical predictions (Dreybrodt 1988). In arid or weakly vegetated sites, growth rates are often lower than predicted by growth rate models, and growth hiatuses that compromise the reliability of age models can occur. The latter may in themselves provide valuable climatic signals, particularly in cases where subtle geochemical changes are recorded in the stalagmite related to a more arid period (e.g., McMillan et al. in press)). At mid– to high–latitudes in the northern hemisphere, speleothem deposition typically ceases during glacial periods (Gordon et al. 1989; Baker et al. 1993), whereas continuous deposition throughout the glacial periods is a feature of many circum–Mediterranean and lower–latitude sub–tropical sites (McDermott 2004).

Figure 1. Schematic diagram of a cave system illustrating several of the variables that can influence the stable isotope signals recorded in speleothems. Columnar ‘constant diameter’ stalagmites depicted near the centre of the diagram are typically fed by slowly dripping vadose seepage water. Longer water residence times result in attenuation of seasonal δ18O variations in rainwater, and drip water δ18O values closely resemble those of the weighted mean δ18O in precipitation. In arid regions, the O isotope ratio of precipitation may be modified by evaporation prior to infiltration, or may be biased by selective infiltration of more intense precipitation events (e.g., Bar–Matthews et al. (2003)). Judicious choice of speleothems for palaeoclimate studies using stable isotopes must take these and other factors (including cave conservation issues) into account.
Recent advances in analytical techniques

The most important analytical developments that have occurred since the pioneering studies of the 1970’s concern improvements in the provision of accurate and precise age estimates for speleothem isotope records. Unlike many other continental archives (e.g., lake sediments, peat bogs) speleothems are not amenable to dating by the radiocarbon method because a variable but difficult to quantify proportion (typically 5–20%) of their carbon is $^{14}$C–dead’ (Genty et al. 2001). Fortunately, speleothems are near–ideal material for dating by U–series, specifically using the ‘daughter deficiency’ $^{230}$Th/U method, and the majority appear to behave as closed systems with respect to uranium and its decay products. Uranium contents in calcite speleothems are rather variable (typically 0.1 – 10 µg/g $^{238}$U) and are about an order of magnitude higher in aragonite–rich speleothems (McDermott et al. 1999; McMillan et al. in press). Much of the renewed interest in the use of speleothems as palaeoclimatic recorders during the past decade can be traced to the development of Thermal Ionisation Mass–Spectrometry (TIMS) techniques for U–series measurements in the late 1980’s (Edwards et al. 1988; Li et al. 1989) that quickly supplanted the established alpha–counting method. TIMS revolutionised U–series dating by allowing a very substantial (10–50 fold) reduction in sample size, and an order of magnitude improvement in analytical precision. Recent technological developments have led to a new generation of high–resolution magnetic sector Multi–Collector Inductive Coupled Plasma mass–spectrometers (MC–ICP–MS) with vastly improved ionisation efficiency for elements such as thorium and protoactinium (Shen et al. 2002; Richards et al. 2003). With the advent of these instruments and with improved within–analysis precision, new issues are beginning to emerge. These include the need for more thorough inter–laboratory comparisons to detect possible systematic errors in mixed $^{229}$Th/$^{236}$U spike calibrations, the need for more careful correction for initial $^{230}$Th in samples with modest amounts of detrital contamination, and the requirement for improved statistical methods to construct speleothem age models from the U–series data. In a minority of speleothems, the presence of annual visible or luminescent bands can provide independent verification of radiometric chronologies (e.g., Wang et al. (2001); Frisia et al. (2003); Hou et al. (2003); Fleitmann et al. (2004)), reducing many of the uncertainties outlined above.

During the past decade there have been numerous efforts to improve the spatial, and therefore the temporal resolution of O and C isotopic analyses in speleothems. A Laser–Ablation Gas–Chromatography Isotope Ratio Mass Spectrometry (LA–GC–IRMS) system developed at Royal Holloway (University of London) for example, offers rapid in–situ O and C isotope analysis of speleothem carbonate at a spatial resolution of 250 µm (McDermott et al. 2001). Comparison of LA–GC–IRMS data with conventional isotope analyses of both dental–drilled and micro–milled traverses indicates that this laser system produces accurate and precise data (McDermott et al. 2001). Replicate analyses of standards indicate that the isotope data are reproducible to better than 0.1‰ for $\delta^1$C and 0.2‰ for $\delta^1$H. While this system offers only a modest improvement in spatial resolution (approximately five–fold) relative to conventional dental drilling methods, data acquisition is rapid and automated.

Several laboratories have invested recently in micro–milling systems to provide samples for conventional stable isotope analysis at a much–improved spatial resolution
compared with that achievable using a conventional dental drill. Frappier et al. (2002) achieved a sampling resolution of just 20 µm by micro–milling, corresponding to a weekly to monthly temporal resolution in a stalagmite from Belize. Importantly, these high–resolution data enabled the recognition of large amplitude (11‰), rapid (sub–seasonal) fluctuations in δ¹³C, interpreted to reflect variations in the El Nino/Southern Oscillation (ENSO). Micro–sampling at such a high spatial resolution requires that the speleothem growth laminae are perfectly flat and parallel to the micro–milled tracks, and resolutions of 70–100 µm are probably routinely achievable.

Ion micro–probes offer excellent spatial resolution (c. 25 µm) for δ¹⁸O analysis (Kolodny et al. 2003), but the relatively poor analytical precision and standardisation problems that characterise the current generation of instruments (c. ± 0.5‰) restricts their use to the study of high–amplitude changes in δ¹⁸O and/or climate transitions. Overall, it appears that micro–milling followed by conventional stable isotope analysis currently offers the best route forward, because although labour intensive, it offers a combination of excellent spatial resolution and analytical precision.

**Oxygen isotope systematics in speleothems**

Assuming that speleothem calcite is deposited at or close to oxygen isotope equilibrium with cave dripwater (but see discussion below), the δ¹⁸O of the precipitated calcite reflects both the δ¹⁸O of the dripwater and the temperature at which calcite deposition occurs. Unfortunately, in common with other continental secondary carbonate archives (e.g., lacustrine carbonates), interpretation of the oxygen isotope signal in terms of palaeotemperature is not straightforward, because the temperature dependence of δ¹⁸O in rainfall (dδ¹⁸Op/dT) is variable and site dependent (Schwarcz 1986; McDermott et al. 1999; Serefiddin et al. 2004). In order to evaluate more critically the extent to which drip–water δ¹⁸O might reflect cave air temperatures, we have compiled the available published oxygen isotope data for modern cave waters and recent carbonate precipitates for those caves whose mean annual air temperature appears to be well documented (Table 1). This compilation encompasses a wide range of cave sites and climatic regimes, with mean annual temperatures ranging from 2.8°C (Soylegrotta, Norway; Lauritzen and Lundberg (1999)) to 26.6 °C (Harrison’s Cave, Barbados; Mickler et al. (2004)). Overall there is a strong correlation between drip water δ¹⁸O and cave air temperature (Figure 2), reflecting the well–known spatial meteoric water δ¹⁸O – air temperature relationship, although the slope is lower than that of most regional meteoric water data–sets (e.g., Rozanski et al. (1993)). Depending on the site however, dδ¹⁸Op/dT could be greater than, equal to, or less than the temperature dependence of δ¹⁸O in calcite (ct) deposited in speleothems (dδ¹⁸Oct/dT). The latter is approximately –0.24‰ °C⁻¹ at 25°C (O’Neil et al. 1969). A similar number of cases have been documented where dδ¹⁸Oc/dT appears to be positive (Goede et al. 1990; Burns et al. 2001; Onac et al. 2002) and negative (Gascoyne 1992; Hellstrom et al. 1998; Frumkin et al. 1999a; 1999b). In principle though δ¹⁸Oc could fortuitously remain invariant to an increase in mean annual air temperature if dδ¹⁸Oc/dT was close to 0.24‰ °C⁻¹, because dδ¹⁸Oc/dT would then be cancelled out by dδ¹⁸Oc/dT. Such cases appear to be rare in the literature but we note that the slope of the data in Figure 2 implies a spatially–determined
A δ¹⁸O value close to 0.26‰ °C⁻¹, and there is no strong relationship between δ¹⁸Oc and cave air temperature in the compiled data (not shown). In general therefore, it remains impossible unambiguously to relate changes in δ¹⁸Oc to changes in mean annual temperature, especially during intervals that lack obvious first-order climate transitions (e.g., glacial to interglacial transitions). These uncertainties underline the need for additional proxy information from the same stalagmite (e.g., annual layer thickness variations, growth-rate changes) to underpin the interpretation of δ¹⁸O (McDermott et al. 1999; Fleitmann et al. 2004; Fairchild et al. in press). In the Fleitmann et al. (2004) study of annually laminated speleothems from Southern Oman for example, there is a good correlation between δ¹⁸O and the thickness of annual layers, providing independent support for their interpretation that δ¹⁸O primarily reflects changes in the amount of precipitation. In other regions (e.g., Israel) it has been documented that changes in δ¹⁸O reflect the so-called 'amount effect', with lower δ¹⁸O values associated with wetter years (Bar–Matthews et al. 1996).

