

- Goodfriend, G. A., Magaritz, M., and Gat, J. R. (1989). Stable isotope composition of land snail body water and its relation to environmental waters and shell carbonate. *Geochimica et Cosmochimica Acta* 53, 3215–3221.
- Heaton, J. H. E., Vogel, J. C., von la Chevallerie, G., and Collet, G. (1986). Climatic influence on the isotopic composition of bone nitrogen. *Nature* 322, 822–823.
- Schwarcz, H. P., and Eyles, N. (1991). Laurentide ice sheet extent inferred from stable isotopic composition (O,C) of ostracodes at Toronto, Canada. *Quaternary Research* 35, 305–320.
- Shackleton, N. J., and Opdyke, N. D. (1973). Oxygen isotope and paleomagnetic stratigraphy of equatorial Pacific core V28-238: oxygen isotope temperatures and ice volumes on a  $10^5$  and  $10^6$  year time scale. *Quaternary Research* 3, 39–53.
- Winograd, I. J., Coplen, T. B., Landwehr, J. M., *et al.* (1992). Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. *Science* 258, 255–260.

## Speleothems

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Speleothems are crystalline deposits of calcium carbonate ( $\text{CaCO}_3$ ) formed in karstic caves as a result of precipitation from dilute aqueous solutions entering the cave, typically as drips from the roof. Karstic caves (q.v.) are formed by dissolution of soluble bedrock, usually a carbonate rock, by the action of meteoric water percolating from overlying soil or bedrock surfaces. This is partly due to organic activity in the soil that generates carbonic acid, which reacts with calcite or dolomite. Karstic dissolution forms cavities varying in size from less than 1 mm to passages many kilometers in length and tens of meters high (Ford and Williams, 1989). Karst can form in other kinds of rock (e.g., evaporitic sulfates), and speleothems can be formed of minerals other than  $\text{CaCO}_3$ . However, this article will deal only with Ca carbonates.

Speleothems can be seen forming today and we can infer that some have formed throughout the Quaternary epoch. They occur in many geometric forms, including stalagmites (which grow upward from the floor of caves beneath a drip site), stalactites (growing downward from the roof of a cave), and flowstone—sheet-like horizontally or inclined layers of calcite produced where water from one or more sources has spread as a film across a cave floor or wall (Fig. 1). When viewed in cross section (axially or longitudinally), many speleothems display a prominent laminated structure (Fig. 2). These preserve records of secular variation in the properties of the speleothem material that can be interpreted as

changes in conditions of deposition in the cave and thus, indirectly, on the Earth's surface above. These properties include the following:

- Chronometric age and rate of growth
- Isotopic composition of the  $\text{CaCO}_3$
- Abundance and isotopic composition of fluid inclusions of water trapped during growth
- Trace element concentrations in  $\text{CaCO}_3$
- Abundance and composition of organic impurities (especially humic substances)
- Mineralogy (calcite, aragonite, etc.)

Here, we focus on the first three items.

## Stable Isotope Systematics in Speleothems

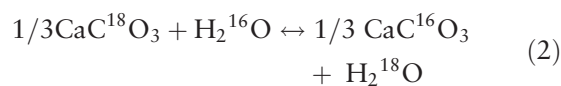
Before percolating through the bedrock, surface water is exposed first to atmospheric  $\text{CO}_2$  and then to soil gases enriched in biogenic  $\text{CO}_2$ . As water percolates through the bedrock overlying a cave, it can react extensively with the rock or may pass through with relatively little chemical interaction, depending on the nature of the openings through which it passes. Under conditions of diffuse flow through relatively tight fractures and joints, the water can approach chemical and isotopic equilibrium with the rock, whereas in larger, open channels entering caves, surface water may enter essentially unchanged. On entering the cave, drip waters can begin to precipitate  $\text{CaCO}_3$  as a result of two discrete processes: evaporation, which increases the concentration (activity) of Ca ions until the solubility of  $\text{CaCO}_3$  is exceeded, and outgassing of  $\text{CO}_2$  from the water, which results in the slow precipitation of  $\text{CaCO}_3$ :



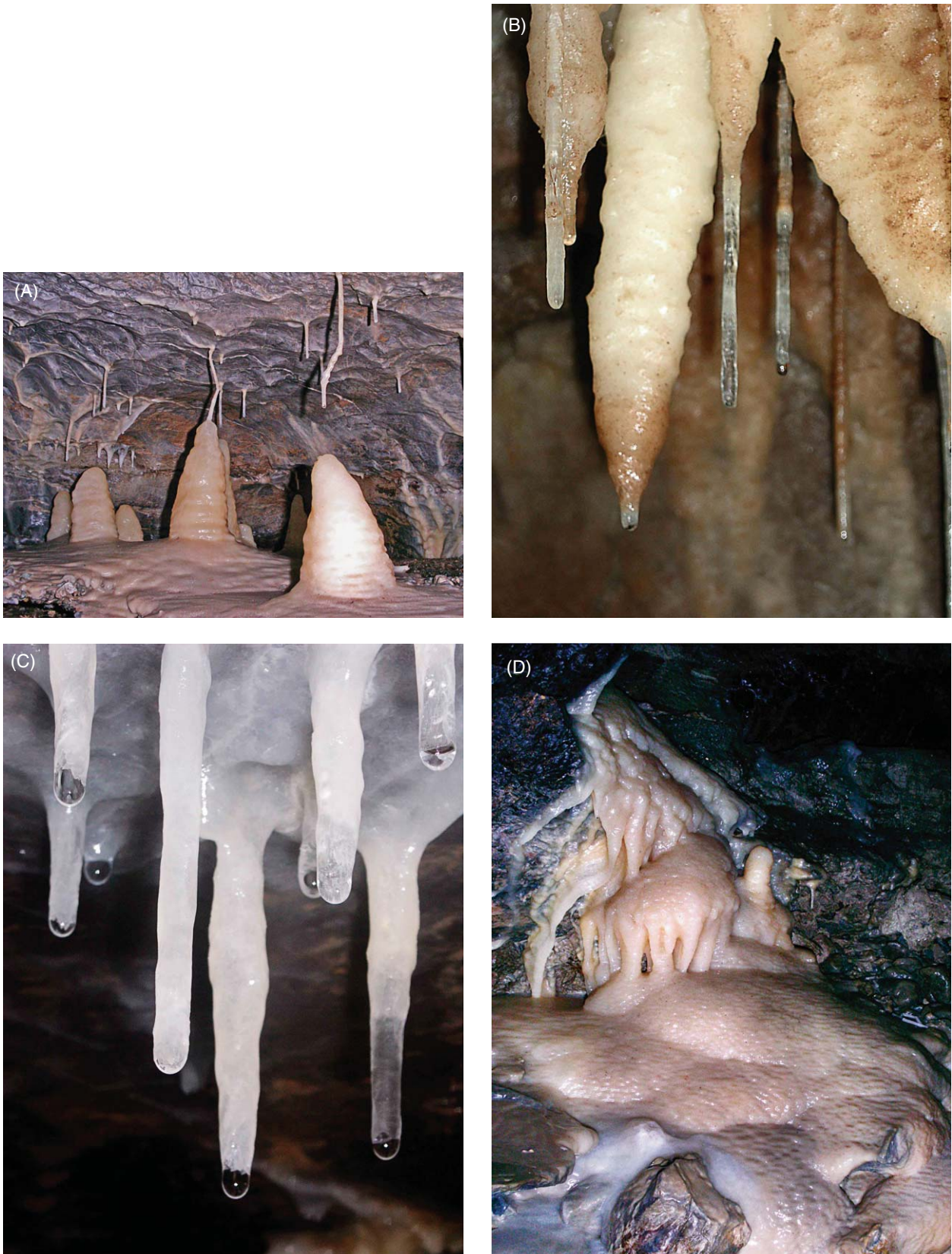
$\text{CaCO}_3$  potentially contains a number of distinct isotopic signals, recorded as variations in the relative abundance of the isotopes of Ca, O, and C. Only the latter two have been extensively studied.

