

TEXTURAL, ELEMENTAL, AND ISOTOPIC CHARACTERISTICS OF PLEISTOCENE PHREATIC CAVE DEPOSITS (JABAL MADAR, OMAN)

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ABSTRACT: Two main types of karst formation are commonly known: the surficial meteoric one and the subsurface (hypogenic) karst, which can be related to both carbonic (H₂CO₃) and sulfuric (H₂S) acids. This paper documents evidence for a third, CO₂-regime related, type of karst that is less commonly described. Petrographic and geochemical properties of exhumed Pleistocene phreatic cave deposits from the diapiric Jabal Madar dome in northern Oman are documented and discussed in a process-oriented context. These calcites form at the interface between two fundamentally different diagenetic and hydrogeological domains: the deep-seated, hydrothermal and the near-surficial, meteoric-vadose one.

Four calcite phases are recognized: (i) acicular, (ii) blocky to stubby elongated, (iii) proto-palisade, and (iv) macro-columnar calcites. The macro-columnar calcites, forming the last stage of precipitation, are conspicuous due to their cyclical red zonation, and they form the main (geochemical) focus of this study. Fluid inclusion data point to fluid temperatures of between 30 to 50°C (monophase liquid inclusions) and elevated salinities (1.6 to 7.3 wt.% NaCl equivalent). Low carbon-isotope data (−8 to −9‰) are in agreement with the influx of soil-zone CO₂ whereas decreasing δ¹⁸O (−15‰) values might point to mixing of saline hydrothermal and ¹⁸O depleted, meteoric freshwater, i.e., two fluid sources. Trace-element and stable-isotope data shift between the different cement phases and vary cyclically across the red zoning in macro-columnar calcites. With respect to the intra-crystal variability, these patterns are perhaps best explained in the context of redox potential. Two interpretations are presented; the one favored here suggests that the cyclical red zoning in macro-columnar calcites is controlled by Pleistocene monsoonal climate patterns.

INTRODUCTION

Meteoric karstic cave systems and their vadose carbonate deposits (stalagmites, stalactites, flowstones) receive considerable attention as archives of global climate change (Thraill et al. 1971; Neff et al. 2001; Treble et al. 2005). In contrast, hydrothermal fluid systems and hypogenic (sulfuric and carbonic acid) karst and related phreatic deposits are often approached from an applied viewpoint (Hill 1990; Palmer 1995; Worden et al. 1996).

Phreatic spelean calcites, deposited in caverns formed under the influence of a changing CO₂ regime, precipitate at the shallow fringes of hydrothermal systems. Phreatic spelean calcites in these caverns link two fundamentally different diagenetic environments: the burial-hydrothermal and the meteoric-karstic realms. Many of the concepts that are of importance for the formation of meteoric cave systems also apply to deep-seated, geothermal dissolution processes. In the burial domain, the origin and distribution of leaching fluids, however, are quite different and

solution rates are less well constrained (Mira and Lu 1992; Zheng and Hoefs 1993; Simmons and Christenson 1994; Palmer 1995; Tritlla et al. 2001). Whereas the processes related to H₂S karstification in oil and gas fields (Palmer 1995; Worden et al. 1996), or the Carlsbad Caverns in New Mexico (Hill 1990) are well studied, only a limited number of authors discuss the role of CO₂-regime changes in creating caves and the associated calcite mineralization in West European and North American scientific literature (Bakalowicz et al. 1987; Dublyansky 1995, 2000a, 2000b; Bottrell et al. 2001).

In this paper, the petrographic and geochemical properties of exhumed Pleistocene phreatic spelean deposits from Jabal Madar in northern Oman (Fig. 1) are documented and discussed in a process-oriented context. Fluid-inclusion data from Jabal Madar precipitates suggest warm, saline waters ascending within the domal diapiric structure that underlies Jabal Madar. In contrast, detrital silt encased within the calcites points to percolating meteoric water. Central to this study are calcite crystals deposited over several phases, of which the latest one recorded cyclical changes in geochemical and stable-isotope properties. Formed at the interface of two realms, the phreatic calcites exposed at Jabal Madar thus represent particular geological archives. Whereas the geochemical and petrographic data presented herein are well constrained, the detailed

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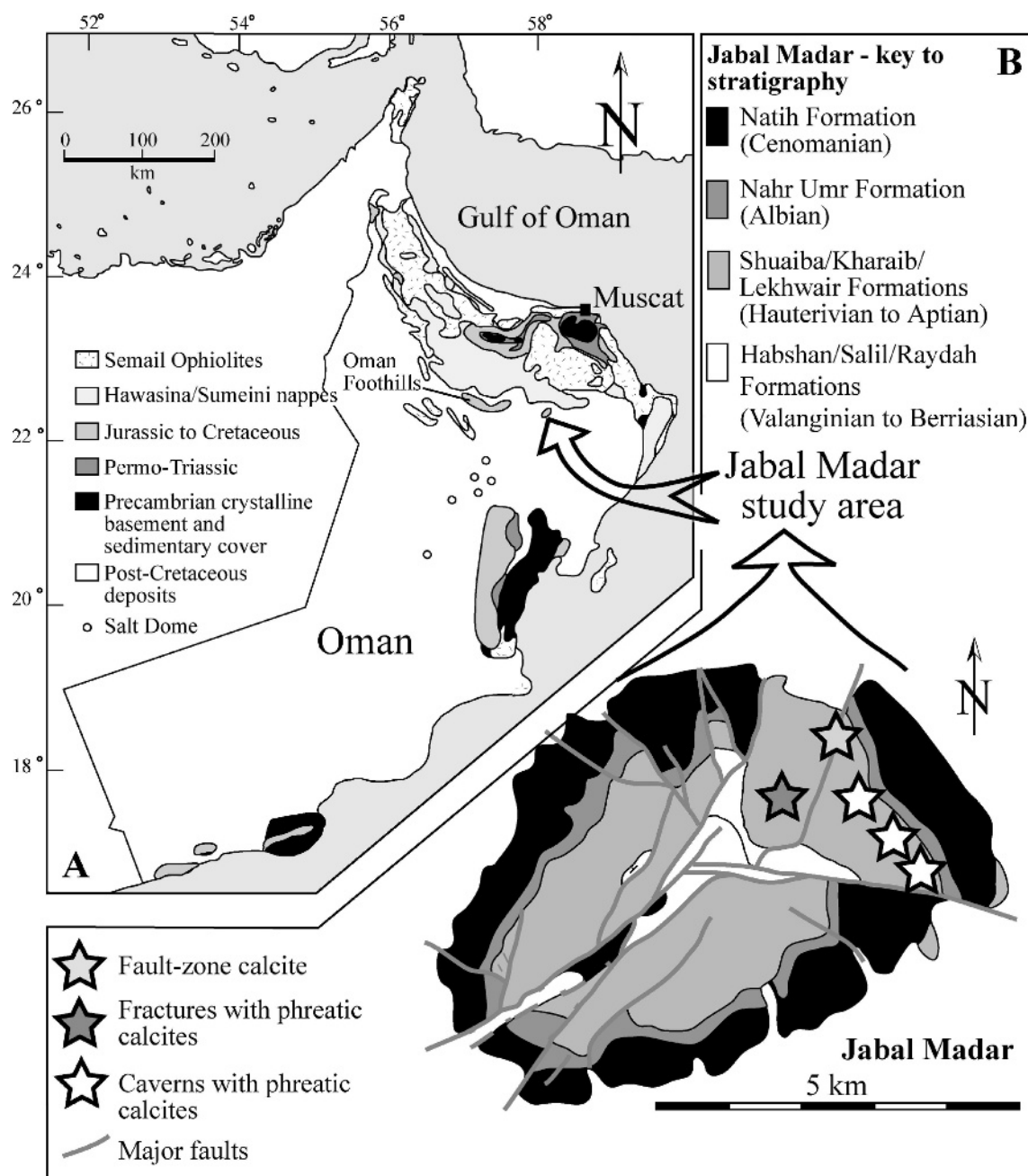


FIG. 1.—A) Regional setting of the study area. B) Blow-up showing the Jabal Madar stratigraphy. Sampling localities are indicated.

interpretation of these data must, for the time being, remain on the level of tentative interpretations. This is due to the inherent complexity of geological archives forming at the interface of two contrasting diagenetic domains.

Geologic Setting

Jabal Madar (N 22° 23' 50.45", E 058° 10' 19.15") lies ca 200 km SSW of Muscat, the capital of Oman (Fig. 1A). Jabal Madar is a salt-cored, diapiric dome structure lifting Jurassic and Cretaceous limestones about 500 m above the surrounding plain (Figs. 1, 2; Montenat et al. 2000). The stratigraphically uppermost level of the dome structure is built of the Cenomanian Natih Formation and carbonates of Berriasian to Valangi-

nian age form its core (Béchenec et al. 1992). The Cenomanian onset of domal uplift is documented in industry-generated 3-D seismic imaging which shows a Cenomanian erosive river system meandering around the incipient Jabal Madar high (C. Grélaud, personal communication 2005). It is unknown whether Jabal Madar still undergoes active uplift.

Portions of a denuded Pleistocene to Holocene cavern system, the topic of this study, are exposed at the eastern dip slope of Jabal Madar (Fig. 1B). The features of this system are characteristically different from those of the probably Cenomanian meteoric karst cavities described by Montenat et al. (2000) from the Natih Formation at Jabal Madar. The exposed portions of the Pleistocene to Holocene caverns are a few meters in width and several tens of meters in length (Figs. 3, 4). The caves have a ramifying pattern with irregular chambers and branches in three

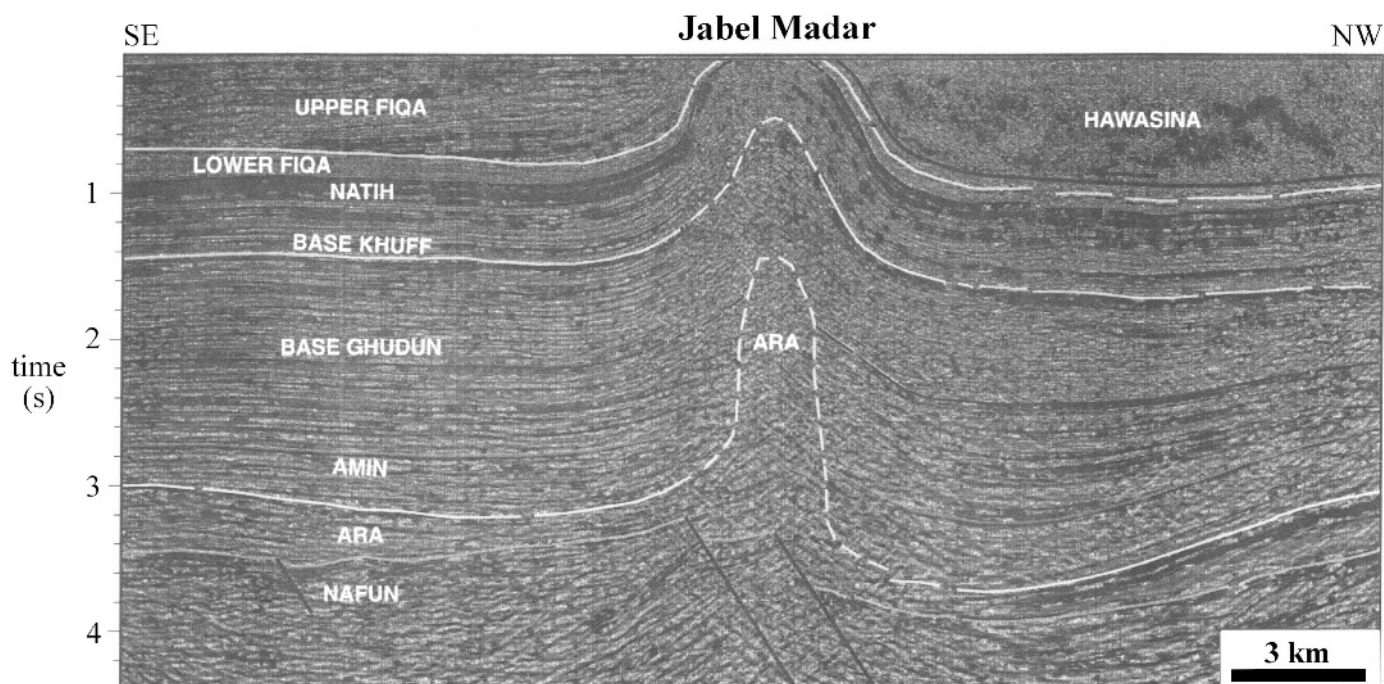


FIG. 2.—Seismic section across Jabal Madar showing diapiric structure due to uplift of the Cambrian Ara Formation salt dome. Vertical axis is two-way travel time. Refer to Mount et al. (1998) for key to formation names (Nafun, Ara, etc.).

dimensions. Stratigraphically, the exposed floors of cavities are situated about eight meters beneath the upper boundary of the Barremian–Aptian Shuaiba Formation (Figs. 3B, C, 4A).

Where exposed, the floors and walls of the cavities are coated with palisades of columnar, centimeters to decimeters long calcite crystals (Fig. 4B). An approximately 5-cm-thick layer of blocky calcite separates the corroded carbonate host rock and the palisade calcites (Fig. 4B). Palisades of similar but generally smaller calcites also line dissolution-widened fractures that are connected with portions of the denuded cavern systems (Fig. 4D, E).

SAMPLES AND ANALYTICAL METHODS

Samples

Nine specimens of macro-columnar calcite of variable size were collected from different cavities and twenty-two specimens were taken from fracture systems (Figs. 1, 3, 4). The contact zone between carbonate host rock and spelean calcite was sampled at two localities. Specimens of blocky calcite from nearby large fault zones were collected at two localities for comparison with the spelean calcites (Fig. 1).

