

PETROGRAPHIC AND GEOCHEMICAL SCREENING OF SPELEOTHEMS FOR U-SERIES DATING: AN EXAMPLE FROM RECRYSTALLIZED SPELEOTHEMS FROM WADI SANNUR CAVERN, EGYPT

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Petrographic and geochemical analyses of four speleothems from Wadi Sannur Cavern in eastern Egypt show that petrography and geochemistry can provide a useful way to screen speleothems prior to dating via U-series analysis. The speleothems vary from inclusion-rich zoned calcite to clear featureless calcite. U concentrations (ranging from 0.01-2.65 ppm) and Sr concentrations (ranging from 0.00-0.11 wt%) are greater in inclusion-rich zoned calcite. U concentrations are also greater in speleothems with small (<1.2 mm wide) columnar calcite crystals than in speleothems with larger crystals. Mg concentrations in the speleothems range from 0.2-2.3 mol% MgCO₃ and show no significant relationship to petrography at the microscopic scale. Geochemical considerations suggest that the Wadi Sannur speleothems were originally mostly aragonite, and that all four have undergone recrystallization. More generally, they suggest that coarse clear columnar calcite and large (>1.0 ppm) ranges of U concentration are warning signs of recrystallization and U loss. However, even finer grained, inclusion-rich columnar calcite may be the result of recrystallization while retaining U contents less depleted than those of associated clear calcite.

Radiometric dating is an essential component in the application of speleothems to paleoenvironmental studies. Such dating, when applied to entire speleothems, allows determination of speleothem growth periods that have been interpreted as wetter phases (e.g., Brook *et al.* 1997). It also allows calibration of paleoenvironmental conditions based on time-series records within individual speleothems (e.g., Dorale *et al.* 1992, 1998). U-series dating is one of the most valuable dating methods, because it yields ages up to roughly 500 ka (Edwards *et al.* 1987) that are readily applicable to Quaternary studies and particularly to the last few glacial-interglacial cycles (Imbrie *et al.* 1993).

Accurate U-series dating requires that isotopic compositions evolve under closed chemical conditions. Loss of U during recrystallization of aragonite, high-Mg calcite, or fine-grained calcite may result in calculated ²³⁰Th/U dates that do not represent true depositional ages. The UO₂²⁺ cation, like most oxocomplexes of cations of high ionic potential, is relatively soluble (Langmuir 1978). It is, therefore, readily mobilized by diagenetic solutions and can be leached from speleothems. On the other hand, Th⁴⁺ is effectively insoluble in most aqueous environments (Kaufman 1969) and commonly remains in carbonates undergoing recrystallization. As a result, diagenetically modified speleothems may have chemically altered ²³⁰Th/²³⁴U ratios that yield anomalously old radiometric ages. For example, Dabous and Osmond (2000) analyzed 32 samples from 8 speleothems from Wadi Sannur Cavern in Egypt and found that 11 of the samples had ²³⁰Th/²³⁴U activity ratios greater than 1 at the 95% confidence level, indicative of U loss in the past. The obvious enhancement of ²³⁰Th/²³⁴U

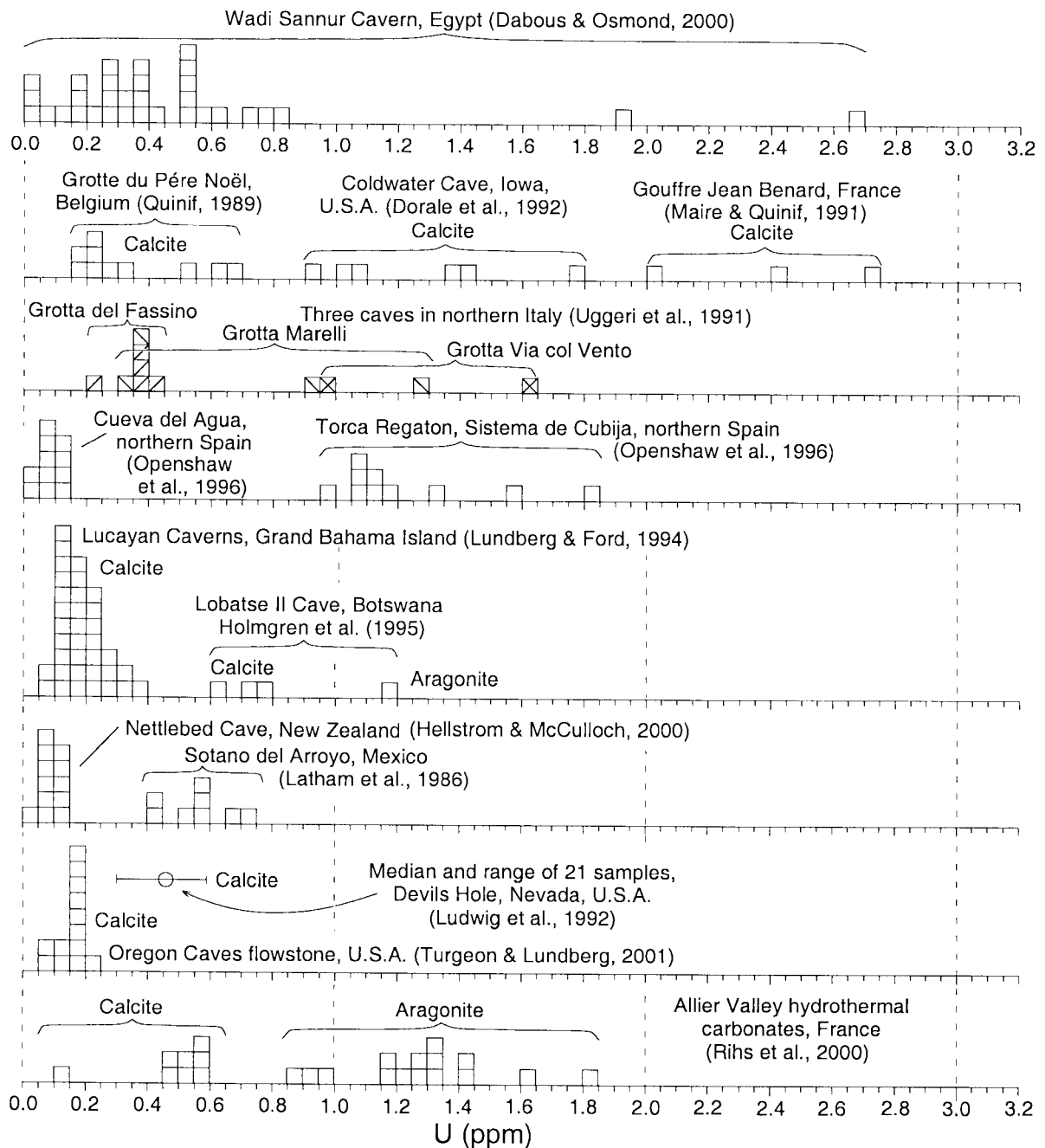
ratios in those samples and likely enhancement of the rest allowed Dabous and Osmond only to infer that the remaining samples were also affected by secondary U mobility and that the dates calculated from ²³⁰Th/²³⁴U - ²³⁴U/²³⁸U activity ratios were probably maximum depositional ages. Other workers commonly report similar problems with U loss and resulting questionable radiometric ages (e.g., Openshaw *et al.* 1996; Whitehead *et al.* 1999). Such problems do not, of course, mean that all U-series ages are suspect, because U-series data can be checked using the γ test (e.g., Ludwig *et al.* 1992; Szabo *et al.* 1994; Ludwig & Paces 2002).