### Oxygen Isotopes

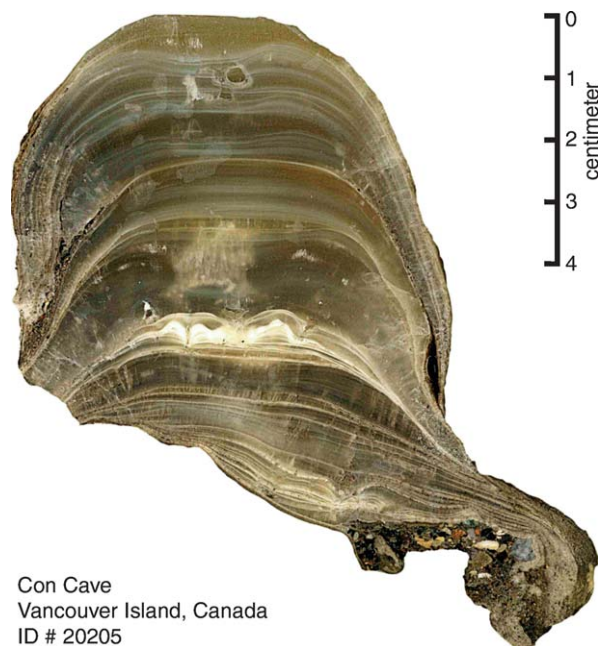
Variations in the  $^{18}\text{O}/^{16}\text{O}$  ratio in water and O-bearing minerals have been widely used as proxies for various environmental records, especially temperature.  $\text{CaCO}_3$  can isotopically exchange with water:



Epstein *et al.* (1953) showed that the equilibrium constant for this reaction,  $K_{\text{ct-w}} = (^{18}\text{O}/^{16}\text{O})_{\text{ct}}/$



**Figure 1** Typical forms of speleothems: (A) stalagmites (middle stalagmite is ~40 cm high); (B) stalactite, ~4 cm in diameter at top, flanked by 'soda straws'; (C) thin stalactites (soda straws), ~5 mm in diameter, showing drip water emerging; and (D) flowstone, ~1 m wide. Photos by P. Beddows.



**Figure 2** Section through a stalagmite showing laminated structures (growth layers). Lighter zones are richer in fluid inclusions; note the detritus-rich layer at base. The color is due to the presence of humic matter in calcite.

$(^{18}\text{O}/^{16}\text{O})_{\text{H}_2\text{O}}$ , depended only on temperature. Therefore, if a sample of  $\text{CaCO}_3$  had precipitated in isotopic equilibrium with water of known  $^{18}\text{O}/^{16}\text{O}$  ratio, we could determine the temperature of precipitation. Hendy (1971) showed that under conditions widely encountered in deep caves, speleothems formed at oxygen isotopic equilibrium with drip waters. This happened if the mode of deposition was by relatively slow outgassing of  $\text{CO}_2$  from the drip water, whereas evaporative deposition (or rapid outgassing) led to disequilibrium precipitation. That is, under the latter conditions the oxygen isotope fractionation was not equal to the equilibrium constant at the temperature of deposition, and deviation from equilibrium increased as drip water traversed the surface of the speleothem. Hendy showed that the calcite precipitated along this path became progressively enriched in  $^{18}\text{O}$ . Therefore, a convenient test for equilibrium was to measure the  $^{18}\text{O}/^{16}\text{O}$  ratio of calcite along several points spaced some centimeters apart on a single growth layer. For equilibrium deposits it was expected that  $(^{18}\text{O}/^{16}\text{O})_{\text{ct}}$  would remain constant, whereas disequilibrium growth layers would display (1) continuously varying  $^{18}\text{O}/^{16}\text{O}$  and (2) a correlation between  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$ . The latter reflects the fact that rapid outgassing or evaporation were usually coupled with variations in the  $^{13}\text{C}/^{12}\text{C}$  ratio of dissolved inorganic carbon (DIC) in the drip water. Speleothems satisfying the criteria of equilibrium deposition are invariably found deep inside long caves (>1 km) or in recently

opened, formerly sealed cavities, where relative humidity was  $\sim 100\%$  and where lack of significant movement of air resulted in high partial pressure of  $\text{CO}_2$  with the result that outgassing of drip water was slow. Recent studies (Mickler *et al.*, 2004) suggest that kinetic effects may prevent the attainment of isotopic equilibrium between calcite and water. However, actively growing stalactites ('soda straws') from deep, high-humidity caves have been shown by other authors to yield isotopic temperatures similar to the temperature in the cave.

The discovery of this means of recognizing speleothems deposited at equilibrium opened up the possibility of using  $(^{18}\text{O}/^{16}\text{O})_{\text{ct}}$  variations in speleothems as a paleothermometer. Far from the entrances to most caves (>100–500 m), the temperature remains constant seasonally and approaches the mean annual surface temperature above the cave. Therefore, a paleotemperature record from an equilibrium speleothem would provide a record of past temperatures on the surface for the duration of growth of the speleothem.

For a given sample of calcite extracted from such an equilibrium deposit, the temperature is given by the paleotemperature equation (Epstein *et al.* 1953):

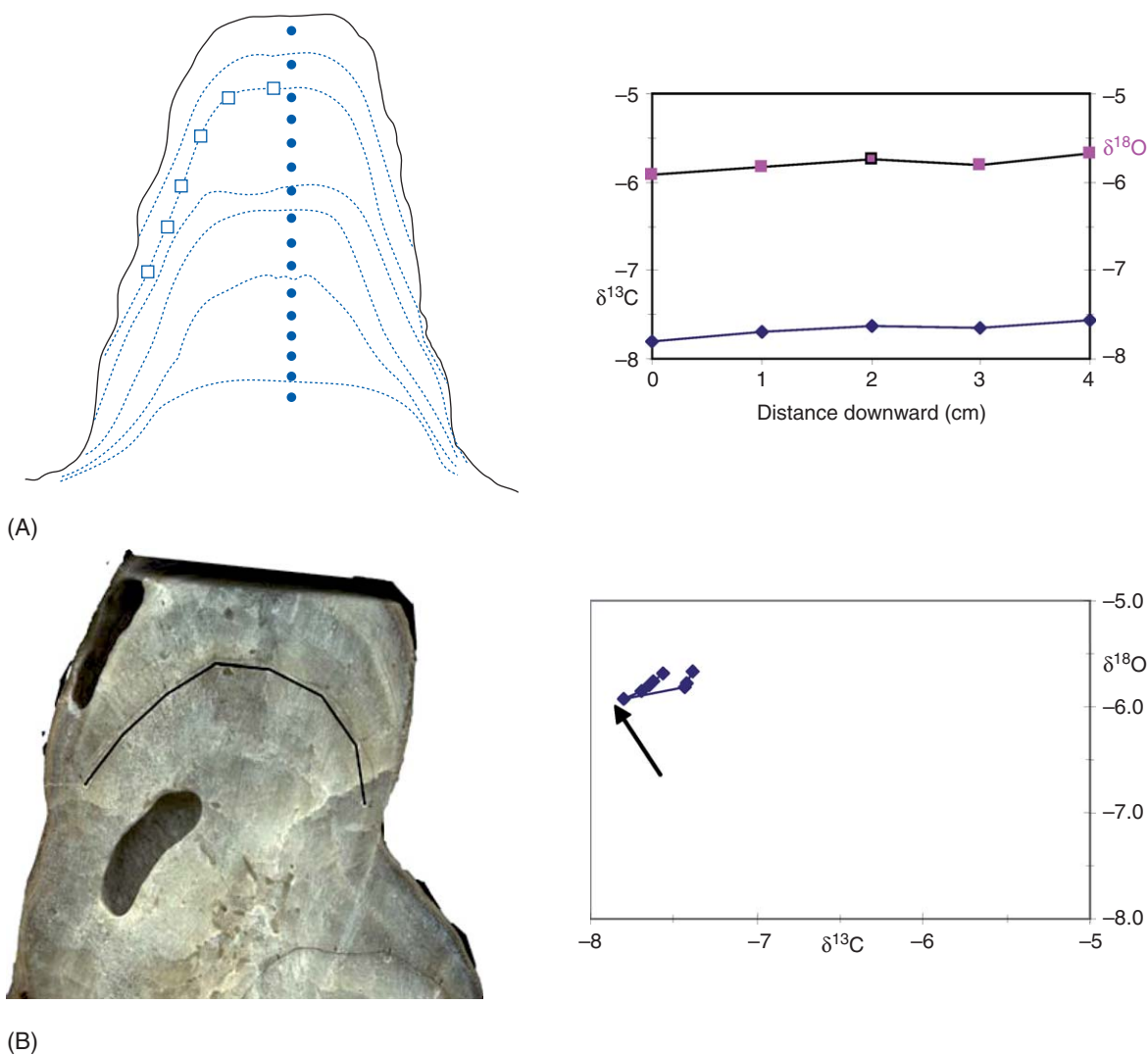
$$T(^{\circ}\text{C}) = 16.5 - 4.3(\delta^{18}\text{O}_{\text{ct}} - \delta^{18}\text{O}_{\text{w}}) + 0.14(\delta^{18}\text{O}_{\text{ct}} - \delta^{18}\text{O}_{\text{w}})^2 \quad (3)$$

