Mineral Assemblages in Theopetra, Greece: A Framework for Understanding Diagenesis in a Prehistoric Cave

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Prehistoric cave sediments are often subjected to severe mechanical and chemical alteration, making it difficult to interpret aspects of their archaeology. Theopetra cave offers unique opportunities to resolve aspects of this problem, particularly in relation to chemical changes, because it has a relatively well defined stratigraphy and its older deposits have been subjected to unusually severe diagenesis. A study of the mineralogy and micromorphology of the sediments, and in particular the phosphatic minerals that formed in the sediments after deposition, shows that each stratigraphic unit has its own pattern of authigenic mineral distribution. In some units these patterns vary sequentially in both lateral and vertical directions. These variations reflect changing degrees of diagenesis and the observed patterns imply that every unit obtained its diagenetic fingerprint fairly soon after burial.

The prominent ash layers in the older sediments were subjected to unusually severe diagenetic alteration, such that most of the relatively stable siliceous components of ash decomposed into amorphous silica. An intimate association between ash minerals and the K, Fe-phosphate mineral leucophosphite was also observed.

The sequential changes in authigenic mineral assemblages in Theopetra are basically similar to those observed in several caves in Israel, raising the possibility that common processes are involved and that information obtained from these detailed studies can be applied to other caves in diverse geographic regions.

Keywords: CAVE SEDIMENTS, DIAGENESIS, PHOSPHATE MINERALS, OPAL, ASH-LAYERS, FIRE, PALAEOLITHIC.

Introduction

The archaeological record is almost always altered by post-depositional modifications. These diagenetic processes can be both mechanical and chemical (Courty, Goldberg & Macphail, 1989). In prehistoric cave sites in particular, the diagenetic processes may be so severe as to seriously compromise the interpretation of the archaeological features (Goldberg, 1979a, b).

One effect of diagenesis is to shift initially incompatible assemblages of minerals toward conditions of chemical equilibrium. The extent to which this occurs at a particular site is in itself a reflection of the severity of diagenesis. This in turn can provide essential information for interpreting aspects of the archaeological record such as bone preservation (Weiner, Goldberg & Bar-Yosef, 1993), dating (Mercier et al., 1995), artefact concentrations and periods of occupation and non-occupation (Schiegl et al., 1996). These aspects of diagenesis are poorly understood in part because of the difficulties in identifying many of the authigenic minerals that form in these environments (Martini & Kavalieris, 1978), and in part because the loose, fine-grained sediments characteristic of caves, are very difficult to study by normal petrographic techniques.

A pioneering study in this regard is the analysis of the sediments in Tabun cave, Israel by Goldberg & Nathan (1975) who identified the presence of dahlite, crandallite and montgomeryite. This approach was continued by Weiner et al. (1993), Weiner et al. (1995) and Schiegl et al. (1996) who monitored a series of diagenetic changes that bones, ashes and carbonate rocks buried in the sediments undergo. These studies of
above studies are reviewed in Weiner (1995). Soluble mineral components of ash have dissolved. The quantities in certain areas of both caves, after all, more siliceous aggregates accumulate in fairly large quantities. Al, K and Fe (Schiegl et al., 1999). About 2% is relatively insoluble and is composed mainly of clusters of soil minerals cemented in an amorphous matrix rich in Si, Al, K and Fe (Schiegl et al., 1994). These so-called siliceous aggregates accumulate in fairly large quantities in certain areas of both caves, after all the more soluble mineral components of ash have dissolved. The above studies are reviewed in Weiner et al. (1995). Table 1 lists the minerals mentioned in the text as well as their chemical formulae. As all the above studies were carried out in a geographically localized environment, there was clearly a need to assess the relevance of these observations to a cave located in a different geographic, lithologic and climatic environment.

Theopetra cave is an archaeological site with an occupational history from the middle Palaeolithic onward (Kyparissi-Apostolika, 1994, 1999). The site is situated in the northwestern edge of Thessaly plain, central Greece (Figure 1), at an elevation of 280 m. It lies on the steep side of an isolated helmet-like mountain feature 1.5 km diameter. The entrance is on the north side overlooking the valley of the Lithaios river, a tributary of the Peneios river, some 100 m below the cave. The cave formed at the contact between an underlying thinly-bedded radiolarian limestone and an overlying massive limestone; both of Cretaceous age (Ardaens, 1978). The monthly mean temperature fluctuates between 5°C (January) and 27°C (July). The annual precipitation is around 1000 mm, and several days of frost are recorded during the colder months of the year.