The possibility of U loss in some speleothems during recrystallization makes methods to recognize such speleothems very desirable. This paper reports the petrography and geochemistry of some of the speleothems studied by Dabous and Osmond (2000), with the goal of identifying tell-tale characteristics of recrystallized speleothems. The results suggest that petrography and geochemistry can indeed be useful in recognizing recrystallized material and in avoiding wasted effort in dating of that material. They further suggest that recrystallization yielding columnar, and seemingly primary, calcite may be more common than frequently thought.

MATERIALS, METHODS, AND PREVIOUS REPORTS

Speleothems 7, 9, 12, and 13 from Wadi Sannur Cavern in northeastern Egypt were described and analyzed previously for U-series isotopes by Dabous and Osmond (2000) and provided the material studied in this project. Dabous and Osmond (2000) divided each speleothem into at least three samples of

Figure 1. Histograms of U concentrations in speleothems (upper 7 histograms) and other terrestrial carbonates (lowest histogram) reported in various studies. Each square represents one analysis. Mineralogy is indicated where reported in the original reference. Note broad range of concentrations from Wadi Sannur samples.



10-20 gm each, and they recorded the position of those samples as “inner” (i.e., near the core of the speleothem), “middle”, and “outer”. Their Table 1 listed U and Th concentrations, $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios determined by alpha spectrometry, and apparent ages for 32 samples from eight speleothems.

Detailed chemical analyses of polished C-coated thin sections of the speleothems were performed on a JEOL JXA 8600 electron microprobe using wavelength-dispersive spectrometers. All analyses were performed using a 15 kV accelerating voltage, a 10 nanoamp beam current, 20 second counting times, and natural carbonate standards (Jarosewich & Macintyre 1983; Jarosewich & White 1987). A 10 μm beam

diameter was used to minimize volatilization during analysis. Our microprobe’s software reports a minimum detection limit of ~ 0.05 wt% Sr, but our previous work (Brook *et al.* 1999: Fig. 4) indicates an MDL of ~ 0.02 wt% Sr and a 95% confidence interval of ~ 0.014 wt% Sr.

Samples of roughly 50 mg were drilled from each of the four speleothems with a dental drill. Mineralogy of these powders was determined by X-ray diffractometry using a Scintag XDS 2000 X-ray diffractometer. Hydrochloric acid dissolved 3.0 mg subsamples of the powders and the resulting solutions were analyzed using a Thermo Jarrell-Ash 965 inductively coupled argon plasma (ICP) spectrometer in the University of Georgia Chemical Analysis Laboratory. Results have standard

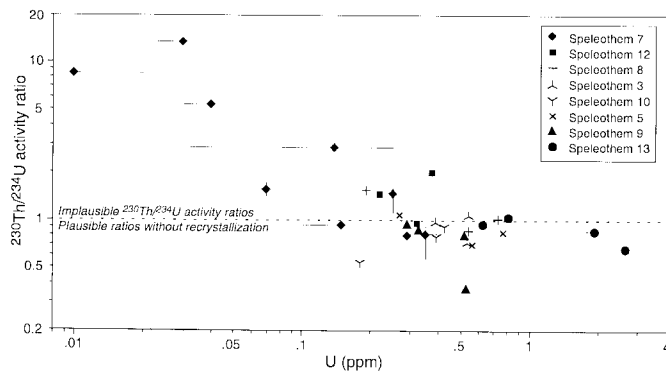


Figure 2. Log-log plot of U concentrations and $^{230}\text{Th}/^{234}\text{U}$ activity ratios of 32 samples from eight speleothems from Wadi Sannur Cavern, Egypt. Filled symbols indicate data from speleothems examined in this study. Error bars are shown where uncertainties significantly exceed size of symbols. Note that a $^{230}\text{Th}/^{234}\text{U}$ activity ratio greater than 1 requires loss of U from the system or addition of Th to it. Data are from Dabous and Osmond (2000).

errors of 0.46% for Ca, 0.30% for Mg, and 0.48% for Sr and have minimum detection limits of 0.001 wt% for Sr and 0.005 mol% MgCO_3 for Mg.

