

Speleothems

OUTLINE

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Speleothems are mineral formations occurring in limestone caves, most commonly as stalagmites and stalactites or slablike deposits known as flowstones. Stalactites (which hang from the ceilings of caves) often have a hollow core, with growth occurring around this central orifice, whereas stalagmites are solid and grow incrementally at the drip site. Thus, stalagmites are generally selected for paleoclimatic analysis. The extensive distribution of karst landscapes (Figure 8.1) means that studies can be undertaken on a worldwide basis. Speleothems are primarily composed of calcium carbonate, precipitated from groundwater that has percolated through the adjacent carbonate host rock. Certain trace elements may also be present (often giving the deposit a characteristic color), and one of these, uranium, can be used to determine the age of a speleothem, as discussed in the text below. Seasonal variations in the trace element composition of dripwaters may also be used to identify annual layers (Treble et al., 2005a). Deposition of a speleothems results from evaporation of water or degassing of carbon dioxide from water droplets. Evaporation is normally only an important process near cave entrances; most speleothems from deep within caves therefore result from the

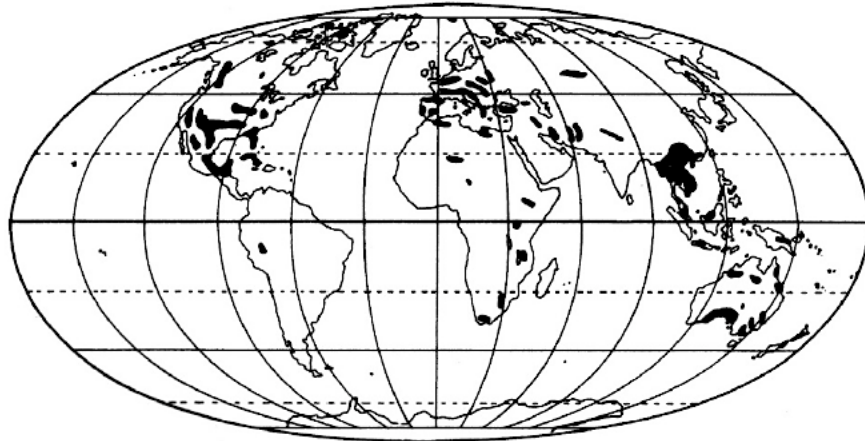


FIGURE 8.1 Distribution of karst in the world, showing the potential sources of paleodimatic information from speleothems.

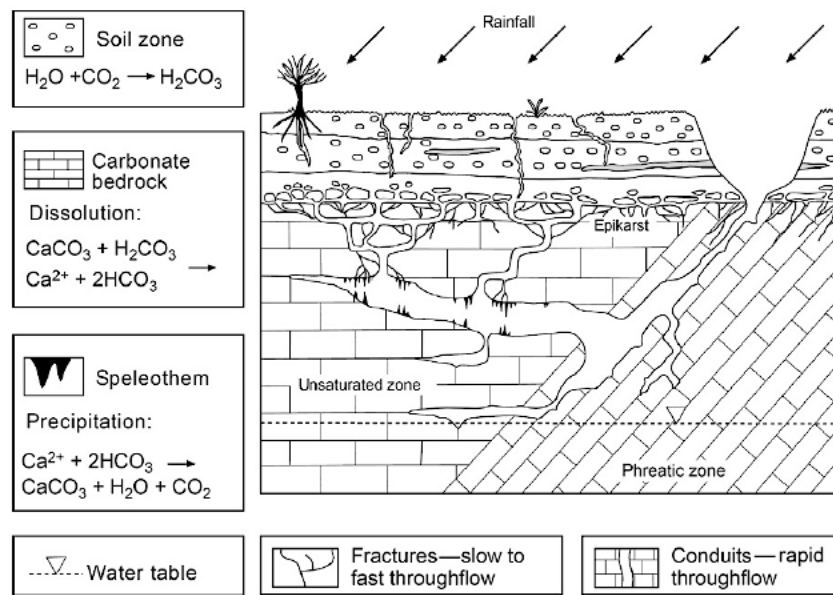
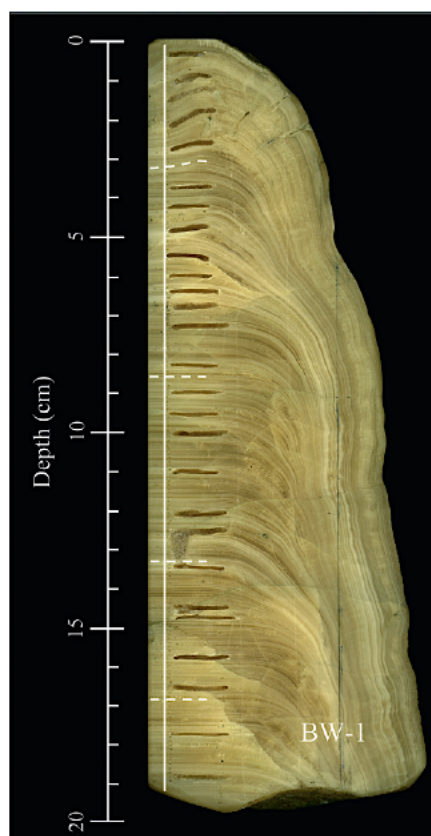


