CAVE SEDIMENTS AND PALEOCLIMATE

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Abstract: This paper is a review of cave sediments: their characteristics and their application as paleoclimate archives. Cave sediments can be separated into two broad categories, clastic sediments and chemical sediments. Of these, stream-transported clastic sediments and calcite speleothems are both the most common and also the most useful as climatic records. Techniques for dating cave sediments include radiocarbon and U/Th dating of speleothems and paleomagnetic reversals and cosmogenic isotope dating of clastic sediments. Cosmogenic isotope dating of clastic sediments in caves with multiple levels or which occur at different elevations provide a geomorphic record of cave ages and river system evolution over the past 5 Ma. Isotope profiles, trace element profiles, color banding and luminescence profiles of speleothems, mainly stalagmites, produce a detailed paleoclimate record with very high time resolution over the past several hundred thousand years. There is potential application of these methods to late Holocene climates with implications for evaluation of current concern over global warming.

INTRODUCTION

Caves are open cavities in the earth. As such they are natural sediment traps. No caver needs to be reminded that caves are muddy. Closer inspection, however, shows that cave deposits are remarkably complicated as are the transport mechanisms that carry the sediments into the caves. Cave sediments have been recognized for as long as there has been scientific interest in caves. However, only in the past several decades has it been recognized that cave sediments contain both hydrogeological and paleoclimatological records. In part, this late recognition is due to the recent development of techniques for assigning dates to cave sediments. With an accurate chronology, the cave archives can be correlated with events on the land surface above. The investigation of cave sediments has moved from an obscure corner of karst science to one of today's hottest topics (e.g., Sasowsky and Mylroie, 2004). There is the very real possibility that cave sediments will take their place along side of ocean sediment cores and continental ice cores (Greenland and Antarctica) as the most important records of how Earth's climate has evolved over the past several million years.

The objective of the present paper is to summarize some of the current state of knowledge of cave sediments. As will be seen, the subject has grown much broader than it was in 1966 on the occasion of the 25th anniversary volume. The literature has become very large. What follows are examples to give some feel for what has been accomplished, particularly in the past 10–20 years. It is not a comprehensive review.

SOME HISTORICAL BACKGROUND

There has always been a distinction between speleothems and clastic sediments in caves. Speleothems are aesthetically pleasing and their bizarre shapes give caves much of their charm. It takes a special point of view to see the same scientific value in a mud bank as in a cluster of stalagmites.

The first descriptions of speleothems are lost in the mists of antiquity. Shaw's (Shaw, 1992) monumental treatise on cave science prior to 1900 devotes 13 chapters to speleothems including accounts of early and somewhat fanciful attempts to explain them. Many descriptions of the various forms of speleothems have appeared, and one of the best and most detailed descriptions of their crystal structures was written nearly a century ago (Prinz, 1908). The correct chemical reaction for the deposition of calcite in caves was described as early as 1812 by Cuvier and in 1820 by Benjamin Silliman the elder (Shaw, 1992). In a now classic paper, Holland et al. (1964) set forth a detailed chemical model for calcite deposition that remains the accepted explanation to the present time.

Clastic sediments are rarely mentioned prior to 1900 (Shaw, 1992). The two main categories, breakdown and stream deposits, are only briefly mentioned in the two most important early 19th Century textbooks (Kyrle, 1923; Trombe, 1952). Clastic sediments did play a central role in the Bretz (1942) model for cave development. According to Bretz, caves formed deep below the water table and then filled with red unctuous clay which filtered down from overlaying soils. Later dissection of peneplains and draining of the caves allowed the sediments to wash out, leaving behind the open cave passages we see today. Many of Bretz's field observations were in Missouri caves where the sticky muds are particularly common. In response, Reams (1968) devoted an entire Ph.D. dissertation to demonstrating that many of the Missouri cave sediments are, in fact, river sediments carried in through sinkholes and by sinking streams. In contrast, Davies (1960) used the sand and gravel sediments in Appalachian caves to

demonstrate that the caves were formed by fast-moving water close to local base levels and not by slow percolation deep below the water table.

Caves sediments came into their own as a significant part of cave science in the 1960s with an important symposium on both chemical and clastic sediments (Dell'Oca, 1961) and the comprehensive research of Renault (1967–1969). The paleoclimatic significance of clastic sediments was recognized in European alpine caves by Schmid (1958). The first two English language textbooks on caves (Jennings, 1971; Sweeting, 1972) had chapters devoted to cave sediments although the coverage was predominantly on chemical sediments. Clastic sediment research in the United States got underway in the mid-1960s with the work of Frank (1965) on the caves of Texas and later work in Australia (Frank, 1969, 1971). Many of these early studies treated clastic sediments in caves as a peculiar sort of sedimentary rock with emphasis on in-cave stratigraphy and provenance of the sediment. One of the most comprehensive studies of sediment source and deposition was an unpublished Ph.D. thesis (Wolfe, 1973) describing cave sediments in the Greenbrier karst of West Virginia.

CLASSIFICATION OF CAVE SEDIMENTS

There is no generally accepted classification scheme for cave sediments. Each of the more recent textbooks on caves and karst (Bögli, 1980; White, 1988; Ford and Williams, 1989, Gillieson, 1996) presents a classification of sediments. These have many points in common but also significant differences. The classification in Figure 1 is a compromise. It lists the main categories of sediment, but does not attempt to provide a pigeon hole for every possible material that might accumulate in a cave.

Sediments are divided into two broad categories: clastic sediments and chemical sediments. Clastic sediments are moved mechanically whereas chemical sediments are formed in place, precipitated from solution in seeping, dripping, or flowing water. Clastic sediments can then be subdivided again into materials that are derived locally within the cave and materials that are transported into the cave from the outside. These are known respectively as autochthonous sediments and allochthonous sediments. Chemical sediments are subdivided into categories based on their composition.

Locally derived clastic material consists of weathering detritus, breakdown, and guano. Weathering detritus is the insoluble component of the bedrock, left behind when the bedrock dissolved. Weathering detritus is one source of the sticky clays found in some caves that have no evidence of stream action. Weathering detritus can include sand, silicified fossil fragments, and chert, the latter in some limestones being a major component of the clastic sediment. Breakdown consists of fragments of broken bedrock in a wide range of sizes. The classification of breakdown and the geologic processes responsible for cave
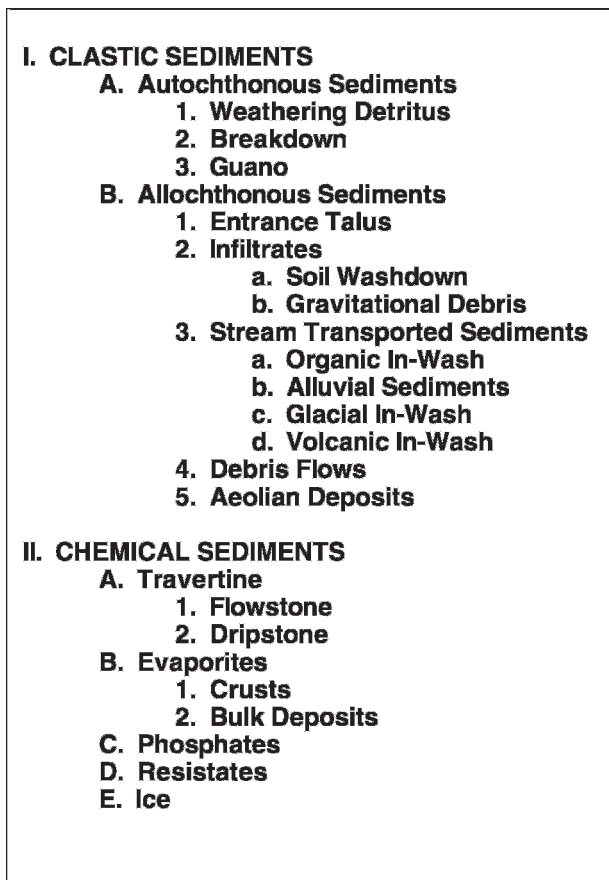
I. CLASTIC SEDIMENTS
   A. Autochthonous Sediments
      1. Weathering Detritus
      2. Breakdown
      3. Guano
   B. Allochthonous Sediments
      1. Entrance Talus
      2. Infiltrates
         a. Soil Washdown
         b. Gravitational Debris
      3. Stream Transported Sediments
         a. Organic In-Wash
         b. Alluvial Sediments
         c. Glacial In-Wash
         d. Volcanic In-Wash
      4. Debris Flows
      5. Aeolian Deposits

II. CHEMICAL SEDIMENTS
   A. Travertine
      1. Flowstone
      2. Dripstone
   B. Evaporites
      1. Crusts
      2. Bulk Deposits
   C. Phosphates
   D. Resistates
   E. Ice

Figure 1. A classification of cave sediments.

passage collapse is more complex than expected (White and White, 1969; Jameson, 1991). Guano is the fecal material deposited in caves by bats and birds. In caves with large bat populations, guano is present in sufficient quantities to be classified as a sediment.

The composition of allochthonous sediment varies depending on the rock types and other materials available in the drainage basin in which the cave is embedded. Cave entrances are usually sites of intensive weathering and the combination of breakdown, downslope movement from other rock units above the cave, soil slumping, and incorporated plant material creates a characteristic pile of roughly stratified debris known as entrance talus. Entrance talus is of importance because it often houses paleontological or archaeological deposits. Infiltrates are sediments that migrate into the cave from the land surface above. They subdivide into soil washdown which is mainly soil from the epikarst that is washed into the cave through solutionally-widened fractures, and gravitational debris which is coarser-grained material that falls down open shafts. Sinking streams carry a great variety of materials into caves including alluvial sediment, glacial tills, volcanic ash and any other unconsolidated material that may be picked up by the stream. Debris flows are essentially avalanches that flow underground. These provide rare but

dramatic cave deposits, for example those found in the caves of the New Guinea highlands (Gillieson, 1986). Finally, quantities of sand and loess can be blown into caves directly by wind action to produce aeolian deposits.

Most common of the chemical sediments are the travertines. The word travertine is here used as a blanket label for fresh-water carbonate deposits of all types. Travertine is used as a rock name whereas speleothem refers to the specific external morphology of the deposits. Cave travertines are chemically similar to the calcareous tufas found as spring and fresh water deposits throughout the world and to the geothermal travertines (Ford and Pedley, 1996). Tufas generally are porous and contain a great deal of plant material in comparison to both cave and geothermal travertines, which are usually dense and compact. Tufas also contain paleoclimatic records (Andrews, 2006).

The term evaporite is used for cave sediments in much the same way that it is used for surface sediments; assemblages of minerals formed by evaporating water. Most common in caves is gypsum, $CaSO_4 \cdot 2H_2O$, but there exist a selection of other sulfate minerals as well as occasional halite deposits. The remaining categories of chemical sediments listed in Figure 1 are volumetrically rather minor. Phosphates, mainly hydroxyapatite, are associated with old and decomposed guano deposits. The resistates, iron and manganese oxides, are usually limited to coatings. Perennial ice occurs in alpine caves and so can reasonably be considered a cave sediment.

CLASTIC SEDIMENTS

Figure 1 provides a systematic categorization of clastic sediments in terms of source area. However, the conduit system acts as a mixing chamber so that the sediments observed in caves or emerging from karst springs contain components from all of the sources. Figure 2 gives the overall concept. The key parameters are flow velocities, flow volumes, particle density, and particle size. Although there may be some contribution of relatively light organic material, most clay, silt, sand, cobbles and boulders have densities not greatly different from that of quartz (2.65 g cm^{-3}). Density variations are not a very significant variable. The size of clastic particles varies over six to eight orders of magnitude from sub-micrometer colloidal and clay particles to boulders approaching one meter. The clastic sediments remaining in caves and the flux of clastic sediments through the aquifer are determined mainly by storm flow and by particle size. Clastic particles flushed through the system are part of the hydrology; clastic particles remaining after the caves are drained become the sediment record.