The cave consists of one chamber with a surface extent of about 500 m² (Figure 1). A few deep karstic cavities in the western rear part of the cave are probably infilled terminations of karstic aquifers. The sedimentary sequence in the central part of the cave is 6-4 m thick. The sequence contains Middle Palaeolithic, Upper Palaeolithic, Mesolithic and Neolithic cultural phases and provides new evidence in an area poorly known in terms of the Palaeolithic and the Mesolithic. Study of the archaeological material (lithic, faunal, palaeobotanical and anthropological remains) is in progress and, therefore, only some preliminary results concerning the lithic industries are reviewed here. The Middle Palaeolithic lithic assemblages record the existence of multiple Levallois and non-Levallois systems of production and a pronounced morphological variability in the tool inventory including scraper sub-types, points, denticulates, chopping tools, truncated-faceted pieces, bifaces and leafpoints. The assemblages are also characterized by a low overall artefact density and a high tool frequency (Panagopoulou, 1999). The Upper Palaeolithic lithic industries exhibit a low tool/debitage ratio and fall under the broad term of Epigravetian. The tool inventory is limited, consisting of backed and retouched bladelets and fewer blades, endscrapers and some truncations (Adam, 1999). The subsequent Mesolithic occupation provides the only evidence of Mesolithic in the area so far. The Mesolithic industries are characterized by a large number of flakes, several retouched forms (truncations, notches, etc), and the lack of bladelets, geometric and microliths and microburins (Adam, 1999). Although stratigraphic correlations are still in progress, in general terms Middle Palaeolithic lithic assemblages are found in Units I, IIA and in the

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
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<tbody>
<tr>
<td>Calcite (C)</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Dahllite (D)05053</td>
<td>Ca₅(PO₄, CO₃)₄(OH)</td>
</tr>
<tr>
<td>Ca, Al-phosphate amorphous (N)</td>
<td>Ca, Al, P-phase, non-stoichiometric</td>
</tr>
<tr>
<td>Crandallite (R)</td>
<td>CaAl₃(OH)₆[PO₄(OH)]₂(OH)₂</td>
</tr>
<tr>
<td>Taranakite (T)</td>
<td>H₃K₂Al₆(PO₄)₈.18H₂O or K₃[Al₂₋₅(H₂O)]₄OH₂ [Al₃P₄₋₅(OH)]₄[PO₄]₂.2H₂O</td>
</tr>
<tr>
<td>Leucophosphate (L)</td>
<td>K₃[Fe⁴⁺(OH)₆(H₂O)]₄[PO₄]₂.2H₂O</td>
</tr>
<tr>
<td>Tinsleyite</td>
<td>K₃(AlFe⁴⁺)₄[PO₄]₃(OH)₂.2H₂O</td>
</tr>
<tr>
<td>Variscite (V)</td>
<td>AlPO₄.2H₂O</td>
</tr>
<tr>
<td>Opal (O)</td>
<td>SiO₂·nH₂O</td>
</tr>
</tbody>
</table>

*Blount (1974); †Smith & Brown (1959); ‡McConnell (1976); §Moore (1972); Dunn et al. (1984); **Nriagu (1984).
Figure 1. Plan view of Theopetra cave showing the excavation grid and profiles XX’ and YY’ depicted in Figures 2 & 3, respectively. Dashed line marks the drip line of the cave. The inset shows the location of the cave in central Greece.
lower part of IIB, whereas Upper Palaeolithic occurs in Units IIB, III, IV; Mesolithic lithic industries are limited to Unit V (Figures 2 & 3). Neolithic pottery remains as well as lithic and bone artefacts are found in Unit VI. One of the most striking finds of Theopetra is the discovery of human footprints in the Middle Palaeolithic deposits of the cave. Their study is in progress and the results will be presented soon.

The areas excavated of Theopetra cave (around 150 m²) reveal a fairly well-defined stratigraphy with marker horizons that can be followed over almost the entire cave. In this respect Theopetra offers singular advantages in studying the complexities of diagenesis, as many other prehistoric caves do not have such well defined stratigraphy. This study focuses on the relation between the stratigraphic units and their diagenesis, and particular attention is paid to the authigenic minerals that form within their sediments.

**Methodology**

The basic sampling strategy was to record the authigenic minerals and map their spatial distribution in three dimensions. During the first stage we collected bulk sediments from different locations. After identifying the major mineral components and their distributions, we proceeded to a detailed examination, attempting to sample every alteration feature in the whole excavated area. Fourier transform infra-red spectrometry (FTIR) was the main technique used for determining the mineralogy of the samples. A 0.5 cm⁻¹ resolution spectrometer (MIDAC Corp., Costa Mesa, CA, U.S.A.) was used. FTIR spectra were obtained by mixing 0.1 mg or less of powdered sample with about 80 mg of KBr. Spectra were collected at 4 cm⁻¹ resolution. For more details see Weiner, Goldberg & Bar-Yosef (1993).