**Figure 2.** Relationship between cave drip water δ¹⁸O and cave air temperature for data compiled in Table 1. There is a broad positive correlation between drip water δ¹⁸O and cave temperature, although the slope of the data (0.26‰ °C⁻¹) is lower than that of most meteoric water compilations (Rozanski et al. 1993). The slope defined by the data is approximately 0.26‰ °C⁻¹, similar to, but of opposite sign to the calcite–water fractionation factor (approximately −0.24‰ °C⁻¹ at 25°C, O’Neil et al. 1969). Three of the five data points that plot clearly above the regression line are from near-coastal sites (S.W. Ireland and two from Tasmania).
Table 1. Compilation of published oxygen isotope data for cave drip–waters and associated modern carbonate precipitates. Values in italics are ± uncertainties (1σ around the mean) in the oxygen isotope values where these have been given in the individual studies. * denotes that winter precipitation recharge values of δ¹⁸O were used in the calculation of temperatures in Figure 3, °indicates experimental precipitates on glass slides from the work of Mickler et al. (2004).

<table>
<thead>
<tr>
<th>Cave site</th>
<th>Modern calcite δ¹⁸O (PDB)</th>
<th>Present–day drip water mean δ¹⁸O (SMOW)</th>
<th>Cave temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calcite precipitates</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Père Noël (Belgium)¹</td>
<td>−5.5 ± 0.6</td>
<td>−7.20 ± 0.08</td>
<td>9.1</td>
</tr>
<tr>
<td>Søylegrotta (Norway)²</td>
<td>−7.3</td>
<td>−10.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Ernesto (Italy)³</td>
<td>−7.0 ± 0.2</td>
<td>−9.0 ± 0.1</td>
<td>6.6</td>
</tr>
<tr>
<td>Frankcombe cave (Tasmania)⁴</td>
<td>−4.0</td>
<td>−5.7 ± 0.1</td>
<td>8.3</td>
</tr>
<tr>
<td>B7 cave (Germany)⁵</td>
<td>−6.3</td>
<td>−8.4 ± 0.6</td>
<td>9.4</td>
</tr>
<tr>
<td>Lynd's cave (Tasmania)⁶</td>
<td>−4.1 ± 0.1</td>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>Little Trimmer cave (Tasmania)⁷</td>
<td>−3.8</td>
<td>−5.68</td>
<td>9.5</td>
</tr>
<tr>
<td>Crag cave (Ireland)⁸</td>
<td>−3.5</td>
<td>−5.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Flint Ridge–Mammoth cave (U.S.)⁹</td>
<td>−5.1 ± 0.3</td>
<td>−5.94</td>
<td>13.5</td>
</tr>
<tr>
<td>Clamouse (France)¹⁰</td>
<td>−4.9 ± 0.6</td>
<td>−6.2 ± 0.4</td>
<td>14.5</td>
</tr>
<tr>
<td>Peqim (Israel)¹¹</td>
<td>−5.2 ± 0.3</td>
<td>−5.50</td>
<td>16.0</td>
</tr>
<tr>
<td>Victoria Fossil Cave (S. Australia)¹²</td>
<td>−4.8</td>
<td>−4.98</td>
<td>16.8</td>
</tr>
<tr>
<td>Cango caves (S. Africa)¹³</td>
<td>−5.4</td>
<td>−5.44</td>
<td>17.5</td>
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<tr>
<td>Cold Air cave (S. Africa)¹⁴</td>
<td>−4.8</td>
<td>−4.0</td>
<td>18.8</td>
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<tr>
<td>Soreq (Israel)¹⁵</td>
<td>−5.4 ± 0.1</td>
<td>−5.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Hoti Cave (Oman)¹⁶</td>
<td>−1.9 ± 1</td>
<td>−1.0 ± 1</td>
<td>23.0</td>
</tr>
<tr>
<td>Harrison's Cave (Barbados)¹⁷</td>
<td>−5.3</td>
<td>−3.3 ± 0.3</td>
<td>26.6</td>
</tr>
<tr>
<td>Harrison's Cave (Barbados)¹⁷</td>
<td>−4.0 ± 0.3</td>
<td>−3.3 ± 0.3</td>
<td>26.6</td>
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<tr>
<td>Harrison's Cave (Barbados)¹⁷</td>
<td>−4.0 ± 0.4</td>
<td>−3.3 ± 0.3</td>
<td>26.6</td>
</tr>
<tr>
<td>Harrison's Cave (Barbados)¹⁷</td>
<td>−4.6 ± 0.3</td>
<td>−3.3 ± 0.3</td>
<td>26.6</td>
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<tr>
<td><strong>Aragonite precipitates</strong></td>
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<td></td>
</tr>
<tr>
<td>Cold Air Cave (S. Africa)¹⁸</td>
<td>−2.93</td>
<td>−3.13</td>
<td>18.0</td>
</tr>
<tr>
<td>Nerja Cave (S. Spain)¹⁹</td>
<td>−4.60</td>
<td>−5.20</td>
<td>20.0</td>
</tr>
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</table>

Overall therefore, in common with other continental secondary carbonate archives, the system is usually under-determined (e.g., Leng and Marshall (2004)), in the sense that there are several inter-related factors that can influence the $\delta^{18}O$ of speleothem calcite, and derivation of absolute temperatures is generally not possible. If in the future, reliable hydrogen and possibly oxygen isotope data can be recovered from speleothem fluid inclusions (see below), this situation will improve.

It is increasingly apparent that on centennial to millennial timescales, variations in speleothem $\delta^{18}O$ probably reflect changes in the $\delta^{18}O$ of precipitation as a consequence of atmospheric circulation changes rather than local temperature changes (Burns et al. 1998; Bar–Matthews et al. 1999; 2000; McDermott 2001; Yuan et al., 2004). A recent study of a five year record of $\delta^{18}O$ in precipitation ($\delta^{18}O_p$) from Tasmania for example (Treble et al. 2005) indicates that there is little correlation between $\delta^{18}O_p$ and air temperature, and instead $\delta^{18}O_p$ is influenced strongly by synoptic patterns that influence air–mass trajectories. $\delta^{18}O$ in precipitation clearly exerts a first–order control on the $\delta^{18}O$ of cave drips, and the meteorological controls on this are discussed in detail elsewhere (e.g. Serefiddin et al. 2004; Treble et al. 2005). Here we note simply that the present–day spatial and seasonal variations in $\delta^{18}O_p$ arises from several so–called “effects” that include latitude, altitude, distance from the sea, amount of precipitation and surface air temperature (Rozanski et al. 1982; 1993; Gat 1996; Fricker and O’Neil 1999). On centennial to millennial timescales, additional factors such as (i) changes in the $\delta^{18}O$ of the ocean surface (ii) changes in the temperature difference between the oceanic vapour source area and the cave site (iii) shifts in moisture sources and/or storm tracks and (iv) changes in the proportion of precipitation derived from non oceanic sources, i.e., recycled from continental surface waters, must also be taken into account (see McDermott et al. (1999) for a discussion).

One prerequisite for the successful use of $\delta^{18}O$ in speleothems as an indicator of $\delta^{18}O_p$ is that carbonate deposition occurred at or close to isotope equilibrium with the cave drip waters. It is often assumed that stalagmite calcite is deposited close to isotope equilibrium with cave drip waters in high humidity caves, but there have been relatively few critical evaluations of this assumption. The most striking result from our compilation of the available data from the literature (Table 1) is that while oxygen isotopes in speleothem calcite are typically in 'quasi–equilibrium' with their drip waters, many appear to be systematically heavier (Figure 3a) than those predicted by recently published equilibrium fractionation factors (Kim and O’Neil 1997). Some speleothem studies (e.g., Holmgren et al. (2003)) have used fractionation factors based on the early empirically–derived O isotope–temperature relationships (the Craig (1965) equation and versions thereof including the Anderson and Arthur (1983) equation). Curiously, these appear to yield temperatures that are closer to the expected (cave air) temperature for modern precipitate–drip water pairs (Figure 3b). In part this may reflect the fact that these early empirical equations were based on mixed calcite–aragonite mineralogies (Leng and Marshall 2004), because published equilibrium fractionation factors for aragonite (Grossman and Ku 1986) predict higher $\delta^{18}O$ in aragonite compared with calcite at a given temperature. It is likely that these early mixed mineralogy empirical calibrations are not appropriate for calcite speleothems.
Figure 3. (a) Plot of $1000 \ln \alpha_{\text{calcite-water}}$ vs. $1/T$ (K) for compiled modern cave calcite (crosses) and aragonite (filled circles) precipitate–drip water pairs (Table 1). Data represent a wide range of cave sites in climatic regimes with mean annual temperatures ranging from 2.8 to 26.6 °C. Error bars represent typical uncertainties on cave air temperatures and present–day $\delta^{18}O$ for compiled data (Table 1). Note that $1000 \ln \alpha_{\text{calcite-water}}$ approximates to $\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{water}}$. (b) Plot of calculated temperatures from modern cave precipitate–drip water pairs illustrating that the perception of equilibrium depends largely on the choice of palaeotemperature equation. Data outlined by box in upper right part of diagram are for glass-slide precipitates (Mickler et al. 2004).
Instead, we prefer to base our assessment of present–day equilibrium deposition on the most recently published experimental calibration for calcite (Kim and O’Neil 1997). On this basis the $\delta^{18}$O values for most modern cave calcites tend to plot above the predicted equilibrium values on a diagram of 1000 ln $\alpha_{\text{calcite-water}}$ vs. 1/T (Figure 3a) with typical enrichments of 0.5–1‰ relative to the predicted values. The reasons for this discrepancy are not well understood. Kinetic enrichments often accompany relatively rapid degassing of the drip waters (Mickler et al. 2004), but the relatively small and constant offset of the data from the Kim and O’Neil (1997) equilibrium fractionation line argues against kinetic effects, because in principle the latter should produce a wide range of enrichments. We note that seasonal biases in calcite precipitation rate cannot readily account for the systematic nature of the observed isotope shift in the modern cave carbonates, because given the range of climatic regimes represented, the latter should produce scatter around the equilibrium values rather than a unidirectional shift.