TRANSPORT MECHANISMS

Sediment transport in open channels occurs by two mechanisms: suspended load and bedload. The suspended load consists of particles taken in suspension by the
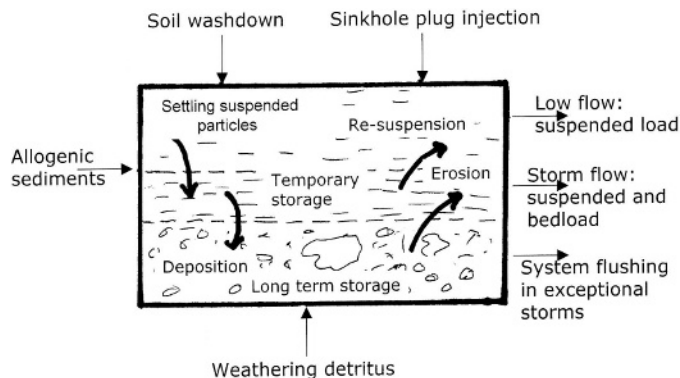

Figure 2. Sketch showing clastic sediment sources and the role of the conduit system as a mixing chamber.

turbulence of stream flow. Such particles tend to settle out, but are held in suspension by the turbulence. The energy required to hold particles in suspension and the rate at which they settle out of suspension depend on particle size. If flow velocities decrease, for example by an expansion of the passage cross-section or by ponding of water behind an obstruction, coarse sediments drop out rapidly but very fine-grained sediments may remain in suspension. Flowing water moves bedload by dragging it along the bed because of the boundary shear between the moving water and the bed material. It is not required that these flows be turbulent although they usually are. The boundary shear necessary to put bed particles in motion increases almost linearly with the particle size and with the square of the flow velocity.

There is a wide range in particle sizes for the material injected into the conduit systems from the sources sketched in Figure 2. Velocities vary along the conduit depending on whether a particular segment is pipe-full or flowing in an open channel, depending on passage cross-sectional area, and depending on obstacles or blockages within the conduit. Velocities also vary depending on whether the system is at base flow or storm flow, and if at storm flow, on the magnitude of the storm. As a result there is a very complex mixing and partitioning of sediment within the conduit system. Small particles in the colloidal or fine clay size range may remain in suspension and provide a continuous flux of sediment at the spring even during base flow conditions. Clay and silt sized particles may settle into temporary storage during base flow but are re-suspended and carried to the spring during storm flow, thus causing the spring to become muddy. Very coarse pebble to cobble size sediments may be swept into the conduit system during large storms and remain in the system in long-term storage until they are swept on through by another exceptional storm. There is a continuous interchange of sediment depending on flow conditions.

Much recent research has been concerned with the hydraulics of sediment transport and with the appearance of suspended sediments at karst springs. Because of the open conduits, many springs discharge very small particles

even under base-flow conditions (Atteia et al., 1998). The fine-grained particles are of importance because they provide a transport mechanism for bacteria (Mahler et al., 2000) and heavy metals (Vesper and White, 2003). Turbid or muddy spring water makes the springs unsuitable as water supplies and as a result there have been many studies of suspended sediment transport to springs (Mahler and Lynch, 1999; Drysdale et al., 2001; Amraoui et al., 2003; Massei et al., 2003; Dogwiler and Wicks, 2004). There has been relatively little recent work on the mechanisms of transport of the coarse fraction that makes up much of the sediment seen in caves. Gale (1984) was able to use the observed sediment particle sizes to back calculate the hydraulic characteristics of the conduit in which they were found. One recent study (Hart and Schurger, 2005) estimated the rate of sediment injection through sinkholes to be 111 $Mg\,km^{-2}\,yr^{-1}$ for a watershed in central Tennessee.

LITHOFACIES

Ultimately, of course, the composition, mineralogy, and lithology of cave clastic sediments depend on the material available in the source areas. Within this constraint, however, the sedimentary deposits depend on the internal dynamics of the conduit system. Thus, cave clastic sediments occur in facies that reflect the way in which injected sediment has been rearranged and deposited. There have been a number of facies schemes proposed depending on the criteria used for identifying the facies (e.g., Gillieson, 1986; Springer and Kite, 1997). The scheme sketched in Figure 3 (Bosch and White, 2004) describes facies according to particle size and the degree of sorting. It will be noted that the axes in Figure 3 have no scale. Further, the boundaries between the facies domains are exceedingly fuzzy.

The widest range of particle size and particle sorting occurs in the most common stream deposits in caves, the channel facies. They occur as roughly stratified layers of sands, silts, and cobble deposits most easily observed where more recent streams have cut through earlier sediments thus exposing the layering in the stream bank. Any given exposure of channel facies is likely to show distinct bedding, but this stratigraphy is rarely continuous along the cave passage. The thalweg facies is a derivative of the channel facies. Thalweg facies are the coarse cobble armoring that forms the beds of many active cave streams. The coarse material is a residual deposit formed by stream action winnowing out the fine-grained material from the channel facies. The other three facies sketched in Figure 3 each involve different transport processes.

Slackwater facies are the thin layers of fine grained silt and clay that often form the final top layer of clastic deposits. This facies is often found in blind side passages, pockets, and other niches in caves unlikely to be reached by flowing streams. The slackwater facies appear to be deposited from suspended sediment that has settled out
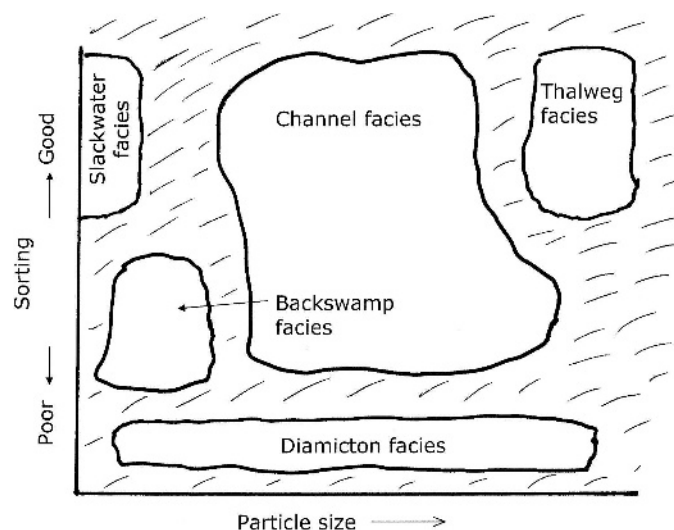

Figure 3. Facies of clastic sediment. Adapted roughly from Bosch and White (2004).

of flooded cave passages. Rising floodwaters fill all available spaces and are then ponded for extended periods of time until the flood recedes. During the time when the passage is water-filled, suspended sediments have time to settle out and form a sediment layer. An investigation of this facies in Agen Allwedd Cave in the UK (Bull, 1981) revealed distinct laminae which were interpreted to be the result of a rhythmic pulsing of sediment-laden water into subterranean lakes in response to surface climate. Careful examination of this microstratigraphy revealed a sequence of climatic events extending back 17,000 years (Bull, 1980).

Diamicton facies are the result of debris flows. These are chaotic deposits containing particles ranging from clays to cobbles tossed together with no bedding and no sorting. Special circumstances, mainly extreme storm intensities and high gradient cave passages, allow entire sediment deposits to be taken into suspension and swept down a cave passage to later be deposited in an undifferentiated mass. Diamicton facies were described from the high gradient caves in New Guinea (Gillieson, 1986).

In some caves, particularly network mazes, flow velocities never reach threshold values for sediment transport. The sediments in these caves tend to be locally derived, either the residual insoluble material from dissolution of the limestone or infiltrating soil from the land surface above. The term "backswamp facies" was chosen because, hydraulically, network mazes and other slow-flow caves tend to behave as the underground equivalent of swamps.

CHEMICAL SEDIMENTS

MINERALOGY

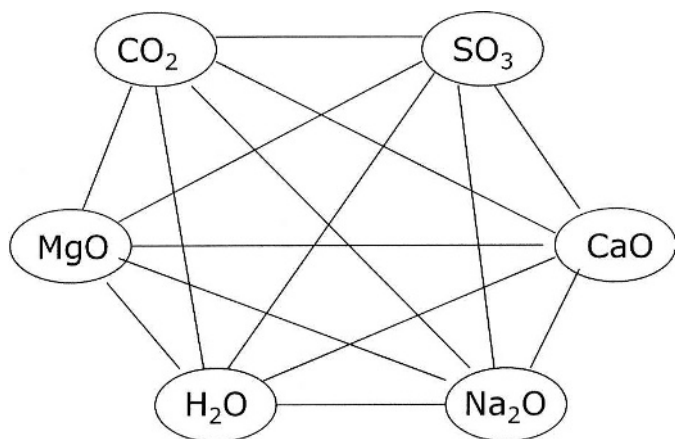Caves, where temperature, water vapor partial pressure, carbon dioxide partial pressure and other environmental

Figure 4. Interconnections of the six oxide components that make up most common cave minerals.

Figure 5. Compositions of the cave carbonate minerals represented on a regular tetrahedron.

parameters either remain constant or cycle through fixed patterns over long periods of time, are effective deposition sites for a surprising range of minerals. Hill (1976) described 74 minerals mainly from caves in the United States. By 1997 when the expanded *Cave Minerals of the World* reached a second edition (Hill and Forti, 1997), the number of identified cave minerals had reached 255. Very few of these occur in sufficient volume to be important as cave sediments.

Ions that occur commonly in carbonate ground waters and would be available for the formation of cave minerals are Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, and SO_4^{2-}, plus, of course, water. Because caves, with some interesting exceptions, are oxidizing environments, the resulting minerals can be described in terms of their component oxides. The system would be $CaO - MgO - Na_2O - CO_2 - SO_3 - H_2O$. Because any material object contains 100 percent stuff, the total concentrations of all components must add up to 100 percent. Therefore, the number of independent composition variables is always one less than the number of components. The chemical system of six oxides requires a five-dimensional space to plot the compositions which is difficult on a two-dimensional sheet of paper. Figure 4 shows the topological relations. If the components are selected four at a time, the compositions of any minerals in these sub-systems can be represented in three dimensions, namely by plotting any combination of four components on the apices of a regular tetrahedron. The principal Ca-Mg-carbonate minerals can be displayed in this fashion (Fig. 5).

Of the minerals plotted on Figure 5, only calcite and to a lesser extent aragonite are significant constituents of cave sediments. In spite of the common occurrence of caves in dolomite rocks, dolomite rarely precipitates from karst waters. Magnesium appears either as a solid solution in calcite or as the fine-grained hydrated magnesium carbonate minerals known as moonmilk.
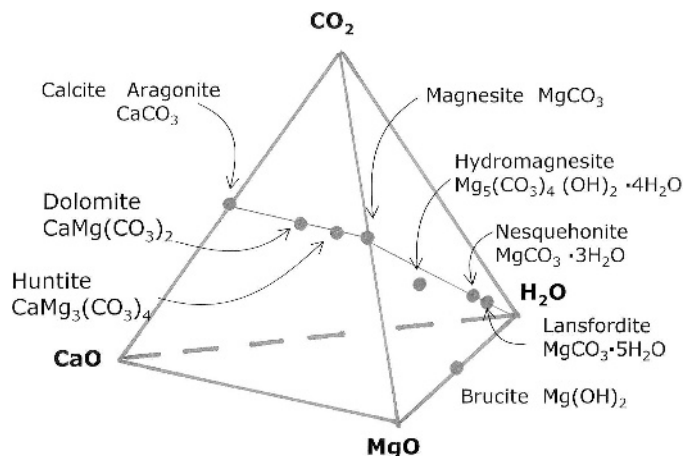
The sulfate minerals require the five-component sub-system $CaO - MgO - Na_2O - SO_3 - H_2O$ to cover the common minerals. Gypsum, $CaSO_4 \cdot 2H_2O$ is the second most common cave mineral and, in terms of sediment volume, is by far the most important sulfate mineral. Others include epsomite, $MgSO_4 \cdot 7H_2O$ and mirabilite, $Na_2SO_4 \cdot 10H_2O$. Both are highly water-soluble and are found only in extremely dry caves. The stability of these minerals can be described in terms of the temperature and water vapor partial pressure (White, 1997).