FIGURE 8.2 Schematic diagram of a cave system and carbonate dissolution and deposition (Fairchild et al., 2006).

degassing process. Water that has percolated through soil and been in contact with decaying organic matter usually accrues a partial pressure of carbon dioxide exceeding that of the cave atmosphere. Thus, when water enters the cave, degassing of carbon dioxide occurs, causing the water to become supersaturated with calcite, which is thus precipitated (Figure 8.2) (McDermott, 2004; McDermott et al., 2006; Fairchild and Baker, 2012).

FIGURE 8.3 A polished section of a stalagmite from Kulishu Cave, near Beijing (39.6°N, 115.6°E, 610 m asl). Holes can be seen where samples were drilled for ^{230}Th dating. The white vertical line shows the track of subsamples for stable isotope analysis, and dashed lines indicate the positions of samples for Hedy test. From *Ma et al. (2012)*.



There has been explosive growth in the number of paleoclimatic studies using speleothems, especially high-resolution studies of stalagmites (Figure 8.3). This has been facilitated by the development of thermal ionization mass spectrometers (TIMS) and multicollector inductively coupled plasma mass spectrometers (MC-ICP-MS) that can provide high-precision uranium-series dates (Edwards et al., 1987a; Shen et al., 2002, 2012; Richards and Dorale, 2003; Eggins et al., 2005; Cheng et al., 2012a) and improved techniques for high-resolution sampling and analysis using laser ablation mass spectrometry, ion microprobes, and micro X-ray fluorescence scanners (e.g., Baldini et al., 2002; Kolodny et al., 2003; Frisia et al., 2005; Orland et al., 2009). Hence, stalagmites can provide insight into episodes of rapid environmental change; dating of these periods can be more precise than ^{14}C dating and times of abrupt change well beyond the range of radiocarbon can be examined. However, for paleoclimatic applications, the resolution of such studies is constrained by the residence time of water in the aquifers, which link surface climatic conditions to subsurface speleothem growth. This effectively acts as a low-pass filter on the environmental record in speleothems, but generally flow rates are high enough