Two modern cave aragonite samples are included in our compilation (from Nerja Cave, southern Spain; Jimenez de Cisneros et al. (2003) and Cold Air Cave, South Africa; Repinski et al. (1999)). The sample from South Africa appears to lie on the equilibrium fractionation line for aragonite (Grossman and Ku 1986), whereas that from Nerja cave exhibits higher $\delta^{18}$O relative to the equilibrium value predicted from its associated drip water and cave air temperature (Figure 3a). Thus, present indications are that while cave calcites are precipitated in quasi–equilibrium with their drip waters, a small (< 1‰) but systematic offset to higher $\delta^{18}$O values appears to occur. If this effect is common, then small amplitude temporal variations in $\delta^{18}$O, in a Holocene stalagmite for example, might simply reflect non–equilibrium effects rather than a direct climate–driven rainfall $\delta^{18}$O signal. This in turn has implications for the signal to noise ratio requirement for the identification of robust climate–related signals in time–series speleothem $\delta^{18}$O records.

The effect of using different ‘palaeotemperature equations’ to calculate carbonate deposition temperatures (and to assess the extent to which equilibrium deposition has been achieved) is illustrated in Figure 3b. Clearly, the empirical Craig–derived equations appear superficially to more closely recover the observed cave (air) temperature, whereas the Kim and O’Neil (1997) equation appears to yield temperatures that are too low. We interpret this to mean that most cave carbonates are not strictly in oxygen isotope equilibrium with their drip waters, as discussed above. Calculated temperatures have a range of about 4°C, and so the choice of fractionation factor is critical in assessing the extent to which equilibrium has been achieved.

Demonstrating that modern carbonate is at or close to oxygen isotope equilibrium with cave drip waters is clearly a useful first step in evaluating the extent to which a particular cave system might be suitable for palaeoclimatic studies. More important however is the need to demonstrate that equilibrium was maintained over the growth history of a stalagmite. The criteria for recognising conditions of equilibrium deposition have been discussed previously (Hendy 1971; Schwarz 1986). Briefly, they are (i) that $\delta^{18}$O remains constant along a single growth layer while $\delta^{13}$C varies irregularly, and (ii) that there is no correlation between $\delta^{18}$O and $\delta^{13}$C along a growth layer. In practice, consistent sampling along single growth layers is often difficult to achieve, not least
because visible layers are often thinner along the flanks of stalagmites compared with
their central growth axis. Nonetheless, the so-called 'Hendy criteria' are used widely by
researchers as a check that carbonate was deposited at or close to isotope equilibrium
with cave drip waters. In some cases it can be demonstrated that calcite deposited along
the flanks of stalagmites exhibit kinetic fractionation effects, but that the material
deposited close to the central growth axis may have been deposited in isotope
equilibrium with the cave drip waters (Talma and Vogel 1992; Spötl and Mangini
2002). It is possible that carbon isotope ratios may be strongly affected by degassing
and prior precipitation of calcite in the water flow–path, but these effects are detectable
by combined stable isotope and trace element studies (see below).

Aside from issues concerning the deposition of carbonate in isotope equilibrium, it is
important to evaluate the hydrogeological factors that influence the oxygen isotope
ratios in the cave waters of individual drip systems in order to interpret correctly
temporal changes in the oxygen isotope composition of speleothems. Selection of
individual speleothems for palaeoclimatic studies depends on the goals of the research
project, and the available temporal resolution in the record. An understanding of the
site–specific hydrological behaviour of cave drips is essential for (i) the optimal
selection of speleothems that can record the isotope signals at the time resolution of
interest and (ii) the correct interpretation of the isotope data in terms of climatic
variables. The δ¹⁸O of slow, so-called 'seepage flow' drip sites with a relatively large
storage component usually reflect the mean annual δ¹⁸O of precipitation (Yonge et al.
1985; Caballero et al. 1996) and speleothems deposited from such drips would be
appropriate for palaeoclimatic studies requiring a multi–annual resolution. Fast or
'flashy' drip sites on the other hand may exhibit large seasonal variations in δ¹⁸O
reflecting minimal storage and homogenisation in the epikarst. Such sites may exhibit
seasonal undersaturation with respect to calcite (Baldini 2004), and are unlikely to
produce the regular geometrically–simple columnar stalagmites favoured for
palaeoclimatic reconstruction, but they may be of value if for example the goal is to
reconstruct high–resolution records of seasonal changes in δ¹⁸Oₚ. At some arid and
semi–arid circum–Mediterranean sites it has been demonstrated that recharge is
dominated by heavy winter rainfall events (Cruz–San Julian et al. 1992; Bar–Matthews
et al. 1996) and speleothems deposited from such sites may preserve seasonal biases in
their δ¹⁸O. Additionally, seasonally variable increases in δ¹⁸O may occur as a result of
near–surface evaporative processes in arid and semi–arid sites (Bar–Matthews et al.
1996; Denniston et al. 1999a; 1999b). Another complication is that soil pCO₂ and drip
water Ca contents often vary seasonally, with the result that calcite deposition rates also
vary seasonally (Genty et al. 2001; Frisia et al. 2003). I is possible therefore that
speleothem calcite might in some circumstances preserve seasonal biases, but this could
be detected by detailed seasonal monitoring of the chosen drip sites to understand the
factors controlling intra–annual variability in growth rates. These issues highlight the
need for detailed site–specific present day monitoring studies to understand better the
relationship between the palaeo–δ¹⁸O signal preserved in speleothem calcite (δ¹⁸Oₛ) and
palaeoclimatic variability. Many of these uncertainties relating to the interpretation of
δ¹⁸Oₛ could be reduced or eliminated if reliable fluid inclusion data are available to
constrain contemporaneous changes in the δ¹⁸Oₚ (see below).
Speleothems as recorders of teleconnections in the climate system

A major strength of speleothem isotope records is their robust chronology (Richards et al. 2003). Ages with a relative error of ± 0.5% are achievable for speleothems younger than about 100,000 years using modern mass spectrometers with high abundance–sensitivity. Perhaps the most feature of recent speleothem studies that serves to underline their remarkable potential as palaeoclimate archives is their ability to detect teleconnections in the climate system on millennial timescales (Wang et al. 2001; Spötl and Mangini 2002; Genty et al. 2003; Yuan et al. 2004). Wang et al. (2001) for example, demonstrated that oxygen isotope ratios in five partially overlapping stalagmites from Hulu Cave in China appear to be sensitive to the Dansgaard–Oeschger (DO) interstadial events documented in the Greenland ice–cores (Figure 4). $\delta^{18}O$ variations in the Hulu stalagmite were interpreted to reflect changes in the ratio of summer/winter precipitation. Importantly these results provide evidence for teleconnections in the climate system and indicate a link between the East Asian Monsoon and Greenland temperatures as predicted by recent modelling results (Chaing and Bitz in press). Similar teleconnections were noted in the Holocene record from Crag Cave (McDermott et al. 2001), although these probably reflect atmospheric circulation changes recorded contemporaneously in mid and high–latitudes.