DEPOSITION OF CALCITE AND ARAGONITE

The deposition of both calcite and aragonite in caves is described by the deceptively simple chemical reaction

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (1)$$

The same reaction written in reverse describes the dissolution of limestone. The equilibrium concentration of dissolved carbonate depends on the partial pressure of CO_2, the temperature, reactions among the various carbonate species, and also on the ionic strength, other ions in solution, and various complexes that may form. Carbonate chemistry is now understood in considerable detail and appears in a variety of textbooks (e.g., Langmuir, 1997). The equilibrium concentration of dissolved Ca^{2+} in a system open to CO_2 is given by

$$m_{Ca^{2+}} = P_{CO_2}^{1/3} \left[\frac{K_1 \, K_C \, K_{CO_2}}{4 \, K_2 \, \gamma_{Ca^{2+}} \, \gamma_{HCO_3^-}^2} \right]^{1/3} \qquad (2)$$

In this equation, K_1 and K_2 are the first and second dissociation constants for carbonic acid, K_{CO_2} is the Henry's law constant for the solubility of CO_2 and the γ's are the activity coefficients for the Ca^{2+} and HCO_3^- ions. The same equation describes the solubility of aragonite if K_C, the solubility product constant for calcite, is replaced by K_A, the solubility product constant for
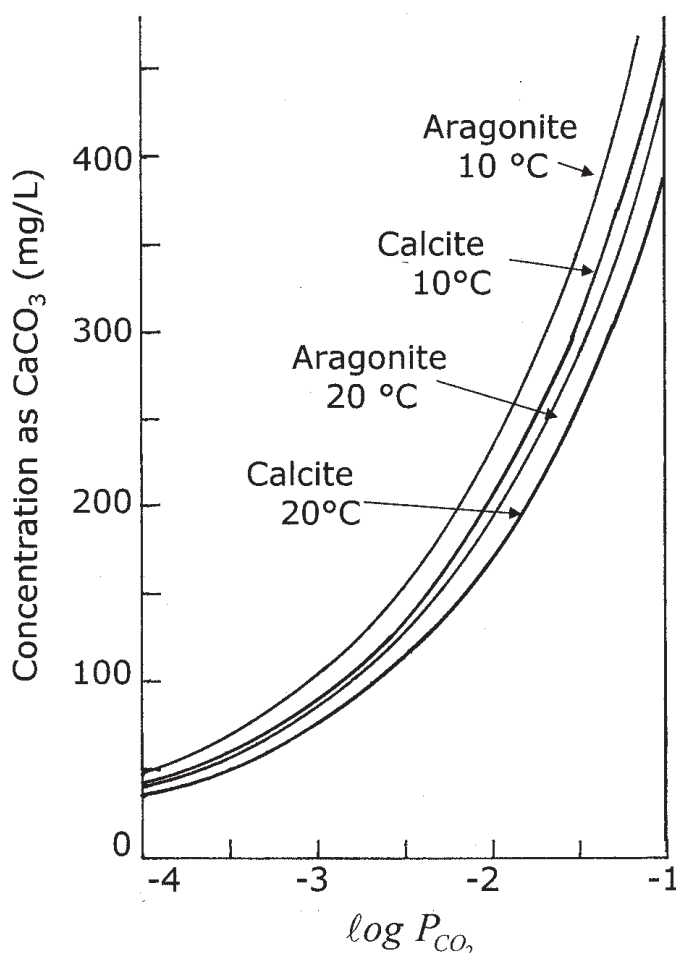
Figure 6. Solubility of calcite and aragonite as a function of CO_2 pressure. Calculated from equation (1) for 10 °C and 20 °C.

aragonite. Numerical values for the constants at various temperatures are given by White (1988). Calculated solubilities for calcite and aragonite are plotted in Figure 6.

The solubility curves in Figure 6 provide a model for the chemistry of carbonate mineral deposition. Rain water contains CO_2 at the concentration of 0.037 volume percent ($log\ P_{CO_2} = -3.43$) but essentially zero dissolved carbonate. When rain water percolates through organic-rich soils, the CO_2 concentration may rise as high as 10% ($log\ P_{CO_2} = -1$). When the CO_2-rich water reaches the bedrock it dissolves the limestone taking Ca^{2+} ions into solution. Ca^{2+}-ion concentrations may reach values in the range of 400 mg L^{-1} as $CaCO_3$ as given by equation (2). These CO_2- and Ca^{2+}-rich percolation waters seep downward along joints until they emerge from the ceilings and walls of cave passages. The CO_2 concentration in cave atmospheres is typically about ten times that of the surface atmosphere ($log\ P_{CO_2} = -2.5$) so in this environment, the dripping waters are highly supersaturated. CO_2 is degassed into the cave atmosphere and $CaCO_3$ is precipitated, until (at equilibrium) the concentration falls back to about

100 mg L^{-1}. Because the cave environment is usually water-saturated, the surfaces of the growing speleothems remain wet. Each successive drop deposits its small load of $CaCO_3$ in register with the ions already present on the growing crystal surface. Thus individual calcite crystals in speleothems in sealed caves tend to be large, often much larger than any that have been grown in the laboratory.

The rate at which calcite dissolves has been the subject of a huge number of investigations (for review see Morse and Arvidson, 2002). Dissolution rate studies are pertinent to the interpretation of cave development (speleogenesis). The reverse rates for calcite or aragonite precipitation and thus of speleothem growth at saturation conditions far from equilibrium tend to follow the same laws as calcite dissolution (with some signs reversed) (Reddy et al., 1981). Near equilibrium, which is the condition in most cave depositional environments, the mechanisms are much more complicated. In order for calcite crystals to grow, the feed solutions must be supersaturated. However, if the supersaturation is too large, new calcite crystals will be nucleated and, instead of one large crystal, the speleothem will consist of many small crystals. $CaCO_3$ growth rates have been studied in the laboratory by controlling supersaturations and measuring growth rates (Gutjahr et al., 1996).

More insight into the details of the process at the atomic scale have been obtained by using the atomic force microscope to actually measure the rate of growth of individual layers within the crystal (Teng et al., 2000). The agreement is generally good between laboratory measurements, calculations of growth rate, and growth rates directly measured in caves (Baker et al., 1998). The trade-off between growth rates of individual crystals and the nucleation and growth of multiple crystals results in a variety of microstructures (also called fabrics or textures) in speleothems which can be examined by polarized light microscopy or by scanning electron microscopy (Frisia et al., 2000). Trace quantities of Mn^{2+} or rare earth elements fluoresce under cathode-ray activation, providing a better visual image of growth patterns than those that can be seen by white light microscopy. Cathodoluminescence microscopy has been used to observe growth patterns in speleothems and produce a paleoclimatic interpretation (Richter et al., 2004).

It has long been established that calcite is the stable polymorph of $CaCO_3$ at all temperatures under ambient pressures (Carlson, 1983). Pressures of 300–500 MPa are required to stabilize the orthorhombic aragonite structure. In what seems to be a direct violation of thermodynamics, aragonite occurs commonly in caves forming anthodites, frostwork, aragonite bushes, and bulk stalactites and stalagmites. The literature on the aragonite problem is very large (see review by Carlson, 1983). Two factors seem to be responsible. One is the sensitivity of calcite nucleation and growth to the presence of impurities. The other is the solubility of aragonite which, as a metastable phase, must be larger than that of calcite. However, as shown by the

curves in Figure 6, the solubility of aragonite is only about 10% greater than that of calcite over a wide range of CO_2 pressures at the same temperature. Indeed, the aragonite curve at 20 °C is almost coincident with the calcite curve at 10 °C. Unlike calcite, aragonite nucleates easily and its growth is relatively insensitive to impurities. It is only necessary to inhibit calcite nucleation sufficiently to allow the supersaturation to build past the aragonite solubility curve and aragonite will precipitate. Sr^{2+} enhances aragonite growth by precipitating a Sr-rich nucleus with the aragonite structure. This acts as a template on which aragonite can grow. Mg^{2+} has long been known as a calcite growth inhibitor (Berner, 1975), an effect confirmed by more recent direct measurements with the atomic force microscope (Davis et al., 2000).

Growth of bulk speleothems, of which stalagmites have been of greatest interest, combines consideration of the growth of individual calcite crystals with considerations of precipitation, flow paths from the surface to the cave, and carbon dioxide concentration contrasts between the soil and the cave atmosphere. A further consideration for near-entrance environments is the role of evaporation as a competitive process with CO_2 loss. Because drip-rate (related to precipitation) and CO_2 pressure vary seasonally in most locations, speleothems develop an annual layering with layers that vary in texture and also sometimes in calcite/aragonite content. The rate of growth can be determined by dating the stalagmite layers, either by counting the layers in contemporary stalagmites or by U/Th dating of samples taken along the stalagmite axis. Typical values are in the range of 0.01 to 0.1 mm y^{-1}. The relationship between growth rate and stalagmite shape has been modeled by Kaufmann (2003).

The thickness, texture, and mineralogy depend primarily on precipitation as the most important external parameter, thus measurement of these quantities provides a paleoclimate indicator. Growth layering has provided information from the past several millenia where confirmation from historical records is possible. Such measurement gave a rainfall proxy record for the past five centuries in Madagascar (Brook et al., 1999). Several thousand years of record of the intensity of Indian monsoons was extracted from a stalagmite from Nepal (Denniston et al., 2000a). Spectral analysis of the layering pattern in the Shihua Cave, China appeared to track climatic cycles (Qin et al., 1999). Older records are also possible.

DEPOSITION OF GYPSUM

Gypsum deposition is a matter of the evaporation of sulfate-bearing solutions. No chemistry is involved. The reaction is:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad (3)$$
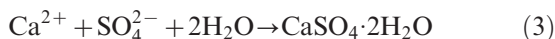
The concentration of dissolved gypsum exactly in equilib-

rium with crystalline gypsum is given by

$$C_{gyp} = M_{gyp} \left[\frac{K_{gyp}}{\gamma_{Ca^{2+}} \; \gamma_{SO_4^{2-}}} \right]^{1/2} \quad (4)$$

C_{gyp} is the concentration of dissolved gypsum in g/L, M_{gyp} is the molecular weight of $CaSO_4 \cdot 2H_2O$, K_{gyp} is the solubility constant for gypsum and the gammas are the activity coefficients for calcium and sulfate ions. $M_{gyp} = 172.17$ atomic mass units. The solubility of gypsum does not depend on pH or CO_2 pressure but does vary with temperature. Other ions in solution affect gypsum solubility through the activity coefficients.

K_{gyp} as a function of temperature is given by

$$\log K_{gyp} = 68.2401 - \frac{3221.51}{T} - 25.0627 \log T \quad (5)$$

Equation (5) is taken from Langmuir and Melchior (1985). In this equation, T is the absolute temperature in kelvins. At the standard reference temperature of 25 °C, the calculated value is $\log K_{gyp} = -4.581$, a value that has been accepted by several contemporary textbooks (e.g., Langmuir, 1997; Drever, 1997). This number is based on direct solubility experiments and is recommended against other values that have been calculated from thermodynamic data.

The sources of gypsum in caves vary depending on the specific cave. Sources that have been identified include:

- Dissolution, transport, and redeposition of gypsum beds that occur interbedded with the carbonate units.
- Oxidation of H_2S to sulfuric acid followed by reaction of the acid with the limestone to form gypsum. This is the source of gypsum in sulfuric acid caves.
- Oxidation of pyrite, FeS_2, that occurs dispersed in the limestone followed by reaction with the limestone to form gypsum.
- Oxidation of pyrite from overlying strata followed by transport of sulfate-bearing solutions to the cave where reaction to gypsum takes place.

Residual gypsum is a key part of the mechanism for the formation of sulfuric-acid caves (Hill, 1987, 1990). Thus far, gypsum has not been found to contain any significant paleoclimatic record. Another sulfate mineral, alunite, $KAl_3(SO_4)_2(OH)_6$, has been found to retain ^{40}Ar from the decay of ^{40}K so that $^{40}Ar/^{39}Ar$ dating of the alunite from Carlsbad Caverns and other Guadalupe Mountain caves was possible (Polyak et al., 1998). Ages ranged from 3.89 Ma in Carlsbad Cavern to the oldest and highest cave examined, Cottonwood Cave, at 12.26 Ma.

ICE

Seasonal ice forms in many caves where winter temperatures fall below freezing. Often the ice takes the form of spectacular, if transient, speleothems near cave entrances. Caves with perennial ice are less common and

Figure 7. Ice speleothems, Scărişoara Ice Cave, Romania.

Figure 8. Ferrihydrite speleothems, Rohrers Cave, Pennsylvania.

usually occur only at high altitudes. Fossil Mountain Ice Cave in Wyoming is an example in the United States. Best known are the big ice caves of the European Alps such as the Eisriesenwelt and the Rieseneishöhle in Austria. Some of the best paleoclimatic records have been recovered from ice cores drilled in the continental glaciers of Greenland or Antarctica. It would seem that drilling the perennial ice in an ice cave would be valuable. Studies have been undertaken in the Scărişoara ice cave in the Apuseni Mountains of Romania (Racovită and Onac, 2000) (Fig. 7).

RESISTATES: IRON AND MANGANESE OXIDES

Among the more widespread minor cave sediments are the oxides and hydroxides of iron and manganese. These compounds are highly insoluble in neutral pH water and so are known as resistates.

Goethite (FeOOH), ferrihydrite (Fe(OH)$_3$) and other hydrated and hydroxylated iron oxides occur widely in caves. Goethite is usually crystalline at the X-ray diffraction scale but the other iron oxides and hydroxides are usually non-crystalline at the X-ray scale. Speleothems of iron hydrates have been found and are well developed in Rohrer's Cave, Lancaster County, Pennsylvania (White et al., 1985) (Fig. 8).