Analytical Methods

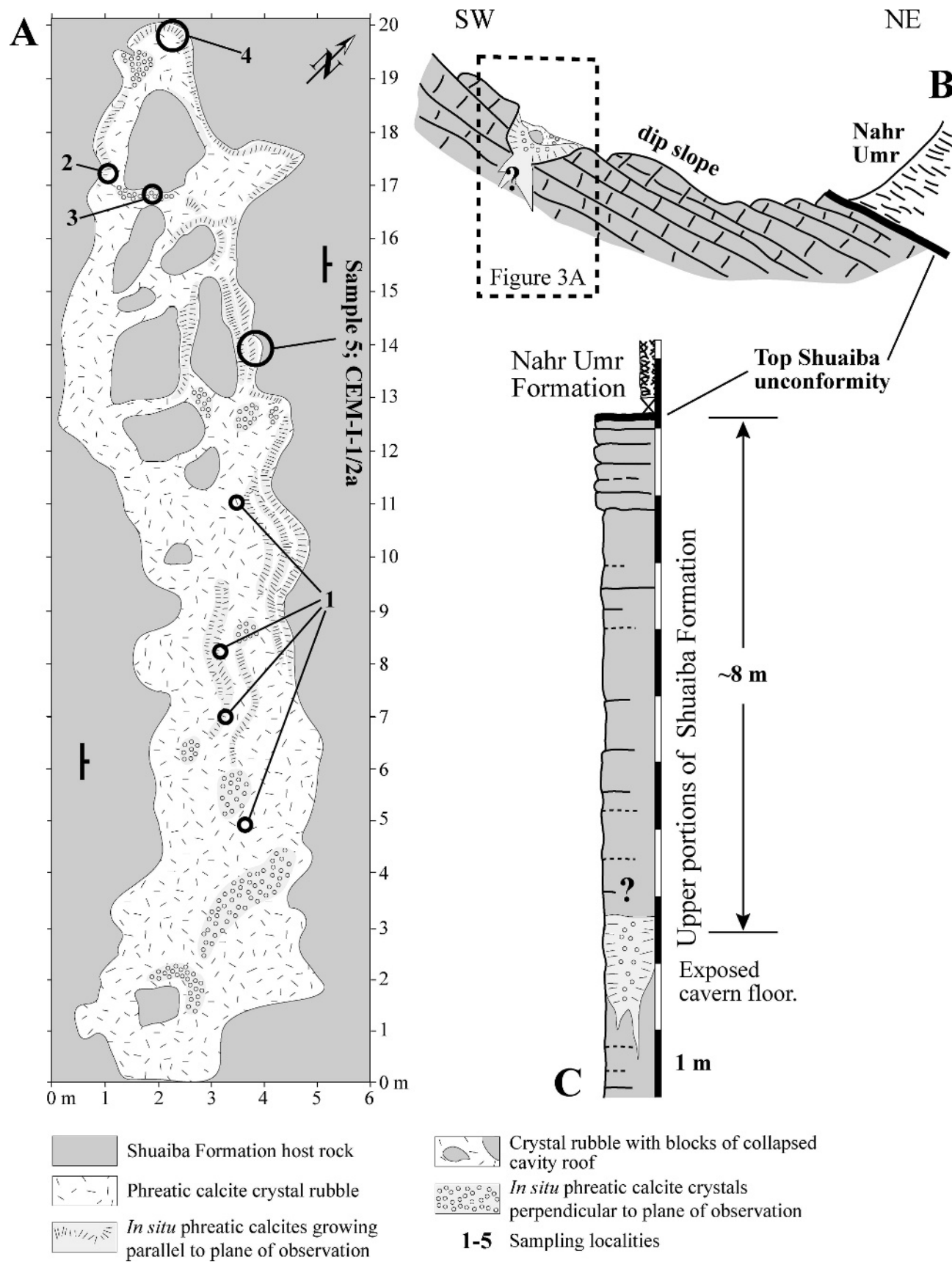
Carbon and Oxygen Isotopes.—Two hundred and forty-eight calcite powder samples (20 to 80 μg) were analyzed on a ThermoFinnigan MAT 252 isotope ratio mass spectrometer at the Vrije Universiteit, Amsterdam, The Netherlands. Repeated analyses of carbonate standards show a reproducibility of better than 0.1‰ for $\delta^{18}\text{O}$ and better than 0.05‰ for $\delta^{13}\text{C}$ ratios. Duplicate samples show scatter of $\pm 0.1\text{‰}$ or less for

both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ratios. All isotope results are reported in ‰ relative to the V-PDB standard.

Water Content and Hydrogen Isotopes from Fluid Inclusions.—Analyses were performed at the Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, USA. Four aliquots from two calcite samples (74 to 760 mg, depending on the content of water) were crushed in a specially designed cell in He flow at 150°C (to keep water in gaseous state and prevent adsorption). The water recovered from inclusions was cryogenically trapped, separated from CO_2 , and then carried into the ThermoFinnigan TC/EA glassy carbon pyrolysis furnace heated to 1450°C. The produced hydrogen was introduced into the ThermoFinnigan Delta^{plus} XL mass spectrometer through an open-split interface. The measured δD values are assessed to be accurate within $\pm 5\text{‰}$. Calibration using injections of different amounts of standard waters allowed the assessment of the amounts of water trapped in inclusions.

Trace Elements.—One hundred calcite powder samples were analyzed for Ca, Mg, Sr, Mn, and Fe elemental concentrations at the Vrije Universiteit, Amsterdam, The Netherlands. The elemental composition was established by inductively coupled plasma–atomic emission spectrometry (ICP–AES) after dissolution of ~ 0.8 to 1 mg of powdered sample in 1 N HNO_3 with subsequent dilution to an ~ 0.1 N HNO_3 solution. The small sample size made accurate measurements of powder weights difficult. Raw solution data were thus converted to Mg/Ca ratios by assuming that all Ca and Mg are present as carbonate-bound cations. The resulting analytical precision of repeated analyses is in the order of $\pm 1.5\%$ for Ca and $\pm 8\%$ for Mg, Sr, Mn, and Fe.

FIG. 3.—**A)** Map view of one of several truncated Holocene caverns at Jabal Madar. **B)** Schematic transect showing the discontinuity at the top of the Shuaiba Formation (Lower Aptian) and overlying aquitard of the Nahr Umr Formation (Albian). **C)** Stratigraphic column of the top of the Shuaiba Formation showing the location of the exposed cavern floor. The height of caverns is unknown due to erosion but might have extended up to the base of the sealing Nahr Umr Formation.



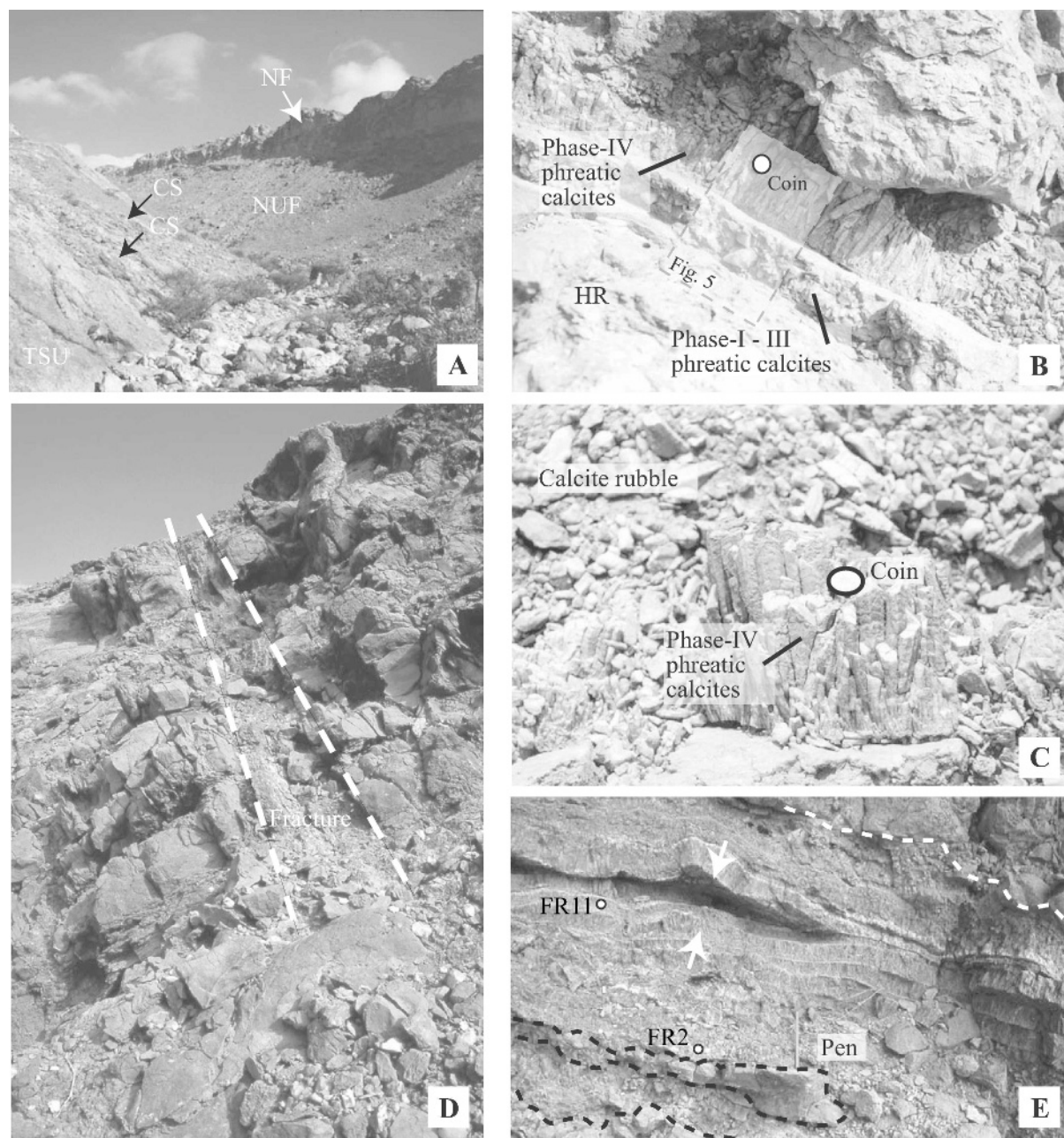


FIG. 4.—**A**) Field photograph of top Shuaiba Formation unconformity (TSU) and overlying Nahr Umr (NUF) and Natih (NF) formations. Positions of two of the cavity systems are indicated (CS). **B**) Portions of the exhumed cavity floor and sidewalls. Phase-I through Phase-IV calcites are indicated. HR = Aptian host rock. **C**) Close-up of Phase-IV calcites. Coin for scale. **D**) Exhumed fracture filled with Phase-IV calcite. **E**) Close-up of fracture shown in Part D with eight consecutive Phase-IV calcite palisades. Note bipolar (arrows) growth direction, pointing to calcite precipitated in phreatic environment. Sampling points for ^{14}C age data (FR2 and FR11) are indicated. Pen for scale.

Cathodoluminescence (CL).—Thin sections of various cement samples were investigated under a cold-stage CL microscope operating at 10 to 14 kV accelerating voltage, 200 to 300 μA beam current, and a beam diameter of 4 mm at the Vrije Universiteit, Amsterdam.

Microprobe Analysis and Scanning-Electron Microscopy (SEM).—Backscatter images of authigenic and accessory minerals were obtained using an electron microprobe operating at 20 kV accelerating voltage, beam current of 0.015 μA , and 13 μm beam diameter (detection limits for Sr = 200 ppm, Mg = 100 ppm, Mn = 200 ppm, Fe = 200 ppm). For

SEM imaging a JSM 6400 scanning-electron microscope was used at the Vrije Universiteit, Amsterdam.

Fluid Inclusion Thermometry.—Doubly polished sections (150–200 μm thick) were analyzed using a Linkam THMS 600 heating/freezing stage at the Vrije Universiteit, Amsterdam. The stage was calibrated using synthetic fluid inclusions. In freezing experiments the temperatures were recorded within $\pm 0.1^\circ\text{C}$. Only the data from those inclusions were accepted in which the vapor phase was present at the moment of the last melting.

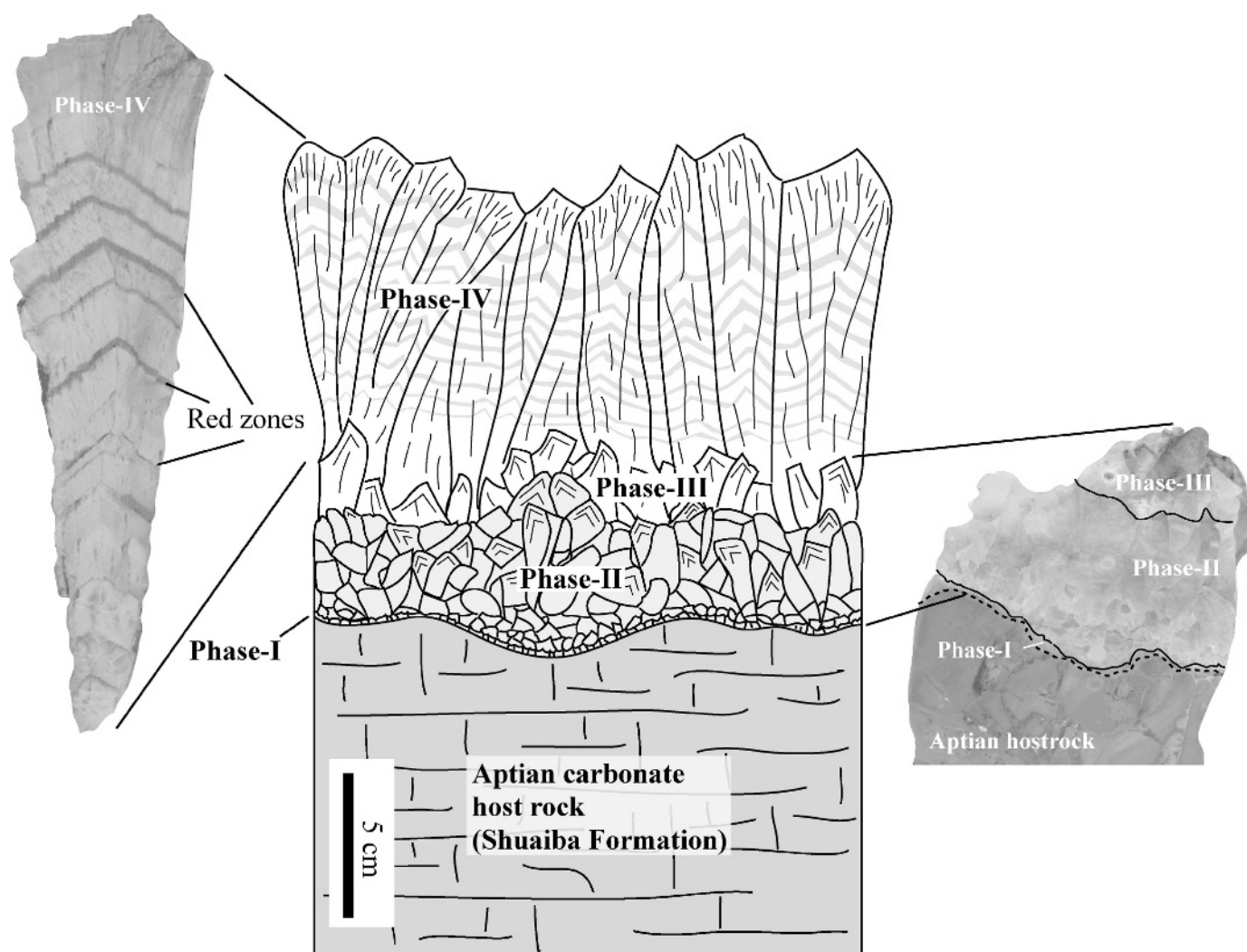


FIG. 5.—Paragenetic sequence of phreatic calcite phases in the exhumed Jabal Madar cave system.

¹⁴C AMS Dating.—Ten calcite samples were analyzed at the Utrecht University, The Netherlands, for their ¹⁴C age using an accelerator mass spectrometer based on a 6 MV tandem Van de Graaff accelerator.