U CONCENTRATIONS AND $^{230}\text{Th}/^{234}\text{U}$ ACTIVITY RATIOS

The U concentrations reported by Dabous and Osmond (2000) range from 0.01–2.65 ppm in a distribution with two outliers at its upper end (Fig. 1). The large range of these U concentrations contrasts sharply with ranges typically observed in speleothems and other terrestrial carbonates (Fig. 1). Consideration of data sets from several speleothems or suites of speleothems reveals a maximum range of only 0.87 ppm (Dorale *et al.* 1992), or only one third of the range in the Wadi Sannur samples. Uranium concentrations from aragonitic hydrothermal near-surface carbonates in France have a range of 0.94 ppm (Rihs *et al.* 2000), but even that range does not approach the range of U concentrations in the samples from Wadi Sannur Caverns.

$^{230}\text{Th}/^{234}\text{U}$ activity ratios show an inverse correlation with U concentrations in the Wadi Sannur samples (Fig. 2). Only (but not all) samples with U concentrations greater than 0.15 ppm have plausible $^{230}\text{Th}/^{234}\text{U}$ activity ratios (i.e., ratios ≤ 1.0), whereas the three samples with U concentrations less than 0.05 ppm have $^{230}\text{Th}/^{234}\text{U}$ activity ratios in excess of 5.0. These observations are compatible with post-depositional U loss.

Uranium concentrations show no strong relationship to position within speleothems (Fig. 3). The mean concentrations of inner, middle, and outer samples are statistically unresolvable. Middle samples, which might be hypothesized to be most protected from recrystallizing waters, have both the highest U concentration reported and the three lowest values reported (Fig. 3).

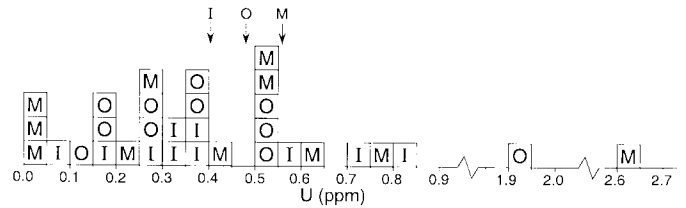


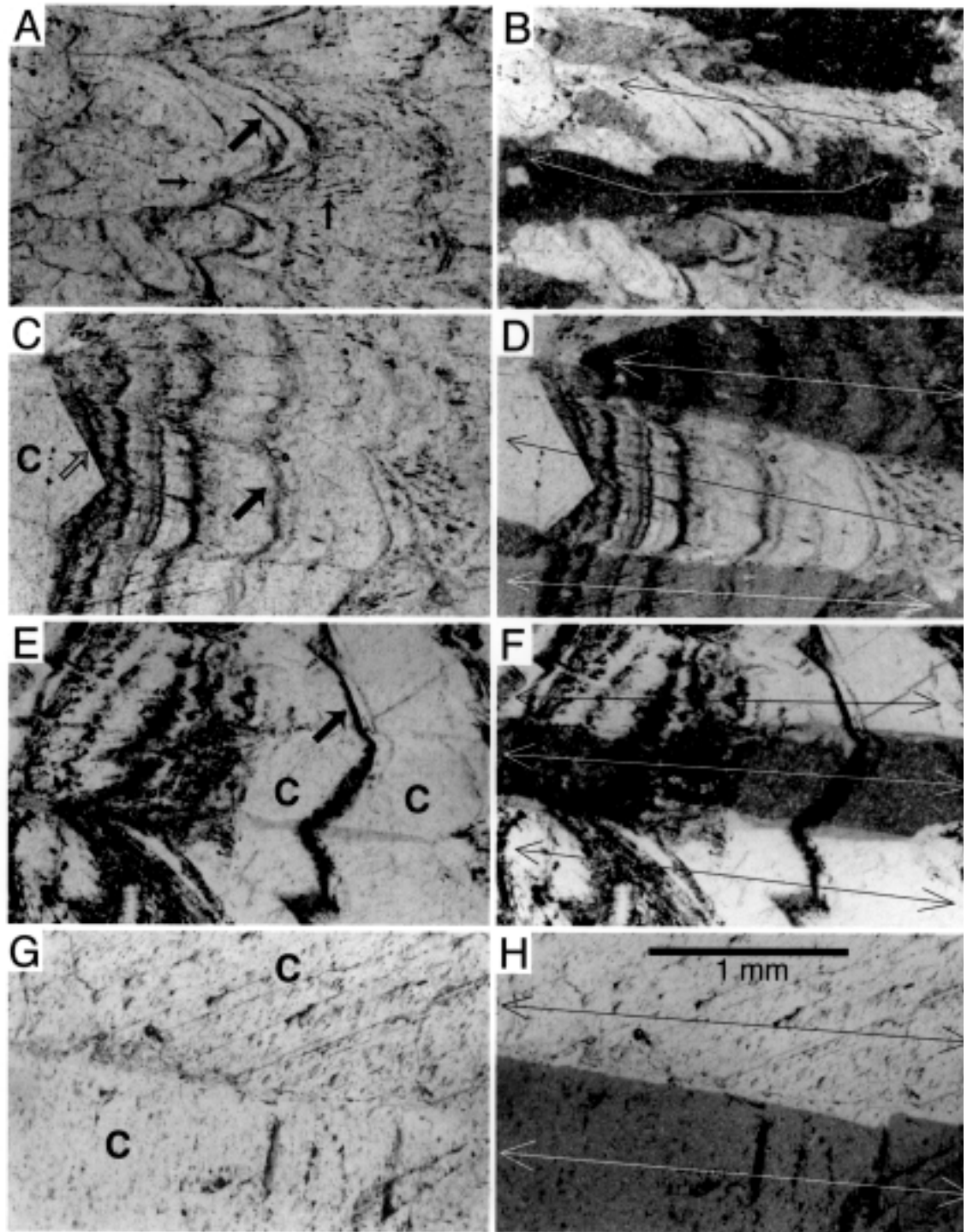
Figure 3. Histogram of U concentrations of 32 samples from eight speleothems from Wadi Sannur Cavern, Egypt. Samples are coded by location within each speleothem: “I” = inner, “M” = middle, and “O” = outer. Arrows above histogram indicate means for each group. Data are from Dabous and Osmond (2000).