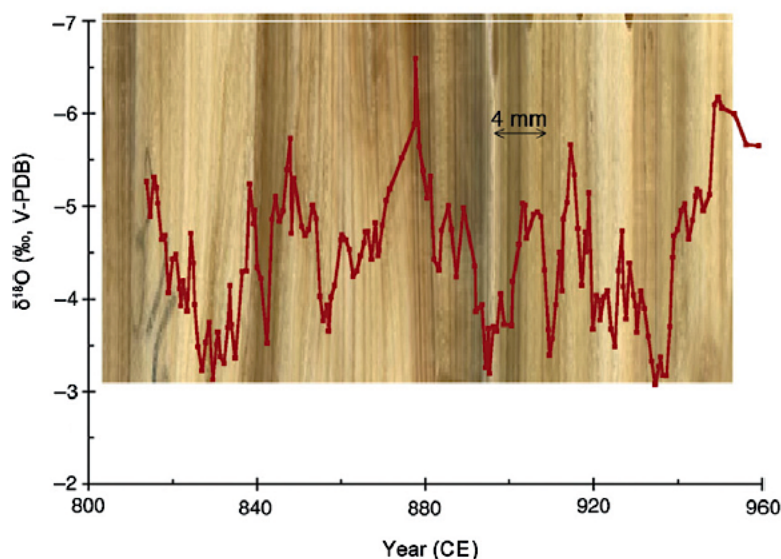


FIGURE 8.4 A cross section through the growth axis of a stalagmite from Chaac Cave, Yucatan peninsula, Mexico (21°N, 89°W), showing distinct laminations during the Mayan Terminal Classic Period. The nearest measured ^{230}Th dates to the sample interval shown in this figure occur at CE 1004 and 780; this gives an age range for the sample of 918-820 (98 years). A total of 85 ± 10 laminations were counted in this section, strongly suggesting that these laminations are annual. The error in lamination counts stems from the different number of laminations in the center of growth compared to the periphery along the same depth interval; often, a single layer observed in the center of growth appears as several bands away from the center. Superimposed on the stalagmite cross section (in red) is the $\delta^{18}\text{O}$ record showing a series of droughts (higher isotopic values) that had severe impacts on the regional population. From *Medina-Elizalde et al. (2010)*.

that annual (or even subannual) variations may be resolved in some situations (Figure 8.4) (cf. *Shopov et al., 1994; Baldini et al., 2002*).

Speleothems are most commonly dated by uranium-series disequilibrium methods (generally $^{230}\text{Th}/^{234}\text{U}$) described in *Chapter 3, Section 3.2.3*. Isotopes of uranium leached from the carbonate bedrock are coprecipitated as uranyl carbonate with the calcite of the speleothems. Normally, the precipitating solution contains no ^{230}Th because thorium ions either are adsorbed onto clay minerals or remain in place as insoluble hydrolysates. Thus, providing the speleothem contains no clay or other insoluble materials, which are carriers of detrital thorium, the activity ratio of ^{234}U to its decay product ^{230}Th will give the sample age (*Richards and Dorale, 2003*). The method is useful over the time range $\sim 500,000$ -100 years BP. A number of precautions are taken to ensure a reliable age estimate, most notably that any samples containing more than 1% of acid-insoluble detritus are likely to be rejected. Also, any indication that recrystallization has occurred (suggesting that the sample may not have remained a closed system) would raise concerns. The latest analytic techniques for U-series dating require very small samples (<100 mg of calcite) and generally yield dates with a 1σ precision of <1% and in some cases as low as 0.1% (*Shen et al., 2012*).

8.1 ISOTOPIC VARIATIONS IN SPELEOTHEMS

Stable isotopes of oxygen and carbon provide the main basis for reconstructing the temperature or precipitation history of a site from speleothems. When air and water movement in a cave is relatively slow, a thermal equilibrium is established between the bedrock temperature and that of the air in the cave, approximating the mean annual surface temperature. During deposition of calcite from seepage (drip) water, as CO_2 is lost, fractionation of oxygen isotopes occurs at a rate that is dependent on the temperature of deposition ($-0.24\text{‰ }^\circ\text{C}^{-1}$; O'Neil et al., 1969). Thus, in theory, oxygen isotopic variations in the speleothem calcite ($\delta^{18}\text{O}_c$) should provide a proxy of temperature variations through time. However, a number of other factors must also be considered (Mickler et al., 2004). First, isotopic paleotemperatures are recorded only if the calcite (or aragonite) is deposited in isotopic equilibrium with the dripwater solution. This can be assessed by determining if $\delta^{18}\text{O}_c$ is constant along a growth layer; if values vary for the same depositional interval, it indicates that deposition was affected by evaporation, not just the slow degassing of CO_2 , and this would alter the simple temperature-dependent fractionation relationship. Another test of isotopic equilibrium that is commonly invoked is the so-called Hendy test. This involves comparing variations in carbon and oxygen isotopes along individual growth layers (Hendy, 1971). If a nonequilibrium situation existed, the isotopic composition would be controlled by kinetic factors and the same fluctuations would be found for both carbon and oxygen isotopes. If no correlation between these two isotopes is found, it can be assumed that the carbonate speleothem was deposited in equilibrium.