Figure 4 Oxygen isotope records for five stalagmites from Hulu Cave (32°30’N, 119°10’E), (China) exhibit good coherence between overlapping stalagmites (upper curve). The Dansgaard–Oeschger (DO) interstadial events (numbered) and the Heinrich events (lower curve) are clearly discernible in the Hulu data (upper curve), suggesting a link between Greenland temperatures and the behaviour of the East Asian Monsoon between about 75 ka and 11 ka. The large amplitude variability (about 5‰) in $\delta^{18}O$ in the Hulu stalagmites was interpreted to reflect temporal changes in the balance between precipitation associated with the summer and winter monsoon. Diagram reproduced with permission from Wang et al. (2001).
Figure 5. Speleothems from Israel have provided a remarkably coherent picture of regional climate variability over the past 250,000 years (Bar–Matthews et al. 1996; 1997; 1999; 2000; 2003). This diagram (Bar–Matthews et al. 2003) combines data from Soreq (31.45°N, 35.03°E, central Israel) and Peqiin caves (32.58°N, 35.19°E, northern Israel). Oxygen isotope ratios exhibit large amplitude variations that closely track changes in the marine δ¹⁸O record (ice volume effect) for the Eastern Mediterranean reconstructed from the planktonic foraminifera *Globigerinoides ruber* (Bar–Matthews et al. 2003), with a relatively constant (5.6±0.7‰) offset. Low δ¹⁸O events coincide with high water stands in caves and with sapropel events in the Mediterranean, indicative of wet conditions. Sapropel event S5 (128–117 ka) is characterised by low δ¹⁸O and high δ¹³C. The latter was interpreted to reflect rapid throughput of meteoric water during deluge events, with high δ¹³C values a consequence of relatively little interaction between infiltrating water and soil CO₂. An alternative explanation for high δ¹³C during sapropel event S5 recorded in a speleothem from a cave in Jerusalem (Frumkin et al. 2000) involved loss of vegetation and soil cover under hot–dry conditions, but this may be difficult to reconcile with the low δ¹⁸O (wet conditions) recorded at Soreq and Peqiin. Reproduced with permission from Bar–Matthews et al. (2003).
Figure 6. Stalagmite (M1–2) deposited during the last glacial at Moomi Cave (Socotra Island, Yemen, 12°30’N 54°E) exhibits relatively low-amplitude δ¹⁸O variability (middle curve) with low δ¹⁸O (wetter conditions) apparently associated with the Dansgaard/Oeschger events identified in the GISP core (plotted using GRIP 2001 chronology, lower curve). Also shown (upper panel) is the relevant part of the O isotope record from Hulu Cave in central China (Wang et al. 2001). The three curves are plotted using their own independent chronologies, and that the age model for the Moomi Cave stalagmite has been revised to correct for a systematic error (Burns et al. 2003). A major finding of the Burns et al. (2003) study is that the tropics (ITCZ) vary in concert with N. hemisphere high-latitude temperature, with increased precipitation in the tropics associated with warmer conditions in Greenland. Reproduced with permission from Burns et al. (2003).
Yuan et al. (2004) investigated the timing and duration of changes in the Asian monsoon over the past 160,000 years using oxygen isotope data for stalagmites from Dongge Cave in China, some 1200 km WSW of Hulu Cave referred to above (Figures 4 and 6). Of particular interest in the context of speleothems as recorders of teleconnections in the climate system is the remarkably good correspondence in $\delta^{18}O$ between stalagmites from Dongge and Hulu caves in times of contemporaneous growth during the last de-glaciation (e.g., Figure 7). The large amplitude of $\delta^{18}O$ variability in these Chinese speleothems indicates that they primarily record changes in $\delta^{18}O_p$, rather than temperature changes. The $\delta^{18}O$ of precipitation reaching the Hulu and Dongge sites largely reflects the progressive rainout of water vapour transported from the tropical Indo-Pacific oceanic source regions to southeastern China. Yuan et al. (2004) argue that higher $\delta^{18}O$ during glacial times (Figure 7) reflect drier conditions, similar to that seen elsewhere (e.g., in Israel, Figure 5). Such millennial–scale changes are interpreted to reflect major and abrupt changes in the Asian Monsoon and appear to be contemporaneous with changes in air temperatures recorded by the high–latitude (Greenland) ice cores. By contrast, low–frequency changes (tens of millennia) recorded by the Dongge and Hulu stalagmites during the past 160,000 years appear to correlate with changes in N. hemisphere insolation (Yuan et al. (2004), not shown).

Figure 7. Diagram from Yuan et al. (2004) showing that stalagmite D4 from Dongge Cave in Guizhou Province, China (25°17', 108°5'E) exhibits a pattern of high–amplitude $\delta^{18}O$ variability over the late–glacial/early Holocene interval that is similar to that from Hulu cave, some 1200 km away (Figure 4). The similar pattern of $\delta^{18}O$ variability in these two widely separated records indicates that these stalagmites have recorded large–scale regional, rather than local climate signals. Reproduced with permission from Yuan et al. (2004).
Speleothems as recorders of solar forcing of Earth’s climate

One of the most remarkable results to emerge from oxygen isotope studies of speleothems in recent years has been the apparent evidence for solar forcing of Earth’s climate on sub–Milankovitch timescales. Neff et al. (2001) argued that δ¹⁸O in a Holocene stalagmite (H5) from Hoti Cave in northern Oman (23°05’N, 57°21’E) correlates strongly with atmospheric Δ¹⁴C (derived from the tree–ring radiocarbon calibration dataset), and they interpreted this to reflect solar forcing of the tropical monsoon (Figure 8a). The high–resolution oxygen isotope record from speleothem H5 was interpreted as a proxy for variations in tropical circulation and monsoon rainfall over this part of Arabia. They argued that the primary control on centennial– to decadal–scale changes in tropical rainfall and monsoon intensity are variations in solar radiation, as reflected in the atmospheric (tree–ring) Δ¹⁴C dataset. These results indicate that the Indian Ocean monsoon system was considerably stronger in the early to mid–Holocene than at present, indicating that the inter–tropical convergence zone (ITCZ) was situated distinctly further north than at present. Lower δ¹⁸O was associated with increased monsoonal precipitation because the so–called ‘amount effect’ is dominant in this region. The high–resolution interval of speleothem H5 (between approximately 8.3 and 7.9 ka) indicates that δ¹⁸O and Δ¹⁴C are also correlated on shorter (decadal) timescales (Figure 8b). Further evidence for probable solar forcing of late Holocene climate was provided by the study of stalagmites from B7 cave in NW Germany by Niggemann et al. (2003). One of the stalagmites studied was deposited during the late Holocene (STAL–B7–7), and its oxygen isotope record appears to correlate with the atmospheric Δ¹⁴C curve in the interval between 4 ka to the present–day. In particular the interval around 2.8 to 2.4 ka that shows strong variability in atmospheric Δ¹⁴C, and for which solar forcing has been suggested previously (van Geel et al. 1998) shows a remarkably close correlation between Δ¹⁴C and δ¹⁸O (Figure 8c). Similar results for a longer interval of the Holocene were reported by Fleitmann et al. (2003) for a stalagmite (Q5) from a different cave in Oman (Qunf Cave, 17°N, 54°18E). Their high–resolution record spans most of the Holocene (10.3 to 2.7 ka and 1.4 to 0.4 ka), and like the record for N. Oman (Hoti Cave) discussed above, the δ¹⁸O variability is interpreted to reflect changes in monsoon precipitation, reflecting the dominance of the amount effect. In the time interval after about 8.0 ka, the intensity of the monsoon system appears to have decreased (higher δ¹⁸O) as northern hemisphere summer insolation decreased gradually. In the early Holocene portion of the Q5 record (before c. 8 ka), changes in the monsoon intensity (inferred from speleothem δ¹⁸O) appear to be in phase with Greenland temperatures as recorded in the δ¹⁸O of the GRIP record. Thus several oscillations in δ¹⁸O in the interval between approximately 9.3 and 8.7 ka appear to be contemporaneous (within the dating errors) in Q5 and GRIP, implying a connection between Greenland temperatures and the position of the ITCZ in this part of Arabia. In the time interval after 8 ka, decadal to centennial timescale variations in δ¹⁸O in Q5 appear to correlate with atmospheric Δ¹⁴C, suggesting that monsoon intensity in southern Oman is linked to relatively high–frequency changes in solar output as had been observed previously in northern Oman (Neff et al. 2001).
Figure 8. (a) The coherent variation of $\delta^{18}O$ and atmospheric (tree–ring) $\Delta^{14}C$ in the Holocene stalagmite H5 (Hoti Cave, Oman) over the time interval between about 9.5 and 6 ka. It was argued that variations in solar output affect the intensity of monsoonal precipitation (Neff et al. 2001). (b) Details of the correlation over a short portion of the Hoti Cave record. (c) The close correlation between $\delta^{18}O$ in the Holocene stalagmite STAL–B7–7 (B7 Cave, Sauerland, Germany) and atmospheric $\Delta^{14}C$ (Niggemann et al. 2003). Dashed curves are for $\delta^{18}O$ and solid curves represent $\Delta^{14}C$. Redrawn after Neff et al. (2001) and Niggemann et al. (2003).
Spectral analysis of both δ¹⁸O records from Oman indicate periodicities that are consistent with solar forcing. In common with all studies that indicate a solar forcing mechanism for high–frequency climate change, the precise mechanism by which relatively small variations in solar output are amplified to produce detectable climate signals on these short timescales remains unresolved.

It should be noted that the chronology of all three stalagmite records reproduced in Figure 8 (H5, Q5 and STAL–B7–7) were 'tuned' within the error bars allowed by the U–series ages in order to maximise the match between the O isotope and Δ¹⁴C records (Neff et al. 2001; Fleitmann et al. 2003; Niggemann et al. 2003). In some cases the dating uncertainties were relatively large (several hundred years), because of relatively low U contents, and so the extent to which the solar signal (atmospheric Δ¹⁴C) might lead the climate signal (δ¹⁸O) on decadal timescales remains difficult to assess.

Frisia et al. (2003) adopted a different approach in investigating the possible role of solar forcing on the thickness of annually deposited laminae in a stalagmite from Grotta di Ernesto (ER76) in northern Italy. In this study, the annual lamina thickness and the ratio of dark to light–coloured laminae in three contemporaneously deposited stalagmites appear to respond to changes in surface air temperature. Particularly noteworthy is the occurrence of dark and thin laminae in stalagmites deposited during the Maunder and Dalton Minima of solar activity and the presence of an 11–year cyclicity in stalagmite growth rate (lamina thickness), attributed to solar forcing. Frisia et al. (2003) argued, on the basis of the factors that control stalagmite growth rates at these sites in the present–day that high–frequency solar forcing somehow modulated the seasonal production of soil CO₂, that in turn affected stalagmite growth rates.

Carbon isotopes in speleothems

Carbon isotope ratios in speleothems usually reflect the balance between isotopically light biogenic carbon derived from the soil CO₂ and heavier carbon dissolved from the limestone bedrock. Conceptually, the processes by which downward percolating drip waters acquire calcium carbonate in the soil and host–rocks above a cave have been described in terms of two end–member systems (Hendy 1971; Salomons and Mook 1986). In an open–system, continuous equilibration is maintained between the downward percolating water and an infinite reservoir of soil CO₂ resulting in a progressive increase in the bicarbonate content of the water as it dissolves more limestone in the unsaturated zone. Under these conditions, the δ¹³C of the dissolved species reflects the carbon isotopic ratio of the soil CO₂, with no detectable contribution to the carbon isotope signal by the carbonate host–rock. In a C3 plant system, the δ¹³C of the dissolved inorganic carbon (DIC) in the percolating solution is typically in the range –14 to –18‰ when the solution reaches saturation with respect to CaCO₃, depending on soil pCO₂ and temperature (Hendy 1971; Salomons and Mook 1986; Dulinński and Rozanski 1990).