PETROGRAPHY

Petrography and X-ray diffraction indicate that the four speleothems examined in this study are all calcite, but their fabrics vary from inclusion-rich and zoned to clear and featureless. Macroscopically, transverse sections of Speleothem 13 show mostly light brown calcite with pronounced fine-scale zonation (Railsback 2000: Fig. B2). Microscopically, Speleothem 13 consists of elongate or columnar calcite crystals radiating from the speleothem’s center. The columnar crystals are as much as 12 mm long and vary in width from 0.15 to 1.2 mm. They are inclusion-rich, rather than clear, and the inclusions consist of at least two types (Figs. 4A & 4B). One type is small (0.1 to 0.4 mm) subequant inclusions of opaque to translucent material. The other type is elongate to linear (typically 0.01 by 0.1 mm) liquid or gaseous inclusions oriented parallel to the long direction and extinction direction of the calcite crystals. Both kinds of inclusions define apparent growth zones that extend across calcite crystals and that can commonly be traced in concentric circles all the way around the central canal. None of the edges of the columnar calcite crystals coincide with the growth zones defined by inclusions.

Macroscopically, Speleothem 9 consists mostly of finely zoned light brown calcite, but the center is clear and vitreous (Railsback 2000: Fig. B2). A single crystal of clear calcite extends outward from the center of the speleothem across concentric zonations that appear to define the original wall of the central canal (Figs. 4C & 4D). Euhedral boundaries of that crystal extend across and into growth zones in inclusion-rich columnar calcite. Columnar calcite crystals that are 0.07 to 1.55 mm wide and as much as 10.1 mm long radiate outward from the central crystal. The interior portions of those columnar crystals are rich in both of the kinds of inclusions described with regard to Speleothem 13, and those inclusions likewise define concentric growth zones (Figs. 4C & 4D). The outer portions (i.e., nearest the outside of the speleothem) are generally inclusion-poor and locally clear. Some patterns of inclusions in the outer areas have the form of euhedral calcite terminations, whereas others appear to follow growth zonations that, if continuous, would define large concentric circles

Figure 4.
Photomicrographs
of speleothems stud-
ied. A and B:
Speleothem 13. C
and D: Speleothem
9. E and F:
Speleothem 7. G and
H: Speleothem 12.
Photomicrographs
in left column are in
plane-polarized
light; photomicro-
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umn are of same
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ized light. Larger
filled arrows in left
column point to lay-
ers defined by small
subequant inclu-
sions; smaller filled
arrows on left point
to elongate to linear
inclusions parallel
to length of crystals;
open arrow in C
points to euhedral
boundary in crystal
that extends to left
into central canal.
“C” indicates clear
calcite. Long thin
arrows in right col-
umn indicate extent
of single optically
continuous crystals.
In A through F,
central canal is to left,
just out of field of
view. Scale bar in H
applies to all eight
photomicrographs.



around the central canal.

Speleothem 7 macroscopically consists partly of light brown calcite with weakly defined zones and partly of clear to white calcite that is only locally zoned (Railsback 2000: Fig. B2). A few crystals of clear calcite extend outward across zones of inclusions that apparently define the original edge of the central canal. Columnar calcite crystals that are as much as 22 mm long and 0.2 to 1.8 mm wide radiate from the central canal (Figs. 4E & 4F). One zone within them is rich in small subequant inclusions of opaque to translucent material; that

zone is ~3 mm thick. The rest of the columnar calcite is generally clear with at most a few linear and small subequant inclusions.

Speleothem 12 consists macroscopically of vitreous calcite in which zonation is only faintly recognizable. The speleothem consists of large crystals of columnar calcite that are up to 2.7 mm wide and some of which are at least 34 mm long. This calcite is almost entirely clear with only a few thin (≤ 0.15 mm) zones that contain inclusions (Figs. 4G & 4H).