U–Th Dating.—The analytical work was performed at the University of Bern, Switzerland and at the IFM-GEOMAR, Germany. In this study a MC–ICP–MS (AXIOM), a double focusing magnetic sector field instrument equipped with 10 Faraday cups and 3 ion counters was used. Refer to Fietzke et al. (2005) and Burns et al. (1998) for details of the methodology.

PETROGRAPHY OF SPELEOTHEMIC AND FRACTURE-ZONE CALCITES

The term “speleothem” refers to a “mineral deposit formed in a cave by the action of water” (Bates and Jackson 1984). Vadose-zone speleothems, such as stalactites or flowstones, precipitate from a thin veneer of water in an air-filled cave system. This makes them fundamentally different from the cave deposits at Jabal Madar, which, judging from the bipolar growth mode of calcites in caverns and widened fractures (i.e., crystals grow from cavern floors, walls, and roofs towards the cavern or fracture center; Fig. 4E), formed in a phreatic environment. In order to avoid potential confusion with meteoric speleothems, we refer to the Jabal Madar precipitates as “phreatic calcites.”

The main morphological varieties of the Jabal Madar phreatic calcite crystals include in paragenetic order: (1) Phase-I acicular calcite crystals occurring in rims, one to a few millimeter thick; (2) Phase-II blocky, in part stubby elongated, transparent calcite forming three to four centimeter thick layers; (3) Phase-III *ca.* one centimeter thick, irregular layers of proto-palisade calcite; and (4) Phase-IV one to eight (in fractures) stacked-up palisade rims of banded, macro-columnar calcite with individual crystals up to 20 cm in length (Figs. 4B, E, 5). For comparison, hydrothermal calcites from large fault zones at Jabal Madar were investigated. The hydrothermal calcite is present as centimeter to decimeter-size whitish calcite crystal rubble covering the desert floor where large fault systems crosscut the outcrops.

Phase I—Acicular Calcite

Solutional cavities in the host carbonate rock, i.e., the Barremian–Aptian Shuaiba Formation, are lined by a first generation of dull to moderately bright (orange) luminescent, zoned calcite crystals. These crystals are acicular in shape and about three millimeters long, and they grew roughly perpendicularly to their substratum (Fig. 5). The contact to the carbonate host rock, commonly a bioclastic, recrystallized micrite

with uniformly dull luminescence, is smooth. The micritic seam separating the bedrock and the Phase-I calcite, about one millimeter wide, is somewhat darker and finer-grained than to the host carbonate.

Phase II—Blocky to Columnar Calcite

The Phase-II, in part blocky and in part stubby elongated, translucent calcites grow on Phase-I calcites and display uniformly dull, dark orange colors under CL. Similar calcites fill cracks and fissures extending into the host-rock carbonate. Following Nielsen et al. (2005) the term “columnar” is used here to describe the coarsely radiating, closely packed calcite crystals of one millimeter to five centimeter in diameter that commonly have a length/width ratio larger than 3:1. The longest axis of crystals is oriented roughly perpendicular to the contact with the host rock (Fig. 5). Some of these short columnar calcites display a clear growth zonation. The zonation—not visible under luminescent microscopy—is enhanced by small inclusions usually bearing a gas and a fluid phase and numerous solid inclusions. Due to geometric competition, crystals generally increase in size with increasing distance away from the substratum (Fig. 5). Free-grown crystal faces are commonly straight to slightly convex. Under crossed polars, individual crystals exhibit uniform extinction.

Phase III—Proto-Palisade Calcite

The Phase-III calcites occur in a one centimeter thick layer between the Phase-II and Phase-IV calcites (Fig. 5). They comprise a crust of short (proto-)palisade crystals that differ from the underlying cement generations by having faint reddish color (as opposed to colorless translucent) and by displaying only rare fluid-filled inclusions (as opposed to abundant aqueous inclusions in Phase-II calcite). Similar to Phase-II calcite, this phase exhibits uniform dull, dark orange CL. Similar to Phase-IV calcite, zonation could be observed in the Phase-III calcite under optical microscopy, but this feature is not apparent under CL.

Phase IV—Palisades of Banded, Macro-Columnar Calcite

Banded palisade calcite, up to 20 cm in length and 1 to 5 cm wide (outward thickening), form the last, most conspicuous crystal phase. The term “palisade calcite” was originally used by Folk and Assereto (1976) for Holocene, formerly aragonitic crystals in the Carlsbad Caverns, New Mexico, forming crusts of parallel, columnar crystals 1 to 10 millimeters long. Following the later work of Dublyansky (1995) and other authors, however, here the term is also applied to calcite crystals of larger dimensions. We furthermore apply the terminology of Nielsen et al. (2005) and use the term “macro-columnar calcite” for this cement phase.

The Jabal Madar palisades are built up of length-fast (i.e., *c* axis parallel to the length of the crystal) macro-columnar calcite crystals (Fig. 5). The crystals form positive rhombohedral tips {1011}. Compromise crystal faces are straight to slightly outwardly curved. Cleavage planes are well developed and intergrowth twinned crystals are very common. The internal microstructure is fibrous and consists of parallel, slightly radiating or converging individual sub-crystals. Under crossed polars, each sub-crystal exhibits a weak composite to slightly undulous extinction, but as a whole the extinction pattern of macro-columnar calcites is nearly uniform, indicating that sub-crystals grew close to optical continuum. This feature is interesting, inasmuch as calcite crystals growing from waters just above the saturation state typically have an internal structure of a single crystal (White 2004).

Macroscopically, the crystals are cream-colored or translucent; in thin sections they appear faintly reddish. Irregular fissures transect crystals. In elongated caverns, these palisade calcites usually form one massive rim with individual crystals reaching 20 cm in length. In widened fractures (Fig. 4E), up to eight, shorter, successive palisade growth stages could be present.

Of particular interest is the conspicuous reddish zoning of this cement phase, transcending the compromise-growth boundaries of individual crystals (Fig. 5). The spacing between red zones is rather uniform (between 1 and 1.75 cm) in all specimens collected. This zoning is broadly consistent with the rhombohedral crystal morphology. Microprobe and SEM analyses of three polished thin sections (sampled at localities 1, 2, and 4 in Fig. 3A) show that the conspicuous red zones of the Phase-IV calcites are enriched in detrital minerals (Fig. 6). Cracks within the etched calcite that builds these zones are filled by mainly vermiculite and illmenite containing accessory detrital minerals including quartz, rutile, apatite, chlorite, and unidentified Ni- and Ba-Mn-oxides. Authigenic barite is also common (Fig. 6A).

The translucent to whitish portions of the macro-columnar calcites of phase IV (Fig. 5) are non-luminescent (black) under CL, with the exception of bright luminescent zones, occurring beneath and above each red interval (Fig. 7). The bright luminescent zone present at the base of each red zone is approximately 1–2 mm thick. The luminescent intervals often display a complex zonation (Fig. 7C). At their upper limit, layers of the zoned, luminescent calcite are etched, corroded, and overlain by the porous non-luminescent calcites forming the red zones (Fig. 7D, E). A thin (< 1 mm) patchy and irregular luminescent zone is found at the upper limit of red zones (Fig. 7E). Here, the luminescence is confined to micro-druses occluded by several generations of luminescent calcite. This upper luminescent zone is then followed by non-luminescent calcites of the next cycle of transparent calcite precipitation (Fig. 7E).

In order to better understand the alternating red and translucent zoning of Phase-IV calcites, and particularly the differences in detrital content, one might refer to the two growth modes of gypsum sand crystals from the Laguna Madre in Texas as described by McBride et al. (1991): a slow mode (non-displacive) where gypsum merely fills pores between sand grains in a passive manner and a fast growth mode (displacive) resulting in gypsum entirely free of sand grains, i.e., the crystal surfaces displace sand grains whilst growing.

The translucent Phase-IV calcite shows characteristic petrographic features of relatively fast precipitation and thus rapid growth and is largely free of detrital phases (displacive growth); in contrast, calcite in the porous red layers apparently precipitated at slower rates, is in places drusy, and is rich in detrital material (non-displacive growth). It is worth noting that precipitation of the red zones commonly follows a hiatus in the calcite deposition, during this hiatus calcite growth stopped and the surface of already deposited crystals was etched. Similarly, some degree of etching of the top of the red zones precedes precipitation of the base of the overlying translucent zone (see Fig. 7 D, E).

Fault-Zone Blocky Calcite

Large volumes of whitish to translucent calcite crystal rubble, covering areas up to 20 meters wide and hundreds of meters long, delineate fault zones at Jabal Madar (Fig. 1). Individual fault-zone crystals are commonly a few centimeters in dimension and are confined by planar cleavage surfaces. Crystals are bright luminescent under CL and contain rare gas-liquid inclusions. Judging from field and petrographic evidence, these calcites are not related to the spelean calcites of phase I to IV. Although not the focus of this study, carbon and oxygen isotope data were measured for comparison with the phreatic calcites.

ANALYTICAL RESULTS

Carbon and Oxygen Isotopes

The summary of the stable-isotope properties of the carbonate materials studied from the Jabal Madar site is shown in Figure 8.

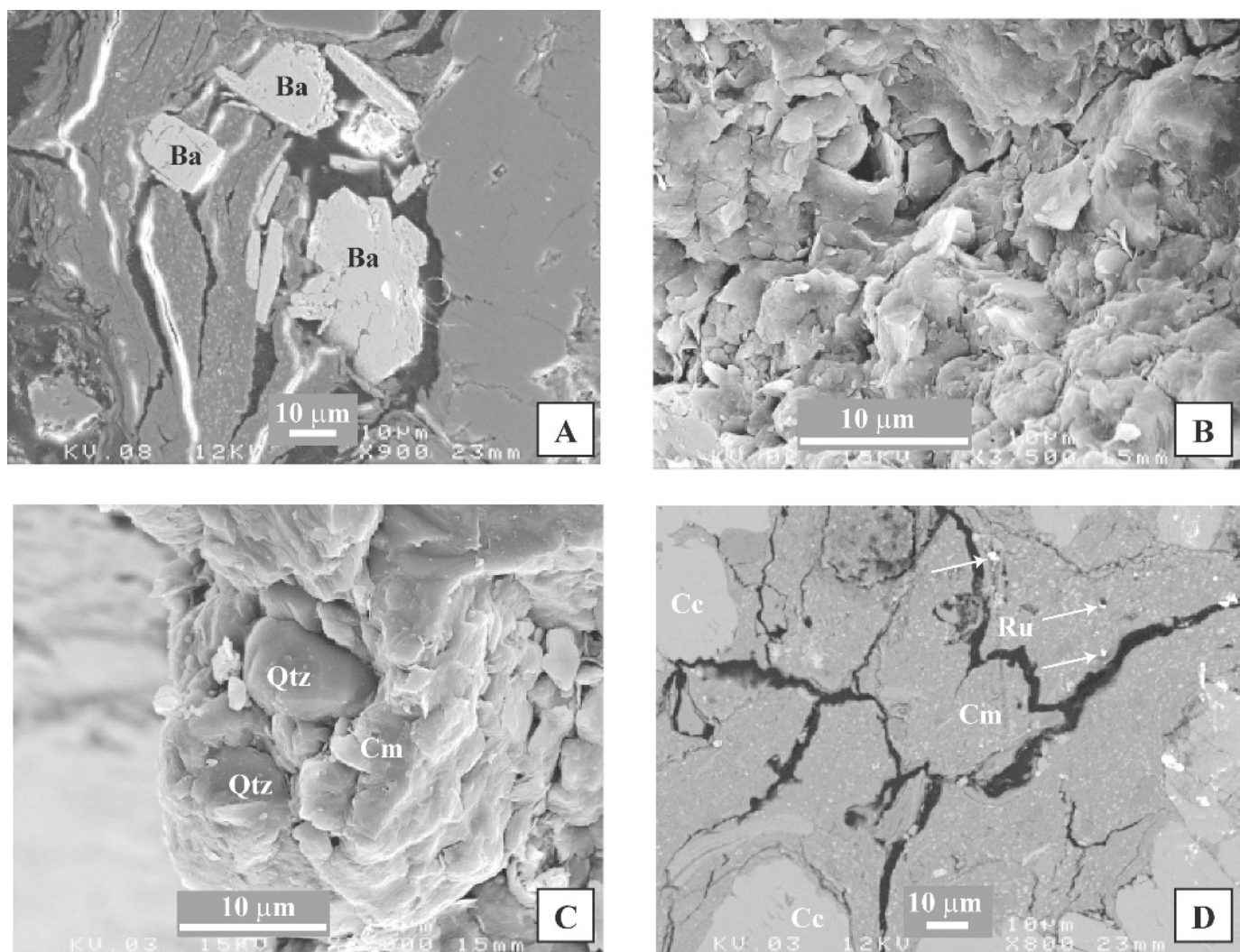


FIG. 6.—Scanning electron microscope (SEM) and microprobe backscatter (MB) imaging of red zones in Phase-IV calcites. **A)** MB image showing authigenic barite (Ba) in clayey matrix. **B)** SEM image close-up of mainly vermiculite occluding fissures in phreatic calcite. **C)** SEM image showing detrital quartz grains (Qtz) embedded in clayey material (Cm). **D)** MB image showing fractured clay matrix filling porosity in calcite (Cc). White arrows point to detrital rutile (Ru).

Carbonate Host Rock.—Mean bulk-matrix micrite values of Shuaiba Formation host rock limestones cluster around $+2.3\text{‰}$ for $\delta^{13}\text{C}$ ($\sigma = 0.56$) and -7.8‰ for $\delta^{18}\text{O}$ ($\sigma = 0.86$; Fig. 8).

Phase-I through Phase-IV Phreatic Calcites.—Phase-I calcite is difficult to sample because of the small size of its crystals (Fig. 5). Only four measurements were made, indicating a range between -0.7 and -1.3‰ for $\delta^{13}\text{C}$ and between -11.8 and -12.3‰ for $\delta^{18}\text{O}$ (Fig. 9). Phase-II blocky calcite shows mean $\delta^{13}\text{C}$ values of -0.7‰ ($\sigma = 0.4$; $n = 21$) and mean $\delta^{18}\text{O}$ values of -11.7‰ ($\sigma = 1.0$; Fig. 9). Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are relatively homogeneous in phase II. Phase-III calcite crystals display an average $\delta^{13}\text{C}$ ratio ($n = 7$) of -2.3‰ ($\sigma = 0.7$) and an average $\delta^{18}\text{O}$ ratio of -11.7‰ ($\sigma = 1.4$; Fig. 9). Whereas $\delta^{18}\text{O}$ values are comparable to those of phase II, $\delta^{13}\text{C}$ records an abrupt shift of *ca.* 2‰ towards lower values (Fig. 9).