By contrast, in a closed system the downward percolating water loses contact with the soil CO₂ reservoir as soon as carbonate dissolution commences (Hendy 1971; Salomons and Mook 1986). CO₂ consumption in the carbonation reaction H₂O + CO₂ → H₂CO₃ limits the extent of limestone dissolution, because in this model the soil CO₂ reservoir is finite. Under closed–system conditions, the carbon isotope ratio of the host–rock exerts
a strong influence on that of the DIC. For a C3 system with soil gas $\delta^{13}C$ of c. –23‰ and a host limestone with $\delta^{13}C$ of +1‰, the DIC $\delta^{13}C$ is typically c. –11‰. In reality most natural systems are likely to be partially open, with the $\delta^{13}C$ of DIC between that predicted by the end-member models (Dreybrodt 1988). Radiocarbon data on independently (e.g., U–Th) dated stalagmites can be used to calculate the mass fraction of $^{14}C$–dead carbon and thereby constrain the balance between open and closed–system dissolution, although other effects such as ageing of organic matter in the overlying soil reservoir must also be taken into account at some sites (e.g., Genty et al. (2001)).

In arid regions, changes in the $\delta^{13}C$ values of speleothem calcite have been interpreted to reflect climate–driven changes in vegetation type (e.g., C3 versus C4 dominated plant assemblages (Dorale et al. (1992); (1998); Bar–Matthews et al. (1997); Frumkin et al., (2000)). In these regions, relatively large shifts in $\delta^{13}C$ can occur because soil respired CO$_2$ in equilibrium with a C3 dominated plant assemblage has $\delta^{13}C$ in the range –26 to –20‰, while that in equilibrium with C4 vegetation is heavier ($\delta^{13}C$ of –16 to –10‰). These differences produce distinctive ranges in $\delta^{13}C$ in secondary carbonates (typically –14 to –6‰ for carbonates deposited in equilibrium with CO$_2$ respired from C3 plants, and –6 to +2‰ for that from C4 plants). In stalagmites from Israel (Figure 5), sapropel event S5 (128-117 ka) is characterised by low $\delta^{18}O$ and high $\delta^{13}C$. The latter was interpreted to reflect rapid throughput of meteoric water during deluge events, with high $\delta^{13}C$ values a consequence of relatively little interaction between infiltrating water and soil CO$_2$.

The interpretation of carbon isotopes in moist temperate zones that lack C4 vegetation is necessarily more tentative, but occasionally a clear climate–related signal can be retrieved. As an example from the recent literature, Genty et al. (2003) noted that stalagmites deposited during the late glacial in the south of France exhibit $\delta^{13}C$ values that are much higher than in those deposited during the Holocene. These differences were attributed to changes in the relative proportions of atmospheric and biogenic (light) carbon. This interpretation implies that periods of climatic amelioration promote the production of soil biogenic CO$_2$, resulting in lighter carbon isotope ratios in the speleothem calcite (Figure 9). Data for the Grotta di Ernesto stalagmites (McDermott et al. 1999; Frisia et al. 2003) indicate that $\delta^{13}C$ values tend to be higher during episodes of thinner laminae in the mid–nineteenth century compared with those associated with thick laminae deposited during the last 50 years. These variations were interpreted to reflect decreases in the production rate of soil CO$_2$ giving rise to higher $\delta^{13}C$ values during the cooler intervals (see below). Critically, many temperate–zone speleothems exhibit $\delta^{13}C$ values $> –6‰$ (Figure 10); higher than predicted to be in equilibrium with the expected C3 vegetation (Baker et al. 1997). Processes within the cave including evaporation and rapid degassing of cave drip waters may cause kinetic fractionation (Hendy 1971). Calcite precipitation in the unsaturated zone above the cave may also produce heavy carbon isotope signatures (Baker et al. 1997; Genty and Massault 1997). The latter process appears may be important in samples for which the highest $\delta^{13}C$ values also exhibit high Mg/Ca (Figure 11), indicative of prior calcite precipitation from the drip waters.
Figure 9. The lower curve shows $\delta^{13}C$ in stalagmite 'Vil9' from Villars Cave in southwest France (45°N, 0.50°E) after Genty et al. (2003). Deposition of Vil9 continued through most of the last glacial, apart from major hiatuses at 78.8–75.5 ka (D2), 67.4–61.2 ka (D3) and 55.7–51.8 ka (D4). The regular increase in $\delta^{13}C$ into event D3 ('Villars cold phase') and the decrease following re-establishment of speleothem growth points to a c. 6,000 year long cold phase with decreased vegetation intensity, leading to higher $\delta^{13}C$. Also shown is the Hulu Cave dataset (Wang et al. 2001). The poor correlation between the Vil9 and Soreq (Israel) records suggests that the latter reflects a Mediterranean (Bar–Matthews et al. (1999); Vaks et al. (2003)) rather than a N. Atlantic signal. Reproduced with permission from Genty et al. (2003).
Figure 10. Histograms of published carbon isotope data for three temperate–zone stalagmites from cave sites where C4 vegetation probably never existed in the late Quaternary. Filled columns are for a stalagmite deposited during the last glacial at Villars, S.W. France, (Figure 9, Genty et al. 2003) and Holocene stalagmites from Père Noël, Belgium and Crag, S.W. Ireland (Verheyden et al. 2000; McDermott et al. 1999). Unfilled segments represent modern precipitates (e.g., soda-straws, incipient stalagmites) from these caves where data are available Père Noël and Crag Cave). Some δ¹³C values are higher than predicted to form in equilibrium with soil CO₂ associated with the C3 vegetation at these sites (> –6 ‰). Mg/Ca ratios are available for two of these stalagmites (Crag and Père Noël), and in both, high δ¹³C appears to be associated with elevated Mg/Ca (Figure 11). This is interpreted to reflect simultaneous degassing and prior calcite precipitation of the drip waters in the flow–paths above the stalagmites, producing a combination of high δ¹³C and high Mg/Ca. In the absence of Mg/Ca data, high δ¹³C could be misinterpreted as a climate–driven vegetation signal in palaeo–records.
In summary, the interpretation of carbon isotopes in regions where changes in the proportion of C3 and C4 plants can be verified independently (e.g., from pollen data) is relatively straightforward. In temperate regions that lack natural C4 vegetation however, the interpretation of carbon isotopes in speleothems remains more difficult, and the data are often interpreted on case–by–case basis. So far, the geochemical criteria for distinguishing between the processes that might be responsible for carbon isotope variations have not been established, yet these are essential if reliable palaeoclimatic information is to be inferred from the $\delta^{13}C$ record of temperate–zone speleothems. If incomplete equilibration between soil CO$_2$ and percolating water is the primary factor responsible for elevated $\delta^{13}C$ in some temperate zone speleothems, then elevated $\delta^{13}C$ should be associated with wetter periods, when the water/soil gas contact times are
shorter. If, on the other hand, seasonal evaporation of water in the unsaturated zone or perhaps within the cave itself is the dominant processes, then high $\delta^{13}C$ should be associated with drier periods. One promising line of research is to combine trace element and carbon isotope data, because depending on the nature of the covariations, several possible mechanisms for changes in $\delta^{13}C$ can be ruled out. In a study of a 31,000 year old speleothem from New Zealand for example, Hellstrom and McCulloch (2000) were able to rule out a reduction in cave seepage water flow rates as an explanation for elevated $\delta^{13}C$. Barium concentrations exhibited a strong negative correlation with $\delta^{13}C$, the opposite to that predicted if high $\delta^{13}C$ was caused by enhanced prior calcite precipitation in the flow path as a result of slower flow rates. Future research should seek to develop further these coupled isotope and trace element criteria and to underpin these with modelling as has been done for some trace elements (Fairchild et al. 2000).

**Fluid inclusions in speleothems: methodologies and some recent results**

*Significance of speleothem fluid inclusions*

Almost all speleothems contain sealed microscopic cavities that are partly or wholly filled with water, referred to generically as fluid inclusions. These represent a valuable archive of palaeo–water. Individual speleothems often preserve intervals of inclusion–poor calcite that appear to alternate with depositional episodes in which abundant fluid inclusions are uniformly and densely dispersed through the calcite. Macroscopically, the presence of fluid inclusions is revealed in thick sections or cut slabs by a milky opacity, typically distributed as layers alternating with clear, apparently inclusion–free calcite. Zones of high fluid inclusion density may correspond to periods when growth rates are changing rapidly, resulting in frequent sealing off of micropores, rather than their being filled by calcite growth from their base. Fluid inclusions in stalagmites and flowstone tend to be in the form of ellipsoidal or irregular tubes, oriented parallel to the crystallographic $c$ axis of the host calcite crystal (Figure 12). Water trapped as inclusions in speleothems makes up, on average, about 0.1% by weight of speleothems, ranging from c. 0.05 to 0.5 wt. %.