In summary, the sequence of speleothems from 13 to 9 to 7

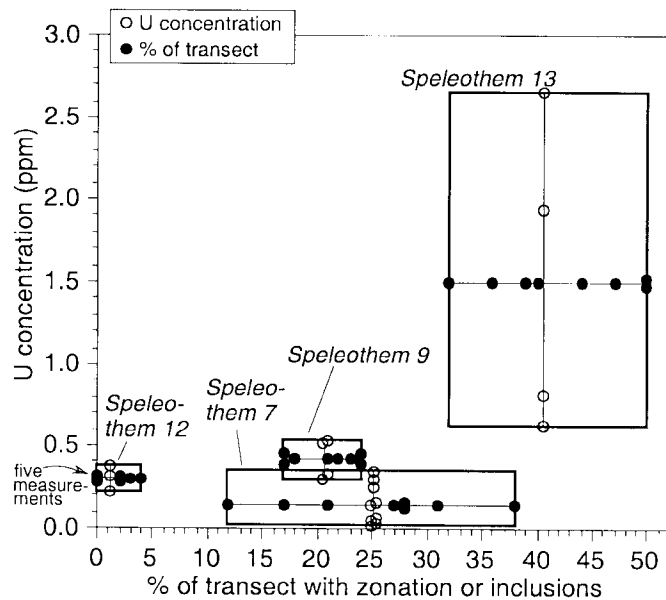


Figure 5. Plot of U concentration (open symbols, on vertical axis) and extent of textural preservation (filled symbols, plotted on horizontal axis) of four speleothems from Wadi Sannur Cavern. Textural preservation was measured by examination of linear transects across thin sections and measurement of the proportion of each transect characterized by inclusion-rich or zoned calcite. Locations of U analyses did not coincide with locations of transects, so each variable is plotted against the average of the other (thin lines) to generate rectangles encompassing range for each speleothem. Some filled symbols have been moved vertically and some open symbols have been moved horizontally to avoid overlap. U concentration data are from Dabous and Osmond (2000).

to 12 represents a spectrum from relatively small inclusion-rich crystals across which growth zonation is evident to relatively coarse clear crystals across which growth zonation is indistinct. None of the speleothems have detectable cathodoluminescence.

RELATIONSHIPS BETWEEN PETROGRAPHY AND GEOCHEMISTRY

The trends in petrography described above are related to U concentration. For example, if randomly chosen linear transects are made across the speleothems and the percentage of each transect crossing zonation or inclusion-rich zones is measured, U concentration of the speleothems is less in speleothems with lower percentage of zoned and/or inclusion-rich material (Fig. 5). (Note that the scale of observation in the petrographic transects is similar to that of sampling to determine U concentrations). Uranium concentration also is less in speleothems with greater width of columnar calcite crystals (Fig. 6).

Petrography is also related to concentration of Sr at the

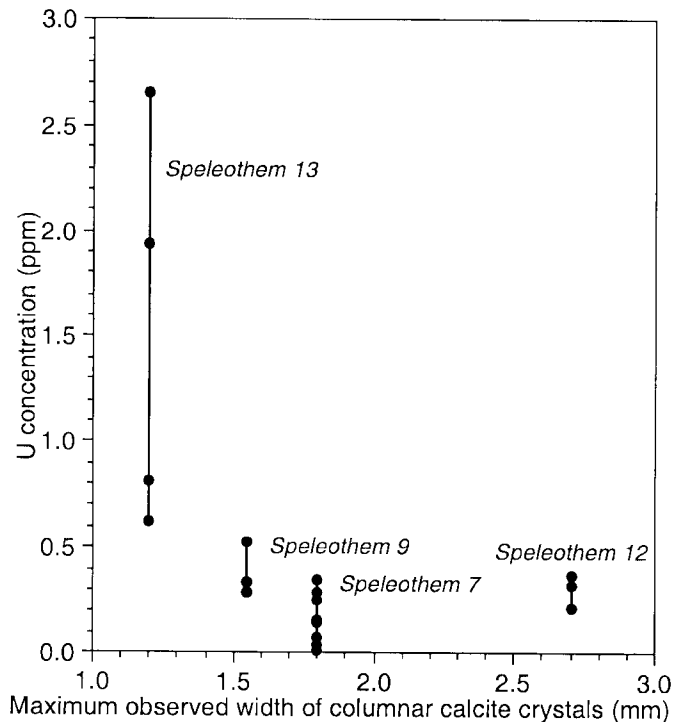


Figure 6. Plot of U concentration (filled circles, on vertical axis) and maximum observed width of columnar crystals (vertical lines, on horizontal axis) of four speleothems from Wadi Sannur Cavern. U concentration measurements are from different parts of speleothems, whereas widths are one maximum from each speleothem, so multiple values of U concentration are plotted against one value of width for each speleothem. Widths are “maximum observed” because widths were measured in thin sections that may have not encountered the greatest crystal width in the entire speleothem. U concentration data are from Dabous and Osmond (2000).

microscopic scale. Microprobe analysis reveals that Sr concentration in inclusion-rich or zoned calcite ranges from 0.00-0.11 wt%, with a mean of 0.046 wt% (Fig. 7). Sr concentration in clear calcite ranges from 0.00-0.11 wt%, with a mean of 0.027 wt% (Fig. 7). Although the ranges are identical, a Student’s t-test reveals that the means differ with statistical significance ($p=0.002$, where p is the probability that the observed difference arose randomly). Means of Sr concentrations in the two kinds of calcite differ with even greater statistical significance ($p=0.001$) in Speleothem 13 (Fig. 8), the petrographically best-preserved speleothem.

Petrography is related to concentration of both Mg and Sr at the macroscopic scale (Fig. 9). ICP analysis of drilled powders yields a Sr concentration of 0.053 wt% and Mg concentration of 0.450 mol% $MgCO_3$ in Speleothem 12, the speleothem with the coarsest crystals and the least zonation and fewest inclusions. In contrast, Speleothems 7, 9, and 13, which have finer crystals and more zonation and inclusions, have Sr concentrations of 0.058-0.069 wt% and Mg concentrations of 0.803-0.920 mol% $MgCO_3$. These ICP results fall in