In three crystals of phase IV the mean $\delta^{13}\text{C}$ value is -7.2‰ ($\sigma = 1.3\text{‰}$) and the corresponding mean $\delta^{18}\text{O}$ value is -14.0‰ ($\sigma = 0.8\text{‰}$). The data from sample CEM 1/2a are shown in Figure 10. Data display a systemic cyclical pattern, with $\delta^{18}\text{O}$ maxima often coinciding or falling directly underneath the red zones. Across red zones

the mean $\delta^{18}\text{O}$ value is -13.5‰ ($\sigma = 1.0\text{‰}$) and the mean $\delta^{13}\text{C}$ value is -6.5‰ ($\sigma = 1.4\text{‰}$). In translucent Phase-IV calcite the mean $\delta^{18}\text{O}$ value is -14.2‰ ($\sigma = 0.7\text{‰}$) and the mean $\delta^{13}\text{C}$ value is -7.5‰ ($\sigma = 1.1\text{‰}$).

Carbon-isotope values typically attain maxima directly beneath red zones (although in some instances it happens within and above them) and then trend toward a minimum at central parts of the intervening translucent intervals. This pattern is clearly visible when sampling at approximately 2 millimeter increments (Fig. 10). In an attempt to resolve a possible higher-frequency pattern, one interval of CEM 1/2a was sampled in one millimeter increments. In terms of absolute values, the two data sets are identical (Fig. 11A). This implies that the observed trends are not artifacts. Horizontal transects, i.e., parallel to the crystal growth surface reveal relatively invariant isotope data (Fig. 11B).

Fault-Zone Blocky Calcites.—In terms of $\delta^{13}\text{C}$ values, values for fault-zone blocky calcite range between host rock and speleothem values, but $\delta^{18}\text{O}$ signatures are closer to spelean phreatic calcites (Fig. 8). The mean $\delta^{13}\text{C}$ value is $+1.0\text{‰}$ ($\sigma = 0.2\text{‰}$) and the mean $\delta^{18}\text{O}$ value is -11.3‰ ($\sigma = 1.2\text{‰}$).

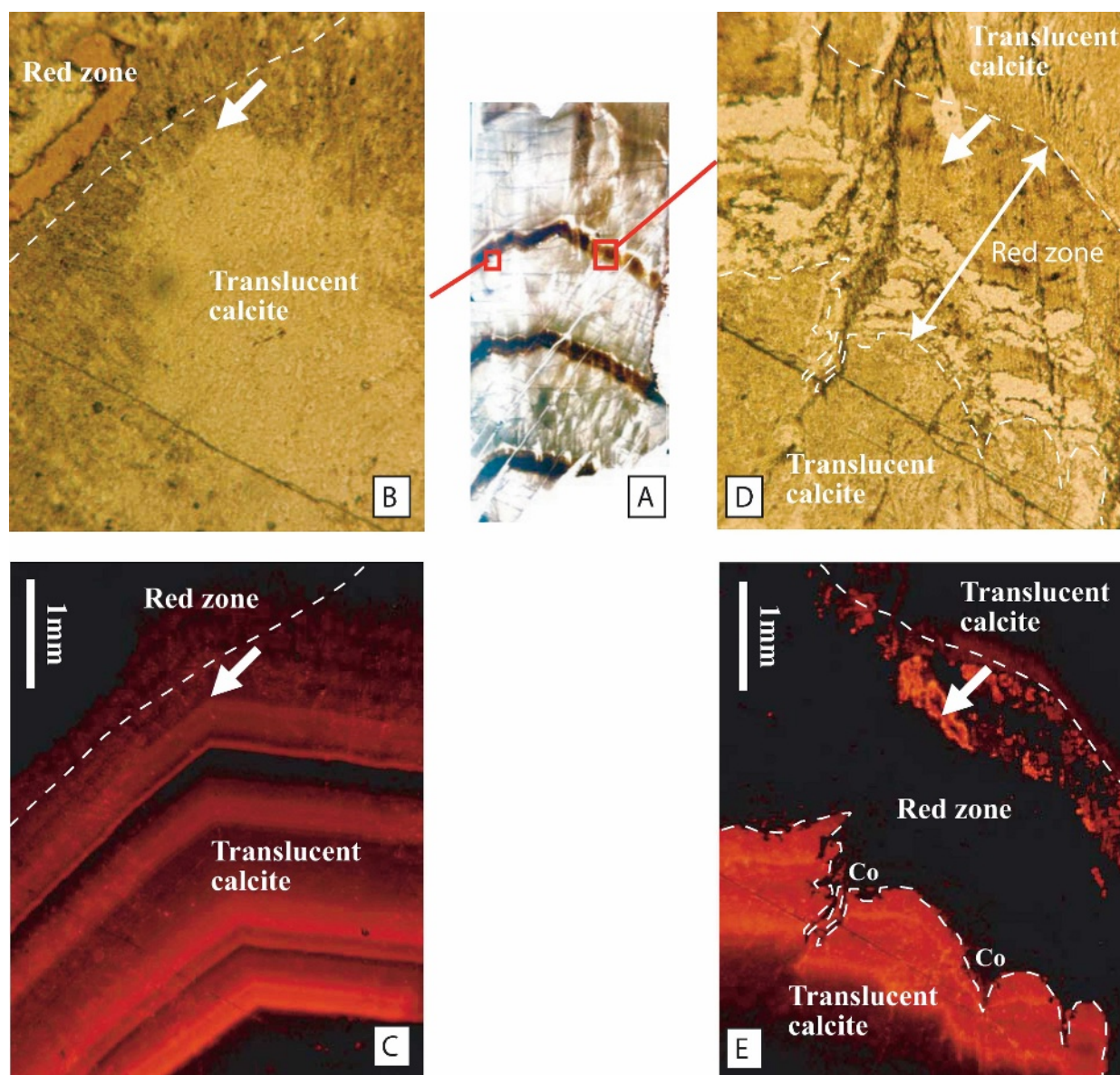


FIG. 7.—A) Thin section of sample CEM 1/2a (Phase-IV calcite). B, C) Portions of translucent calcite beneath red zones under transmitted light and under CL. Arrows for orientation. Stippled line denotes lower limit of red zone. D, E) Red zone under transmitted light and under CL. Dissolution pores in etched upper portions of red zone are filled with several generations of bright luminescent calcite (arrow). Note corrosion (Co) of the translucent calcite at the base of the red zones.

Trace Elements

Phase-II through Phase-IV Phreatic Calcites.—Samples drilled from Phase-I phreatic calcite crystals were too small for trace-element analysis requiring about 0.5 to 1 milligram of powder (Fig. 5). Trace-element data from the Phase-II and Phase-III calcites are shown in Figure 12. Iron concentrations range from below detection limit to about 114 ppm (mean = 54 ppm; σ = 54 ppm). Magnesium contents range between 2593 and 5550 ppm (mean = 3722 ppm; σ = 1598 ppm). The manganese contents are rather uniform with a range of 246 to 257 ppm (mean = 256 ppm; σ = 9 ppm). Strontium contents range from 193 to 356 ppm (mean = 260 ppm; σ = 85; Fig. 12).

Trace-element data from a macro-columnar Phase-IV calcite (sample CEM 1/2a) are illustrated in Figures 12 and 13. Basically, trace-element values in red zones (rz) differ significantly from those in translucent zones (tz). Iron in CEM 1/2a and three other phreatic Phase-IV crystals ranges

from below detection limit to 1700 ppm (mean_{rz} = 958, σ_{rz} = 541 ppm; mean_{tz} = 608, σ_{tz} = 304 ppm); Mg is between 700 and 3100 ppm (mean_{rz} = 2359, σ_{rz} = 630 ppm; mean_{tz} = 2690, σ_{tz} = 335 ppm); and Mn ranges from below detection limit to 200 ppm (mean_{rz} = 113, σ_{rz} = 80 ppm; mean_{tz} = 59, σ_{tz} = 47 ppm). Strontium concentrations lie between below detection limit and 720 ppm (mean_{rz} = 226, σ_{rz} = 144 ppm; mean_{tz} = 212; σ_{tz} = 119 ppm).

The trace-element compositions display a cyclical pattern that appears to be similar to that of the isotope data. More specifically, Fe, Mn, and Sr co-vary with $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, whereas Mg shows the opposite pattern (Fig. 13). A noteworthy feature of the trace-element pattern is the reciprocal nature of the Fe and Mg contents, so that the sum of the Fe + Mg content remains more or less constant. On the basis of mathematical treatment of elemental and isotope data and of the optical image of sample CEM 1/2a (Fig. 10), three distinct growth regions of this specific crystal were defined (Fig. 13). An implication of this is that

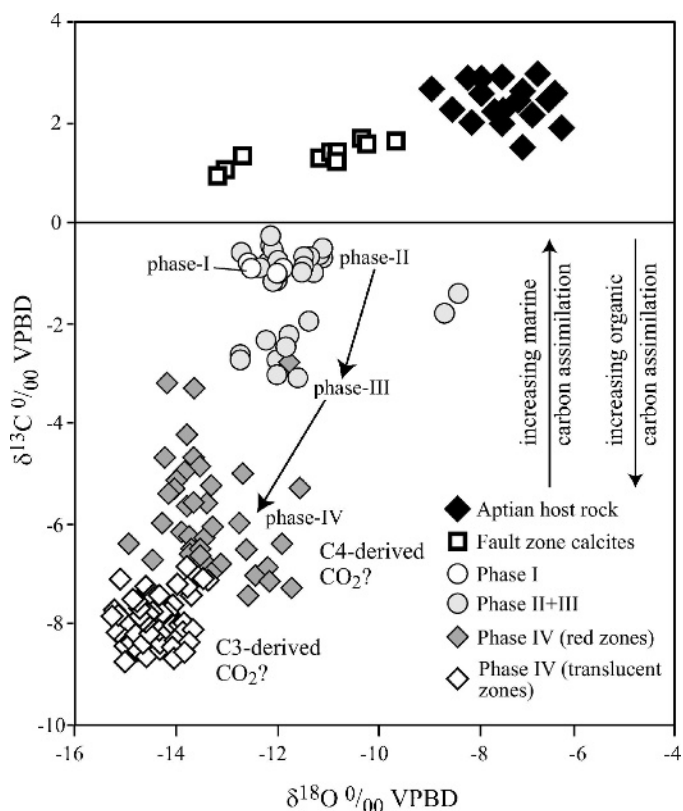


FIG. 8.—Cross-plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ of various carbonate phases. Differences in $\delta^{13}\text{C}$ between red and translucent zones in Phase-IV calcites are tentatively explained by the influence of the soil-zone CO_2 derived from different vegetation types adapted to alternating humid (C3) and dry (C4) climate.

correlations between geochemical properties must be analyzed within individual areas of crystal growth, and the direct correlation of the whole data set would not be correct from the standpoint of the mathematics. A detailed documentation and discussion of the outcome of the mathematical treatment of these data, however, is beyond the scope of this publication and will be reported elsewhere.

Fluid-Inclusion Thermometry

Fluid-Inclusion Petrography.—Two samples representing Phase-II and Phase-IV calcite were examined for the presence of fluid inclusions. In the Phase-II calcite, inclusions are abundant. Most of them are all-liquid aqueous. In some groups individual inclusions contain vapor bubbles. The bubbles are large, and have vapor-to-liquid (L:V) ratios of ca. 0.5 to 0.8, suggesting that those inclusions are artifacts, either related to the stretching and leakage of inclusions or to heterogeneous entrapment of vapor and liquid phases during mineral growth. Sizes of inclusions vary over two orders of magnitude (from tens to hundreds of micrometers), with the largest inclusions being invariably the least equidimensional.

In the Phase-IV calcite, aqueous inclusions are very small and located mostly along fractures. The latter are curved and appear to be randomly oriented, showing no relation to the crystallography of the host mineral. Much more rarely, large (up to 100 μm) three-dimensional inclusions are found in this calcite. Inclusions typically have irregular shapes, and most of them are leaked.

In both Phase-II and Phase-IV calcites, typical vadose-zone inclusions (i.e., thorn- or spindle-shaped) were not observed. The morphological appearance of individual inclusions and fluid-inclusion assemblages (FIAs) is typical of the phreatic-zone calcite.

Microthermometry.—Microthermometric experiments have been carried out only for the Phase-II calcite, since the phase IV one did not contain suitable inclusions. Homogenization experiments were performed

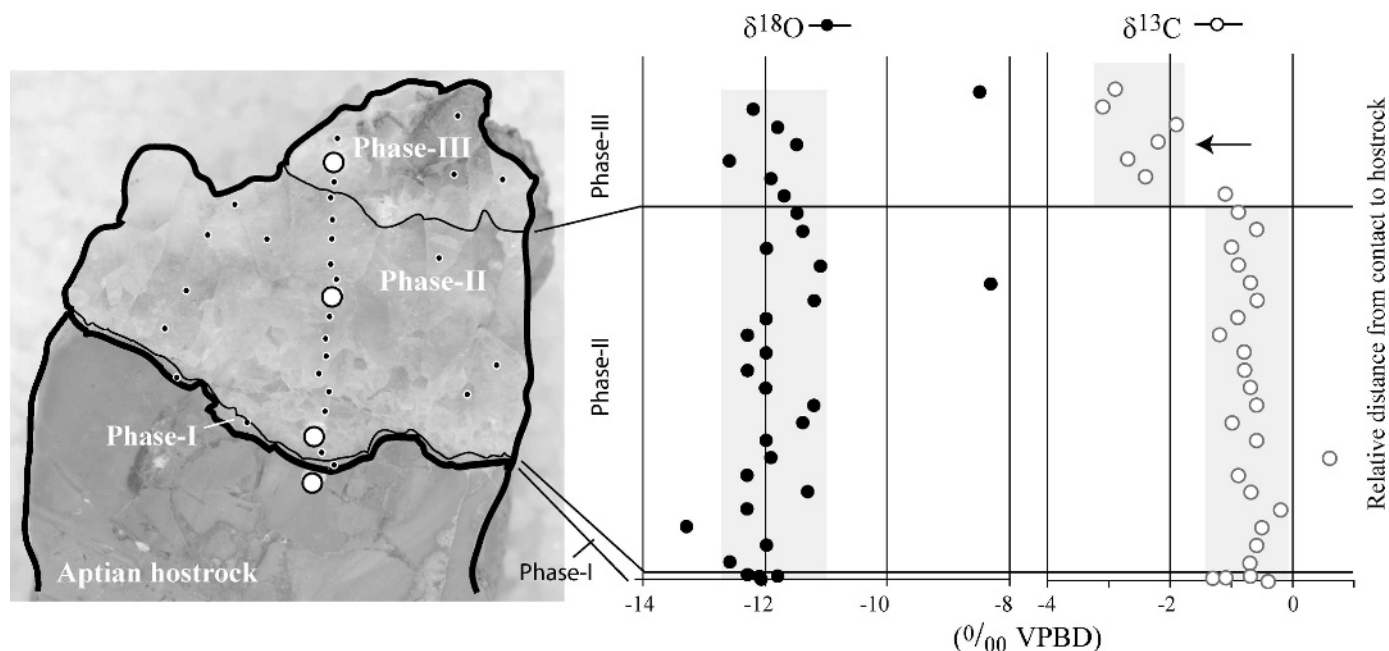


FIG. 9.—Isotope transect of Phase-I through Phase-III phreatic calcites overlying Aptian carbonate host rock. Note abrupt decrease in $\delta^{13}\text{C}$ values for Phase-III calcite by ca. 2‰. White circles denote sampling localities for larger volume bulk samples.