A few other factors also have to be considered in reconstructing paleotemperature from $\delta^{18}\text{O}_c$. Although the fractionation factor between calcite and water decreases with an increase in cave temperature (causing a decrease in $\delta^{18}\text{O}_c$ values), changes in air temperature at the surface are almost certainly accompanied by changes in the isotopic composition of precipitation, such that (in midlatitudes, at least) the $\delta^{18}\text{O}$ value of dripwater tends to increase with higher temperatures (see Chapter 5, Section 5.2.3). The relative importance of these opposing effects must therefore be evaluated. Also, during glacial periods, the growth of ^{18}O -depleted continental ice sheets led to an increase in $\delta^{18}\text{O}$ of oceanic water (of up to 1‰) and hence also of precipitation. Thus, for a given climatic shift, several (often opposing) factors come into play, and in some locations, it may be difficult to assess *a priori* in which direction the $\delta^{18}\text{O}_c$ might have changed (Thompson et al., 1976; Harmon et al., 1978a). Ideally, when sample resolution is comparable to that of instrumental or historical data, a direct comparison can be made during the period when records overlap. Thus, Mangini et al. (2005) used regional temperature reconstructions (from Luterbacher et al., 2004) to calibrate variations in $\delta^{18}\text{O}$ in a stalagmite from Spannagel Cave in the central Alps of Austria. They then used this regression to derive temperatures at the cave over the last 2000 years, at near-annual resolution. Similarly, Burns et al. (2002) were able to show that there was strong relationship between regional rainfall and $\delta^{18}\text{O}$ in Oman stalagmites during the twentieth century, thereby quantifying their interpretation of the longer stalagmite record in terms of rainfall variations. Direct monitoring of dripwater is also extremely useful, in order to understand the environmental factors that are important in the most recent period of deposition (e.g., Genty et al., 2001; McDonald and Drysdale, 2004; Cruz et al., 2005a; Treble et al., 2005b; Matthey et al., 2008).

In some speleothems, dripwater, trapped as tiny liquid inclusions as the speleothem grew, has been isolated to provide a more direct measure of the changing isotopic composition of rainwater (e.g., van Breukelen et al., 2008) or to extract noble gases for direct paleotemperature estimation (e.g., Kluge et al., 2008). These inclusions vary in abundance and when present in large amounts (>1% by weight) give speleothems a milky appearance (Thompson et al., 1976; Harmon et al., 1979). Because it is possible that the inclusion water may have continued to exchange oxygen isotopes with the surrounding calcite following its entrapment, it is preferable to measure the deuterium-hydrogen (D/H) ratio, since there is no hydrogen in the calcite with which hydrogen in the water might have exchanged. The relationship between δD and $\delta^{18}O$ in dripwater should approximate the Meteoric Water Line (MWL), first noted in precipitation by Craig (1961c):

$$\delta D = 8\delta^{18}O + 10$$

and

$$d = \delta D - 8\delta^{18}O$$

where d is the *deuterium excess* parameter (see Section 5.2.5). Providing this relationship (or perhaps a similar relationship, with a different d -value) has remained constant over time, the former $\delta^{18}O$ values of rainfall over very long periods of time can be estimated. Using this approach to account for the amount of rainfall-related isotopic change, McGarry et al. (2004) were then able to constrain the probable range of temperatures experienced at Soreq Cave, Israel, since the last interglacial. According to this analysis, temperatures fell from around 20 °C during marine isotope stage 5e to ~10 °C at the Last Glacial Maximum (LGM). In contrast, Fleitmann et al. (2003a) ruled out temperature changes as an explanation for the presence of much lighter hydrogen isotopes in fluid inclusions and much lighter $\delta^{18}O_c$ of the associated calcite in stalagmites from northern Oman, during the LGM and earlier glacial episodes. They argued that the changes reflect stronger monsoon rainfall in the region at those times, which brought more isotopically depleted water into the cave systems. In fact, throughout the Tropics, temperature changes on glacial-interglacial timescales have been relatively small (2-4 °C), equivalent to less than 1‰ in $\delta^{18}O_c$, and so the oxygen isotope signal in tropical speleothems is predominantly that of rainfall variations. This has proven to be a powerful tool for understanding past climatic conditions, particularly changes in monsoon circulation regimes, revealing important details about how climate changes in the Tropics and at high latitudes are dynamically linked, on both long and short timescales.

8.2 TROPICAL AND SUBTROPICAL PALEOCLIMATE VARIABILITY FROM SPELEOTHEMS

Speleothems from China have provided remarkable insights into monsoon climate variability over the last half a million years (Wang et al., 2008; Cheng et al., 2012b). As an example, Figure 8.5 shows $\delta^{18}O$ variations spanning the last 224 ka in a set of stalagmites from northeastern and central China, within an area dominated by the East Asian monsoon regime. These records are synchronous with Northern Hemisphere July insolation at 65°N, which