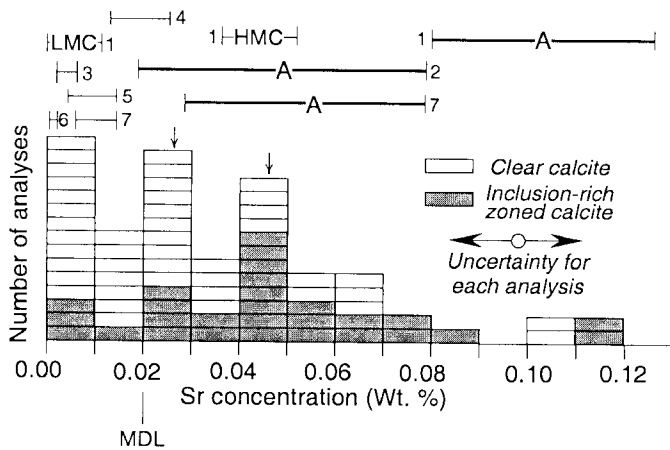


Figure 7. Histogram of microprobe measurements of Sr concentration in four speleothems from Wadi Sannur Cavern. Shading indicates degree of textural preservation; arrows indicate mean Sr concentration for each group. At top, thick horizontal bars labeled “A” are ranges of Sr concentration in aragonite in speleothems reported in literature; thin unlabeled bars show ranges of Sr concentration in calcite in speleothems reported in literature; “LMC” and “HMC” indicate reported ranges for low-Mg calcite and high-Mg calcite. Sources of data are 1: Bar-Matthews *et al.* (1991); 2: Brook *et al.* (1999); 3: Gascoyne (1983); 4: Goede & Vogel (1991); 5: Goede *et al.*, (1998); 6: Huang & Fairchild (2001); 7: Railsback *et al.* (1997).

the middle of the ranges of the microprobe results, which is to be expected because they represent larger samples that necessarily include a greater range of petrographic characteristics.

Petrography is not correlative with concentration of Mg at the microscopic scale. Mg concentration in inclusion-rich zoned calcite ranges from 0.19-2.30 mol% MgCO₃ with a mean of 0.87 mol% MgCO₃, and Mg concentration in clear calcite ranges from 0.04-2.30 mol% MgCO₃ with a mean of 0.78 mol% MgCO₃ (Fig. 8). Those means do not differ with statistical significance ($p=0.25$). Only in data from Speleothem 12 does the mean Mg concentration of inclusion-rich zoned calcite differ with statistical significance from that of clear calcite ($p=0.043$). Even that significance is eliminated if one notes that four sets of data (Fig. 8) are tested and, therefore, uses a Bonferroni correction and divides α by 4, reducing α from 0.05 to 0.0125. A Bonferroni correction is required because repeated tests of one hypothesis are made. If four tests were made with $\alpha=0.05$, the probability that random numbers would yield $p<0.05$ in one of those tests would be 0.20 (an unacceptably high probability of a faulty inference) rather than 0.05 (the standard value in the earth sciences).

CONCLUSIONS AND DISCUSSION

CONCLUSIONS SPECIFIC TO THE WADI SANNUR SPELEOTHEMS

The relatively high Sr concentrations in inclusion-rich por-

tions of the Wadi Sannur speleothems (Fig. 7, 8, & 9) and the high U concentrations of some of the samples from the speleothems (Fig. 1) suggest that some, and perhaps much, of the material in these speleothems was originally aragonite. Sr concentrations in inclusion-rich portions of the speleothems are equal to Sr concentrations of spelean aragonite, whereas they exceed Sr concentrations in primary spelean calcites (Fig. 7). In fact, most Sr concentrations in *clear calcite* from the Wadi Sannur speleothems also exceed those reported in primary spelean calcites (Fig. 7). High U concentrations similarly argue for an original aragonite mineralogy, because the distribution coefficient for U is much larger in aragonite than in calcite (Kitano & Oomori 1971; Meece & Benninger 1993).

Although the Wadi Sannur speleothems were probably partly to mostly aragonite when they formed, the Mg content of their calcite suggests that the speleothems also originally contained calcite with a non-trivial Mg content. The distribution coefficient for incorporation of Mg in aragonite (0.002) reported by Brand and Veizer (1983) would imply aragonite precipitation from a water with Mg/Ca = 11.8 to allow the greatest Mg concentrations observed in the speleothems (2.3 mol% MgCO₃). Mg/Ca ratios are typically not that great in cave waters (Fig. 10), suggesting that the Mg was not incorporated in primary aragonite. The distribution coefficient for incorporation of Mg in spelean calcite (~0.03) (Gascoyne 1983; Huang & Fairchild 2001) would, on the other hand, imply calcite precipitation from a water with Mg/Ca = 0.8 to allow the greatest Mg concentrations observed in the speleothems (2.3 mol% MgCO₃). Cave waters with Mg/Ca = 0.8 are relatively common (Fig. 10), so that the Mg concentrations of the calcites could have resulted from precipitation of primary magnesian calcite. Two conclusions are possible: 1) Some of the original material of the Wadi Sannur speleothems was Mg-bearing calcite; 2) Recrystallization of aragonite to calcite took place in waters sufficiently Mg-rich to result in the present Mg content.

The geochemical considerations discussed above and the petrographic character of the Wadi Sannur speleothems combine to suggest that all four speleothems underwent significant recrystallization. Petrographic evidence (preservation of zonation and relative fine calcite crystal size) and geochemical evidence (high U concentration and distinct Sr-rich zones) indicate that Speleothem 13 underwent the least recrystallization. However, even Speleothem 13 appears to have undergone recrystallization, because its high Sr content is incompatible with an original calcite mineralogy and because the boundaries of all of the elongate calcite crystals have no relationship to zonation defining the speleothem's growth layers. The coarser crystals and lesser preservation of original fabric in Speleothems 9, 7, and 12 suggest that they underwent even more recrystallization than Speleothem 13.