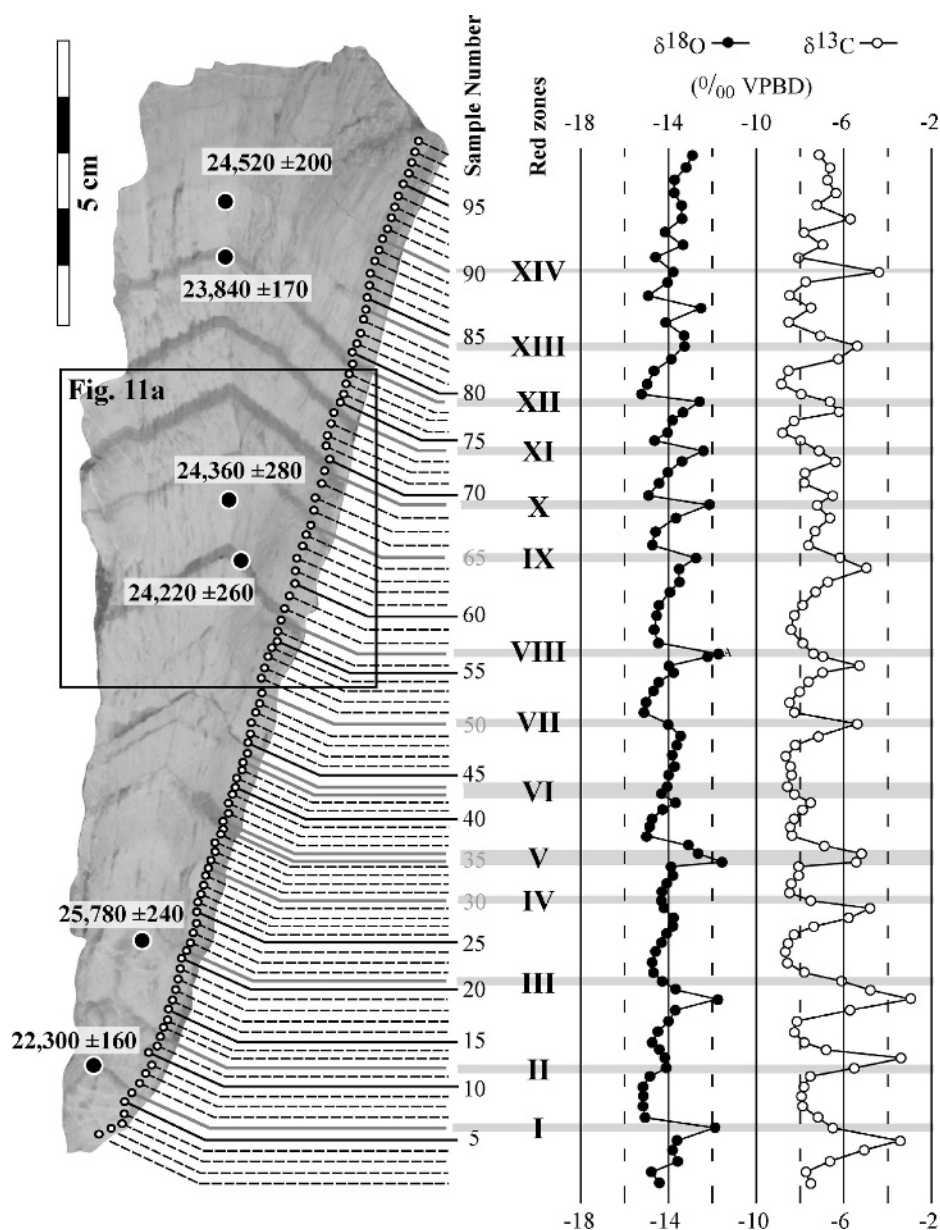


FIG. 10.—Isotope stratigraphy of macro-columnar calcite (Phase-IV; sample CEM 1/2a). Gray bands indicate position of red zones within crystal. Sampling points are indicated. Sampling localities for ^{14}C age dating and resulting uncorrected ages are shown.

on a number of FIAs; several inclusions showed, on a visual basis, similar L:V ratios (with the remainder being monophasic liquid). Measured homogenization temperatures were relatively high (79 to 160°C). In the three cases when more than one T_h has been measured from the same FIA, the scatter of data was significant, ranging from 9 to 56°C. The relatively high homogenization temperatures along with the monophasic character of the majority of inclusions, and the scattered character of the temperatures indicate that the two-phase character of these inclusions is likely an artifact, so that the measured homogenization temperatures do not reflect the temperature of the mineral forming waters.

Salinities of paleo-waters were determined through measurements of the final ice melting temperatures. Inclusions were stretched by over-heating prior to freezing experiments so that the vapor bubbles were present in inclusions during the melting of the last ice crystal. The measured freezing depression temperatures ranged from -0.9 to -4.6°C, corresponding to salinities from 1.6 to 7.3 wt.% NaCl equivalent (Fig. 14).

Fluid-Inclusion Stable-Isotope Analysis

Water Content in Calcite.—Samples of Phase-II calcite contain substantially more water (2.7 to 10.4 $\mu\text{l/g CaCO}_3$), as compared to the Phase-IV calcite (0.9 to 1.1 $\mu\text{l/g CaCO}_3$), which is consistent with the fluid-inclusion petrographic observations. Both values are greater than those measured in samples of the typical vadose-zone (stalagmite) calcite from, for example, northeastern Italy (0.02 to 1.0 $\mu\text{l/g CaCO}_3$), which is consistent with the phreatic character of the Oman calcite.

Hydrogen Isotope Composition of Water Trapped in Inclusions.—Both samples (Phase-II and Phase-IV calcite) showed similar δD values of waters recovered from fluid inclusions (-66 and -67‰ V-SMOW, respectively). These results should be considered tentative, since they are based on only four measurements (two from each sample; Fig. 15).

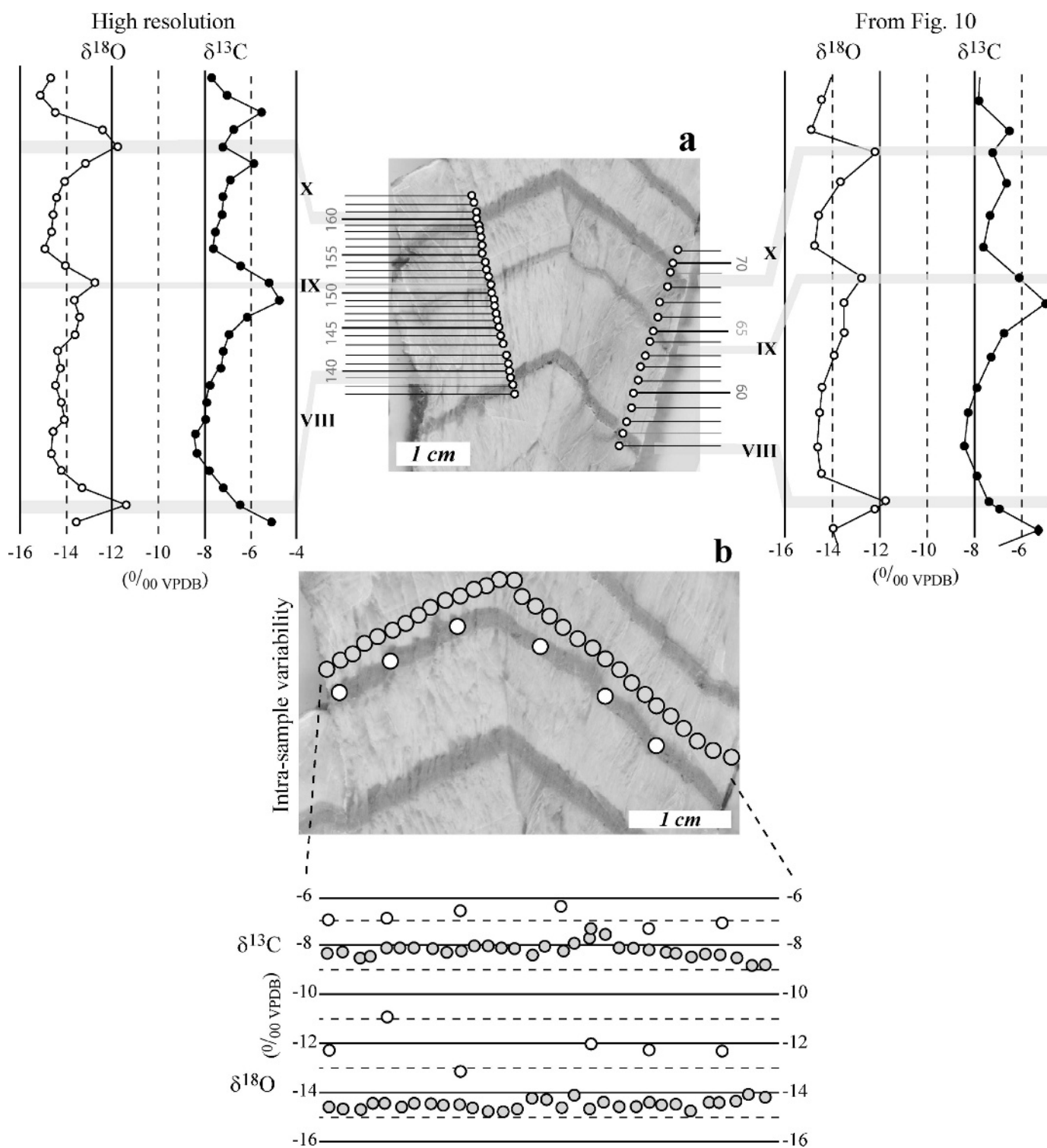


FIG. 11.—A) High-resolution isotope sampling (1 mm increments) across red zones VIII-IX is shown to the left (see Fig. 10). Plot to the right shows results of sampling at 2 mm or less resolution. Note that absolute values and overall pattern correlate well. B) Sampling of the macro-columnar crystal parallel to the inferred growth surfaces (red zone X of Fig. 10). Note that lateral variability of isotope values in translucent calcites is small, whereas it is somewhat more pronounced within red zones.

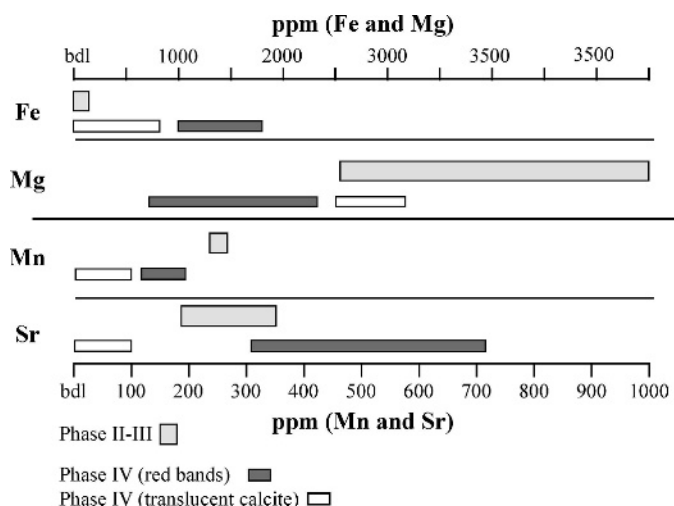


FIG. 12.—Comparison of trace-elemental data from Phase-II/III and Phase-IV calcites.

¹⁴C AMS Dating and U–Th Dating

¹⁴C AMS analysis of a Phase-IV calcite (sample CEM 1/2a; Fig. 10) yielded uncorrected radiocarbon ages ranging between $22,300 \pm 160$ to $25,780 \pm 240$ yr. BP (mean = 24,138 yr; $\sigma = 1246$ yr). Two additional ¹⁴C AMS analyses were obtained from the first and the last generations of Phase-IV calcite from the fracture shown in Figure 4E (FR 2 and 11). The uncorrected age is $26,220 \pm 210$ yr BP for the first Phase-IV palisade (FR 2) and $24,200 \pm 190$ yr for the last Phase-IV phase (FR 11).

Uranium-series age dating was performed from Phase-II/III and from Phase-IV calcites, and the resulting data are summarized in Table 1 and Figure 16. Samples were taken from localities 4 and 5 in Figure 3A and from fault-zone calcites (Table 1). The ages range from older than 600 kyr to younger than 200 kyr, but four samples cluster in an age range between 150 and 300 kyr, i.e., the middle Pleistocene.

DISCUSSION

Origin of Cavities Hosting the Phreatic Calcites

The original dimensions of the Jabal Madar cave system are not well constrained (Figs. 3, 4). To our knowledge, cavity systems with a comparable mineral infilling have not been reported from elsewhere in the Oman Foothills (Fig. 1A). It is thus possible that the cavity-forming processes responsible for the development of this cave system are specific to Jabal Madar, which is diapiric in origin (Fig. 2), whereas other outcrops of the Foothills are anticlinal structures (Hanna 1990).

The specific position of the Jabal Madar caverns, situated underneath a regional low-porosity aquitard (the Nahr Umr Formation shales, Figs. 3B and 4A), merits discussion. Similar to the processes discussed in Giles and De Boer (1989), a model for phreatic (hydrothermal) cave formation (related to CO₂ but not to H₂S) was laid out in Dublyansky (1995 and references therein; Fig. 17). The advantage of this model is that it explains both carbonate dissolution (cavity formation) and phreatic calcite precipitation. As summarized by Dublyansky (2000a), the solubility of calcite (S_{calc}) in a phreatic hydrothermal environment is controlled by three major parameters: (1) the CO₂ regime ($S_{calc} \sim pCO_2^{1/3}$); (2) temperature ($S_{calc} \sim T^{-1}$); and (3) ionic strength of a solution ($S_{calc} \sim I$; Holland and Malinin 1979). In turn, the amount of dissolved CO₂ and its phase state in the system depends on temperature and pressure. Malinin (1979) modeled that the solubility of calcite in the water ascending from depth toward surface gradually increases over most

of the path (Fig. 17), so that the ascending water is able to dissolve carbonate bedrock. Only near the surface, at a depth of 0.5 to 0.2 km, the CO₂ loss to the gaseous phase acquires the “runaway” character, which leads to the abrupt reversal of the trend and results in rapidly decreasing solubility of calcite. The fluid becomes supersaturated, and the calcite dissolved when water moved through the deep-seated part of the system is deposited. The actual depth of the calcite deposition zone depends on many parameters, including temperature, pCO₂, ionic strength, and velocity of upwelling.