where  $\delta^{18}\text{O}_x$  is defined as

$$\delta^{18}\text{O} = \left\{ \left[ \frac{(^{18}\text{O}/^{16}\text{O})_x}{(^{18}\text{O}/^{16}\text{O})_{\text{std}}} \right] - 1 \right\} \times 1000 \quad (4)$$

where w is drip water, and std refers to one of the two international standards for  $^{18}\text{O}/^{16}\text{O}$  ratios: Vienna Pee Dee Belemnite (VPDB) or Vienna Standard Mean Ocean Water. The units of  $\delta^{18}\text{O}$  are ‰ (per mil). The precision of analyses of  $\delta^{18}\text{O}$  is typically approximately  $\pm 0.1\text{‰}$ . Note, however, that in order to determine  $T$ , it is necessary to have values for  $\delta^{18}\text{O}$  of both the calcite and the water from which it was precipitated.

$\delta^{18}\text{O}_{\text{ct}}$  is usually determined by reacting samples  $\geq 100 \mu\text{g}$  with 100% phosphoric acid and analyzing the resultant  $\text{CO}_2$  on a gas-source, isotope ratio-detecting mass spectrometer. Most studies of long-term variation in  $\delta^{18}\text{O}_{\text{ct}}$  of speleothems have been done on stalagmites using axial sections (Fig. 3) oriented more or less in a diametric section of the stalagmite. Samples are drilled out of the polished surface of the section. High-resolution records (with micrometer spacing) have been obtained using computer-driven milling machines (Mangini *et al.*, 2005) and laser heating to decompose  $\text{CaCO}_3$  to  $\text{CaO} + \text{CO}_2$  (McDermott *et al.*, 2001). In most studies of



**Figure 3** Analysis of layers: (A) Drawing of stalagmite showing sampling localities for Hendy test (squares) and climate records (circles); (B) Hendy test of a growth layer in a Holocene stalagmite from Marengo Cave, Indiana (R. Zhang, unpublished data). (Top graph)  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  along the left side of the growth layer are indicated by the curved line. (Bottom graph) Lack of correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ; arrow marks the top of the growth layer.

secular variation in  $\delta^{18}\text{O}_{\text{ct}}$ , the authors use the so-called Hendy test to ensure that the deposits were formed in oxygen isotopic equilibrium, reporting  $\delta^{18}\text{O}_{\text{ct}}$  and  $\delta^{13}\text{C}_{\text{ct}}$  values for samples taken along single growth layers.

It has proven much more difficult to determine values for  $\delta^{18}\text{O}_{\text{w}}$ . Various approaches to this problem are discussed next.

### Carbon Isotopes

The  $^{13}\text{C}/^{12}\text{C}$  ratio of the carbonate in calcite is always measured at the same time as  $\delta^{18}\text{O}_{\text{ct}}$  during analysis of  $\text{CO}_2$  gas on isotope ratio mass spectrometers. Data are reported as  $\delta^{13}\text{C}_{\text{ct}}$  with respect to the VPDB standard. The precision of analysis is  $\pm 0.1\%$ . Variations in  $\delta^{13}\text{C}_{\text{ct}}$  are not significantly temperature

dependent but are rather a consequence of various mixing processes during the formation of DIC.

### Dating

Ages of speleothems have been obtained principally by  $^{14}\text{C}$  and uranium (U) series dating. Electron spin resonance has been applied with limited success, possibly due to the short lifetime of trapped charges in calcite.

### Radiocarbon

$^{14}\text{C}$  is introduced into DIC and thus into speleothems through oxidation of plant-derived organic matter in the soil. Ages must be corrected for the presence of dead carbon, nonradioactive C introduced into DIC

during dissolution of calcite in the soil zone. From Eq. (1), it appears that approximately half of the C atoms in  $\text{HCO}_3^-$  ions should be derived from the bedrock calcite, which in most circumstances contains no  $^{14}\text{C}$ . Therefore, modern cave-deposited calcite should have a  $^{14}\text{C}/^{12}\text{C}$  ratio approximately half that of modern carbon. The initial percentage of dead carbon (dcp) is in fact observed to range from ca. 5 to <40% (Genty *et al.*, 2001). Lower values are presumably a result of continued exchange between soil-derived  $\text{CO}_2$  and recharge water as it percolates through air-filled passages on the way to the cave. The initial dcp cannot be assumed to be constant at a given site but may vary as a result of changing soil activity. Errors due to uncertainty in dcp decrease with age. Speleothems dated by U series have also been used to reveal large oscillations in atmospheric  $^{14}\text{C}$  activity (Beck *et al.*, 2001).

### U series

$^{238}\text{U}$  decays to a series of short-lived daughter isotopes; after a long time (>2 My), the activity of each of these isotopes (in disintegrations per minute in a given sample) should equal the activity of the parent  $^{238}\text{U}$ . However, the daughter isotopes can be geochemically separated from the parent U prior to deposition of calcite because uranium is soluble in groundwater, whereas daughter Th and Pa are insoluble. The age of calcite is determined from the extent of growth of the daughter isotopes thorium-230 ( $^{230}\text{Th}$ ) and  $^{234}\text{U}$  into secular equilibrium with  $^{238}\text{U}$  and that of protactinium-231 ( $^{231}\text{Pa}$ ) into equilibrium with  $^{235}\text{U}$  (Richards and Dorale, 2003). The activity ratio  $^{230}\text{Th}/^{234}\text{U}$  increases from zero at the time of deposition to a maximum value of 1 at infinite age. The ratio of  $^{234}\text{U}$  to  $^{238}\text{U}$  also varies because the radiogenic  $^{234}\text{U}$  is a 'hot atom' whose chemical properties during weathering are different from those of its parent  $^{238}\text{U}$ .

Speleothems are well suited to U-series dating because their calcite crystals are usually large and have little tendency to recrystallize after deposition. Speleothem calcite typically contains between 100 and 1,000 parts per billion (ppb) U, whereas aragonitic speleothem contains up to 100 ppm U. Some speleothems contain detritus, which is trapped in the calcite during flooding events in caves and which contaminates the samples with  $^{230}\text{Th}$  so that the apparent age of the freshly deposited calcite is greater than zero. Analyses of such 'dirty' calcites can be obtained by use of isochrons, in which a nonradiogenic isotope,  $^{232}\text{Th}$ , is used to estimate the amount of detritus (Bischoff and Fitzpatrick, 1991). Individual analyses can be corrected by using the  $^{230}\text{Th}/^{232}\text{Th}$  ratio to estimate the amount of 'detrital'  $^{230}\text{Th}$  present in the sample.

U-series isotopes are analyzed using thermal ionization mass spectrometry (TIMS; Edwards *et al.*, 2003) or multicollector inductively coupled plasma mass spectrometry. The precision of analyses of speleothems is better than 1% of the age. Older analyses done by counting of  $\alpha$  particles were of lower precision (5–10% of age). The practical age limit for U-series dating is approximately 500,000 years. U-Pb dating by TIMS can be used for older speleothems, although the method requires moderately high U concentrations and analysis of coeval samples with varying U/Pb ratios (Richards *et al.*, 1998).