In detail, the mechanism of formation of inclusions is poorly understood, but is presumably the result of closing over of intercrystalline spaces on the growth surface of the speleothem (Kendall and Broughton 1978). Inclusions range in size from a few hundred nanometers to several cubic centimeters, but the majority range from 1 to 100 μm in maximum dimension. The fluid is usually a two–phase assemblage, a lower zone of water capped by a bubble of included air (Figure 12).
Preservation of the fluid inclusion isotope signals

Hendy (1971) observed that for speleothems formed at equilibrium with their drip water, their temperature of formation could be determined from the oxygen isotope fractionation between calcite and the drip water. Schwarcz et al. (1976) suggested that fluid inclusions might provide samples of that water, but noted that over the multi-millennial history of a speleothem it was likely that the \(^{18}\text{O}/^{16}\text{O}\) ratio would have changed due to re-equilibration with calcite in the wall of the inclusion. This might occur for example by diffusive exchange around the perimeter of the inclusion, or by dissolution–recrystallization at the water–calcite interface. However the extent to which re-equilibration of oxygen isotope ratios occurs remains poorly understood. Theoretical calculations suggest that diffusive exchange of oxygen isotopes in a water–calcite system should proceed very slowly at Earth surface temperatures, approaching isotopic equilibrium by only one part in \(10^3\) on a timescale of \(10^6\) years for an inclusion with a radius \(<10^{-2}\) m (P. Dennis, pers. comm. to PJR). For example, Rye and O’Neil (1968)

Figure 12. Photomicrographs showing fluid inclusions in speleothems. Images A and B show typical distribution of fluid inclusions in relation to (sub-horizontal) growth laminae. Inclusions are often 'thorn shape' with their long axis parallel to the crystallographic C axis of the calcite crystals. White bars in images A and B are 200 microns long. C and D are close-up images of inclusions, some of which have a trapped gas bubble. Inclusions are typically 10-30 microns in width in these images.
noted that only 26–29% of possible oxygen isotope exchange had occurred between fluid inclusion water and the 38 Ma hydrothermal calcite host deposits at Providencia, Mexico. It appears therefore that this mechanism would produce negligible modification of the $\delta^{18}$O of fluid inclusion waters on Pleistocene timescales. Dissolution–reprecipitation process might in principle affect the $\delta^{18}$O of the fluid inclusion water and is likely to be concentrated in the recesses of irregular shaped inclusions (many are thorn–shaped or have triangular cross sections) as their morphology gradually modifies towards shapes that minimise surface area and energy. The extent to which this process alters the $\delta^{18}$O of the fluid inclusion water depends on inclusion volume and age, and the relative temperatures at time of formation and alteration. However, no evidence of such alteration has been observed during petrographic examination of large numbers of speleothems of Pleistocene age (A. Kendall, pers. comm. to PJR). These observations, combined with the slow diffusive exchange of oxygen isotopes in the water–calcite system suggests that $\delta^{18}$O re–equilibration is a less acute problem than anticipated in the early studies (see example below however), but further investigation of the issue is certainly desirable.

By contrast with the $^{18}$O/$^{16}$O ratio, there is more confidence that the D/H ratio of the trapped water should remain intact after entrapment, because no opportunity exists for isotope exchange within a speleothem. In order to avoid possible problems associated with re–equilibration of the oxygen isotope ratios, Schwarcz et al. (1976) measured D/H ratios, and then calculated the initial oxygen isotope ratios of the fluid inclusion water using a meteoric water line relationship. Today, drip waters from many caves have been shown to resemble the global meteoric water line of Craig (1961) for which $\Delta D = 8 \delta^{18}$O + 10. Schwarcz et al (1976) assumed the same relationship for ancient waters and obtained temperatures for deposition of speleothems from various sites in North America. A subsequent study by Harmon et al. (1979) showed that, using a deuterium excess ($d$) of 10‰, many samples yielded impossibly low palaeotemperatures (<0°C). This problem could be avoided if 0 < $d$ < 10‰ during Ice Ages, as had been shown on theoretical grounds by Merlivat and Jouzel (1979), and as observed recently in high–latitude ice cores (Stenni et al. 2004).

In general, the emphasis in speleothem fluid inclusion research has now shifted from attempts to calculate absolute palaeotemperatures to the more attainable goal of reconstructing temporal changes in the $\delta^{18}$O of palaeo–rainfall. Provided that drip waters are not evaporated, their isotope composition will, as discussed above, reflect that of the local rainwater, and the global distribution of isotopes in precipitation is amenable to modelling by isotope–enabled GCMs and so provide a useful test for such GCMs. If isotope ratio measurements of the inclusions were sufficiently precise, it should be possible to determine the deuterium excess in precipitation, which can be interpreted in terms of temperature and humidity at the moisture source areas. Documentation of this parameter through time for any given location would provide insights into vapour source changes under different climatic regimes. The noble gas content of inclusions, if determined with sufficient precision (e.g., Stuart et al., 1995), could in principle be used as an independent thermometer recording cave temperature through time using the principles outlined by Stute and Schlosser (1993). Preliminary experiments at McMaster University, however, suggest that it may be difficult to correct for the "excess air" component.
Extracting inclusion water for isotope analysis – a historical perspective

Aside from a minority of speleothems that contain fluid inclusions large enough to permit the water to be withdrawn using a syringe (Genty et al. 2002), the recovery of inclusion water from the speleothem calcite without fractionating the oxygen and hydrogen isotopes in the process has proven to be an exceptionally difficult task. The historical development of the analytical methodologies is outlined here in order to provide a context for the more recent work. In the pioneering studies at McMaster University (1974 –1983), fluid inclusions were extracted by placing a saw–cut, c.1g block of calcite inside a stainless steel tube sealed with gaskets to a vacuum line, and crushing the block with a hydraulic press (Harmon et al 1979). A single crushing typically yielded 10–50 ìl water, adequate for D/H analyses. In later experiments Yonge (1982) progressively heated samples and continuously converted the released water to hydrogen gas using metallic U at 800°C, allowing him to obtain a thermal release history. Water was also extracted by calcining samples at c. 800°C (CaCO\textsubscript{3} \rightarrow CaO + CO\textsubscript{2}), and by separating water from CO\textsubscript{2} on a vacuum line (Schwarz and Yonge 1983). These early studies established the two primary techniques in use for extracting inclusion water for isotope measurement that are still employed today, namely thermal decrepitation and crushing. Both are carried out under high vacuum (<10\textsuperscript{−5} torr) in order to minimise the mean free path of the water vapour molecules during recovery from the calcite and subsequent manipulation steps.

Initial studies by the McMaster group encouragingly showed that $\delta^D$ of fluid inclusions from small stalactites (“soda straws”) agreed with that of coeval drips in caves. In addition, it was demonstrated that replicate analyses of $\delta^D$ from the same level in a single flowstone from Bermuda agreed within the precision of analysis (c. 1‰). In these experiments $\delta^{18}O$ of the water was analysed by reaction with BrF\textsubscript{5} and conversion of the resultant O\textsubscript{2} gas to CO\textsubscript{2} by reaction with graphite (M. Yamamoto, unpublished data). Replicate analyses within single growth layers of a flowstone from Bermuda agreed within analytical error (± 0.2‰), but $\delta^{18}O$ differed between layers. These analyses showed that waters trapped in Pleistocene stalagmites from N. America did not lie on the meteoric water line, but were displaced to an extent unaccountable for by shifts in $\delta^D$ alone (Schwarz 1986). This was interpreted to reflect exchange between water and calcite as a result of change in environmental temperature between the time of entrapment and today, underlining persistent concerns about re–equilibration of the oxygen isotope ratios (but not hydrogen) of the fluid inclusion water.

Importantly, the McMaster experiments also revealed that the D/H ratios of water released by thermal decomposition of calcite were depleted by 22‰ with respect to cave drip waters. No explanation was given for this effect, and the offset was simply corrected for in calculations of palaeotemperatures. It was also observed that, with progressive decrepitation up to c. 500°C, later (higher–T) fractions of water were systematically more D–depleted. On calcining the residue after such a decrepitation sequence, Yonge (1982) found that an additional amount of water was released, comparable in volume to that liberated through all prior decrepitation steps, and which was also D–depleted by up to 80‰ with respect to drip water. The significance of this high–temperature water release is discussed further below in the context of new insights into the various forms of water that appear to be present in speleothem calcite.
In their initial paper, Schwarcz et al. (1976) used the relationship between fluid inclusion–derived temperatures and inferred δ¹⁸O of drip waters to determine the local, long–term relation between these two quantities. They observed that the T–dependence of δ¹⁸O of meteoric precipitation d(δ¹⁸O_p)/dT, varied between 0 and 0.3‰/°C and was always less than the short–term average of c. 0.7‰/°C observed today in North America and other temperature regions (Rozanski et al. 1993). Harmon et al. (1983) observed a significant drop in average äD over North America during glacial periods. In a study of a speleothem from Coldwater Cave, Iowa, although δ¹⁸O of calcite was almost constant throughout the growth history of this 83 cm long stalagmite, äD varied by 12‰, indicating that the temperature of deposition had varied by 5°C (Harmon et al. 1979).