CONCLUSIONS GENERALLY APPLICABLE TO SPELEOTHEMS

The most general conclusion from this work is that microscopic petrography is a valuable tool in evaluating

Figure 8. Plots of Sr and Mg concentration determined by microprobe analysis of four speleothems from Wadi Sannur Cavern.

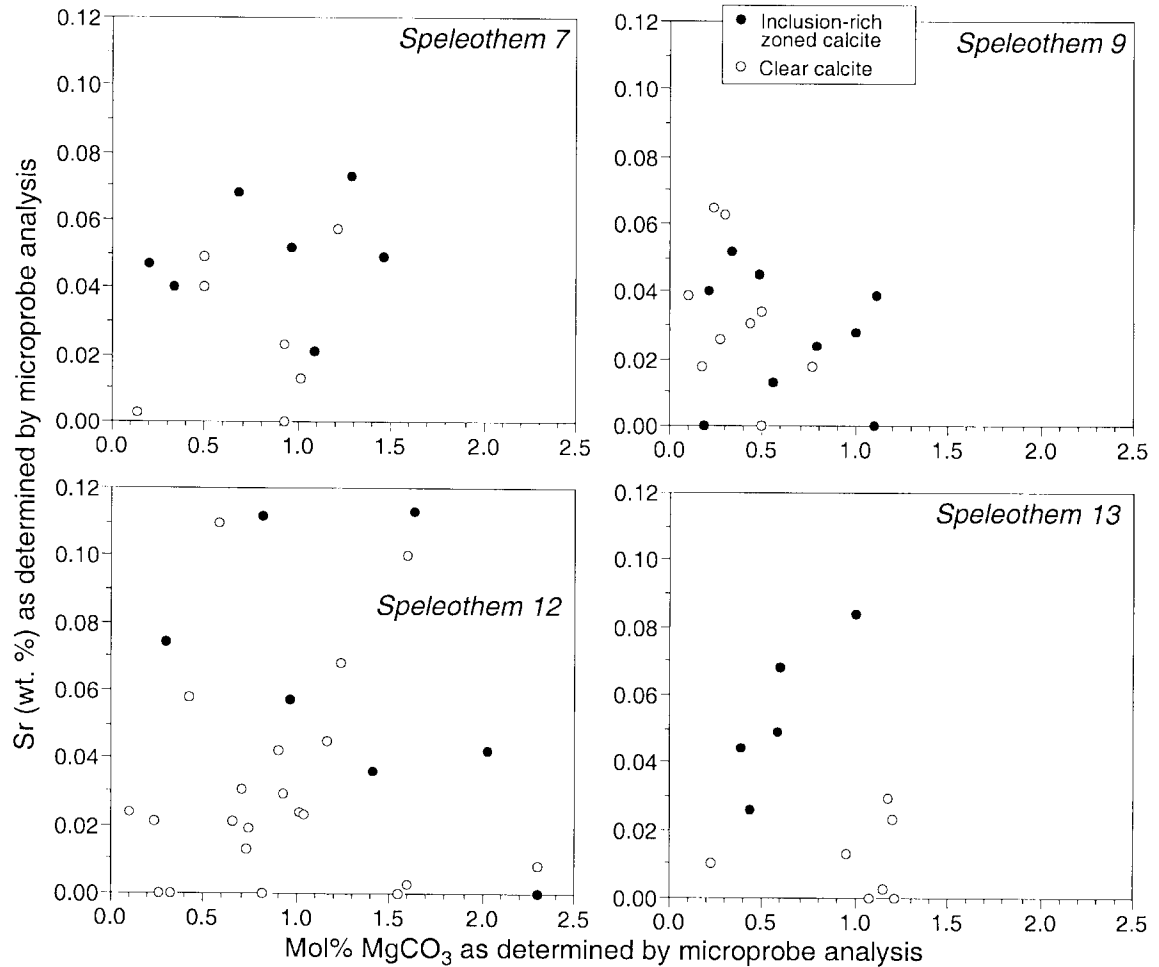
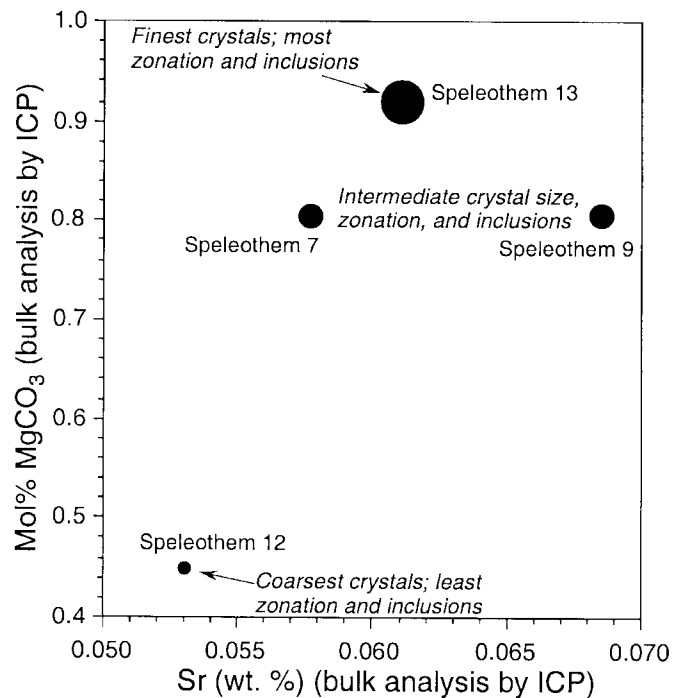
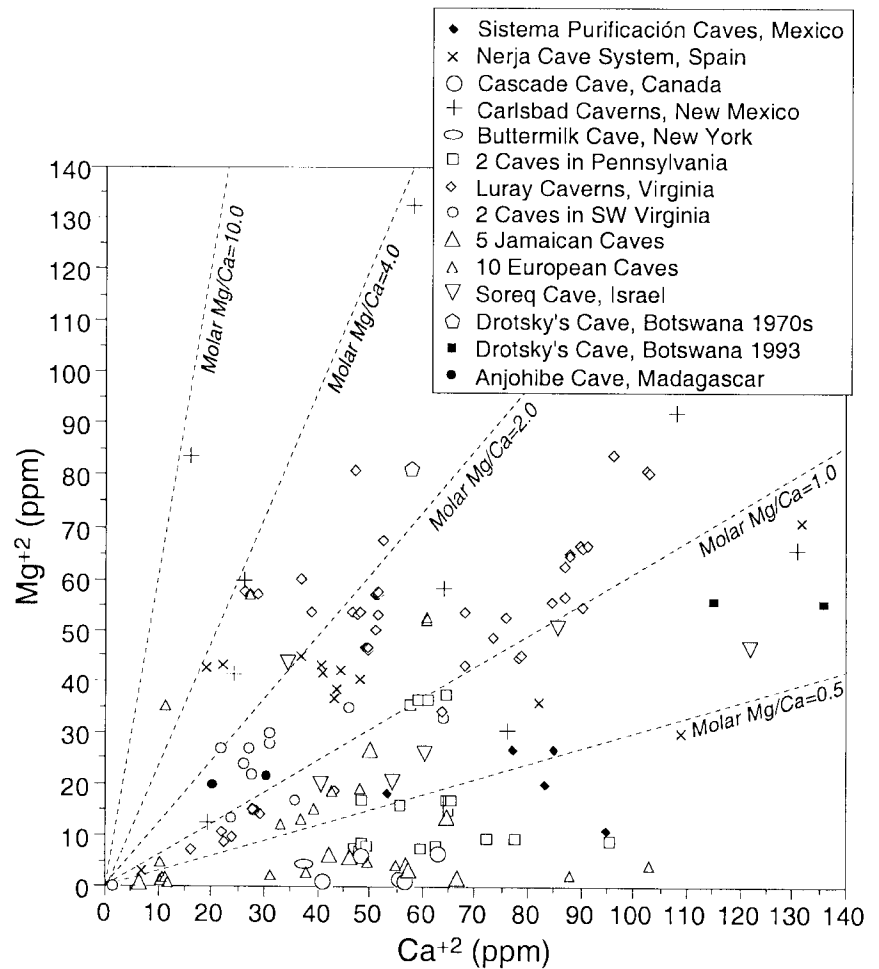