Black coatings that occur widely on stream sediments are usually described as manganese oxide. Usually the manganese oxides appear only as thin ($<$ 1 mm) coatings although thicker and more massive deposits occur. Although at least nine manganese oxide minerals have been reported from caves (Hill and Forti, 1997), most of the identified deposits are composed of birnessite, the δ polymorph of MnO_2, but with a composition approximately $(Na,Ca,Mn^{2+})Mn_7O_{14} \cdot 2.8H_2O$. The manganese oxides act as scavengers for heavy metals. Concentrations from parts per million to more than one percent of Zn, Cu, Ni, Co, V, and Cr have been found. Likewise, rare earth elements have been found in manganese oxide deposits (Onac et al., 1997). Deposition of the manganese oxide minerals requires oxidation of Mn^{2+} in the cave water to Mn^{4+}, a process that is likely microbially mediated (Tebo et al., 1997; Northup and Lavoie, 2001).

AGE MEASUREMENTS ON CAVE SEDIMENTS

The widespread interest in cave deposits as paleoclimate archives arises because of well-developed and reliable methods for assigning dates to the deposits. Different sediments provide different information and different methods are used to date them. The sections that follow give a short summary of the most important of the dating techniques.

CARBON 14

Spallation of ^{14}N by cosmic rays in the upper atmosphere produces the radioactive isotope of carbon, ^{14}C. The ^{14}C is oxidized to $^{14}CO_2$ which then mixes with other $^{12}CO_2$ in the lower atmosphere thus producing a constant radioactive component. The same constant radioactive background is present in plants which grow by extracting CO_2 from the atmosphere. The basis for C-14 dating is that when plants die, the exchange of CO_2 with the atmosphere ceases, the incorporated ^{14}C begins to decay according to its 5730 year half-life. Measurement of the residual ^{14}C in wood and charcoal then allows the calculation of the time that has elapsed since the wood or charcoal was part of a growing plant. The usual time limit for C-14 dating is about ten half-lives or 50,000 years, but there are many corrections and caveats to the calculation of dates (Taylor et al., 1992).

The calcite in speleothems is derived from limestone dissolved at the soil/bedrock contact above the cave for which the chemical reaction is

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + HCO_3^- \qquad (6)$$
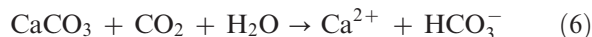
In the cave the calcium and bicarbonate ions are recombined to precipitate calcite in the growing speleothem. Half of the carbon in the precipitated calcite comes from CO_2 and the other half from the $CaCO_3$ in the limestone. The CO_2 is derived partly from the atmosphere and partly from the decomposition of organic material in the soil. The organic material originated as living plants and thus also contains the background concentration of ^{14}C. One might expect, therefore, that the carbon in the bicarbonate ions that form speleothems should consist of about half young carbon from the atmosphere and soil CO_2 and half old, dead, carbon from the limestone. C-14 dating of speleothems should therefore be possible by taking account of the fraction of young, zero age, carbon in the calcite.

The isotopic chemistry of calcite deposition is more complicated. There is carbon-isotope exchange in the soil and in the dissolution and deposition processes. As a result, speleothems typically contain about 85% young carbon, a circumstance that actually makes C-14 dating a little easier. There have been relatively few C-14 dates of speleothems. One critical comparison on speleothems in the Lobatse II Cave (Holmgren et al., 1994) showed that C-

14 dates compared well with U/Th dates back to 20,000 years.

U/TH DATING OF SPELEOTHEMS

U/Th-dating has become the gold standard for speleothem dating (Dorale et al., 2004; Richards and Dorale, 2003). The common uranium isotope, ^{238}U, undergoes a long and complicated decay chain before reaching the stable isotope ^{206}Pb (see Figure 1 in Field, 2007). Along that chain of mostly short-lived intermediates are two long-lived isotopes, ^{234}U (half life = 248,000 years) and ^{230}Th (half-life = 75,200 years). Measurement of the ratio of $^{234}U/^{238}U$ and $^{230}Th/^{234}U$, assuming no thorium in the initial sample, allows the calculation of an age. What makes U/Th isotope dating particularly useful for calcite speleothems is a quirk in the geochemistry of these two elements. Both uranium and thorium have 4+ valence states which produce compounds that are highly insoluble. Uranium also has a 6+ valence state which usually appears as the UO_2^{2+} ion. Thorium does not. The uranyl ion further complexes in carbonate waters and becomes highly mobile (Langmuir, 1997). As a result, speleothems often contain tens to hundreds of parts per million uranium but no thorium. The radiogenic thorium that accumulates in the calcite is a direct measure of the time elapsed since the calcite was deposited.

Uranium/thorium dating of speleothems was pioneered by Derek Ford, Henry Schwarcz, and their students at McMaster University. Age dates combined with oxygen isotope ratios and deuterium ratios produced paleoclimatic records for caves in West Virginia (Thompson et al., 1976). These early measurements used alpha particle spectroscopy to measure uranium and thorium isotope concentrations, a technique that required tens of grams of sample (Harmon et al., 1975). Many dates were obtained by multiple laboratories and a picture was framed for northern North America and northern Europe of abundant speleothem growth during the Holocene and during the Eemian (Sangamon) interglacial (isotope stage 5; 100,000–130,000 years B.P.). Relatively little growth occurred during the periods of glacier advancement (Hennig et al., 1983; Gascoyne, 1992). Although some U/Th dating by alpha-counting continues, for example, the demonstration of four episodes of speleothem deposition in level IV of the Demanova Caves in Slovakia (Hercman et al., 1997), better resolution is necessary to probe the paleoclimate records in detail. The breakthrough was the use of heavy ion mass spectroscopy to measure isotope concentrations (Li et al., 1989). More precise isotope concentrations allowed extension of the dating range from 350,000 years for alpha counting techniques to approaching the theoretical limit of about 600,000 years. Heavy ion mass spectroscopy and later accelerator mass spectroscopy also reduced the required sample size so that dates could be obtained from milligrams rather than tens of gram quantities of speleothem. Thus a stalagmite could be
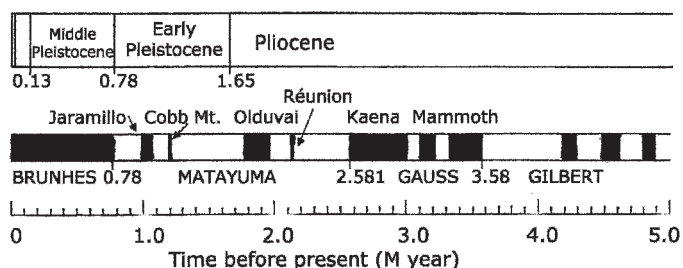
Figure 9. Geomagnetic time scale through the Pliocene. Drawn from data of Cande and Kent (1995), Berggren et al. (1995) and Singer et al. (2004). The precise dates for some of the reversal events are not in complete agreement between literature sources. Labeling at bottom gives the main paleomagnetic periods (or chrons). At top are labeled some secondary events.

sectioned along its long axis, then sampled at close intervals along the axis to obtain a complete chronology of the stalagmite's growth history.

PALEOMAGNETIC CHRONOLOGIES

The Earth's magnetic field reverses at irregular intervals during which the magnetic north pole and the magnetic south pole exchange places. Intervals where the north pole is near its present location are called normal; the other intervals are called reversed. The geophysics of the magnetic field have been extensively investigated (e.g., Channell et al., 2004) and a geomagnetic stratigraphy established well back into geologic time. The paleomagnetic time scale shown in Figure 9 has been drawn only for the past five million years since this is the time interval of most interest in karst processes.

Fine-grained clastic sediments contain small amounts of magnetic minerals. As these sediments settle, the magnetic grains rotate to orient with the Earth's magnetic field as it was at the time of the event. Once the grains have settled, their magnetic orientation is locked in place and can be determined by careful measurement of the magnetic properties of oriented samples. The measurements require very high sensitivity equipment because there are only a small number of magnetic grains and most of these have only weak magnetic moments

If paleomagnetic reversals can be identified in cave sediments, they provide time markers and thus dates for sediments and the passages in which they occur. Because of the long time spans between reversals, the method is best applied to tiered caves where the total sequence of cave passages and their sediments represent equally long times. Within a single cave passage, sediments are expected to be stacked in the usual stratigraphic fashion with the oldest sediments on the bottom. Cave passages, however, are arranged in the opposite order, with the youngest passages near present day base levels and older passages higher on the ridges (Fig. 10). This arrangement must be taken into
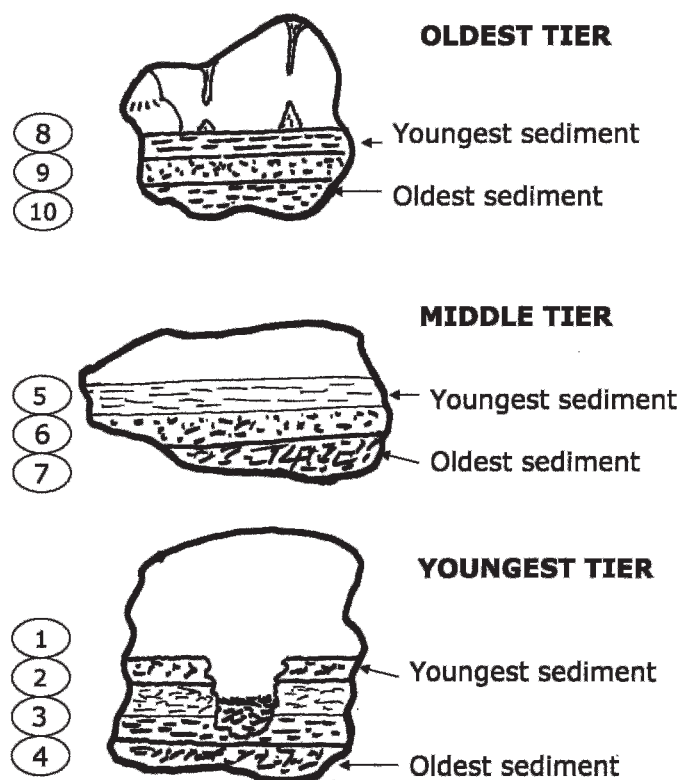

Figure 10. Sketch showing sediment stratigraphic relations in tiered caves. The schematic sediment layers are numbers from youngest to oldest, 1 to 10.

account in the interpretation of paleomagnetic data. The best samples are obtained from the slackwater facies where the sediment grains settle out in quiet water. Often what is available are the channel facies, and these may very well have been reworked by later flood events so that the paleomagnetic signals are scrambled. If a complete sedimentary sequence is not available, identification of a reversal in a sediment pile in a high-lying cave leaves open the question of which reversal is being observed.

Paleomagnetic stratigraphy has been determined for clastic sediments in Mammoth Cave (Schmidt, 1982), the caves of the Obey River Gorge in the western Cumberland Escarpment of Tennessee (Sasowsky et al., 1995), the caves of the Cheat River Gorge in West Virginia (Springer et al., 1997), and Kooken Cave, Pennsylvania (Sasowsky et al., 2004). Because of limited availability of sensitive magnetic measuring apparatus, and because the reversals provide only widely spaced time markers, this method of sediment dating has seen limited application.

COSMOGENIC ISOTOPE DATING

The Earth is under constant bombardment by cosmic rays, which are extremely energetic particles from space. These particle streams and their spallation products from collisions in the upper atmosphere, rain down on the surface where they can induce nuclear reactions in surface

materials. These reaction products are known as cosmogenic isotopes and can be used as an interpretative tool (Gosse and Phillips, 2001). The isotopes of importance for cosmogenic isotope dating of cave sediments are [10]Be (half-life = 2.18 Ma) and [26]Al (half-life = 1.02 Ma). Both are formed from the secondary cosmic ray neutron and muon bombardment of quartz, [10]Be from oxygen and [26]Al from silicon.

If quartz, either as pebbles or sand, is left exposed on or near the land surface, a certain very tiny concentration of [10]Be and [26]Al will build up. If sinking streams then wash the quartz sediment into a cave, the quartz will be shielded from cosmic rays and the accumulated [10]Be and [26]Al will begin to decay. Although the initial concentrations of the cosmogenic isotopes are not known, the ratio of the concentrations will change so that the time since burial can be extracted (Granger and Muzikar, 2001). Careful sample preparation is needed and, because concentrations are measured in millions of atoms, an accelerator mass spectrometer is needed to determine the isotope ratios.