Following the renaissance in interest in speleothems as palaeoclimate recorders in the 1990s, the group at the University of East Anglia (UEA) have been active in developing techniques for the reliable extraction of isotope data from speleothem fluid inclusions (Dennis et al. 2001). They focussed on crushing procedures in order to investigate the δ¹⁸O signal. Investigation of the latter is precluded by decrepitation techniques since the calcite is strongly heated, typically to ~500°C to rupture the inclusions by vapour pressure, or to ~900°C to disintegrate the sample by conversion of CaCO₃ to CaO. At such elevated temperatures, rapid exchange of oxygen isotopes occurs between the released water and the large quantities of CO₂ produced. After the trapped water is released and transferred to the vapour phase, fractionation can occur by preferential adsorption of the heavier isotopes (¹⁸O, D) onto the reactive surfaces of freshly crushed calcite (see below) or onto the surfaces of the extraction apparatus. Conversely, there may be preferential escape of the lighter isotopes (¹⁶O, ¹H) during sample manipulation in the high–vacuum handling lines. Fractionation must be minimised in order to maximise the signal–to–noise ratio since the amplitude of changes in the oxygen isotope ratio of groundwater is generally very low on other than glacial–interglacial timescales. Uncertainties of >±1‰ for oxygen and >±8‰ for hydrogen are of limited use for validating GCMs, or for calculating cave temperatures to a precision of better than ±5°C.

Crushing can be achieved either with the sample attached to a vacuum line by screw crushers, hammer crushers or electro–magnetically operated pistons, or offline by crushing sample capsules in a vice or agitating calcite in a ball mill. It is necessary to heat samples moderately (~150°C) to desorb the water from the freshly activated calcite surfaces and to drive the water out of those inclusions that have been accessed by narrow cracks only. Dennis et al. (2001) devised an improved method of crushing speleothem samples that quantitatively removed inclusion water in a controlled fashion. In a series of experiments in which anhydrous Iceland Spar was crushed with water of known mass and isotope composition sealed in capillary tubes, Dennis et al. (2001) showed that when released, the water adsorbed strongly onto the fresh calcite grain surfaces, probably in a series of monolayers. Attempts to desorb the water cryogenically at room temperature resulted in recoveries of only 50–80% for H₂O/CaCO₃ mass ratios of 1–2 mg g⁻¹, typical of observed speleothem values. The recovered water was invariably isotopically depleted by up to 25‰ for hydrogen, and 10‰ for oxygen. Following Gammage and Gregg (1972), Dennis et al. (2001) found that heating the sample to 150°C completely desorbed the water, and allowed recovery of the correct
isotope ratios. These results contrast with those of some inclusion studies on hydrothermal deposits, e.g., Yang et al. (1995), who successfully recovered water from crushed dolomite without sample heating.

Crushing and decrepitation techniques both require that the water is recovered cryogenically to a liquid nitrogen trap at \(-196^\circ C\) and the temperature raised to boil off any trapped CO\(_2\). The water is then transferred to an appropriate vessel for analysis, generally a pyrex tube that can be flame sealed or closed with a tap. The recovered water (typically 0.1 to 5 \(\mu\)L for calcite samples of 0.1–several grams) may be subjected to both oxygen and hydrogen isotope measurements, or to hydrogen isotope measurements only. In the former case, a metered amount of CO\(_2\) of known isotope composition is transferred into the sample vessel with the water. It is sealed and the oxygen isotopes allowed to exchange between H\(_2\)O and CO\(_2\) for several days at a carefully controlled known temperature, usually 25\(^\circ C\), until equilibration is completed (Kishima and Sakai 1980; Socki et al. 1999). The CO\(_2\) and water are cryogenically separated at \(-75^\circ C\) and the water transferred for high temperature reduction to hydrogen using zinc (Coleman et al., 1982, Tanweer et al. 1988), chromium (Donnelly et al. 2001), manganese (Shouakar–Stash et al. 2000) or uranium (Hartley 1980). The isotope composition of the CO\(_2\) and the hydrogen are then measured directly by mass spectrometry.

Applying the crushing and heating technique to a speleothem from SW England, Dennis et al. (2001) were able to produce an oxygen and hydrogen isotope record of mid–late Holocene drip water. The data plotted on, or very close to, the Global Meteoric Water Line, with the youngest samples plotting within the field of modern drip water compositions. This result would not be expected if post–trapping exchange of oxygen with calcite had occurred, but it should be noted that (i) the samples analysed were all of Holocene age and little temperature change is expected to have occurred over this interval; and (ii) the duration of storage is relatively short. On balance, caution is urged in inferring \(\delta^{18}O\) values of drip water directly from corresponding analyses of fluid inclusion waters, but the alternative approach of inferring drip water \(\delta^{18}O\) from measured D/H ratios is also problematic because it hinges on the correct choice of \(d\).

The latter issue was highlighted in the Matthews et al. (2000) decrepitation study of fluid inclusions from Soreq Cave in Israel where today \(d = 22\%o\). Matthews et al. (2000) showed that drip water was enriched in D by 30\%o compared to trapped inclusions, comparable to the 22\%o offset observed by Schwarcz and Yonge (1983). When waters trapped during ice ages (MIS 3 and 4) were used to calculate palaeotemperatures, agreement with independent estimates of temperature was best if the authors assumed a deuterium excess of 10\%o (Craig’s (1961) modern global meteoric water line). The implication is that \(d\) changes significantly between glacial and interglacial climate states, and it underlines the difficulty in objectively choosing the appropriate value for the deuterium excess.

Evidence for multiple forms of water in speleothems

An improved understanding of the nature of trapped waters in speleothems may provide useful insights into how best to improve fluid–inclusion extraction techniques in the future. As alluded to above, Yonge (1982) observed that even clear, apparently
inclusion–free speleothems yielded, on decomposition, significant amounts of water, confirming that water was present in some form other than microscopically resolvable fluid inclusions. In recent years the nature of this 'residual' water became the subject of further investigation at McMaster University. Schwarcz (unpublished data) prepared portions of inclusion–rich stalagmites by grinding them to particles <10 μm, and heating them to 500 °C in a furnace prior to analysis using Fourier Transform Infrared Spectrophotometry (FTIR). In all cases, a broad absorption peak at c. 3400 cm⁻¹ corresponding to liquid water was observed in these heated samples (Figure 13).

![Figure 13. Fourier transform infra–red absorption spectrum of a powdered sample of a stalagmite from Coldwater Cave, Iowa. Superimposed spectra at –11 °C and –36 °C are indistinguishable from spectrum at 25°C (not shown). The broad peak centered at 3400 cm⁻¹ indicates the presence of liquid (but not solid) H₂O (H. Schwarcz, unpublished data).](image)

Importantly, this did not appear to be due to the presence of water of hydration (lattice–bound H₂O). For example, gypsum (CaSO₄ 2H₂O) displays a number of discrete peaks in this spectral region, but no peak due to liquid water. Also, no hydroxyl (OH) peak was observed, except where they had been inadvertently overheated leading to calcination and subsequent formation of CaOH. Attempts to freeze the water by carrying out FTIR measurements at –30°C showed no change in the shape of the peak, whereas the IR spectrum of liquid water attached to calcite was seen to transform to that of ice. Although considerable care was taken not to expose the samples to atmospheric water vapour after heating, it was possible that this broad water peak was due to water inadvertently adsorbed prior to FTIR analysis. To test this, freshly heated calcite was exposed to a saturated vapour of D₂O. No absorption peak for liquid D₂O (at 2470 cm⁻¹) was observed, nor was there any change in the intensity of the 3400 cm⁻¹ peak, leading to the conclusion that liquid water was still present inside these strongly decrepitated samples.
G. Rossman and C. Verdel at the California Institute of Technology (pers. comm. to HPS, 2004) suggested recently that this water might be trapped in these samples as inclusions 100nm in maximum dimension, which would not be liberated by crushing. (pers. comm. to HPS 2004). These sub-im–sized inclusions might also be present in optically clear calcite since their small size would not lead to detectible scattering of light. During heating, the vapour pressure of steam in a nano inclusion would be insufficient to fracture the surrounding calcite. Also, at sub-zero temperatures they might remain supercooled due to lack of nuclei for freezing. Water in these nano inclusions might be isotopically fractionated with respect to water in larger inclusions, due to larger surface/volume ratio of the inclusions, as a result of surface/water interactions during trapping which would tend to preferentially trap H2O vs D2O. This proposal is currently under experimental investigation by the McMaster group.

It is noteworthy that ion–probe analyses of the hydrogen contents of speleothems (Fairchild et al. 2001) provide an independent line of evidence for the nature of trapped water. Hydrogen is typically present at concentrations of 100–1000 ppm, with a continuous distribution on the scale of a few microns. These observations are consistent with the presence of molecular or nano–inclusion hosted water.

Recent applications of fluid inclusion studies

Fleitmann et al. (2003) used a 'Dennis–type' crusher to extract fluid inclusions from speleothems from Oman. They observed large excursions in δD, the highest values approaching those of modern precipitation in the area of the cave, while mid–glacial stage values were up to 60‰ lower. From these data they inferred changes in atmospheric circulation, but did not attempt to calculate palaeotemperatures. They were able to identify the Indian Ocean as the dominant moisture source for groundwater recharge during Mid–Pleistocene interglacial periods based upon the δD values of the fluid inclusions.

Construction of a 'Dennis–type' crusher at the McMaster laboratory allowed Serefiddin et al. (2002) to obtain a series of palaeotemperatures on stalagmites from a cave in South Dakota, USA. Here, coeval portions of stalagmites deposited a few metres apart in a single chamber of the cave were found to differ in δ18O by up to 2‰ (Serefiddin et al. 2004). However, agreement was found between fluid inclusion based palaeotemperatures for the coeval deposits, showing that the difference in δ18O was due to systematic difference in δ18O of drip waters feeding the two sites. This was ascribed to differential delivery of winter vs summer precipitation to the recharge areas feeding these two stalagmites. As in earlier studies, it was necessary to assume d < 10 to avoid obtaining palaeotemperatures lower than 0°C.