### Paleoclimate Inferred from O Isotope Records in Speleothems

Eq. (1) shows that for speleothems formed at oxygen isotopic equilibrium, we can infer the temperature of deposition from  $\delta^{18}\text{O}_{\text{ct}}$  and  $\delta^{18}\text{O}_{\text{ppt}}$ . In general, we can express a change  $\delta^{18}\text{O}_{\text{ct}}$  as

$$\Delta\delta^{18}\text{O}_{\text{ct}} = [(d\varepsilon_{\text{ct-w}}/dT) + (d\delta^{18}\text{O}_{\text{ppt}}/dT)]\Delta T + \Delta\delta^{18}\text{O}_{\text{sw}} + \Delta\delta^{18}\text{O}_{\text{s}}$$

where sw is seawater: All meteoric water is derived from the ocean; thus, changes in  $\delta^{18}\text{O}$  of seawater during the Pleistocene as a result of changes in ice volume would be reflected in  $\delta^{18}\text{O}_{\text{ppt}}$ . The last term is a correction to represent changes in the source of water as a result of secular shift in the average path of storm tracks.  $\varepsilon_{\text{ct-w}} = (\alpha_{\text{ct-w}} - 1) \times 1,000$ , and  $d\varepsilon_{\text{ct-w}}/dT$  is the temperature ( $T$ ) dependence of the calcite-water fractionation, approximately  $-0.25\text{‰}/^\circ\text{C}$ . The second term,  $d\delta^{18}\text{O}_{\text{ppt}}/dT$ , refers to the long-term (secular) dependence of  $\delta^{18}\text{O}_{\text{ppt}}$  on temperature, which is not necessarily equivalent to short-term temperature dependence as observed, for example, in annual records at a single site. The latter  $T$  dependence is typically equal to approximately  $0.7\text{‰}/^\circ\text{C}$  (Rozanski *et al.*, 1993). If the secular  $T$  dependence were also  $\sim 0.7\text{‰}/^\circ\text{C}$ , then the net  $T$ -dependent change in  $\delta^{18}\text{O}_{\text{ct}}$  would be approximately  $0.4\text{‰}/^\circ\text{C}$ . In tropical and subtropical regions,  $\delta^{18}\text{O}$  of drip waters can also change as a result of the so-called 'amount effect,' in which  $\delta^{18}\text{O}_{\text{ppt}}$  decreases with increasing volume of individual rain events (Rozanski *et al.*, 1993). From the previous relationship, we would expect to find a positive correlation between temperature of deposition and  $\delta^{18}\text{O}_{\text{ct}}$ . We can test the nature of this correlation in a number of ways:

- Comparison of  $\delta^{18}\text{O}_{\text{ct}}$  of modern (or interglacial) speleothems with glacial age samples
- Comparison of  $\delta^{18}\text{O}_{\text{ct}}$  record with other coeval, dated paleoclimate records, such as  $\delta^{18}\text{O}$  of foraminifera from deep-sea cores or ice cores or

temperatures obtained from Mg/Ca or alkenone ratios in foraminifera

- Association between a deposit and sedimentary or paleontological deposits of known climatic signature

In published studies of  $\delta^{18}\text{O}_{\text{ct}}$  vs age, the correlation between inferred paleotemperature (i.e., paleoclimate, ranging between glacial (cold) and interglacial (warm)) is either positive or negative. We can express this fact in terms of the sign of  $\gamma = d(\delta^{18}\text{O}_{\text{ct}})/dT$ , which can be positive or negative. This represents the tendency of  $\delta^{18}\text{O}_{\text{ct}}$  to rise or fall as local climate becomes warmer or cooler. In principle, we can also have sites with  $\gamma = 0$ , where the positive and negative climatic effects on  $\delta^{18}\text{O}_{\text{ct}}$  exactly cancel out.

### Determination of $\delta^{18}\text{O}$ of Paleowaters

In order to determine paleotemperatures from speleothems deposited at isotopic equilibrium, it is necessary to determine  $\delta^{18}\text{O}_{\text{w}}$  of the drip water from which the speleothem formed (see Eq. 3).  $\delta^{18}\text{O}$  of drip water is close to the annual average of  $\delta^{18}\text{O}_{\text{ppt}}$ , the  $\delta^{18}\text{O}$  value of precipitation falling on land surface above the cave (Yonge *et al.*, 1985; Spötl *et al.*, 2005), but may be locally affected by factors such as surface evaporation and transpiration or selective recharge of seasonal precipitation (e.g., snow meltwater). Most papers reporting  $\delta^{18}\text{O}_{\text{ct}}$  data do not explicitly attempt to evaluate variation in  $\delta^{18}\text{O}_{\text{ppt}}$  but merely show comparisons between excursions in  $\delta^{18}\text{O}_{\text{ct}}$  and other paleoclimate proxies as noted previously. However, at least three distinct approaches have been used to estimate isotopic composition of paleowaters:

- Assuming that secular variation in  $\delta^{18}\text{O}_{\text{ppt}}$  is the same as annual (seasonal) variation (Dorale *et al.*, 1992). This assumes a particular value for  $d(\delta^{18}\text{O}_{\text{ppt}})/dT$ .
- Analysis of fluid inclusions in speleothem, which are presumed to represent the drip water present during growth (Schwarcz *et al.*, 1976). This water can be extracted by crushing the sample in vacuum, and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  can be determined (Dennis *et al.*, 2001). Although oxygen isotopes may have been exchanged postdepositionally with the calcite, the  $\delta\text{D}$  value of the water should be unchanged and can be used to reconstruct  $\delta^{18}\text{O}_{\text{ppt}}$  from the meteoric water relationship  $\delta\text{D}_{\text{ppt}} = 8 \delta^{18}\text{O}_{\text{ppt}} + \delta_0$ , where  $\delta_0$  is the so-called deuterium excess. For most continental regions of the world,  $\delta_0 = 10\text{‰}$ , but this value may have changed through the Pleistocene. For a detailed discussion of the use of fluid inclusions, see McDermott *et al.* (2006).

- Specific models for variation in  $\delta^{18}\text{O}_{\text{ppt}}$ , such as derivation of water vapor from seawater whose  $\delta^{18}\text{O}$  varied in a known fashion (Frumkin *et al.*, 1999).

### Application to Paleoclimate Studies

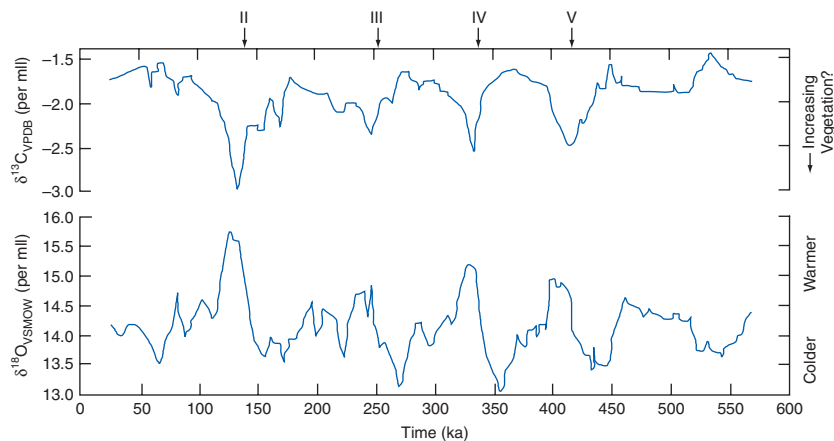
#### $\delta^{18}\text{O}_{\text{ct}}$

More than 100 papers report secular variation in  $\delta^{18}\text{O}_{\text{ct}}$  of U-series dated speleothems deposited during the past 200,000 years. Most use  $\delta^{18}\text{O}_{\text{ct}}$  as a proxy for paleoclimate, an approach that is analogous to the use of  $\delta^{18}\text{O}$  analyses of foraminifera from deep-sea sediments or  $\delta^{18}\text{O}$  (and  $\delta\text{D}$ ) measurements of ice cores. Most studies identify features (excursions or trends) in the speleothem records that match coeval isotopic excursions in the better known proxy records as well as records of pollen, fauna, trace elements in sediments, etc. Thus, we can describe the use of most speleothem  $\delta^{18}\text{O}_{\text{ct}}$  data as providing a formal (but not quantitative) proxy for Quaternary paleoclimate. Correlations with  $\delta^{18}\text{O}_{\text{ct}}$  records from U-series dated speleothems can be used to give precise dates for critical climatic transitions in other proxy records; they also have been interpreted as indicating how local climate was coupled to global climate change.