Figure 9 (Right). Plot of Sr and Mg concentration determined by ICP analysis of drilled powders of four speleothems from Wadi Sannur Cavern. Symbol size reflects petrographic parameters (see horizontal axes of Figs. 5 & 6) and is proportional to inferred degree of preservation of original texture. Analytical uncertainty is less than size of smallest symbol. Sample sizes for these analyses were much larger than for the microprobe analyses reported in Figures 7 and 8, but the minimum detection limits were much lower (offscale to left and bottom of this figure).



speleothems for potential U-series dating. Visual examination of hand samples is often used by practitioners of speleothem geochemistry as their sole means to evaluate preservation. However, Speleothem 13 demonstrates that macroscopic observation of well-defined concentric zonation is not sufficient to disprove possible recrystallization. Instead, positive relationships of U concentration with quantified measures of petrography (Figs. 5 & 6) and differences in Sr concentration with petrography (Figs. 7, 8, & 9) indicate that thin-section petrography provides an effective method to evaluate the preservation of speleothems for U-series dating and perhaps for other geochemical applications as well.

Figure 10. Plot of Ca^{+2} and Mg^{+2} concentrations in waters reported from caves around the world. Sources of data are Carrasco *et al.* (1995) (Spain), Cooke (1975) (Botswana), Even *et al.* (1986) (Israel), Feeney (1997) (New York), Fischbeck (1976) (Europe), Gascoyne (1983) (Canada & Jamaica), Gonzalez and Lohmann (1988) (New Mexico), Holland *et al.* (1964) (Luray Caverns & Pennsylvania), Hose (1996) (Mexico), and Murray (1954) (southwest Virginia). Only a selection of samples from Figure 3.7 of González and Lohmann (1988) are shown because their data were not tabulated. Data from caves near marine shorelines have been excluded to preclude inclusion of waters with Mg-enrichment from seawater.



The large range of U concentration in the Wadi Sannur speleothems and the smaller ranges reported in other terrestrial carbonates shown in Figure 1 suggest that large ranges of U concentration in monomineralic speleothems may also serve as a warning that at least some of the material has undergone recrystallization and loss of U. The condition “in monomineralic speleothems” must be added because the distribution coefficient for U is much larger in aragonite than in calcite (Kitano & Oomori 1971; Meece & Benninger 1993). Lev *et al.* (2000) likewise argued that a large range in U concentration is evidence of post-depositional remobilization in shales.

Finally, the presence of Sr-rich, inclusion-rich columnar calcite in some of the Wadi Sannur speleothems is evidence that inclusion-rich columnar calcite in speleothems can be secondary, rather than primary. The origin of columnar calcite in speleothems has been the subject of vigorous debate (e.g., González *et al.* 1992, 1993; Kendall 1993; Frisia *et al.* 2000). The results of this study cannot lead to a general statement about the origin of all columnar calcites, but they do provide an example in which spelean columnar calcite with inclusion-rich and inclusion-poor bands preserving original zonation seems to be the result of recrystallization of aragonite (and perhaps magnesian calcite).

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