McGarry et al. (2003) employed a modified thermal decrepitation technique to provide δD measurements of fluid inclusions for speleothems from three caves in Israel. As in previous studies (Matthews et al. 2000), a large (30‰) fractionation in δD was observed between the recovered and parent fluid inclusion water. After correcting for this effect, a range of δ18O values were inferred for the included water using both the global and Mediterranean meteoric water lines (MWL and MMWL). On the basis of these inferred δ18O data, a range of depositional temperatures were calculated using the
associated carbonate $\delta^{18}O$ values and a carbonate–water temperature equation. This approach yielded a trend of progressive cooling during the interval between about 130–20 ka, broadly in line with those inferred from independent marine (alkenone) based palaeotemperature estimates from the Eastern Mediterranean and Crete (Emeis et al. 1998; 2000; Kallel et al. 2000).

Current and future developments

Despite the very significant technical and analytical difficulties that surround the extraction of reliable fluid inclusion stable isotope data, such studies are worth pursuing because of their potential to unlock important insights into several issues in palaeoclimatology including:

(i) Reconstruction of secular variation in $\Delta D$ of meteoric water during shifts from glacial to interglacial climates in temperate and subtropical regions. Studies of fluid inclusions in dated speleothems could provide evidence of climate–controlled shifts in circulation patterns and sources of water vapour, and provide valuable tests for isotope–enabled GCMs;

(ii) Comparison of $\Delta D$ in nanoinclusions vs macroinclusions (>1 ìm) may reveal a source of 'noise' in fluid inclusion isotope data, and may lead to strategies for selecting a population of inclusions more representative of the drip waters;

(iii) Comparison of $\Delta D$ of fluid inclusions along single growth layers (or even more grossly, between axial and distal parts of the same stalagmite) may provide a more unequivocal test of whether evaporation occurred during deposition, possibly leading to disequilibrium deposition of CaCO$_3$;

(iv) High resolution measurement of palaeotemperature variations on a scale of a few decades to hundreds of years will require development of techniques for analysis of fluid inclusions in smaller amounts of calcite and sub–ìl amounts of water. Advances in continuous flow isotope ratio mass spectrometer (CF–IRMS) technology now allow hydrogen isotopes ($^{1}H^{1}H$ and $^{1}H^{2}H$) to be measured without interference from the He carrier gas ($^{4}He$) (e.g., Prosser and Scrimgour (1995); Begley and Scrimgour (1997)). This provides the opportunity for using the high temperature pyrolysis furnaces that are routinely used in CF work to reduce H$_2$O samples online to CO and H$_2$ (Eiler and Kitchen 2001; Sharp et al. 2001), thus avoiding the time consuming and difficult offline equilibration and liquid–gas separation steps necessary for dual inlet mass spectrometry. The omission of these sample–handling steps is likely to compensate for any slight loss of precision using the CF technique. Water samples ~0.1 ìl can have both oxygen and hydrogen isotopic ratios determined in ~10 minutes. This compares with minimum sample size of about 0.3 ìl and measurement times of 20 minutes each for O and H$_2$ using dual inlet mass spectrometry. It may be possible, therefore, to improve the resolution of fluid inclusion studies by up to an order of magnitude from the 300–1000 year range normally attempted at present. Such advances in measurement procedures do not, however, reduce the problems inherent in extracting the inclusion water from the calcite matrix, except insofar as they may permit the extraction device to be coupled to a mass spectrometer sample introduction system, thus streamlining sample handling.

(iv) A remaining question is the cause of the inhomogeneous distribution of fluid inclusions in speleothems? Without knowing the mechanism of entrapment, we cannot
fully comprehend why, during extended growth periods, the abundance of fluid inclusions can drop nearly to zero, resulting in the precipitation of optically clear calcite (which may still of course contain nano-inclusions). A related issue is that the temporal resolution for inclusion studies may ultimately be dictated by their closure rate, which may be on the order of decades, depending on the growth rate of the speleothem.

**Summary**

In summary, despite the apparently widespread 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 $\delta^{18}$O of meteoric water that falls on a cave site. Several studies have demonstrated that speleothems can record details of past climates such as the Dansgaard/Oeschger events that were previously accessible only via ice cores. The apparently synchronous changes in the position of the ITCZ and Greenland temperatures recorded by several mid–latitude northern hemisphere speleothems and ice cores respectively, yields important new insights into the operation of the climate system during the last glacial and explanations of these phenomena are currently the subject of modelling work. Speleothem O isotope data have also provided unexpected and challenging new insights into the probable influence of solar forcing on monsoonal systems on centennial to millennial time–scales in the Holocene, and underline the need to improve our understanding of the amplification mechanisms of solar forcing. Despite these undoubted successes it remains essential to check, on a sample by sample basis, that isotope equilibrium was achieved and maintained during the growth history of individual stalagmites using Hendy–type tests. Present–day monitoring studies of cave drip waters are also essential to understand fully the site–specific relationships between speleothem $\delta^{18}$O and meteorological variables at the surface.

Temporal changes in speleothem $\delta^{13}$C 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 (e.g., Dorale et al. (1998); Genty et al. (2003)). However carbon isotope data should ideally be accompanied by appropriate trace element data (e.g., Ca/Mg ratios) in order to evaluate other possible causes for temporal changes in $\delta^{13}$C. 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 $\delta^{13}$C values unrelated to changes in vegetation type or intensity.

By virtue of their strong chronological control and the long–term integrity of their stable isotope signals, speleothems offer considerable potential for the identification of teleconnections that in turn can provide new tests for both internal and external forcing mechanisms that drive Earth's climate on a variety of time scales. Thus, the emphasis in recent studies has been on the identification of relatively large shifts in the $\delta^{18}$O recorded by speleothems, and the evaluation of the extent to which these changes are recorded on a hemispheric scale. A remarkable result to emerge during the past few years has been evidence for strongly coherent in–phase climate signals on millennial timescales during the last glacial (e.g., Dansgaard–Oeschger events), between the Greenland ice core records and several northern hemisphere speleothem records such as
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Caves in China (Wang et al. 2001; Yuan et al. 2004), Kleegruben Cave in the Austrian Central Alps (Spötl and Mangini 2002), Moomi Cave in Socotra Island, Yemen (Burns et al. 2003) and Villars Cave in south-west France (Genty et al. 2003). At some northern tropical sites (e.g., Burns et al. 2003) the oxygen isotope signals have been interpreted to reflect changes in the meridional position of the ITCZ, that in turn may be linked to changes in high latitude (e.g., Greenland) air temperatures. These observations can provide tests for emerging models for teleconnections between high latitude ice sheets and the ITCZ (e.g., Chiang and Bitz in press), but a key issue is that chronological control on all records must be improved to test the exact phase relationships between these effects. It is likely that the speleothem records will continue to refine the chronology for the high–latitude ice core records. There is still a dearth of long well–dated speleothem records from equivalent low to mid–latitudes in the southern hemisphere, and so it remains difficult to delineate the southern limit of the apparent coherence between Greenland temperatures and the ITCZ.

On shorter timescales, in the Holocene for example, there has been considerable progress in providing high–resolution speleothem records. One of the most striking results to emerge from some of these datasets is the surprisingly strong coherence between oxygen isotope ratios in speleothems and atmospheric $\Delta^{14}C$, pointing to a solar influence on centennial to millennial timescales (Neff et al. 2001; Niggemann et al. 2003; Fleitmann et al. 2003). These correlations with $\Delta^{14}C$ are best seen in speleothem records in which the 'amount effect' appears to dominate the speleothem oxygen isotope record, suggesting that on these timescales solar forcing may cause changes in atmospheric circulation that in turn lead to changes in precipitation amount at a given site. In the case of the sub–tropical sites, reduced solar irradiance (high $\Delta^{14}C$) appears to cause a reduction in the intensity of monsoonal rainfall intensity (inferred from heavier $\delta^{18}O$), possibly related to southward shifts in the position of the ITCZ (Neff et al. 2001; Fleitmann et al. 2003). Similarly, in the case of the central European site (Germany), periods of reduced insolation during the late Holocene were associated with drier conditions. If similar data sets can be established for a range of latitudes it may be possible to test the competing models for the amplification of weak changes in solar irradiance (Shindell et al. 2001; Bond et al. 2001). In the early Holocene there is evidence from a variety of northern hemisphere proxy records including speleothems (McDermott et al. 2001; Fleitmann et al. 2003) and lake sediments (Andresen et al. 2004) that subtle variability in climatic conditions were contemporaneous with changes in Greenland air temperatures.

Few available continental archives record climate–driven changes in, for example the oxygen isotope ratio of meteoric water, with the resolution, faithfulness and chronological control offered by speleothems. During the past decade, stable isotope studies of speleothem carbonate have provided important new insights into the operation of the Earth's past climate, arguably rivalling those from the high–latitude ice cores. As with the ice cores, the quantitative interpretation of stable isotope shifts in speleothems is seldom straightforward, and a detailed knowledge of the meteorological variables that control these in modern cave systems is essential to provide a sound interpretation of past climates. Demonstration that speleothem carbonate was deposited at or close to isotope equilibrium with cave drip waters and an understanding of the site–specific relationships between the $\delta^{18}O$ of the latter and that of local meteoric water.
are also important requirements. Replication of records both within and between caves in the same region (e.g., Bar–Matthews et al. (2003); Wang et al. (2001); Yuan et al. (2004)), would do much to improve confidence in the climate signals and clearly should be a goal of future studies. 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.

References


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