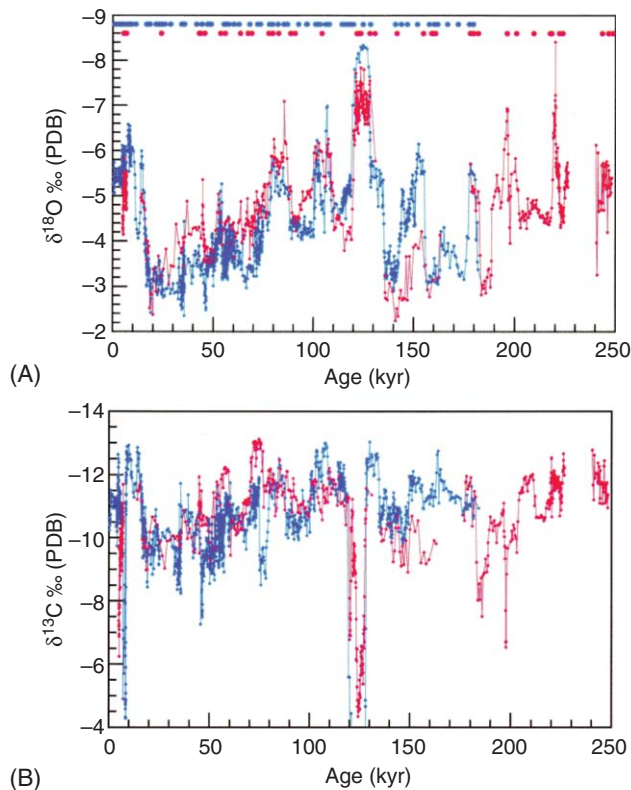
An example of a formal proxy is the study of subaqueous calcite precipitated from thermal water in a fissure at Devil's Hole, Nevada (Winograd *et al.*, 1992). In all significant respects, this is identical to studies of speleothems, specifically in that it presents a detailed U-series dated sequence of analyses of  $\delta^{18}\text{O}_{\text{ct}}$  for a laminated deposit formed at relatively low temperatures. The  $\delta^{18}\text{O}_{\text{ct}}$  record (Fig. 4) shows signals corresponding to all the major climatic cycles observed in deep-sea cores from 500 to 70 ka. The timing of the  $\delta^{18}\text{O}_{\text{ct}}$  cycles at Devil's Hole is distinctly discordant to that inferred from the Milankovitch theory (e.g., Termination II is approximately 15,000 years earlier than expected).

$\delta^{18}\text{O}_{\text{ct}}$  records from speleothems found in the Soreq Cave and other caves in Israel (Bar-Matthews and Ayalon, 2003; Frumkin *et al.*, 2000) show striking formal agreement between the  $\delta^{18}\text{O}_{\text{ct}}$  record and data from ice cores and deep-sea sediments (Fig. 5). The correspondence persists over eight oxygen isotope stages, back to 250,000 BP.  $\gamma < 0$  for these sites. McGarry *et al.* (2004) measured  $\delta\text{D}$  in fluid inclusions at Soreq. Noting that  $\delta_0 = 20\text{‰}$  for Israel today, they used comparisons between alkenone-based sea-surface temperatures and  $\delta^{18}\text{O}_{\text{ct}}$  values to infer secular change in  $\delta_0$ .

The latter two studies made use of records that spanned glacial-interglacial transitions marked by



**Figure 4**  $\delta^{18}\text{O}$  record for Devil's Hole, Nevada. U-series dates are shown at top. From Winograd, I., Landwehr, J., Ludwig, K. R., Coplen, T., and Riggs, A. C. (1997). Duration and structure of the past four glaciations. *Quaternary Research* **48**, 141–154. Reproduced with permission from the National Speleological Society.



**Figure 5**  $\delta^{18}\text{O}$  (A) and  $\delta^{13}\text{C}$  (B) records for speleothems from Soreq (blue) and Peqin Cave (red), Israel. Circles in A show U-series ages. From Bar-Matthews, M., and Ayalon, A. (2003). Sea-land oxygen isotopic relationships from planktonic Foraminifera and speleothems in the eastern Mediterranean region and their implication for paleorainfall during interglacial intervals. *Geochimica et Cosmochimica Acta* **67**, 3181–3199. Reproduced with permission.

large shifts in  $\delta^{18}\text{O}_{\text{ct}}$ . Studies at other sites where the dated speleothem record did not cross a termination generally display smaller scale variations in  $\delta^{18}\text{O}_{\text{ct}}$ , which nevertheless have been correlated with shorter

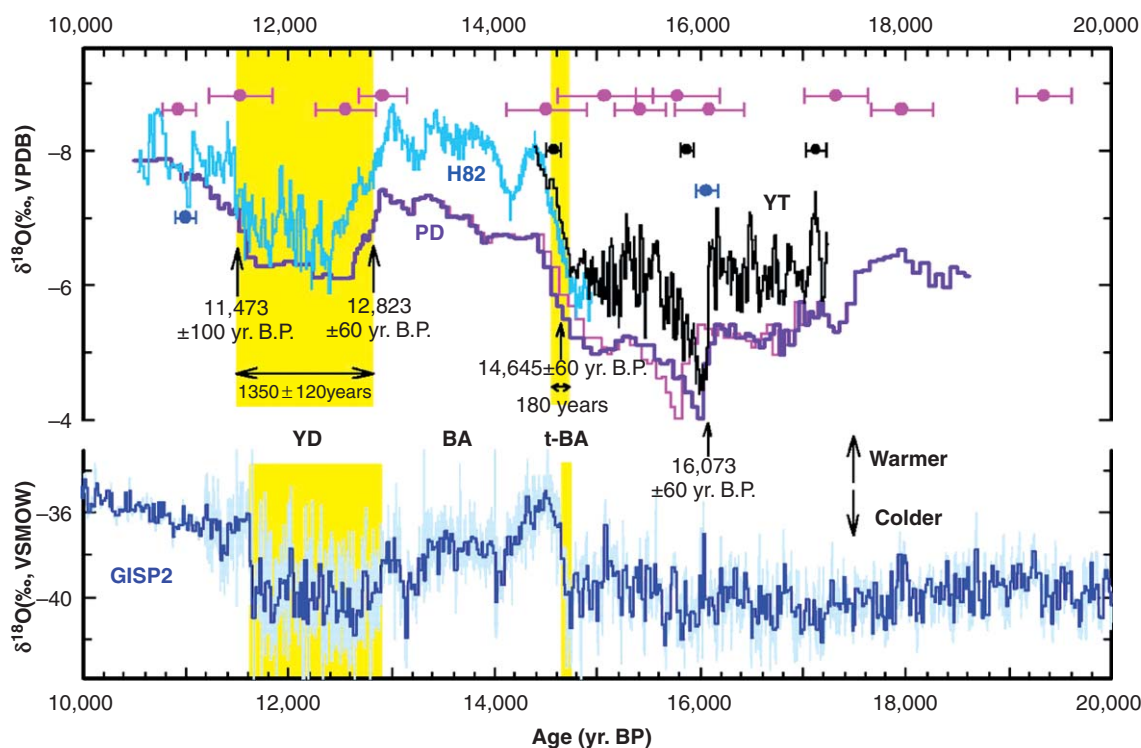
term cycles in the global paleoclimate record, such as Heinrich events and Dansgaard–Oeschger (D-O) cycles. Examples follow:

*Hulu Cave, China:* Several speleothems give concordant, partially overlapping records that span a 70,000-year period from ca. 80 to 10 ka (Fig. 6). Cycles with amplitudes of 0.5–1‰ ( $\gamma < 0$ ) are correlated by these authors with coeval Heinrich events (cooler periods lasting a few kiloyears or less). The authors infer that these cycles record variations in monsoon activity (Wang *et al.*, 2001).

*Oman:* Speleothems from caves in Oman record climatic cycles on a time scale ranging from hundreds of years to 330 ka (Fleitmann *et al.*, 2004).  $\delta^{18}\text{O}_{\text{ct}}$  in series of relatively short-lived stalagmites ranges over 8‰ ( $\gamma > 0$ ). These represent pluvial periods during which the source of moisture has shifted between a continental and monsoonal pattern, as shown by changing  $\delta\text{D}$  of fluid inclusions.

*Austrian Alps:* At the Kleegruben Cave, oscillations in  $\delta^{18}\text{O}_{\text{ct}}$  appear to match D-O cycles seen in Greenland ice cores (Spötl and Mangini, 2002; Fig. 7) and were used to provide an improved chronology for these cycles; from the correlation with D-O cycles, we infer that  $\gamma > 0$  at this site.