Cosmogenic isotope dating is one of the most promising recent techniques. It covers a time scale back to 5 Ma which is the time scale for most active karst systems. The quartz that is dated is part of the channel facies sediment load and these materials are usually deposited when the cave passage is part of the active drainage system. To a reasonable approximation, the cosmogenic date of the sediment is also a measure of the age of the cave passage. By using cosmogenic isotope dating of cave sediments, it was possible to establish a rate of downcutting for rivers in the Sierra Nevada (Stock et al., 2004).

THE PALEOCLIMATIC RECORD

AVAILABLE ARCHIVES

The study of cave sediments, as has been demonstrated above, has come a long way. From a beginning of simply trying to understand why speleothems have their observed shapes and mineralogy, investigations of cave sediments are now delving into sediments as archives of critically important paleoclimatic information. Cave sediments have come into their own as the unopened history book of the Pleistocene.

Of the main classes of cave sediments listed in Figure 1, carbonate speleothems have the greatest information content. Clastic sediments appear as facies which reflect the hydraulics of the flow systems that deposited them. Previous episodes of intensive flooding can sometimes be recognized, but clastic sediments do not record much detail and do not provide much time resolution. Speleothems, in contrast, are deposited from solution and thus carry a record of texture, mineralogy, trace element content, and isotope content. Dated speleothems provide a microstratigraphy with a very high time resolution (Perrette, 1999).
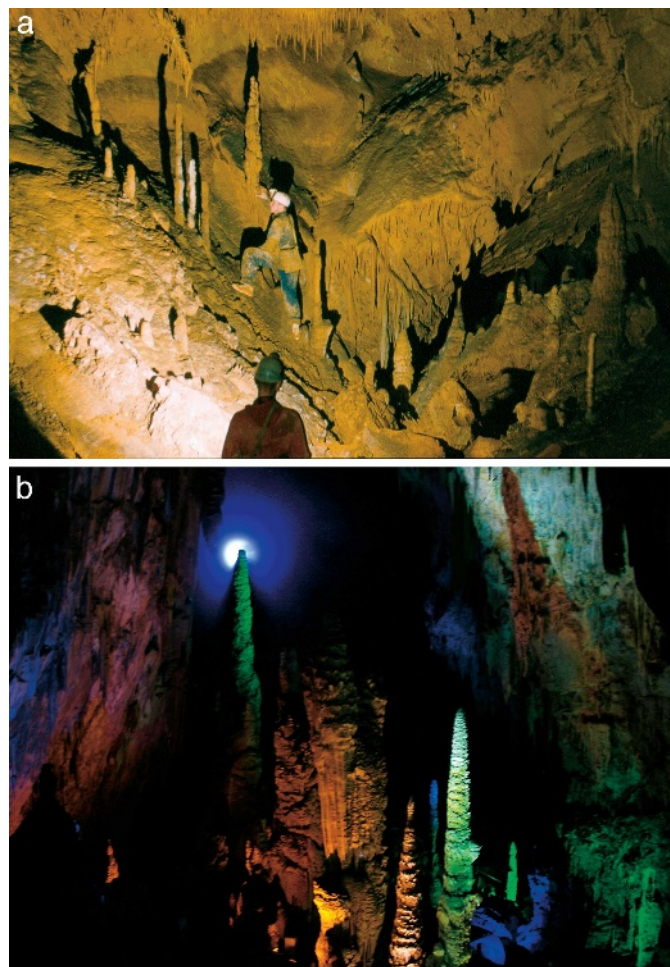
Figure 11. Cylindrical stalagmites. (a) Type of stalagmites typically sampled for paleoclimatic studies. Sites Cave, Pendleton County, W.Va. (b) Large stalagmites in Furong Cave, Chongqing Province, China.

Cylindrical (broomhandle) stalagmites are the speleothem of choice (Fig. 11a). Stalagmites grow, layer by layer, as water drips onto their tops. A stalagmite of uniform diameter is evidence of uniform growth rate over long periods of time. Uniform growth also implies uniform drip rates and uniform chemistry. Stalagmite growth rates mostly fall in the range of 0.01 to 0.1 mm y^{-1}. If there are no breaks in the growth, such stalagmites provide time spans of 100,000 years to 10,000 years per meter of stalagmite. Most stalagmites examined thus far have been less than two meters in length. Much larger stalagmites exist (Fig. 11b). Measurements on these stalagmites pose the technical problem of removing and longitudinally sawing the specimen. Speleothem work also raises a very serious ethical question: Is the scientific information obtained from the stalagmite worth the damage done to the cave in order to collect it?

Because annual growth layers in a typical stalagmite are fractions of a millimeter thick, high time resolution

depends on micro-samples and micro-analysis. With sufficient micro-sampling it is possible to construct parameter profiles along the stalagmite axis, which, of course, is also a time axis. Quantities that have been measured include:

- Oxygen isotope ratios
- Carbon isotope ratios
- Deuterium/hydrogen ratios
- Trace elements – typically Mg, Sr and Ba, and many others
- Layer-to-layer color variations (color banding)
- Layer-to-layer variations in luminescence intensity (luminescence banding)

Most widely measured are the isotope ratios for $^{18}O/^{16}O$ and $^{13}C/^{12}C$. The oxygen isotope ratio is related to temperature and is widely interpreted as a paleoclimate thermometer. However, a temperature calibration depends on speleothem deposition under conditions of isotopic equilibrium which may not be achieved (Hendy, 1971; Mickler et al., 2006). The carbon isotope ratio is related to the type of vegetation on the land surface above and has been used to distinguish forest from grassland.

Calcite speleothems appear in a variety of colors mostly ranging from white to shades of tan, orange, and brown. The most common sources of color are humic substances derived from the overlying soil (White, 1981). Likewise, speleothem calcite is usually strongly phosphorescent under long wave UV excitation due mostly to the fulvic acid fraction of the humic substances (van Beynen et al., 2001). An important discovery made in the 1980s by Yavor Shopov (Shopov et al., 1994) is that the luminescence is banded on a micrometer scale and that the individual bands represent an annual cycle. There has been a tremendous amount of interest in luminescence and color banding. These appear to be a measure of precipitation, but calibration in terms of specific climatic variables has been difficult.

There are a range of pertinent time scales and associated questions. These are dealt with individually in the following sections. For a much more complete discussion of the other paleoclimatic data into which the speleothem results are merged, see Bradley (1999).

THE PLIOCENE/EARLY TO MIDDLE PLEISTOCENE: 5 MA TO 300 ka

Much of today's landscape, including most of the caves and surface karst, has been sculptured during the past 5 Ma, that is the Pliocene, the Pleistocene and the Holocene. Near the beginning of this period the mild climate of the Eocene and Miocene gave way to a climatic cycling from warm to cold and back to warm periods. In high northern and southern latitudes and at high altitudes these cycles were accompanied by advances and retreats of glaciers. Sea level rose and fell as significant volumes of water were sequestered in continental ice sheets and later
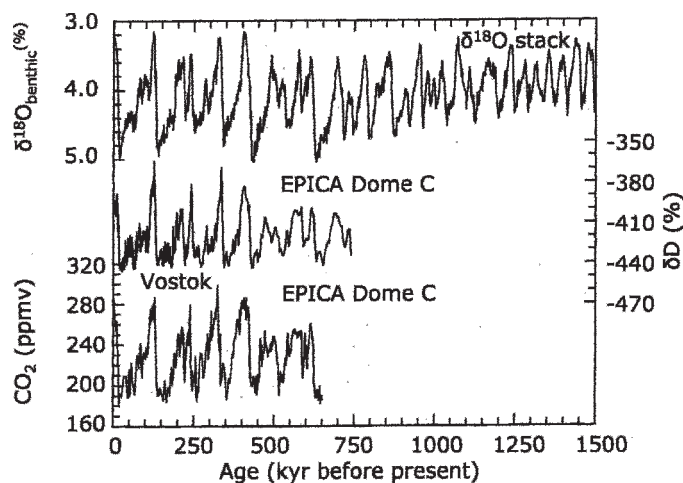

Figure 12. Climatic cycles over the past 1.5 Ma based on ice core records. From Brook et al. (2006). Oxygen isotope data are the benthic record. Vostok and Epica Dome C are ice cores from Antarctica.

released as the ice melted. The climatic oscillations occur in regular cycles: 41,000 years at the beginning of the period of oscillations and switching to a 100,000 year cycle about 800,000 years ago. The cycles are known in considerable detail because of data extracted from the long ice cores drilled in Greenland and Antarctica (Fig. 12).

Events prior to about 500,000 years are beyond the range of U/Th dating. Information from the Pliocene and Early to Middle Pleistocene must be extracted from clastic sediments which can be dated by cosmogenic isotope methods and by paleomagnetic reversals. At about the time that the 25th anniversary issue of this journal was being published, Davies' (1960) view that master trunk caves were formed close to regional base levels was becoming accepted (White and Schmidt, 1966). Fossil caves could, in principle, be dated by their relation to nearby river terraces. However, the evolution of surface valleys is destructive, with earlier valley floors and channels being dissected and lost as surface streams continue to downcut. As a result, the dating of terraces was always highly uncertain. In recent years, the situation is reversed. Cosmogenic isotope dating of clastic sediment in master trunk caves gives very accurate dates which can then be applied to the terrace level toward which the cave passage is graded.

Cosmogenic isotope dating has been used to establish a chronology for the main trunk passages in Mammoth Cave (Granger et al., 2001) and for major caves in the western Cumberland Plateau of Kentucky and Tennessee (Anthony and Granger, 2004). The caves chosen for dating span the entire time period of cave and karst development in the south-central Kentucky karst and the Appalachian plateaus. The main conclusions from these investigations are summarized in Figure 13. These studies have locked in a time scale for most cave development in the eastern

MAMMOTH CAVE	CUMBERLAND PLATEAU
	Caves graded to Highland Rim (Harrisburg Surface?) 5.7 – 3.5 Myr
Level A: Highest level passages 3.6 Myr Sediment infilling	Caves related to Parker Strath 3.5 – 2.0 Myr
Level B: Main cave in Mammoth 2.15 Myr Sediment infilling	Caves graded to stillstands in Cumberland River. 2 – 1.5 Myr
Level C: Mid-level tubes with little sediment infilling 1.55 Myr	
Level D: Smaller passages 1.45 Myr	Caves formed after 1.5 Myr
Massive regional sedimentation event at ~0.8 Myr	

Figure 13. Chronologies for caves and erosion surfaces in the Mammoth Cave area and the Cumberland Plateau. Information compiled from Granger et al. (2001) and Anthony and Granger (2004).
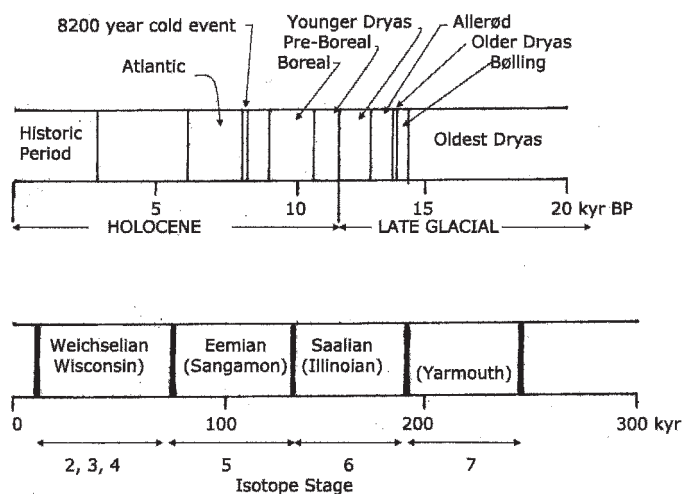

Figure 14. Sketch showing climate periods of the late Pleistocene and the Pleistocene-Holocene transitional period, the period most easily accessible to U/Th dating.

United States. By relating the oldest Cumberland Plateau caves to the dissection of the Highland Rim surface at 5.7 to 3.5 Ma, by implication, the same time scale should apply to caves related to the Harrisburg Surface in the Valley and Ridge Province of the Appalachians (White and White, 1991).

One of the events common to both Mammoth Cave and the Cumberland Plateau was a massive sediment in-filling at about 800,000 years B.P. Such a sedimentation event implies high precipitation and flooding on the land surface above. This time interval also corresponds to the transition from 41,000 year to 100,000 year climatic cycles. Whether this is merely a coincidence or whether the cave sedimentation is recording the global shift in climatic cycles should be further investigated.

THE LATE PLEISTOCENE AND THE EEMIAN INTERGLACIAL

The younger end of the Pleistocene lies in the time range for U/Th dating so that full use can be made of the speleothem records. For reference, Figure 14 gives the usual time divisions. It was a period of extensive climatic variation with both glacial and interglacial periods.