It is likely that the upwelling (moderately thermal) water in the diapiric structure remained undersaturated with respect to CaCO₃ along most of its path. The result is the dissolution of the Cretaceous carbonate host rock preferentially along fractures that act as fluid pathways and are leached and widened by the undersaturated fluids (Figs. 4D, E). Once reaching the top of the Shuaiba Formation, and the base of the overlying seal facies of the argillaceous Nahr Umr Formation, the undersaturated fluids are trapped and lateral dissolutional cavities are formed. If the process delineated above occurs associated with the overall diapiric uplift of the Jabal Madar and ongoing erosion of the overlying sedimentary units, the calcite dissolution zone, where solutional cavities developed at early stages of the process, will be moved into the calcite deposition zone. This led to the precipitation of the phreatic calcites described in this paper.

Other models for the formation of the non-meteoric caves, such as the H₂S or the seacoast mixing one (Hill 1990; Palmer 1995), do not seem to be relevant in the case of the Jabal Madar due to the lack of any mineralogical or geochemical evidence suggesting the involvement of the sulfur species and the absence of a nearby Pleistocene coastline.

Age of Phreatic Calcites

Age of Phreatic Crystals.—The AMS ¹⁴C age data from Phase-IV calcites CEM 1/2a (Fig. 10) and FR 2 and 11 (Fig. 4E) represent an age overestimate because of the incorporation of dead carbon from the Aptian carbonate host rock. From vadose speleothems, Genty et al. (2001) documented an increase in dead carbon proportion (dcp) from 22 to 38% from 3780 years ago to the present. In the case of the Jabal Madar samples, the uncorrected 23 to 27 kyr time interval as indicated by the ¹⁴C method falls into a period of little or no speleothem growth in northern Oman, whereas the period between 6 and 10.5 kyr is characterized by summer monsoon precipitation and enhanced phreatic speleothem growth (Fleitmann et al. 2003a; Fleitmann et al. 2003b). In order for the Jabal Madar vadose crystals to match this 6 to 10.5 kyr time interval, a dcp of roughly 85% must be assumed. Greater proportions of dead carbon can be expected when referring to deep-seated circulation through relatively old carbonate-rich formations, but these considerations remain speculative and are contrasted with the results of the U-series disequilibrium data, which, for Phase-IV calcite, yielded ages of 158 to 212 ka (Table 1). Consequently, the radiocarbon ages are not considered to be meaningful.

Precise U-series disequilibrium dating of Phase-II to Phase-IV calcites has not been possible perhaps due to detrital contamination and leaching of U, similar to the problems mentioned in Burns et al. (1998), Fleitmann et al. (2003a), and Fleitmann et al. (2003b). Although large U/Th age uncertainties are observed (Table 1), the U/Th age data cluster between roughly 150 and 320 ka (with the exception of sample II-A indicating an age of more than 500 ka, Table 1). In addition, the two samples taken from Phase-II/III calcites are consistently older than those of the subsequent Phase-IV data. This is considered to be meaningful.

Assuming that these observations are correct, the Jabal Madar phreatic calcites seem to have ages between approximately 320 and 150 ka. Older than 150 ka, at least two intervals centered at ~ 200 and ~ 315 ka of enhanced speleothem deposition occurred in northern Oman (Fig. 16).

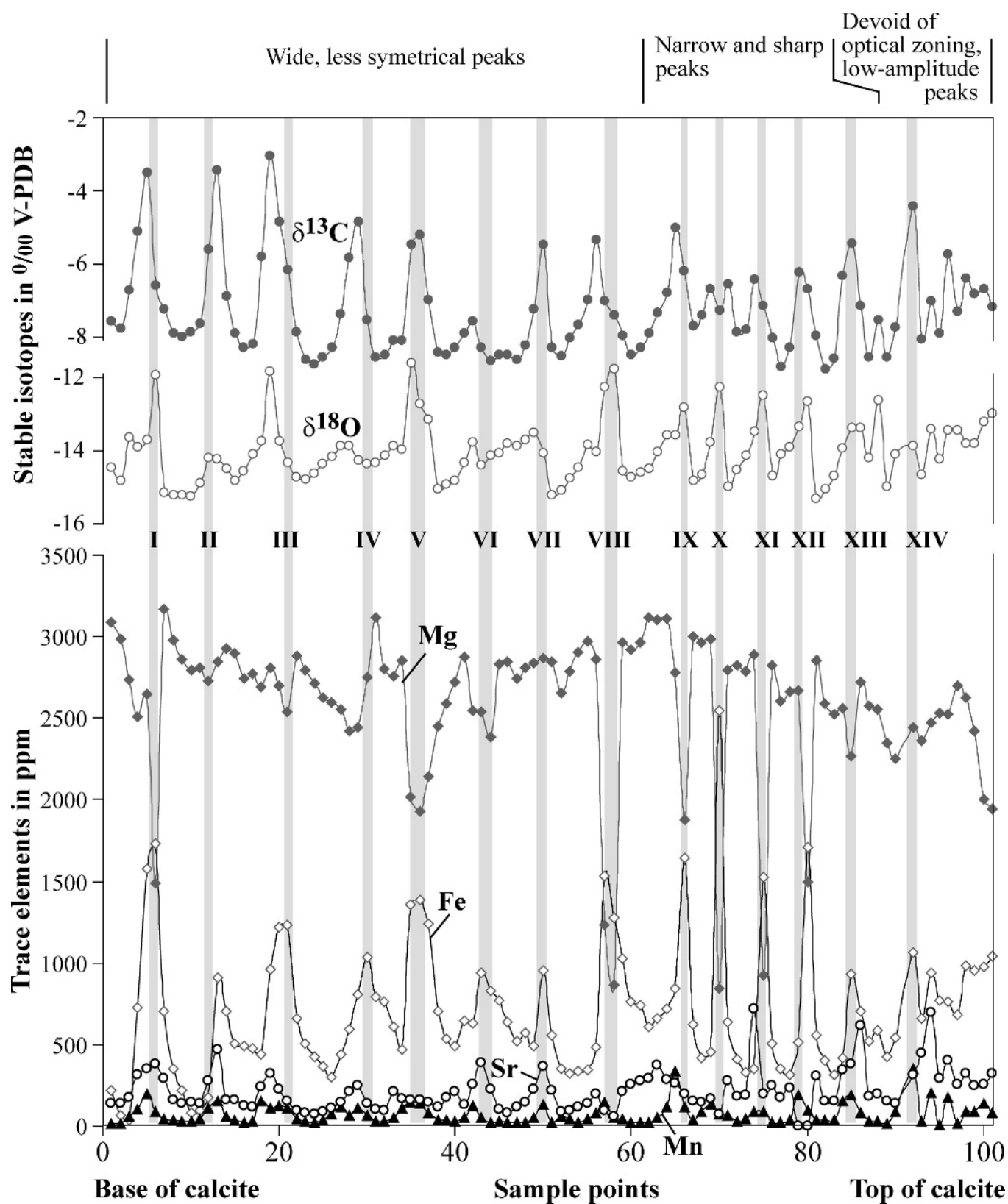


FIG. 13.—High-resolution trace-element stratigraphy of macro-columnar calcite (Phase-IV; sample CEM 1/2a). Gray bands indicate position of red zones within crystal. Isotope data are shown for comparison. On the basis of mathematical treatment of elemental and isotope data and of the optical image, three distinct growth regions of this specific crystal can be separated. Note the reciprocal character of the Mg and Fe contents.

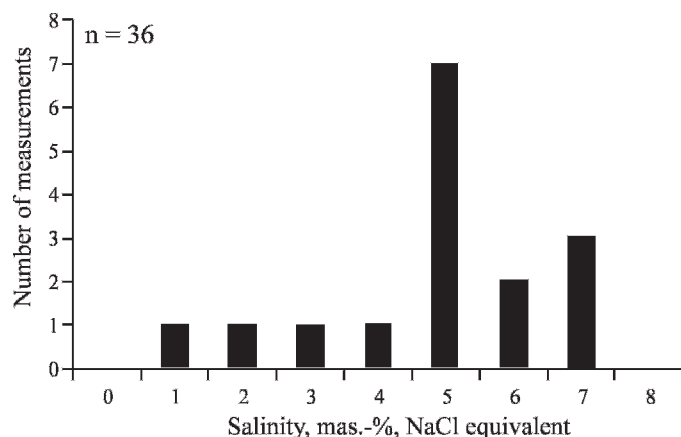


FIG. 14.—Salinities of waters trapped in inclusions from sample JM-P1 (Phase-II) determined by freezing experiments.

Whereas the charging of the aquifers in northern Oman is probably related to increased monsoonal precipitation, the precipitation of phreatic calcites does not necessarily respect climate, and such calcites mostly do not form in the peak interglacial periods. Accepting that, within limitations, aquifer charging and calcite precipitation could be two temporally separate processes, it is conceivable that the Jabal Madar phreatic calcite precipitation was related to, but not necessarily coeval with, intervals when northern Oman was affected by summer monsoon precipitation (Burns et al. 2001; Fleitmann et al. 2003a).

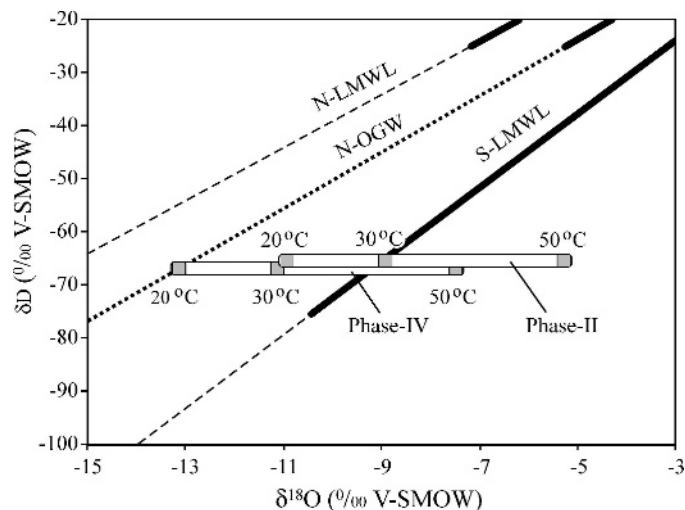


FIG. 15.—Measured values of δD of water recovered from inclusions and calculated values of $\delta^{18}O_{\text{water}}$ from Phase-II and Phase-IV calcites. For calculations, mean values of $\delta^{18}O_{\text{calcite}}$ of -12.4 and -14.5% for Phase-II and Phase-IV, respectively, were accepted. N-LMWL and S-LMWL are northern and southern Oman local meteoric water lines, and S-OGWL is the southern Oman groundwater line (Weyhenmeyer et al. 2000). Bold part of the lines shows characteristic values of precipitation. Meteoric water lines for North and South Oman are from Fleitmann et al. (2003b). The depleted character of δD measured in fluid inclusions suggest that waters which deposited phreatic calcite were recharged by southern moisture sources. Note that calculations for 20 and 30°C yield results plotting to the left of the meteoric-water line of South Oman, which would not be realistic. The data thus suggest the temperatures of water somewhat above 30–35°C.

Interpretation of Analytical Results

Aptian Carbonate Host Rock.—Interpretation of the stable-isotope data from the Aptian host rock (Fig. 8) is straightforward. The $\delta^{13}C$ values of $+1$ to $+3\%$ are in the range of many Lower Aptian limestones (Menegatti et al. 1998). The ^{18}O values are clearly ^{18}O depleted, which, in combination with the dull luminescence of the matrix micrites, points to a burial diagenetic overprinting (and perhaps early meteoric diagenesis) of marine values (Immenhauser et al. 2001).

Blocky Fault-Zone Calcites.—The origin of the whitish, inclusion-rich calcite from the fault zones at Jabal Madar (Fig. 1) is obviously phreatic and likely hydrothermal (Fig. 8). The $\delta^{13}C_{\text{calc}}$ values are close to that of the marine limestone, suggesting that the Cretaceous carbonates acted as carbon reservoir. The data show ^{18}O depletion relative to the carbonate host-rock values, suggesting elevated temperatures during the precipitation of the fault-zone calcites.

Phase-I to Phase-IV Fluid Inclusions.—The fluid-inclusion method does not yield numerical results when the temperature at which inclusions are trapped is not sufficiently high to generate, upon cooling, the shrinkage bubbles. In fluid-inclusion practice, minerals that contain only all-liquid aqueous inclusions are typically characterized as being formed at temperature of less than *approximately* 50°C (Goldstein and Reynolds 1994). This is the case with the Jabal Madar Phase-II and Phase-IV phreatic calcites. They contain fluid-inclusion assemblages consisting of the all-liquid inclusions; all two-phase liquid to vapor inclusions are likely artifacts related either to stretching and leakage of inclusions or to heterogeneous entrapment of random amounts of liquid and the ex-solved gas phase (effervescence). This implies that from the fluid inclusion data alone it is not possible to tell whether the mineral forming waters had ambient temperatures or were slightly thermal.

The depositional temperatures could be further constrained by isotope data obtained from calcite and from fluid inclusion waters. Figure 15 shows the measured δD values of the inclusion waters along with the calculated values of the $\delta^{18}O$ for the mineral-forming waters. The latter values were calculated using the $\delta^{18}O$ values of calcite and the calcite–water fractionation coefficients (calculated using equation reported in Kim and O’Neil 1997) for 20, 30, and 50°C. It is apparent from the figure that values calculated for 20 and 30°C plot to the left of the South Meteoric Water Line (Fig. 15). This would be difficult to explain, since there are no obvious geochemical mechanisms that would cause evolution of waters in this direction (e.g., Clark and Fritz 1997). The depositional temperatures, thus, could be bracketed by (approximately) 30–35 and 50°C.

Noteworthy is the depleted δD values measured in fluid inclusions. Waters originated from a northern moisture source (Mediterranean frontal systems) have $\delta D = -25$ to $+5\%$, and similar values were measured from modern ground waters in North Oman (N-OGW in Fig. 15; see also Weyhenmeyer et al. 2000). The low δD values suggest the leading role of the southern moisture sources (monsoons and cyclones from Indian Ocean) in recharge of the groundwater responsible for deposition of calcites at Jabal Madar.

Elevated salinities of the mineral-forming waters trapped in inclusions (1.6 to 7.3 wt.% NaCl equivalent; Fig. 14) strongly suggest involvement of the ascending deep-seated waters that possibly acquired their elevated salt content from the upper Precambrian to Lower Cambrian Ara Formation evaporites (Peters et al. 2003), which form much of the salt dome underneath Jabal Madar (Fig. 2).