*North America:* At Crevice Cave, Iowa (Dorale *et al.*, 1998), the form of the  $\delta^{18}\text{O}_{\text{ct}}$  record is correlated to that of the deep-sea record from 75 to 25 ka BP (with  $\gamma > 0$ ). At Reed's Cave, South Dakota (Sereffiddin *et al.*, 2003), oscillations in  $\delta^{18}\text{O}_{\text{ct}}$  are matched to cycles in Greenland ice cores. Two speleothems from this site have opposite polarities of  $\gamma$ , which the authors attribute to differences in the seasonality of the supply of recharge water. Significant differences in  $\delta^{18}\text{O}$  of coeval



**Figure 6**  $\delta^{18}\text{O}$  of stalagmites from Hulu Cave, China (purple, black, and blue) and Greenland Ice (dark blue, 20-year averages; gray, 3-year averages) vs age. YD, Younger Dryas; BA, Bolling–Allerod; t-BA, transition into B. From Wang, Y. J., Cheng, H., Edwards, R. L., An, Z. S., Wu, J. Y., Shen, C. C., and Dorale, J. A. (2001). A high-resolution absolute-dated late Pleistocene monsoon record from Hulu Cave, China. *Science* **294**, 2345–2348. Reproduced with permission.

calcite deposits have been observed in speleothems from other caves.

**Holocene records:** Records of  $\delta^{18}\text{O}_{\text{ct}}$  from Holocene speleothems have shed light on short-term, recent changes in climate in many regions. For example, Burns *et al.* (1998), who studied the Hoti Cave in Oman, identified pluvial periods in the early Holocene as well as the last interglacial. In Coldwater Cave, Iowa, early Holocene speleothems gave significant differences in  $\delta^{18}\text{O}_{\text{ct}}$  between coeval deposits, attributable to evaporative effects on the recharge waters (Denniston *et al.*, 1999); secular changes in  $\delta^{18}\text{O}_{\text{ppt}}$  are attributed to shifts in storm tracks over the site. Niggeman *et al.* (2003) showed a high-resolution  $\delta^{18}\text{O}_{\text{ct}}$  record from a cave in south Germany, in which power spectrum analyses revealed the influence of solar cycles on  $\delta^{18}\text{O}_{\text{ppt}}$ .

The vast literature affords many other records of interest. For example, Bard *et al.* (2002) accounted for a drop in  $\delta^{18}\text{O}_{\text{ct}}$  in an Italian speleothem approximately 170 ka BP as a result of the amount effect. This effect increased during a wet period identified by the occurrence of a sapropel layer in coeval sediments of the Mediterranean Sea (Fig. 8).

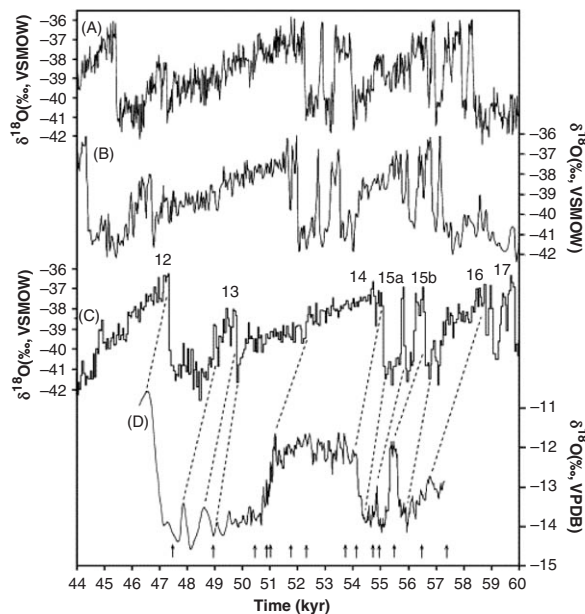
## Paleotemperature Records

Relatively few studies have attempted to interpret variations in  $\delta^{18}\text{O}_{\text{ct}}$  as paleotemperatures, even where Hendy tests gave positive results. Dorale *et al.* (1992) and van Beynen *et al.* (2004) assumed that the secular  $T$  dependence of  $\delta^{18}\text{O}_{\text{ppt}}$  was equal or similar to the seasonal value and used that relationship to derive temperatures for speleothems in Iowa and New York state (Fig. 9). Although Dennis *et al.* (2001) analyzed fluid inclusions in speleothems, they did not use the data to calculate temperatures; Serefiddin *et al.* (2005) did this for three stalagmites and showed that coeval stalagmites with differing  $\delta^{18}\text{O}_{\text{ct}}$  also differed in  $\delta\text{D}$  of inclusions so that the calculated temperatures of deposition were the same. Mangini *et al.* (2005) calibrated the relationship between  $\delta^{18}\text{O}_{\text{ct}}$  and  $T$  by correlating historically reconstructed average annual temperature with  $\delta^{18}\text{O}_{\text{ct}}$  values for speleothem SPA from an Alpine cave.

## Carbon Isotopes

Values of  $\delta^{13}\text{C}_{\text{ct}}$  directly reflect the isotopic composition of the drip water from which the speleothem

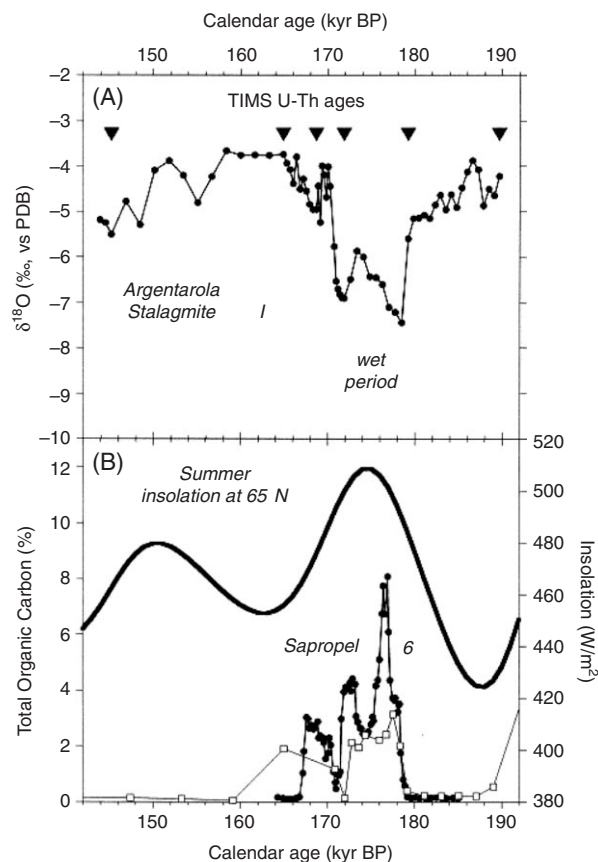




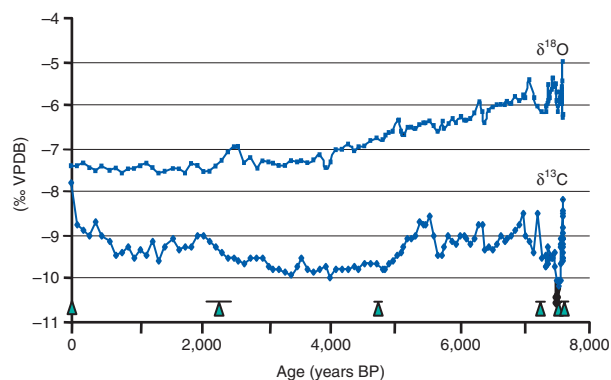
**Figure 7** Comparison of oxygen isotope records of the Greenland ice cores and stalagmite SPA 49 from Kleegruben Cave, Austrian Alps: (A) GISP2 record; (B) GRIP, 1995 time scale; (C) GRIP, 2001 chronology; and (D) stalagmite SPA 49. Numbers refer to Greenland Interstadials. Upward arrows indicate positions of U-series samples. Dashed lines indicate major marker events used for cross-correlation. From Spötl, C., and Mangini, A. (2002). Stalagmite from the Austrian Alps reveals Dansgaard–Oeschger events during isotope stage 3; Implications for the absolute chronology of Greenland ice cores. *Earth and Planetary Science Letters* **203**, 507–518. Reproduced with permission.

grew because the temperature dependence of the carbon isotopic fractionation between calcite and DIC is relatively small. The  $\delta^{13}\text{C}$  value of DIC depends critically on the sources of carbon: atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C} \sim -7\text{‰}$ ), carbonate derived from the bedrock ( $\delta^{13}\text{C} \sim -5$  to  $5\text{‰}$ ), and oxidation of soil organic matter ( $\delta^{13}\text{C} \sim -26$  to  $-9\text{‰}$ ). Large variations in  $\delta^{13}\text{C}_{\text{ct}}$  are observed on various timescales ranging from years (Frappier *et al.*, 2002) to tens of kiloyears. Variations in  $\delta^{13}\text{C}_{\text{ct}}$  (the  $\delta^{13}\text{C}$  value of the  $\text{CaCO}_3$ ) can be caused by two distinct effects, both of which are potentially influenced by climate change:

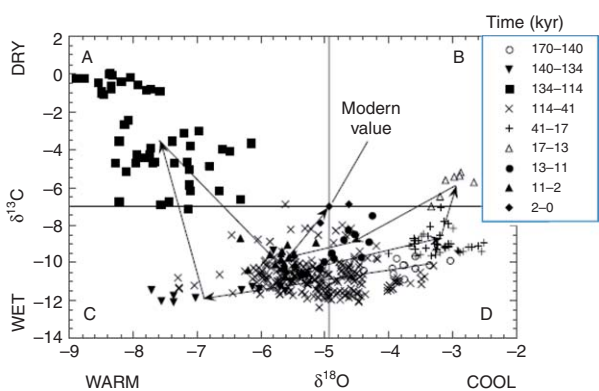
- Change in proportion of  $\text{C}_3$  to  $\text{C}_4$  plants growing above the cave:  $\delta^{13}\text{C}$  values of  $\text{C}_4$  plants are  $17\text{‰}$  higher than those of  $\text{C}_3$  plants; most  $\text{C}_4$  plants are grasses; shifts from forest to grassland can cause an increase in  $\delta^{13}\text{C}_{\text{ct}}$  (Dorale *et al.*, 1998).
- Change in the density of vegetation above the cave: Dissolution of limestone in the absence of soil cover occurs by reaction with atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C} \sim -7\text{‰}$ ), leading to higher  $\delta^{13}\text{C}$  values of DIC in recharge water compared to that produced under  $\text{C}_3$ - and even  $\text{C}_4$ -based soils (Frumkin *et al.*, 2000).



**Figure 8** (A)  $\delta^{18}\text{O}$  vs. age for stalagmite from Argentarola Cave, Italy. Triangles: U-series dated points. (B) Upper curve: summer insolation at  $65^\circ\text{N}$ ; lower curves: wt% total organic carbon in two nearby marine cores. From Bard, E., Delaygue, G., Rostek, F., Antonioli, F., Silenzi, S., and Schrag, D. P. (2002). Hydrological conditions over the western Mediterranean basin during the deposition of the cold sapropel 6 (ca. 175 kyr BP). *Earth and Planetary Science Letters* **202**, 481–494. Reproduced with permission.



**Figure 9**  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  record for stalagmite MF 1, McFail's Cave, New York state; gradient in  $\delta^{18}\text{O}$  following hypsithermal at 7,500 BP represents temperature decrease of ca.  $5^\circ\text{C}$ . From van Beynen, P. E., Schwarcz, H. P., Ford, D. C., and Morrison, J. (2004). Holocene climatic variability measured by speleothems in McFail's Cave, New York. *Journal of Karst and Cave Studies* **66**, 20–27. Reproduced with permission.



**Figure 10** Isotopic and age data for stalagmite AF12 from Jerusalem, Israel, showing the relationship with climate.  $\delta^{13}\text{C}$  increases with decreasing rainfall due to a decrease in the contribution of soil  $\text{HCO}_3^-$  to drip water.  $\delta^{18}\text{O}$  increases with decreasing temperature (Frumkin *et al.*, 1999), inferred from correlation with marine record. From Frumkin, A., Ford, D. C., and Schwarcz, H. P. (2000). Paleoclimate and vegetation of the last glacial cycles in Jerusalem from a speleothem record. *Global Biogeochemical Cycles* **14**, 863–870. Reproduced with permission.

In addition, the extent of exchange of the recharge water with bedrock (limestone) may affect  $\delta^{13}\text{C}$  of DIC of the emerging drip waters, depending on whether or not continued air exchange is possible in the passages (fissures and joints) through which the water flows (Hendy, 1971). Finally, during progressive outgassing of  $\text{CO}_2$  into the cave atmosphere, both equilibrium and kinetic effects can affect the  $\delta^{13}\text{C}$  of the precipitated calcite (Mickler *et al.*, 2004). These effects might be detectable as gradients in  $\delta^{13}\text{C}_{\text{ct}}$  on growth layers.

Some studies have reported correlated shifts in  $\delta^{18}\text{O}_{\text{ct}}$  and  $\delta^{13}\text{C}_{\text{ct}}$  reflecting coupled changes in vegetation (e.g.,  $\text{C}_3/\text{C}_4$  ratios) and temperature (as reflected in  $\delta^{18}\text{O}_{\text{ct}}$ ), whereas other studies show distinctly independent trends for each isotopic signal. Frumkin *et al.* (2000) showed that the trajectory of  $\delta^{18}\text{O}_{\text{ct}}$  and  $\delta^{13}\text{C}_{\text{ct}}$  defines simultaneous coupled changes in rainfall and temperature (Fig. 10).

### Future Directions and Problems

Instrumental advances in the analysis of speleothems may allow further paleoclimatic insights. Higher resolution sampling of  $\delta^{18}\text{O}_{\text{ct}}$  (and  $\delta^{13}\text{C}_{\text{ct}}$ ) may be obtained using lasers or micromilling methods. Analyses of fluid inclusions for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  may provide better paleotemperatures, but these kinds of studies are challenged by problems in extraction and analysis of sub-microliter volumes of water. There may also be isotopic heterogeneity within the population of inclusions (Schwarcz and Yonge, 1983), partly revealed by infrared analysis (Fourier transform infrared spectroscopy) of calcite (unpublished data).

Future studies must take account of two concerns—one ethical and the other practical. Speleothems are admired for their natural beauty and should be disturbed as little as possible. Researchers must collect samples in a way that does not alter the appearance of the cave, either by using already broken stalagmites or working in caves that are in risk of destruction by erosion or human exploitation of the landscape. Second, we must be aware that, with the exception of actively growing speleothems, it is currently impossible to estimate the age of a speleothem *a priori*. Therefore, in general we cannot target a specific pre-Holocene period for study. As speleothem studies progress, previously analyzed, dated speleothems should be carefully archived for possible future research.

*See also:* **Carbonate Stable Isotopes: Non-Lacustrine Terrestrial Studies.** **Ice Core Records: Correlations Between Greenland and Antarctica.** **Radiocarbon Dating: Calibration.** **U-Series Dating.**

### References

- Bar-Matthews, M., and Ayalon, A. (2003). Sea-land oxygen isotopic relationships from planktonic Foraminifera and speleothems in the eastern Mediterranean region and their implication for paleorainfall during interglacial intervals. *Geochimica et Cosmochimica Acta* **67**, 3181–3199.
- Bard, E., Delaygue, G., Rostek, F., Antonioli, F., Silenzi, S., and Schrag, D. P. (2002). Hydrological conditions over the western Mediterranean basin during the deposition of the cold sapropel 6 (ca. 175 kyr BP). *Earth and Planetary Science Letters* **202**, 481–494.
- Beck, J. W., Richards, D. A., Edwards, R. L., Silverman, B. W., Smart, P. L., Donahue, D. L., Herrera-Osterheld, S., Burr, G. S., Calsoyas, L., Jull, A. T., and Biddulph, D. (2001). Extremely large variations of atmospheric  $^{14}\text{C}$  concentration during the last glacial period. *Science* **292**, 2453–2458.
- Bischoff, J., and Fitzpatrick, J. (1991). U-series dating of impure carbonates; An isochron technique using total-sample dissolution. *Geochimica et Cosmochimica Acta* **55**, 543–554.
- Burns, S. J., Matter, A., Frank, N., and Mangini, A. (1998). Speleothem-based paleoclimate record from northern Oman. *Geology* **26**, 499–502.
- Dennis, P. F., Rowe, P. J., and Atkinson, T. C. (2001). The recovery and isotopic measurement of water from fluid inclusions in speleothems. *Geochimica et Cosmochimica Acta* **65**, 871–884.
- Denniston, R. F., Gonzalez, L. A., Asmerom, Y., Baker, R. G., Reagan, M. K., and Bettis, E. A., 3rd (1999). Evidence for increased cool season moisture during the middle Holocene. *Geology* **27**, 815–818.
- Dorale, J. A., Gonzalez, L. A., Reagan, M. K., Pickett, D. A., Murrell, M. T., and Baker, R. G. (1992). A high-resolution record of Holocene climate change in speleothem calcite from Cold Water Cave, northeast Iowa. *Science* **258**, 1626–1630.
- Dorale, J. A., Edwards, R. L., Ito, E., and Gonzalez, L. A. (1998). Climate and vegetation history of the midcontinent from 75 to 25 ka: A speleothem record from Crevice Cave, Missouri, USA. *Science* **282**, 1871–1874.
- Edwards, R. L., Gallup, C. D., and Cheng, H. (2003). Uranium-series dating of marine and lacustrine carbonates. *Reviews in Mineralogy and Geochemistry* **52**, 363–405.