The mineral component of particularly complex samples were also determined by X-ray powder diffraction patterns. They were collected with a Ziemens 5005 using Cu-Kα-radiation. Scans were made from 3 to 75 2θ at a scan speed of 0.02°/sec. The interpretation of the data was conducted with a Ziemens Diffrac Plus-EVA system software using Fourier transform analysis.
Undisturbed samples were collected for petrographic study. The samples were impregnated with polyester resin, cut with a rock-saw, mounted on a glass slide and ground to a thickness of 30 μm. Micromorphological observations were made using a polarizing microscope in plane and crossed polarized light.

Elemental analyses were performed on a set of polished thin sections coated with carbon, using a Jeol Superprobe 737 with an energy dispersive X-ray spectrometry (EDS) Tracor system. Very low currents were used of 0.3 × 10⁻⁸ A in order to avoid burning and dehydration of the samples.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were conducted on the same polished thin sections, using a Jeol 6400 scanning electron microscope with an EDS Link (Oxford Instruments) operating system. Images were recorded in the back-scattered electron (BSE) mode.

Radiocarbon dating was performed on the charcoal-rich burnt layers. The samples were manually cleaned by removing visible debris such as rootlets, treated with 1N HCl to remove all inorganic carbonate, and then oxidized in chromic acid to extract the organic carbon dioxide. The final form of the sample was benzene, which was counted in a Quantalus liquid scintillation counter (Wallac Oy, Finland).

Results

The following description of Theopetra cave deposits is based mainly on the central profile (Z7–9), where the thickest part of the sedimentary sequence is observed (Figures 1 & 2). Additional aspects are described from profile A9-Z9 (Figures 1 & 3). In this study, the mineralogy and alteration features are presented in detail, and the lithostratigraphic data are mentioned only briefly. For a full description of the lithostratigraphy of this profile, see Karkanas (1999). Six lithostratigraphic units separated by stratigraphic gaps are discerned from bottom to top (Figures 2 & 3).

Unit I is a strongly lithified sediment composed mainly of quartz and clay cemented by variscite. It rests upon the limestone bedrock of the cave (Figure 2). The presence of rounded sediment aggregates with silt coatings is the result of freeze–thaw activity (van Vliet Lanoe, Cautard & Pissart, 1984; Courty, Goldberg & Macphail, 1989). The upper boundary of this unit has an erosional surface which clearly differentiates it from the overlying loose sedimentary sequence. An unknown stadial period is ascribed to this unit.

Unit IIA consists of light and dark coloured organic-rich layers alternating with layers of quartz, clay and other silicate minerals. A striking feature of this unit is the deformation structures of the coloured layers. Folding of layers with different plasticity produced the pinched boudinage structures (Figure 4). The layers dip gradually towards the entrance of the cave in the north. The inclined folding planes have the same dip which records the sense of the differential movement.

The quartz and clay-rich sediments exhibit microscopic stratification indicating that they were laid down under water in a low energy environment [Figure 5(a)]. They also contain organic and phytolith-rich laminae, and some diatom concentrations. A major component of this layer is the clay-size groundmass which is isotropic, phosphate-rich and almost calcium deficient. Pale brown silt-size opal with isotropic nodular shapes was also observed. It is composed of almost pure Si. Silcrete-like, laminated microscopic crusts of opal are also present [Figure 5(b)].

The light and dark coloured layers are themselves composed of alternating reddish, black, grey and white sub-layers (Figure 4). The black sub-layers consist mainly of charcoal fragments and the reddish ones of reddish stained clay and other silicate minerals. The grey and white sub-layers are dominated by a spongy continuous pale-brown isotropic mass, and occasionally thin laminated isotropic void-infillings. Many phytoliths are incorporated in the groundmass together.
with a small amount of silicate minerals. BSE images show the same morphological features as seen in the optical microscope, namely a broad spectrum of silica phases. These include a grey matrix with a spongy fabric (silt quartz and tiny mica flakes are embedded in it), fragments of seed coats, phytoliths, and finely laminated coatings (Figure 6). All these phases are composed of almost pure Si, although small amounts of mainly Al, K, P, and Mg (Table 2) are detected in most of the analysis. The FTIR spectra also show that the sediments are composed of almost pure SiO₂. Some spectra show no splitting of the absorption around 800 cm⁻¹, which is indicative of amorphous silica (opal). Others, however, show some splitting of the absorption peak; a property reminiscent of siliceous aggregates (Schiegl et al., 1994). Occasionally, microscopic seams of spherulites are also present, with the characteristic pseudo-extinction patterns in crossed polarized light (see Courty, Goldberg & Macphail, 1989). These spherulites are composed of an Al-rich leucophosphate.