Phase-I to Phase-IV Stable Isotopes.—Phase-I to Phase-III phreatic calcites show a 2‰ shift in $\delta^{13}C$ ratios from Phase-II to Phase-III whereas

TABLE 1.— *U and Th isotope concentrations and calculated ages and uncorrected AMS ^{14}C ages for Jabal Madar phreatic speleothems.*

Uranium series							
Sample Number	Phase	Concentration ^{238}U ppm	Concentration ^{232}Th ppb	Concentration ^{230}Th ppt	Age, kyr	Minimum, kyr	Maximum, kyr
CEM-U	Phase IV	156.006 ± 0.395	72.235 ± 0.438	Not determined	158,447¹	155,151	161,743
CEM-O	Phase IV	98.938 ± 0.254	50.108 ± 0.770	Not determined	212,402¹	202,636	222,168
II-A	Phase II	0.1144 ± 0.0003	0.406 ± 0.010	1.893 ± 0.011	527,000²	413,600	infinite
II-B	Phase II	0.1022 ± 0.0002	1.205 ± 0.011	1.615 ± 0.006	284,500²	270,100	301,500
II-C	Phase II	0.0606 ± 0.0001	18.031 ± 0.101	0.972 ± 0.006	256,200²	228,100	295,500
FZCA	Fault zone calcite	0.5772 ± 0.0005	4.134 ± 0.021	9.670 ± 0.032	Infinite²	574,700	infinite
AMS ^{14}C					^{14}C ages, uncorrected		
FR2							
FR11							
CEM 1/2a-1					22,300	22,140	22,460
CEM 1/2a-2					25,780	25,540	26,020
CEM 1/2a-3					24,220	23,960	24,480
CEM 1/2a-4					24,360	24,080	24,640
CEM 1/2a-5					23,840	23,670	24,010
CEM 1/2a-6					24,520	24,320	24,720

¹ Bern University data; not corrected for detrital contamination.² Kiel University (IFM-GEOMAR) data; for the correction for detrital ^{230}Th , a $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of 0.6 ± 0.2 was used.

$\delta^{18}\text{O}$ values remains largely constant (Fig. 9). This pattern in $\delta^{13}\text{C}$ ratios might indicate the incorporation of variable amounts of ^{12}C derived from the oxidation of soil-zone organic carbon (Machel and Cavell 1999). The low $\delta^{13}\text{C}$ values probably did not form from thermochemical sulfate reduction, because there are no indications of sour gas or any of the common by-products of this process (Worden et al. 1996) in these rocks.

In the Oman Hoti cave of northern Oman (Fig. 1), vadose speleothems, have $\delta^{13}\text{C}$ values that are between -1 and -6‰ (Burns et al. 1998). In many modern vadose speleothems, where the pathway from soil to the cave is short, the carbon is a one-to-one mixture between the carbonate rock ($\delta^{13}\text{C} = 0 \pm 3\text{‰}$) and soil-zone CO_2 ($\delta^{13}\text{C} = -22 \pm 5\text{‰}$; Genty et al. 2001). At Jabal Madar, the host rock has $\delta^{13}\text{C}$ values of $2 \pm 1\text{‰}$, and assuming a soil zone CO_2 $\delta^{13}\text{C}$ value for C_3 plants of -25‰ , values of approximately -11‰ would be expected if the considerations above were applicable. In fact the Phase-IV phreatic calcite $\delta^{13}\text{C}$ ranges between -3 and -9‰ (Fig. 8) and Phase-I to Phase-III data are between -0.2 and -3.5‰ . Furthermore, the pathways of precipitating fluids of the Jabal Madar calcites were probably long. Hence, the ^{13}C -enriched values must be explained differently.

It is unclear where the fluids entered the system. In the case of a long pathway, involving deep circulation of the meteoric waters through various sedimentary rocks, the $\delta^{13}\text{C}$ values could become buffered by the $\delta^{13}\text{C}$ ratio of the bedrock. The meteoric water that enters the bedrock is

charged with isotopically light soil- CO_2 -derived carbon. As it moves through the rock, it dissolves CaCO_3 , thus acquiring isotopically heavy rock carbon. When it becomes saturated with respect to calcite, dissolution comes to a halt. Yet, even at chemical equilibrium, isotopic exchange between water and bedrock may continue through dissolution-precipitation reactions. If the water continues traveling through the bedrock, going to the deeper levels where the temperatures and pCO_2 are higher, some calcite would be precipitated to maintain chemical equilibrium. Then, on the upwelling limb (Fig. 17) the solution becomes again undersaturated, causing dissolution of the bedrock, and the solution becomes further enriched with bedrock-derived ^{13}C .

Yet another mechanism that would tend to shift carbon in these waters toward higher values is degassing of CO_2 , which should occur in the deposition zone (Fig. 17). This degassing leads to kinetic fractionation, whereby lighter isotopes of carbon tend to concentrate in the gas phase, thus enriching the carbon remaining in solution with ^{13}C .

The average $\delta^{18}\text{O}$ ratio of Phase-I through Phase-III calcites is about 2‰ higher than the mean of Phase-IV calcites (Fig. 8). This might have various reasons, but given the only slightly warmer fluid temperatures ($30\text{--}50^\circ\text{C}$; Fig. 15), temperature is perhaps not a main controlling factor. In addition, the lower $\delta^{18}\text{O}$ values of the Phase-IV calcites would suggest that the fluid temperatures were higher at this stage than those of the previous stages. A perhaps more likely interpretation is to see the

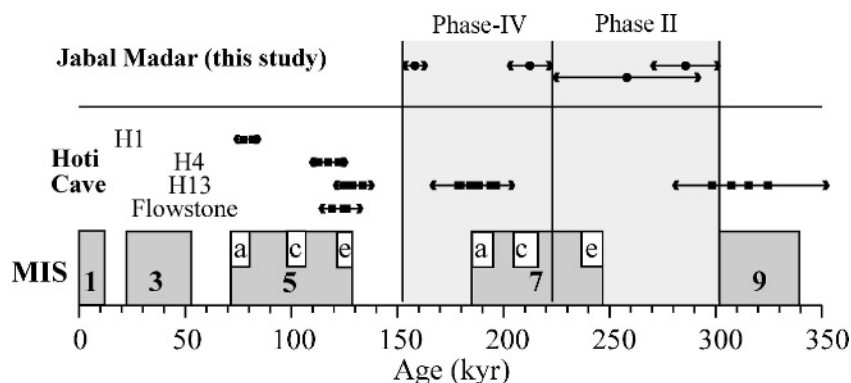


FIG. 16.—Plot of results of Phase-II and Phase-IV Jabal Madar uranium-series age dating with error bars and marine oxygen-isotope stages (MIS). Note cluster of four U/Th age data between 150 and 320 kyr (shaded light gray). Intervals of vadose speleothem deposition in Oman (Hoti cave; Fleitmann et al. 2003b) are indicated. Note that phreatic calcite precipitation does not necessarily coincide with peak interglacials.

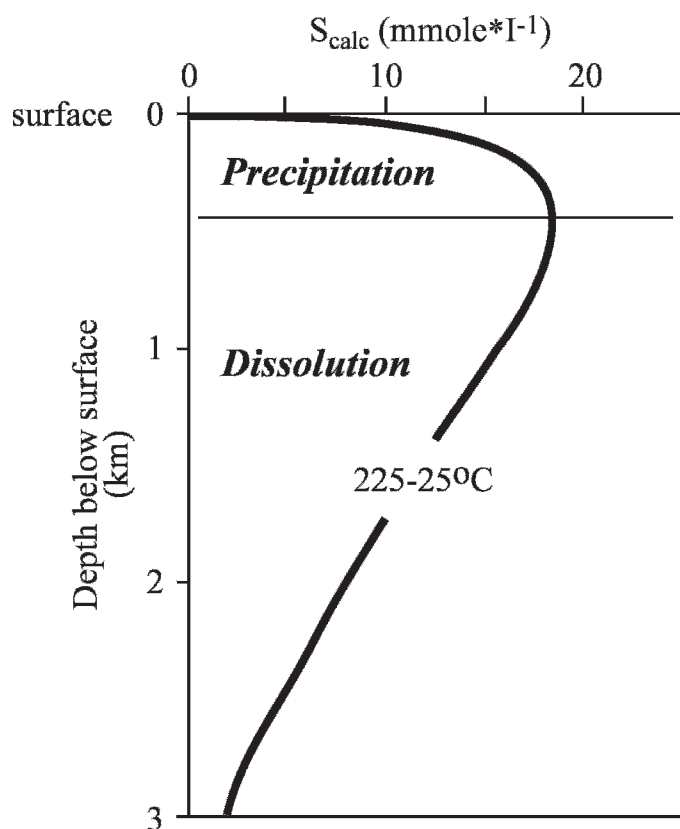


FIG. 17.—Physicochemical model for the formation of phreatic (hydrothermal) caves (Dublyansky 1995). The curve depicts the change in solubility of calcite (limestone) in CO_2 -saturated aqueous solution ascending toward the surface and cooling from 225 to 25°C . Note rapid change from dissolution to precipitation (expressed as a sharp bend of the curve) near the surface, which is related to the onset of the rapid loss of CO_2 to the gas phase at this depth.

observed trend in concert with the possible mixing of hydrothermal (^{18}O -enriched and saline) and meteoric (^{18}O -depleted and low-salinity) waters during Phase-IV precipitation.

Phase-I to Phase-IV Trace Elements.—Trace-element contents of Phase-II/III calcites differ from those of Phase-IV. In addition, trace-element contents fluctuate cyclically within Phase-IV calcites (Figs. 12, 13). Both of these patterns might be best explained by either one or a combination of two end-member models. These are (i) assuming two different parent fluids with a different trace-element composition: one precipitating Phase-II/III calcites and another (or the same with variable admixtures of perhaps meteoric water) precipitating Phase-IV calcites. This setting is common where upwelling thermal waters meet descending meteoric fluids (Dublyansky 1995). The alternative assumption is that (ii) variable physicochemical parameters have resulted in the precipitation of geochemically different cement phases from a single parent fluid.

Considering the second scenario first, i.e., one parental fluid but changing physicochemical parameters over time, the following parameters are important: partitioning coefficients, precipitation rates, and redox states. Whereas the effect of fluid temperature on the partitioning coefficient (distribution coefficient K_d) of Sr in calcite is moderate, it is potentially more important for Mg, Mn^{2+} , and Fe^{2+} (Dromgoole and Walter 1990; Carpenter and Lohmann 1992; Rimstidt et al. 1998). Moreover, K_d is a function of the rate of precipitation, the solution composition, and the concentration of the other trace elements. This renders assumptions regarding the effects of temperature and pre-

cipitation rates on K_d for specific elements difficult. Nevertheless, assuming precipitation of Phase-II through Phase-IV calcites from the same parent fluid, an enrichment in Mg and Sr ($K_d < 1$) with time is predicted, hence resulting in increasingly higher abundances of these elements with each subsequent phase. This is not the case for Mg which is higher in Phase-II/III than in Phase-IV as well as for Sr (translucent Phase-IV calcites; Fig. 12).

In case of growth rates being an important factor of changing $K_{d\text{Mg}}$ and $K_{d\text{Sr}}$, the decrease of Mg across red zones within Phase-IV calcites might point to considerably lower precipitation rates. In contrast, Sr is higher within or underneath red zones (Fig. 13). Assuming constant precipitation rates, a decreasing trend from Phase-II to Phase-IV would be predicted for Fe^{2+} and Mn^{2+} ($K_d > 1$); this is the case for Mn and in part (translucent zones) for Fe (Fig. 12). This implies that the partitioning coefficients and temperature gradients can explain the observed trends in calcite geochemistry only when pronounced differences in precipitation rates are involved (see discussion in de Leeuw 2002).

Partitioning coefficients predict that Mn^{2+} is removed from solution more rapidly than Fe^{2+} ($D_{\text{Mn}^{2+}} > D_{\text{Fe}^{2+}}$), hence compositional trends will tend to exhibit a greater change in $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratios (Dromgoole and Walter 1990). In fact Mn^{2+} and Fe^{2+} co-vary, but the order of magnitude of shifts across red-translucent couplets is many hundreds of ppm for Fe^{2+} but only between 100 and 200 ppm for Mn^{2+} . This observation is not in concert with an enhanced removal of Mn^{2+} from the solution, and a fluid containing more Fe and less Mn would explain the above observation. In summary, K_d seems a possible but not a main controlling factor of the elemental trends observed.

Another aspect that merits consideration is the redox potential of elements in the precipitating fluids. Under sub-oxic (burial) conditions Fe and Mn usually appear in their divalent state (Fe^{2+} and Mn^{2+}), whereas under oxidizing conditions Fe is likely to be oxidized to its trivalent state (Fe^{3+}), and the same accounts for Mn (Mn^{3+} or Mn^{4+}). Magnesium and strontium are not affected by these changes in redox potential. The result of the oxidation of Fe and Mn is that their ionic radii become considerably larger, thus affecting the partitioning coefficients (Barnaby and Rimstidt 1989).

Iron and Mn co-vary within Phase-IV calcite, which is consistent with a redox control. Phase-II/III calcites are more difficult to interpret (low Fe^{2+} , higher Mn^{2+}). However, this difference could be explained by the redox sensitivity of Mn^{2+} versus Fe^{2+} (Barnaby and Rimstidt 1989). More strongly reducing fluids are required to bring Fe^{2+} into solution. Hence Phase-II/III fluids might have been reducing enough to bring Mn^{2+} into solution but not sufficiently reducing for Fe^{2+} . Possibly, Phase-II/III calcites precipitated from fluids that were mildly reducing (enough for Mn but not enough for Fe). The later Phase-IV cements precipitated from more evolved or mixed fluids that were more strongly reducing.

Cathodoluminescence is mostly a function of Mn^{2+} (activator) and Fe^{2+} (quencher), and the Mn content of the dull orange luminescent Phase-II/III calcites is up to five times that of the non-luminescent Phase-IV calcite (and vice versa for Fe). The luminescent nature (suggesting the sub-oxic precipitation environment) of Phase-II/III calcites is in concert with the moderately elevated temperatures, as suggested by δD and fluid-inclusion data (Fig. 15). In a first approximation, similar considerations might account for the complex luminescent zoning underneath red intervals in the Phase-IV macro-columnar calcites (Fig. 7). But whereas the complex luminescence micro-pattern itself (Fig. 7C) could be explained by changes in the Fe and Mn ratio of the precipitating fluid, Mn and Fe abundances fluctuate beneath different red zones (Fig. 13). This implies that the relation between elemental abundances and luminescence patterns is more complex.

Generally, red bands are enriched in Fe, Mn, and Sr, whereas they are depleted in Mg (Fig. 13). Iron might be stripped from clay minerals during precipitation of secondary cements and for instance vermiculite is

abundant in the red layers (Fig. 6). Nevertheless, along with Fe, vermiculite also contains Mg, and Mg decreases towards the red zones, whereas Sr and Mn, which are not a constituent of any of the analyzed clay minerals, are enriched (Fig. 13). This implies that the stripping of elements from clay minerals is a poor explanation of the patterns observed. The changes in elemental composition from Phase-II to Phase-IV, and cyclical changes within Phase-IV, thus reflect genuine changes in the fluid trace-element composition. These considerations, combined with geochemical data, support the assumption that Phase-IV calcites precipitated from a fluid that was different from (or an admixture with) the parent fluid present during precipitation of precursor phases I to III.