In areas of coastal karst, lowering sea levels during the glacial maxima allowed the development of air-filled caves that were then flooded when the glacial ice melted. These caves often contain speleothems which can be U/Th dated and there may be overgrowths on the speleothems that deposited after the caves re-flooded. One of the first accomplishments of U/Th dating of speleothems was to identify sea-level lowering during the Illinoian glaciation (Gascoyne et al., 1979). Sea level minima can be tracked by dating speleothems from submerged caves (Lundberg and Ford, 1994; Richards et al., 1994). Likewise sea level stands higher than present sea level can be measured by dating the overgrowths that form under phreatic conditions (Vesica et al., 2000).

Oxygen isotope profiles along Tasmanian stalagmites produced an oxygen isotope profile from the Eemian interglacial well into the Wisconsin glacial period (Goede et al., 1986; Goede et al., 1990). The profiles were interpreted in terms of temperature changes during the period of record. Deuterium/hydrogen profiles obtained by extracting fluid inclusions in dated spelethems traced temperature over the past 140 ka in the eastern Mediterranean (McGarry et al., 2004). It has long been argued that the arid regions of the Near-East were much wetter during interglacial periods. A speleothem record from Oman shows rapid calcite growth and an oxygen isotope record consistent with high rainfall at 6.5–10.5, 78–82, 120–135, 180–200, and 300–325 ka (Burns et al., 2001). An oxygen and carbon-isotope record in three stalagmites from Missouri clearly shows transitions from forest to savanna to prairie to forest through the Wisconsin glacial period, 75 to 25 ka (Dorale et al., 1998).

THE END OF THE LAST ICE AGE: EXTREME CLIMATIC OSCILLATIONS

The end of the Wisconsin ice age was a tumultuous time with some extreme climatic excursions before the climate settled into the more stable period of the Holocene. Figure 14 names these periods and gives their approximate time intervals. It should be noted that not all sources give the same time boundaries for these periods. The cold glacial climate of the Oldest Dryas gave way to a period of warming, but oscillating climate in the Bølling/Older Dryas/Allerød. At about 12,900 years B.P., according to ice core data (Alley et al., 1993), the northern climate plunged into a 1300 year cold period, the Younger Dryas, from which it emerged with an abrupt warming marking the beginning of the Holocene at 11,640 years B.P. The transition from glacial cold to pre-boreal climate appar-

ently required no more than a decade. The last gasp of the ice age was an event at 8200 years B.P., an abrupt cold snap that lasted for about 200 years. It was identified in ice cores among other records (Alley et al., 1997).

Much of the data on climatic events at the close of the last glaciation come from studies at northern latitudes. There is always the question of how these climatic excursions appeared in temperate or tropical climates or in the southern hemisphere. The intense cooling period of the Younger Dryas appeared in a speleothem record from Australia (Goede et al., 1996). Climatic fluctuations appeared in speleothem records from New Zealand (Williams et al., 2004). Speleothem texture combined with trace element concentrations and heavy metal isotopes were used to sort out wet/dry and warm/cool periods in the Soreq Cave, Israel (Ayalon et al., 1999).

In the American Southwest, there was the onset of a wet climate at 12,500 years B.P. near the beginning of the Younger Dryas. Based on stalagmite growth as dated by U/Th methods, the wet period persisted about 2000 years taking it into beginning of the Holocene and ending at 10,500 years B.P. when the climate shifted to the present arid regime (Polyak et al., 2004). The 8200 year B.P. event appeared as a weakened monsoon in tropical Costa Rica according to speleothem data (Lachniet et al., 2004). It was also found as an anomaly in trace element profiles in a stalagmite from Crag Cave, southwestern Ireland (Baldini et al., 2002)

THE HOLOCENE: 11,650 YEARS TO PRESENT

There were climatic fluctuations during the Holocene, but these were generally less pronounced than those at the end of the glacial period. The Holocene is usually considered to extend from a beginning at 11,500 to 11,700 years B.P. (variably stated in different sources) to the present. The beginning date given above is from Alley et al. (1993). Shifts in climate as reflected in the oxygen isotope profiles of dated speleothems have been measured for Europe (McDermott et al., 1999), Israel (Frumkin et al., 1999), southern Africa (Lee-Thorpe et al., 2001), and China (Wang et al., 2005; Zhang et al., 2004).

A series of studies of carbon isotopes from a variety of caves in the American Midwest has allowed the tracking of vegetation over the course of the Holocene (R.G. Baker et al., 1998; Denniston et al., 1999a; Denniston et al., 1999b; Denniston et al., 2000b). Nearly all trees, shrubs, and cool-season grasses preferentially are enriched in the ^{12}C isotope (C_3 vegetation) whereas grasslands (C_4 vegetation) contain more of the ^{13}C isotope. A pattern of shifts from forest to grassland and back to forest has been documented, but the timing of the shifts varies with location. Generally, there is good agreement with pollen records.

Measurement of $^{87}Sr/^{86}Sr$ ratios in a speleothem from Harrison's Cave, Barbados, showed a systemic change through the Holocene (Banner et al., 1996). This record correlates with rainfall.
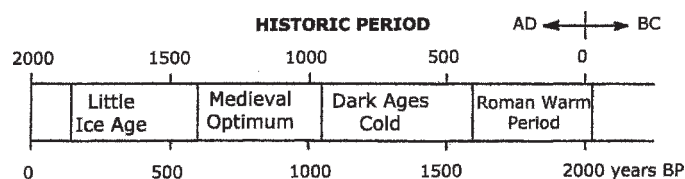

Figure 15. Sketch showing climate periods for the historical period as recorded in Europe. The boundaries are not sharp and vary somewhat between regions.

THE HISTORIC PERIOD: THE PAST SEVERAL THOUSAND YEARS OF THE HOLOCENE

An issue of national and international importance at the time of this writing is that of global warming. It seems that on the average, winters have become warmer, summers hotter, glaciers are retreating, hurricanes have increased intensity, and sea levels are rising. On one side are those who assign these changes to a greenhouse effect brought on by the anthropogenic increase in carbon dioxide and other greenhouse gases in the atmosphere. On the other side are some who assert that the whole idea of human-induced global warming is a myth and that these fluctuations are part of a natural cycle. The implications are enormous. Prolonged warming sufficient to melt the Greenland and Antarctic ice caps (as well as other glacial ice) would raise sea levels, shift ocean currents, drown coastal cities, and change atmospheric circulation patterns so that productive farm lands might become dust bowls. Are human beings creating a disaster or are we simply riding yet another climatic cycle, this one on a centuries time scale?

Climate has indeed oscillated over the past several millennia with a period of oscillation of several centuries (Fig. 15). The warm climates during the flowering of the Roman Empire gave way to cold climates in Europe during what is known as the Dark Ages. Climate warmed again during the Medieval period and then shifted into what historically has been called the Little Ice Age. Since the late 19th Century, climate in North America and Europe has been warming. The "grandfather winters" are fading from memory.

There is some accumulating evidence that these more subtle recent climatic events can be teased from the speleothem record. Spikes in the ^{13}C record in a stalagmite from Belize over a 30 year period from 1970 to 2000 correlated with the southern oscillation index – a measure of El Niño events (Frappier et al., 2002). Oxygen isotope profiles taken from three stalagmites from a cave in southern Oman provided a 780 year record of monsoon activity. The record revealed the transition from the Medieval Warm Period to the Little Ice Age at AD 1320 (Fleitmann et al., 2004). Speleothem records from South Africa indicate that the Little Ice Age, which extended from roughly AD 1300 to 1800, was about 1 °C cooler than present while the Medieval Warm Period may have been 3 °C warmer (Tyson et al., 2000). The boldest proposal has

been to calculate a 3000 year temperature record from stalagmite color banding from South Africa (Holmgren et al., 2001). What is needed, and what more accurately calibrated speleothem records may provide, is an assessment of whether the present day warming is comparable to other warm periods of the past several millennia, or whether we are entering a new, and possibly quite dangerous, climatic regime.

CONCLUSIONS

Cave sediments have the potential for providing detailed paleoclimate archives with value comparable to ice cores and deep sea sediment cores. Techniques for establishing accurate dates on high resolution records in speleothems are in place for the time scale from the late Pleistocene to the present. Cosmogenic isotope dating of clastic sediments extends the measurable time scale back to the early Pliocene but with much less time resolution. The problem remains of establishing reliable relationships between measurable parameters, trace element profiles, isotope profiles, color and luminescence profiles, and the actual climatic variables for which the measurements are a proxy (McDermott, 2004).

Climate, as recorded in cave sediments, is very much a matter of the local climate in the immediate vicinity of the cave. In order to obtain a broader regional or even global picture of climate at some time interval, many more data are needed. Cave sediment – paleoclimate studies are in their infancy.

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REFERENCES

Alley, R.B., Meese, D.A., Shuman, C.A., Gow, A.J., Taylor, K.C., Grootes, P.M., White, J.W.C., Ram, M., Waddingon, E.D., Mayewski, P.A., and Zielinski, G.A., 1993, Abrupt increase in Greenland snow accumulation at the end of the Younger Dryas event: Nature, v. 362, p. 527–529.

Alley, R.B., Mayewski, P.A., Sowers, T., Stuiver, M., Taylor, K.C., and Clark, P.U., 1997, Holocene climatic stability: A prominent widespread event 8200 yr ago: Geology, v. 25, p. 483–486.

Amraoui, F., Razack, M., and Bouchaou, L., 2003, Turbidity dynamics in karstic systems: Example of Ribaa and Bittit springs in the Middle Atlas (Morocco): Hydrological Sciences Journal, v. 48, p. 971–984.

Andrews, J.E., 2006, Palaeoclimatic records from stable isotopes in riverine tufas: Synthesis and review: Earth-Science Reviews, v. 75, p. 85–104.

Anthony, D.M., and Granger, D.E., 2004, A late Tertiary origin for multilevel caves along the western escarpment of the Cumberland Plateau, Tennessee and Kentucky established by cosmogenic [26]Al and [10]Be: Journal of Cave and Karst Studies, v. 66, p. 46–55.

Atteia, O., Perret, D., Adatte, T., Kozel, R., and Rossi, P., 1998, Characterization of natural colloids from a river and spring in a karstic basin: Environmental Geology, v. 34, p. 257–269.

Ayalon, A., Bar-Matthews, M., and Kaufman, A., 1999, Petrography, strontium, barium and uranium concentrations, and strontium and uranium isotope ratios in speleothems as palaeoclimatic proxies: Soreq Cave, Israel: The Holocene, v. 9, p. 715–722.

Baker, A., Genty, D., Dreybrodt, W., Barnes, W.L., Mockler, N.J., and Grapes, J., 1998, Testing theoretically predicted stalagmite growth rate with Recent annually laminated samples: Implications for past stalagmite deposition: Geochimica et Cosmochimica Acta, v. 62, p. 393–404.

Baker, R.G., Gonzalez, L.A., Raymo, M., Bettis, III, E.A., Reagan, M.K., and Dorale, J.A., 1998, Comparison of multiple proxy records of Holocene environments in the midwestern United States: Geology, v. 26, p. 1131–1134.

Baldini, J.U.L., McDermott, F., and Fairchild, I.J., 2002, Structure of the 8200-year cold event revealed by a speleothem trace element record: Science, v. 296, p. 2203–2206.

Banner, J.L., Musgrove, M.L., Asmerom, Y., Edwards, R.L., and Hoff, J.A., 1996, High-resolution temporal record of Holocene groundwater chemistry: Tracing links between climate and hydrology: Geology, v. 24, p. 1049–1053.

Berggren, W.A., Kent, D.V., Swisher, III, C.C., and Aubry, M.-P., 1995, A revised Cenozoic geochronology and chronostratigraphy, in Berggren, W.A., Kent, D.V., Aubry, M.P., and Hardenbol, J., eds., Geochronology: Time scales and global stratigraphic correlation, Society of Sedimentary Geology Special Publication 54, p. 129–212.

Berner, R.A., 1975, The role of magnesium in the crystal growth of calcite and aragonite from sea water: Geochimica et Cosmochimica Acta, v. 39, p. 489–504.

Bögli, A., 1980, Karst hydrology and physical speleology: Berlin, Springer-Verlag, 294 p.

Bosch, R.F., and White, W.B., 2004, Lithofacies and transport of clastic sediments in karstic aquifers, in Sasowsky, I.D., and Mylroie, J.E., eds., Studies of cave sediments: New York, Kluwer Academic/Plenum Publishers, p. 1–22.