- Epstein, S., Buchsbaum, R., Lowenstam, H. A., and Urey, H. C. (1953). Revised carbonate-water isotopic temperature scale. *Bull. Geol. Soc. Amer* **64**, 1315–1326.
- Fleitmann, D., Burns, S. J., Neff, U., Mudelsee, M., and Mangini, A. (2004). Palaeoclimatic interpretation of high-resolution oxygen isotope profiles derived from annually laminated speleothems from southern Oman. *Quaternary Science Reviews* **23**, 935–945.
- Ford, D. C., and Williams, P. W. (1989). *Karst Geomorphology and Hydrology*. Unwin Hyman, London.
- Frappier, A., Sahagian, D., Gonzalez, L. A., and Carpenter, S. J. (2002). El Nino events recorded by stalagmite carbon isotopes. *Science* **298**, 565.
- Frumkin, A., Ford, D. C., and Schwarcz, H. P. (2000). Paleoclimate and vegetation of the last glacial cycles in Jerusalem from a speleothem record. *Global Biogeochemical Cycles* **14**, 863–870.
- Frumkin, A., Ford, D. C., and Schwarcz, H. P. (1999). Continental paleoclimatic record of the last 170,000 years in Jerusalem. *Quaternary Research* **51**, 317–327.
- Genty, D., Baker, A., Massault, M., Proctor, C., Gilmour, M., Pons-Branchu, E., and Hamelin, B. (2001). Dead carbon in stalagmites: Carbonate bedrock paleodissolution vs. ageing of soil organic matter. Implications for  $^{13}\text{C}$  variations in speleothems. *Geochimica et Cosmochimica Acta* **65**, 3443–3457.
- Hendy, C. H. (1971). The isotopic geochemistry of speleothems—The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochimica et Cosmochimica Acta* **35**, 801–824.
- Mangini, A., Spötl, C., and Verdes, P. (2005). Reconstruction of temperature in the Central Alps during the past 2000 yr from a  $\delta^{18}\text{O}$  stalagmite record. *Earth and Planetary Science Letters* **235**, 741–751.
- McDermott, F. C., Matthey, D. P., and Hawkesworth, C. J. (2001). Holocene climate variation insights from an exceptionally high-resolution speleothem  $\delta^{18}\text{O}$  record from SW Ireland. *Science* **294**, 1328–1331.
- McDermott, F., Schwarcz, H. P., and Rowe, P. (2006). Isotopes in speleothems. In *Developments in Paleoenvironmental Research, Vol. 10: Isotopes in Paleoenvironmental Research* (M. Leng, Ed.) Kluwer, Dordrecht, pp. 185–226.
- McGarry, S., Bar-Matthews, M., Matthews, A., Vaks, A., Schilman, B., and Ayalon, A. (2004). Constraints on hydrological and paleotemperature variations in the eastern Mediterranean region in the last 140 ka given by the  $\delta\text{D}$  values of speleothem fluid inclusions. *Quaternary Science Reviews* **23**, 919–934.
- Mickler, P. J., Banner, J. L., Stern, L., Asmerom, Y., Edwards, R. L., and Ito, E. (2004). Stable isotope variations in modern tropical speleothems; Evaluating equilibrium vs. kinetic. *Geochimica et Cosmochimica Acta* **68**, 4381–4393.
- Niggemann, S., Mangini, A., Mudelsee, M., Richter, D. K., and Wurth, G. (2003). Sub-Milankovitch climatic cycles in Holocene stalagmites from Sauerland, Germany. *Earth and Planetary Science Letters* **216**, 539–547.
- Richards, D. A., and Dorale, J. A. (2003). Uranium-series chronology and environmental applications of speleothems. *Reviews in Mineralogy and Geochemistry* **52**, 407–460.
- Richards, D. A., Bottrell, S., Cliff, R. A., Stroehle, K., and Rowe, P. J. (1998). U-Pb dating of a speleothem of Quaternary age. *Geochimica et Cosmochimica Acta* **62**, 3683–3688.
- Rozanski, K., Araguás-Araguás, L., and Gonfiantini, R. (1993). Isotopic patterns in modern global precipitation. In *Climate Change in Continental Isotopic Records* (P. K. Swart et al., Eds.), Geophysical Monograph No. 78, pp. 1–36. American Geophysical Union, Washington, DC.
- Schwarcz, H. P., and Yonge, C. (1983). Isotopic composition of paleowaters as inferred from speleothem and its fluid inclusions. In *Paleoclimates and Paleowaters: A Collection of Environmental Isotope Studies* (R. Gonfiantini, Ed.), Proceedings of Advisory Group Meeting STI/PUB/621, pp. 115–133. International Atomic Energy Agency, Vienna, Austria.
- Schwarcz, H. P., Harmon, R. S., Thompson, P., and Ford, D. C. (1976). Stable isotope studies of fluid inclusions in speleothems and their paleoclimate significance. *Geochimica et Cosmochimica Acta* **40**, 657–665.
- Serefiddin, F., Schwarcz, H. P., Ford, D. C., and Baldwin, S. (2003). Late Pleistocene paleoclimate in the Black Hills of South Dakota from oxygen isotope records in speleothems. *Palaeogeography, Palaeoclimatology, Palaeoecology* **203**, 1–17.
- Serefiddin, F., Schwarcz, H., and Ford, D. (2005). Use of hydrogen isotope variations in speleothem fluid inclusions as an independent measure of paleoclimate. In *Isotopic and Elemental Tracers of Cenozoic Climate Change* (G. Mora and D. Surge, Eds.), Geological Society of America, Special Publication 395, p. 43–53.
- Spötl, C., and Mangini, A. (2002). Stalagmite from the Austrian Alps reveals Dansgaard-Oeschger events during isotope stage 3; Implications for the absolute chronology of Greenland ice cores. *Earth and Planetary Science Letters* **203**, 507–518.
- Spötl, C., Fairchild, I. J., and Tooth, A. (2005). Cave air control on dripwater geochemistry, Obir Caves (Austria): Implications for speleothem deposition in dynamically ventilated caves. *Geochimica et Cosmochimica Acta* **69**, 2451–2468.
- van Beynen, P. E., Schwarcz, H. P., Ford, D. C., and Morrison, J. (2004). Holocene climatic variability measured by speleothems in McFail's Cave, New York. *Journal of Karst and Cave Studies* **66**, 20–27.
- Wang, Y. J., Cheng, H., Edwards, R. L., An, Z. S., Wu, J. Y., Shen, C. C., and Dorale, J. A. (2001). A high-resolution absolute-dated late Pleistocene monsoon record from Hulu Cave, China. *Science* **294**, 2345–2348.
- Winograd, I. J., Coplen, T. B., Landwehr, J. M., Riggs, A. C., Ludwig, K. R., Szabo, B. J., Kolesar, P. T., and Revesz, K. M. (1992). Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. *Science* **258**, 255–260.
- Winograd, I., Landwehr, J., Ludwig, K. R., Coplen, T., and Riggs, A. C. (1997). Duration and structure of the past four glaciations. *Quaternary Research* **48**, 141–154.
- Yonge, C., Ford, D. C., Gray, J., and Schwarcz, H. P. (1985). Stable isotope studies of cave seepage water. *Isotope Geoscience* **58**, 97–105.

## Thermokarst Topography

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### Introduction

Thermokarst terrain exhibits a pitted relief formed from the melting of ground ice. 'Thermokarst' is used widely to describe all processes and landforms that are associated with melting ground ice, but thermokarst, or thaw, lakes are probably the most well-known features (Fig. 1) (French, 1996). Thermokarst processes are generally only considered with respect to permafrost terrain, and soil