Is this conclusion in contrast to the similar δD values (Fig. 15) measured in fluid inclusions from Phase-II and Phase-IV calcites that point to one fluid only? Perhaps, but it should be kept in mind that δD is not a function of the redox potential and does not change substantially when rain water is charged into an aquifer and chemically altered during descent and upwelling. In contrast, D is controlled mostly by source water (precipitation). Therefore, if infiltration occurred on a reasonably short time scale, so that the overall δD of meteoric waters did not change significantly—both upwelling waters and infiltrating ones could have similar δD . In addition, the data set available is not large, and hence it is suggested that sophisticated conclusions should be avoided.

Origin of Zoning in Phase-IV Macro-Columnar Calcites

The red zones within Phase-IV calcites represent “snapshots” marking the propagation of the outside surface of the palisade aggregate during the course of growth, and each red zone is sealed by an overlying translucent phase (Fig. 5). Nevertheless, in order to better understanding the controlling mechanisms of the red zoning, more work is required and the concepts presented hereafter should be treated as tentative interpretations only. Given the formation of these calcites at the burial–meteoric interface, two fundamentally different mechanisms might explain the Phase-IV calcite zoning: (i) the rhythmical tectonic expulsion of deep-seated fluids, or (ii) a monsoon-driven climatic pattern.

Hot Flush (Squeeze) Expulsion.—Tectonic expulsion of formation fluids was originally proposed by Oliver (1986) for the Appalachian foreland basin of the United States. Subsequent workers adapted this concept (Karsten et al. 2003) and introduced the term “squeeze” flow, in analogy to a rubber roller used by, e.g., photographers to push liquid across a surface.

Given the diapiric nature of the Jabal Madar structure, flushes of overpressured slightly thermal fluid, driven by neotectonics, could be envisioned. The main building phase of the Oman Mountains occurred during the Neogene, but subduction of Arabia underneath Eurasia is ongoing in the Persian Gulf. It is at least conceivable that Holocene neotectonic activity in the Persian Gulf caused high-frequency, far-field (~ 300 km) flushes of fluids causing pulses of warm fluids to rise within the Jabal Madar dome (Fig. 2), and precipitation of phreatic calcites from these fluids. Nevertheless, across up to eight palisade Phase-IV calcite phases in one of the widened fractures (Fig. 4E) a total of 37 red/translucent couplets were counted. Using the uranium-series ages, a frequency distribution of approximately one red/translucent couplet per 3,400 yr results but obviously a large error bar must be attributed to this value.

Data on relatively short-lived, low-flux events (hot flushes) during Laramide thrusting in the Rocky Mountain Foreland Basin are discussed in Machel and Cavell (1999). In tectonically active regions such as California, 167 potentially damaging earthquakes of magnitude six or larger have been identified since 1850 (Topozada and Branum 2004; i.e., 1.1 event/yr) and strike-slip rates in modern California (22–27 mm/yr; Johnson and Segal 2004) are comparable to subduction rates in the

Persian Gulf (32 mm/yr). Nevertheless, although possible, it seems difficult to imagine that each red/translucent couplet within Phase-IV calcites should reflect a specific tectonics pulse in the Persian Gulf. A particular problem is the pronounced periodicity of red and translucent zones in Phase-IV calcites, requiring constantly pulsating plate convergence and related far-field flushes of burial fluids.

Monsoon-Driven Precipitation Changes.—The Pleistocene of Oman is characterized by summer monsoon precipitation (Burns et al. 1998; Neff et al. 2001). During wet periods, heavy rainfall might have charged the aquifer underneath the Nahr Umr Formation seal. The water was chemically altered and heated on the way downward. When reaching the Ara salt dome the undersaturated fluids, driven by buoyancy, would rise within the Jabal Madar dome, leaching host limestones at greater depths and subsequently precipitating calcite within cavities at shallower depths.

Petrographic and geochemical evidence suggest that Phase-IV translucent calcites precipitated rapidly, hence displacing silt-size detrital grains, from these warm, saline waters. The rhombohedral crystal forms of Phase-IV calcites are typical of fluid supersaturation of less than six; more specifically the simple crystal shapes (non-dendritic or branching) point to a supersaturation of less than two (González et al. 1992). This assumption is also supported by the nearly single-crystal character pointing to waters just above the supersaturation state. The fact that relatively few but large crystals formed (few nucleation sites), indicates stagnant or nearly stagnant waters.

Phase-IV red zone calcites might have resulted from drier periods when less meteoric water was inserted into the aquifer, causing the water table within the Jabal Madar cavern system to decline (Fig. 18). During these dry periods, occasional thunderstorms generated large water volumes in short periods of time and slackwater, carrying abundant runoff from overlying caprock temporarily re-flooded the cavern system via conduits. The main detrital and authigenic components within red zones (quartz, vermiculite, ilmenite, barite) are in agreement with a caprock origin.

Meteoric slackwater is expectedly undersaturated with regard to CaCO_3 and charged with humic acids from the overlying soil system, perhaps dominated by C4 plants, which are better adapted to a dry climate. Undersaturated, acidic meteoric waters are in agreement with the observed etching of the top of translucent calcites (Fig. 7E). Gradually falling slackwater levels caused the suspended silt to settle on the corroded surface of the underlying translucent calcite phase, and nondisplacive, slow calcite growth encased this material. With the beginning of the next humid period, more meteoric water reached the caverns and detrital material in the cavern-filling waters was diluted. As a result, the next translucent phase of Phase-IV calcites was precipitated. The observed shifts in stable-isotope composition could be explained by alternating humid and dry periods (Fig. 18).

The combination of the displacive versus nondisplacive precipitation mode and a monsoon-driven cyclical charging of the aquifer fluids moving through the cavern system offers a possible explanation for the red zoning observed in Phase-IV calcites. Neff et al. (2001) documented spectral analyses from stalactites in Oman indicating monsoonal periodicities at 1018, 226, 28, 10.7, and 9 years, respectively. The frequency distribution of red/translucent couplets as based on the U–Th ages ($\sim 3,400$ years) is apparently beyond this spectrum but the precision of the U–Th age data is insufficient to exclude the possibility that the red zoning reflects monsoonal periodicity in the millennium time domain. Based on the above arguments and the depleted δD values measured in fluid inclusions pointing to southern (Indian Ocean) moisture sources, the monsoonal model is favored by the authors. This model, however, must be treated as a tentative interpretation until more precise age data are available.

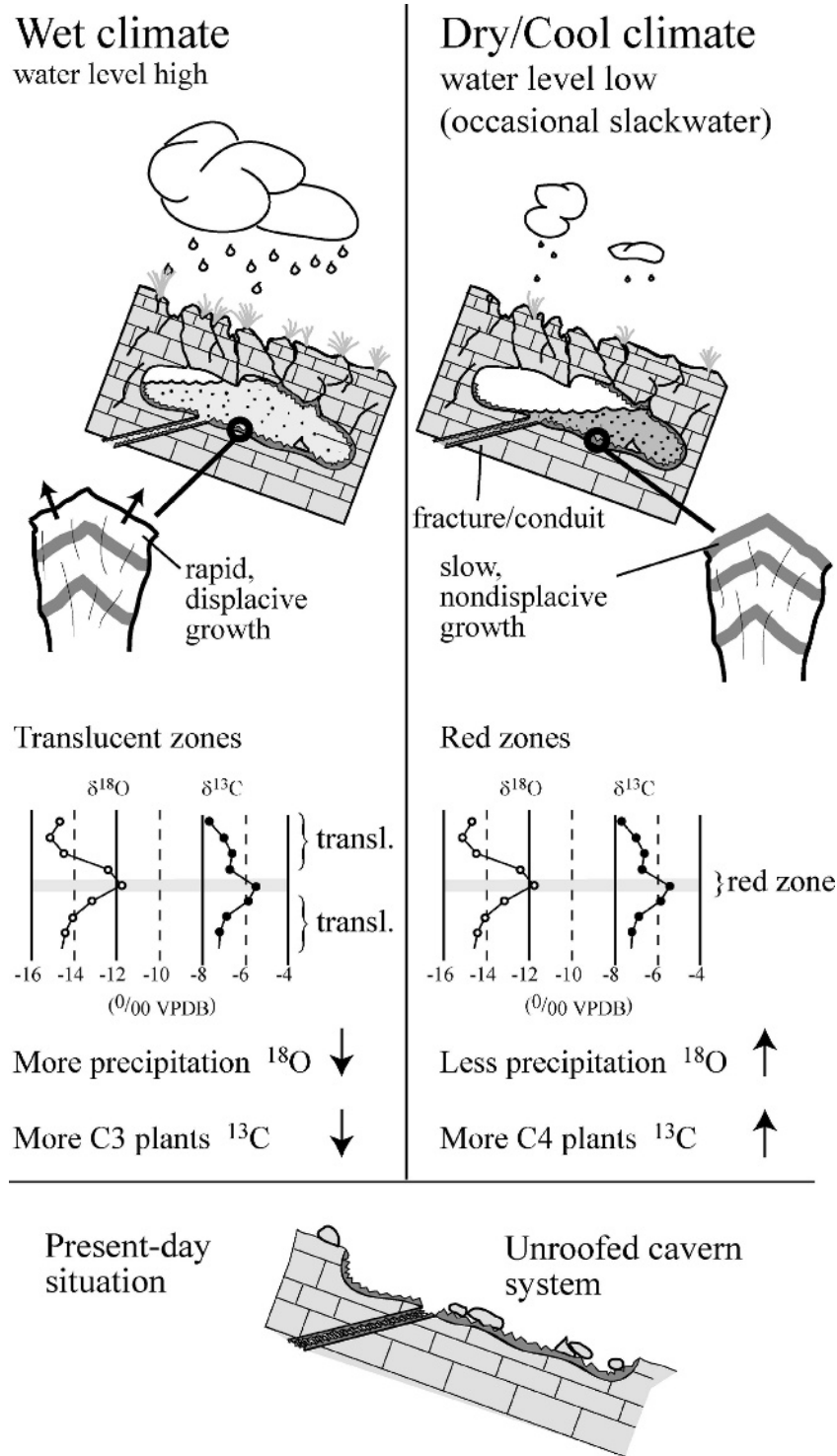


FIG. 18.—Sketch of the “monsoonal model” showing possible relation of alternating wet/dry climate modes and translucent/red zoning in Phase-IV phreatic calcites. See text for discussion.

Comparison with Other Phreatic Calcites

The denuded caves exposed at Jabal Madar and their phreatic spelean calcite filling should not be compared with H_2S -generated cavern systems and related precipitates such as the Carlsbad Caverns of New Mexico and West Texas (Hill 1990), or the Cupp-Coutunn/Promeszutochnaya caves in Turkmenia, central Asia (Bottrell et al. 2001). A main difference is the CO_2 origin (Dublyansky 1995) of the Oman caverns and the absence of

native sulfur, gypsum, or hydrothermal mineralization products at Jabal Madar rules out H_2S karstification.

In contrast, one occurrence of calcite deposits similar to that of the Phase-IV calcite from Jabal Madar was reported from the Buda Hills, Hungary (Dublyansky 1995). There, dissolutional cavities several meters in size were exposed in the walls of a limestone quarry. Some cavities were filled with crusts of columnar calcites 30 to 80 centimeters thick. The crusts were composed of the large individual crystals (tens of centimeters

along the L_3 axis) confined by the compromise growth surfaces. The latest free-growth surfaces exposed in the central openings carried rhombohedral faceting. Similar to Jabal Madar, fluid-inclusion studies revealed only all-liquid aqueous inclusions interpreted as an indication of depositional temperatures of less than approximately 50°C. Similar to Jabal Madar, the columnar calcite exhibited growth-related zonation that was continuous across multiple adjacent crystals. The zonation was consistent with rhombohedral morphology. In the Hungarian quarry, zoning was defined by fine grayish clay particles, which, unlike the Jabal Madar case, did not show any apparent periodicity but more or less irregularly spaced bands of clayey material. In the case of the Hungarian phreatic calcites, the zoning is probably related to crystallization forces. That is, the surface of the growing crystal pushed the impurities, including clay particles, outward. At some point, the concentration of the particles becomes too high, so the crystal can no longer push the load; therefore it overgrows the impurities, thus trapping the clay-enriched zone.

Another example of phreatic calcites was reported by Bakalowicz et al. (1987) from the Black Hills cave (South Dakota). There, euhedral spar, as much as 15 centimeters long, lines the walls of the cavern system. Carbon and oxygen isotope properties of this calcite were consistent with a slightly thermal character of mineral-forming waters. Unpublished work of Y. Dublyansky from fluid inclusion in Jewel Cave palisade calcite has also revealed mostly all-liquid inclusions. Only several two-phase inclusions were found, and they yielded homogenization temperatures of about 35°C. According to Bakalowicz et al. (1987), the large calcite crystals contain as many as 20 distinct growth layers that appear to show a cyclic pattern. Mean $\delta^{18}\text{O}$ values of euhedral palisade sparite range from -16 to -12‰ , and $\delta^{13}\text{C}$ ratios lie between -2 and -7‰ . These values are remarkably close to the range of isotope data obtained from the Oman Phase-IV calcites.

CONCLUSIONS

Phreatic calcites, exposed in denuded Pleistocene cavern systems at diapiric Jabal Madar, Oman, provide a complex record of two fundamentally different diagenetic realms: the burial-hydrothermal realm and meteoric-climatic realm. Four paragenetic calcite phases are recognized, of which Phase-IV (macro-columnar calcites), representing the last stage of precipitation, is macroscopically conspicuous due to its cyclical zonation.

Fluid-inclusion data from calcite phases II and IV point to moderately elevated fluid temperatures of between 30 and 50°C and elevated salinities, both of these parameters suggest heating and chemical alteration of deeply circulating meteoric fluids that rose within the diapiric core of Jabal Madar. Two features, (i) low calcite $\delta^{13}\text{C}$ suggest the influx of soil-zone CO_2 and (ii) detrital material, encased in the phreatic calcites during nondisplacive, slow-growth phases, point to percolating meteoric water as the other fluid source. It is suggested that the first three paragenetic phases (I–III) precipitated predominantly from the warm ascending fluids whereas Phase-IV calcites recorded a cyclical mixing of ascending and descending water, i.e., two fluid sources. The red zonation and the related patterns in trace elements and stable isotopes record cyclical changes in fluid flow. The co-variance of Fe^{2+} and Mn^{2+} is in agreement with a redox control and supports the concept of two fluid sources.

The Jabal Madar phreatic calcites formed at the interface of the burial and the meteoric domains, and consequently mechanisms active in either realm might explain the zoning: (i) high-frequency, far-field tectonic expulsion of formation fluids linked to the subduction of Arabia underneath Eurasia, and (ii) alternating wet and dry periods linked to monsoon-driven, sub-Milankovitch climate patterns. The later interpretation is favored.

Both the formation mechanism of the Jabal Madar caverns, related to changes in the fluid CO_2 -domain and the phreatic spelean deposits, differ from the much better studied H_2S -related, hydrothermal cave systems (e.g., Carlsbad Caverns) or the well known meteoric karst type related to carbonic acid. In contrast, the Oman phreatic calcites share similarities with phreatic spelean calcites in the Buda Hills, Hungary, and the Black Hills in South Dakota, USA.

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