Bradley, R.S., 1999, Paleoclimatology, 2nd ed.: San Diego, Academic Press, 613 p.

Bretz, J H., 1942, Vadose and phreatic features of limestone caverns: The Journal of Geology, v. 50, p. 675–811.

Brook, E.J., Dahl-Jensen, D., Fischer, H., and Steig, E.J., 2006, The future of ice coring: International partnerships in ice core sciences (IPICS): PAGES News, v. 14, p. 6–10.

Brook, G.A., Rafter, M.A., Railsback, L.B., Sheen, S.-W., and Lundberg, J., 1999, A high-resolution proxy record of rainfall and ENSO since AD 1550 from layering in stalagmites from Anjohibe Cave, Madagascar: The Holocene, v. 9, p. 695–705.

Bull, P.A., 1980, Towards a reconstruction of time-scales and palaeoenvironments from cave sediment studies, in Cullingford, R.A., Davidson, D.A., and Lewin, J., Timescales in geomorphology: London, John Wiley, p. 177–187.

Bull, P.A., 1981, Some fine-grained sedimentation phenomena in caves: Earth Surface Processes and Landforms, v. 6, p. 11–22.

Burns, S.J., Fleitmann, D., Matter, A., Neff, U., and Mangini, A., 2001, Speleothem evidence from Oman for continental pluvial events during interglacial periods: Geology, v. 29, p. 623–626.

Cande, S.C., and Kent, D.V., 1995, Revised calibration of the geomagnetic polarity timescale for the late Cretaceous and Cenozoic: Journal of Geophysical Research, v. 100, p. 6093–6095.

Carlson, W.D., 1983, The polymorphs of $CaCO_3$ and the aragonite-calcite transformation: Reviews in Mineralogy, v. 11, p. 191–225.

Channell, J.E.T., Kent, D.V., Lowrie, W., and Meert, J.G., 2004, Timescales of the paleomagnetic field: Geophysical Monograph 145, American Geophysical Union, 320 p.

Davies, W.E., 1960, Origin of caves in folded limestone: National Speleological Society Bulletin, v. 22, p. 5–29.

Davis, K.J., Dove, P.M., and De Yoreo, J.J., 2000, The role of Mg^{2+} as an impurity in calcite growth: Science, v. 290, p. 1134–1137.

Dell'Oca, S., 1961, Riempimenti naturali di grotte: Como, Italy, Rassegna Speleologica Italiana, 277 p.

Denniston, R.F., Gonzalez, L.A., Semken, Jr., H.A., Asmerom, Y., Baker, R.G., Recelli-Snyder, H., Reagan, M.K., and Bettis III, E.A., 1999a, Integrating stalagmite, vertebrate, and pollen sequences to investigate

Holocene vegetation and climate change in the southern midwestern United States: Quaternary Research, v. 52, p. 381–387.

Denniston, R.F., Gonzalez, L.A., Baker, R.G., Asmerom, Y., Reagan, M.K., Edwards, R.L., and Alexander, Jr., E.C., 1999b, Speleothem evidence for Holocene fluctuations of the prairie-forest ecotone, north-central USA: The Holocene, v. 9, p. 671–676.

Denniston, R.F., Gonzalez, L.A., Asmerom, Y., Sharma, R.H., and Reagan, M.K., 2000a, Speleothem evidence for changes in Indian summer monsoon precipitation over the last ~2300 years: Quaternary Research, v. 53, p. 196–202.

Denniston, R.F., Gonzalez, L.A., Asmerom, Y., Reagan, M.K., and Recelli-Snyder, H., 2000b, Speleothem carbon isotopic records of Holocene environments in the Ozark Highlands, USA: Quaternary International, v. 67, p. 21–27.

Dogwiler, T., and Wicks, C.M., 2004, Sediment entrainment and transport in fluviokarst systems: Journal of Hydrology, v. 295, p. 163–172.

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, v. 282, p. 1871–1874.

Dorale, J.A., Edwards, R.L., Alexander, Jr., E.C., Shen, C.-C., Richards, D.A., and Cheng, H., 2004, Uranium dating of speleothems: Current techniques, limits and applications, in Sasowsky, I.D., and Mylroie, J.E., eds., Studies of cave sediments: New York, Kluwer-Academic/Plenum, p. 177–226.

Drever, J.I., 1997, The geochemistry of natural waters, 3rd ed.: Upper Saddle River, N.J., Prentice Hall, 436 p.

Drysdale, R., Pierotti, L., Piccini, L., and Baldacci, F., 2001, Suspended sediments in karst spring waters near Massa (Tuscany), Italy: Environmental Geology, v. 40, p. 1037–1050.

Field, M.F., 2007, Risks to cavers and cave workers from exposures to low-level ionizing α radiation from ^{222}Rn decay in caves: Journal of Cave and Karst Studies, [this issue].

Fleitmann, D., Burns, S.J., Neff, U., Mudelsee, M., Mangini, A., and Matter, A., 2004, Palaeoclimatic interpretation of high-resolution oxygen isotope profiles derived from annually laminated speleothems from Southern Oman: Quaternary Science Reviews, v. 23, p. 935–945.

Ford, D.C., and Williams, P.W., 1989, Karst geomorphology and hydrology: London, Unwin-Hyman, 601 p.

Ford, T.D., and Pedley, H.M., 1996, A review of tufa and travertine deposits of the world: Earth-Science Reviews, v. 41, p. 117–175.

Frank, R.M., 1965, Petrologic study of sediments from selected central Texas caves: [M.A. thesis]: Austin, The University of Texas, 116 p.

Frank, R.M., 1969, The clastic sediments of Douglas Cave, Stuart Town, New South Wales: Helictite, v. 7, p. 3–13.

Frank, R.M., 1971, The clastic sediments of the Wellington Caves, New South Wales: Helictite, v. 9, p. 3–26.

Frappier, A., Sahagian, D., Gonzalez, L.A., and Carpenter, S.J., 2002, El Niño events recorded by stalagmite carbon isotopes: Science, v. 298, 565 p.

Frisia, S., Borsato, A., Fairchild, I.J., and McDermott, F., 2000, Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and southwestern Ireland: Journal of Sedimentary Research, v. 70, p. 1183–1196.

Frumkin, A., Carmi, I., Gopher, A., Ford, D.C., Schwarcz, H.P., and Tsuk, T., 1999, A Holocene millennial-scale climatic cycle from a speleothem in Nahal Qanah Cave, Israel: The Holocene, v. 9, p. 677–682.

Gale, S.J., 1984, The hydraulics of conduit flow in carbonate aquifers: Journal of Hydrology, v. 70, p. 309–327.

Gascoyne, M., 1992, Palaeoclimate determination from cave calcite deposits: Quaternary Science Reviews, v. 11, p. 609–632.

Gascoyne, M., Benjamin, G.J., Schwarcz, H.P., and Ford, D.C., 1979, Sea-level lowering during the Illinoian glaciation: Evidence from a Bahama "blue hole": Science, v. 205, p. 806–808.

Gillieson, D., 1986, Cave sedimentation in the New Guinea highlands: Earth Surface Processes and Landforms, v. 11, p. 533–543.

Gillieson, D., 1996, Caves: processes, development, management: Oxford, Blackwell, 324 p.

Goede, A., Green, D.C., and Harmon, R.S., 1986, Late Pleistocene palaeotemperature record from a Tasmanian speleothem: Australian Journal of Earth Sciences, v. 33, p. 333–342.

Goede, A., Veeh, H.H., and Ayliffe, L.K., 1990, Late Quaternary palaeotemperature records for two Tasmanian speleothems: Australian Journal of Earth Sciences, v. 37, p. 267–278.

Goede, A., McDermott, F., Hawkesworth, C., Webb, J., and Finlayson, B., 1996, Evidence of Younger Dryas and neoglacial cooling in a Late Quaternary palaeotemperature record from a speleothem in eastern Victoria, Australia: Journal of Quaternary Science, v. 11, p. 1–7.

Gosse, J.C., and Phillips, F.M., 2001, Terrestrial in situ cosmogenic nuclides: theory and application: Quaternary Science Reviews, v. 20, p. 1475–1560.

Granger, D.E., and Muzikar, P.F., 2001, Dating sediment burial with in situ-produced cosmogenic nuclides: theory, techniques and limitations: Earth and Planetary Science Letters, v. 188, p. 269–281.

Granger, D.E., Fabel, D., and Palmer, A.N., 2001, Pliocene – Pleistocene incision of the Green River, Kentucky determined from radioactive decay of cosmogenic ^{26}Al and ^{10}Be in Mammoth Cave sediments: Geological Society of America Bulletin, v. 113, p. 825–836.

Gutjahr, A., Dabringhaus, H., and Lacmann, R., 1996, Studies of the growth and dissolution kinetics of the $CaCO_3$ polymorphs calcite and aragonite. I. Growth and dissolution rates in water: Journal of Crystal Growth, v. 158, p. 296–309.

Harmon, R.S., Thompson, P., Schwarcz, H.P., and Ford, D.C., 1975, Uranium-series dating of speleothems: National Speleological Society Bulletin, v. 37, p. 21–33.

Hart, E.A., and Schurger, S.G., 2005, Sediment storage and yield in an urbanized karst watershed: Geomorphology, v. 70, p. 85–96.

Hendy, C.H., 1971, The isotopic geochemistry of speleothems – I. 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, v. 35, p. 801–824.

Hennig, G.J., Grün, R., and Brunnacker, K., 1983, Speleothems, travertines, and paleoclimates: Quaternary Research, v. 20, p. 1–29.

Hercman, H., Bella, P., Glazek, J., Gradzinski, M., Lauritzen, S.E., and Løvlie, R., 1997, Uranium series dating of speleothems from Demänova Ice Cave: A step to age estimation of the Demänova Cave System (The Nizke Tatry Mts., Slovakia): Annales Societatis Geologorum Poloniae, v. 67, p. 439–450.

Hill, C.A., 1976, Cave minerals: Huntsville, Ala., National Speleological Society, 137 p.

Hill, C.A., 1987, Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas: New Mexico Bureau of Mines and Mineral Resources Bulletin 117, 150 p.

Hill, C.A., 1990, Sulfuric acid speleogenesis of Carlsbad Cavern and its relationship to hydrocarbons, Delaware Basin, New Mexico and Texas: American Association of Petroleum Geologists Bulletin, v. 74, p. 1685–1694.

Hill, C.A., and Forti, P., 1997, Cave minerals of the world, 2nd ed.: Huntsville, Ala., National Speleological Society, 463 p.

Holland, H.D., Kirsipu, T.V., Huebner, J.S., and Oxburgh, U.M., 1964, On some aspects of the chemical evolution of cave waters: Journal of Geology, v. 72, p. 36–67.

Holmgren, K., Lauritzen, S.-E., and Possnert, G., 1994, ^{234}Th/^{234}U and ^{14}C dating of a late Pleistocene stalagmite in Lobatse II Cave, Botswana: Quaternary Science Reviews, v. 13, p. 111–119.

Holmgren, K., Tyson, P.D., Moberg, A., and Svanered, O., 2001, A preliminary 3000-year regional temperature reconstruction for South Africa: South African Journal of Science, v. 97, p. 49–51.

Jameson, R.A., 1991, Concept and classification of cave breakdown: An analysis of patterns of collapse in Friars Hole Cave System, West Virginia, in Kastning, E.H., and Kastning, K.M., eds., Appalachian Karst: Huntsville, Ala., National Speleological Society, p. 35–44.

Jennings, J.N., 1971, Karst: Cambridge, Mass., The M.I.T. Press, 252 p.

Kaufmann, G., 2003, Stalagmite growth and palaeo-climate: the numerical perspective: Earth and Planetary Science Letters, v. 214, p. 251–266.

Kyrle, G., 1923, Grundriss der theoretischen Speläologie: Wien, Austria, Österreichischen Staatsdruckerei, 353 p.

Lachniet, M.S., Asmerom, Y., Burns, S.J., Patterson, W.P., Polyak, V.J., and Seltzer, G.O., 2004, Tropical response to the 8200 yr B.P. cold event? Speleothem isotopes indicate a weakened early Holocene monsoon in Costa Rica: Geology, v. 32, p. 957–960.

Langmuir, D., 1997, Aqueous environmental geochemistry: Upper Saddle River, N.J., Prentice Hall, 600 p.

Langmuir, D., and Melchior, D., 1985, The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas: Geochimica et Cosmochimica Acta, v. 49, p. 2423–2432.

Lee-Thorp, J.A., Holmgren, K., Lauritzen, S.-E., Linge, H., Moberg, A., Partridge, T.C., Stevenson, C., and Tyson, P.D., 2001, Rapid climate shifts in the southern African interior through the mid to late Holocene: Geophysical Research Letters, v. 28, p. 4507–4510.

Li, W.-X., Lundberg, J., Dickin, A.P., Ford, D.C., Schwarcz, H.P., McNutt, R., and Williams, D., 1989, High precision mass-spectrometric uranium-series dating of cave deposits and implications for palaeoclimate studies: Nature, v. 339, p. 534–536.

Lundberg, J., and Ford, D.C., 1994, Late Pleistocene sea level change in the Bahamas from mass spectrometric U-series dating of submerged speleothem: Quaternary Science Reviews, v. 13, p. 1–14.

Mahler, B.J., and Lynch, F.L., 1999, Muddy waters: temporal variation in sediment discharging from a karst spring: Journal of Hydrology, v. 214, p. 165–178.

Mahler, B.J., Personné, J.-C., Lods, G.F., and Drogue, C., 2000, Transport of free and particulate-associated bacteria in karst: Journal of Hydrology, v. 238, p. 179–193.

Massei, N., Wang, H.Q., Dupont, J.P., Rodet, J., and Laignel, B., 2003, Assessment of direct transfer and resuspension of particles during turbid floods at a karstic spring: Journal of Hydrology, v. 275, p. 109–121.

McDermott, F., Frisia, S., Huang, Y., Longinelli, A., Spiro, B., Heaton, T.H.E., Hawkesworth, C.J., Borsato, A., Keppens, E., Fairchild, I.J., van der Borg, K., Verheyden, S., and Selmo, E., 1999, Holocene climate variability in Europe: Evidence from $\delta^{18}O$, textural and extension-rate variations in three speleothems: Quaternary Science Reviews, v. 18, p. 1021–1038.

McDermott, F., 2004, Paleo-climate reconstruction from stable isotope variations in speleothems: a review: Quaternary Science Reviews, v. 23, p. 901–918.

McGarry, S., Bar-Matthews, M., Matthews, A., Vaks, A., Schilman, B., and Ayalong, A., 2004, Constraints on hydrological and paleotemperature variations in the eastern Mediterranean region in the last 140 ka given by the δD values of speleothem fluid inclusions: Quaternary Science Reviews, v. 23, p. 919–934.

Mickler, P.J., Stern, L.A., and Banner, J.L., 2006, Large kinetic isotope effects in modern speleothems: Geological Society of America Bulletin, v. 117.

Morse, J.W., and Arvidson, R.S., 2002, The dissolution kinetics of major sedimentary carbonate minerals: Earth-Science Reviews, v. 58, p. 51–84.

Northup, D.E., and Lavoie, K.H., 2001, Geomicrobiology of caves: A review: Geomicrobiology Journal, v. 18, p. 199–222.

Onac, B.P., Pedersen, R.B., and Tysseland, M., 1997, Presence of rare-earth elements in black ferromanganese coating from Vântului Cave (Romania): Journal of Cave and Karst Studies, v. 59, p. 128–131.

Perrette, Y., 1999, Les stalagmites: archives environnementales et climatiques à haute resolution: Karstologia, no. 34, p. 23–44.

Polyak, V.J., McIntosh, W.C., Güven, N., and Provencio, P., 1998, Age and origin of Carlsbad Cavern and related caves from $^{40}Ar/^{39}Ar$ of alunite: Science, v. 279, p. 1919–1922.

Polyak, V.J., Rasmussen, J.B.T., and Asmerom, Y., 2004, Prolonged wet period in the southwestern United States through the Younger Dryas: Geology, v. 32, p. 5–8.

Prinz, W., 1908, Les cristallisations des grottes de Belgique: Nouveaux Mémoires de la Société belge de géologie, de paleontology et d'hydrologie, Ser. 4, 90 p. (English translation in Cave Geology, v. 1, p. 191–258, 1980).

Qin, Y., Tan, M., Liu, T., Wang, X., Li, T., and Lu, J., 1999, Spectral analysis of a 1000-year stalagmite lamina-thickness record from Shihua Cavern, Beijing, China, and its climatic significance: The Holocene, v. 9, p. 689–694.

Racoviță, G., and Onac, B.P., 2000, Scărişoara Glacier Cave: Cluj-Napoca, Romania, Editura Carpatica, 139 p.

Reams, M.W., 1968, Cave sediments and the geomorphic history of the Ozarks [Ph.D. thesis]: St. Louis, Mo., Washington University, 167 p.

Reddy, M.M., Plummer, L.N., and Busenberg, E., 1981, Crystal growth of calcite from calcium bicarbonate solutions at constant P_{CO2} and 25 °C: A test of a calcite dissolution model: Geochimica et Cosmochimica Acta, v. 45, p. 1281–1289.

Renault, P., 1967–1969, Contribution a l' etude des actions mécaniques et sédimentologiques dans la spéléogenèse: Annales de Spéléologie, Introduction, v. 22, p. 5–17. I Les actions mécaniques a l'échelle du massif, v. 22, p. 209–267; II Les effets mécaniques a l'échelle de la cavité, v. 23, p. 259–307; III Les facteurs sédimentologiques, v. 23, p. 529–596; Répertoire Géographique, v. 24, p. 317–337.

Richards, D.A., Smart, P.L., and Edwards, R.L., 1994, Maximum sea levels for the last glacial period from U-series ages of submerged speleothems: Nature, v. 367, p. 357–360.

Richards, D.A., and Dorale, J.A., 2003, Uranium-series chronology and environmental applications of speleothems: Reviews in Mineralogy and Geochemistry, v. 52, p. 407–460.

Richter, D.K., Götte, T., Niggemann, S., and Wurth, G., 2004, REE^{3+} and Mn^{2+} activated cathodoluminescence in late glacial and Holocene stalagmites of central Europe: evidence for climatic processes?: The Holocene, v. 14, p. 759–767.

Sasowsky, I.D., Schmidt, V.A., and White, W.B., 1995, Determination of stream-incision rate in the Appalachian plateaus by using cave-sediment magnetostratigraphy: Geology, v. 23, p. 415–418.

Sasowsky, I.D., Clotts, R.A., Crowell, B., Walko, S.M., LaRock, E.J., and Harbert, W., 2004, Paleomagnetic analysis of a long-term sediment trap, Kooken Cave, Huntingdon County, Pennsylvania, USA, in Sasowsky, I.D., and Mylroie, J.E., eds., Studies of cave sediments: New York, Kluwer Academic/Plenum, p. 71–81.

Sasowsky, I.D., and Mylroie, J.E., 2004, Studies of cave sediments: New York, Kluwer Academic/Plenum Publishers, 329 p.

Schmid, E., 1958, Höhlenforschung und Sedimentanalyse: Schriften des Institutes für Ur- und Frühgeschichte der Schweiz, no. 13, 186 p.

Schmidt, V.A., 1982, Magnetostratigraphy of sediments in Mammoth Cave, Kentucky: Science, v. 217, p. 827–829.

Shaw, T.R., 1992, History of Cave Science: Broadway, New South Wales, Australia, Sydney Speleological Society, 338 p.

Shopov, Y.Y., Ford, D.C., and Schwarcz, H.P., 1994, Luminescent microbanding in speleothems: High-resolution chronology and paleoclimate: Geology, v. 22, p. 407–410.

Singer, B.S., Brown, L.L., Rabassa, J.O., and Guillou, H., 2004, $^{40}Ar/^{39}Ar$ chronology of Late Pliocene and Early Pleistocene geomagnetic and glacial events in southern Argentina, in Channell, J.E.T., Kent, D.V., Lowrie, W., and Meert, J.G., eds., Timescales of the paleomagnetic field: Geophysical Monograph 145, American Geophysical Union, p. 175–190.

Springer, G.S., and Kite, J.S., 1997, River-derived slackwater sediments in caves along Cheat River, West Virginia: Geomorphology, v. 18, p. 91–100.

Springer, G.S., Kite, J.S., and Schmidt, V.A., 1997, Cave sedimentation, genesis, and erosional history in the Cheat River Canyon, West Virginia: Geological Society of America Bulletin, v. 109, p. 524–532.

Stock, G.M., Anderson, R.S., and Finkel, R.C., 2004, Pace of landscape evolution in the Sierra Nevada, California revealed by cosmogenic isotope dating of cave sediments: Geology, v. 32, p. 193–196.

Sweeting, M.M., 1972, Karst landforms: London, Macmillan, 362 p.

Taylor, R.A., Long, A., and Kra, R.S., eds., 1992, Radiocarbon after four decades: New York, Springer-Verlag, 596 p.

Tebo, B.M., Ghiorse, W.C., van Waasbergen, L.G., Siering, P.L., and Caspi, R., 1997, Bacterially mediated mineral formation: Insights into manganese (II) oxidation from molecular genetic and biochemical studies: Review of Mineralogy, v. 35, p. 225–266.

Teng, H.H., Dove, P.M., and De Yoreo, J.J., 2000, Kinetics of calcite growth: Surface processes and relationships to macroscopic rate laws: Geochimica et Cosmochimica Acta, v. 64, p. 2255–2266.

Thompson, P., Schwarcz, H.P., and Ford, D.C., 1976, Stable isotope geochemistry, geothermometry and geochronology of speleothems from West Virginia: Geological Society of America Bulletin, v. 87, p. 1730–1738.

Trombe, F., 1952, Traité de spéléologie: Paris, France, Payot, 376 p.

Tyson, P.D., Karlén, W., Holmgren, K., and Heiss, G.A., 2000, The Little Ice Age and medieval warming in South Africa: South African Journal of Science, v. 96, p. 121–126.

Van Beynen, P., Bourbonniere, R., Ford, D.C., and Schwarcz, H.P., 2001, Causes of colour and fluorescence in speleothems: Chemical Geology, v. 175, p. 319–341.

Vesica, P.L., Tuccimei, P., Turi, B., Fornós, J.J., Ginés, A., and Ginés, J., 2000, Late Pleistocene paleoclimates and sea-level change in the

Mediterranean as inferred from stable isotope and U-series studies of overgrowths on speleothems, Mallorca, Spain: Quaternary Science Reviews, v. 19, p. 865–879.

Vesper, D.J., and White, W.B., 2003, Metal transport to karst springs during storm flow: An example from Fort Campbell, Kentucky/Tennessee, U.S.A.: Journal of Hydrology, v. 276, p. 20–36.

Wang, Y.-J., Cheng, H., Edwards, R.L., He, Y.-Q., Kong, X.-G., An, Z.-S., Wu, J.-Y., Kelly, M.J., Dykoski, C.A., and Li, X.-D., 2005, The Holocene Asian monsoon: Links to solar changes and North Atlantic Climate: Science, v. 308, p. 854–857.

White, E.L., and White, W.B., 1969, Processes of cavern breakdown: National Speleological Society Bulletin, v. 31, p. 83–96.

White, W.B., 1981, Reflectance spectra and color in speleothems: National Speleological Society Bulletin, v. 44, p. 20–26.

White, W.B., 1988, Geomorphology and hydrology of karst terrains: New York, Oxford University Press, 464 p.

White, W.B., 1997, Thermodynamic equilibrium, kinetics, activation barriers, and reaction mechanisms for chemical reactions in karst terrains: Environmental Geology, v. 30, p. 46–58.

White, W.B., and Schmidt, V.A., 1966, Hydrology of a karst area in east-central West Virginia: Water Resources Research, v. 2, p. 549–560.

White, W.B., Scheetz, B.E., Atkinson, S.D., Ibberson, D., and Chess, C.A., 1985, Mineralogy of Rohrer's Cave, Lancaster County, Pennsylvania: National Speleological Society Bulletin, v. 47, p. 17–27.

White, W.B., and White, E.L., 1991, Karst erosion surfaces in the Appalachian Highlands, in Kastning, E.H., and Kastning, K.M., eds., Appalachian karst: Huntsville, Ala., National Speleological Society, p. 1–10.

Williams, P.W., King, D.N.T., Zhao, J.-X., and Collerson, K.D., 2004, Speleothem master chronologies: combined Holocene ^{18}O and ^{13}C records from the North Island of New Zealand and their palaeoenvironmental interpretation: The Holocene, v. 14, p. 194–208.

Wolfe, T.E., 1973, Sedimentation in karst drainage basins along the Allegheny Escarpment in southeastern West Virginia, U.S.A. [Ph.D. thesis]: Toronto, McMaster University, 455 p.

Zhang, M., Yuan, D.-X., Lin, Y., Qin, J., Bin, L., Cheng, H., and Edwards, R.L., 2004, A 6000-year high-resolution climatic record from a stalagmite in Xiangshui Cave, Guilin, China: The Holocene, v. 14, p. 697–702.