All the above mentioned features of the multi-layered coloured sediments are consistent with the presence of ash remains that have been subjected to severe diagenesis. The dipping of layers is also a secondary feature as burnt layers are not normally found on an inclined slope. A consequence of the dip is the production of the deformation structures (Figure 4) owing to slow creep of the overburden sediments. Deformation is absent and horizontality is maintained.
towards the eastern wall of the cave (Figure 3). In this area dahlite is the main constituent of the burnt layer.

Carbon-14 dating of the uppermost burnt layer in the central profile indicated that this unit formed before 36,550 BP (Table 3: RT2878).

Unit IIB consists of several layers composed of quartz, clay and other silicate minerals. Micromorphological examination shows that these layers are finely laminated indicating that this unit was also deposited in a low energy water environment. Platy and lenticular microstructures [Figure 5(c)], rounded aggregates and a highly deformed upper boundary with convolutions are attributed to strong freeze–thaw activity (van-Vliet Lanoé, Coutard & Pissart, 1984) that affected the whole unit. In particular, the observed microstructures are characteristic of seasonal frozen soils (van-Vliet Lanoé, Coutard & Pissart, 1984; Courtby, Goldberg & Macphail, 1989). In the case of Theopetra this was favoured by the north-facing entrance of the cave as well as by the great water content of the sediments.

Taranakite is a major authigenic component of Unit IIB. It is found either as whitish soft nodules of granular size, or as fine irregular banded, lenticular, forms. Both incorporate clay and quartz impurities. The nodular form truncates the lenticular to planar microstructures of the surrounding matrix showing that it formed after the layer was affected by freeze–thaw activity. The banded forms are owing to the complete infilling of planar voids produced by cryogenic activity. Cracking of the altered sediments produces a planar appearance as well. This is the outcome of freeze–thaw activity, after the formation of taranakite. These features imply that taranakite-bearing layers were not altered simultaneously from a single alteration-front, but formation of the mineral was interrupted by depositional as well as freeze–thaw episodes.

In the upper northern part of the profile, towards the entrance, taranakite gives way to a series of non-stoichiometric Ca,Al-phosphate minerals together with dahlite in nodular shapes. The Ca,Al-phosphates are amorphous in the X-ray diffractograms and FTIR spectra, and usually bear appreciable amounts of Si, K and Fe. Some of the latter presumably represent silicate impurities.

Only one multi-coloured layer is present in Unit IIB (Figure 2). It is in the upper part of this unit and has the same features as the burnt layers of the underlying unit. A very Al-rich leucophosphate (tinsleyite after Dunn et al., 1984) dominates the groundmass in the form of a continuous isotropic mass [Figure 5(c)], together with amounts of tiny spherulitic iron-rich leucophosphate [Figure 5(d)]. The BSE image shows that leucophosphate is formed at the expense of tinsleyite [Figure 5(d)]; a fact that illustrates the continuous chemical alteration process that characterizes the diagenesis of ashes. Microscopic seams consisting almost only of phytoliths were also observed. Dating of this layer in several parts of the cave gave an age of about 25,000 BP (Table 3: RT2879, RT2870, RT2874).

Unit III has a tongue-like shape thinning from the entrance of the cave towards the centre (Figure 2). It consists of layers rich in limestone fragments alternating with layers rich in quartz, clay and other silicate minerals. Well-rounded sediment aggregates, sand void-infillings and vertical orientation of fragments, together with the general shape of the unit, are indications of creep owing to freeze–thaw activity (van-Vliet Lanoé, Coutard & Pissart, 1984; Coutry, Goldberg & Macphail, 1989). This unit was probably deposited towards the last Glacial Maximum as it overlies Unit IIB (whose upper part is younger than 25,000 BP) and has also been affected by freeze–thaw activity.

### Table 2. Compositional variations of opal phases (in atom %) in the burnt layers of Unit IIA—determined by EDS and EMPA. An analysis of a phytolith is presented for comparison

<table>
<thead>
<tr>
<th>Matrix (10)*</th>
<th>Coating (4)*</th>
<th>Phytolith</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>99.12–86.92</td>
<td>91.48–93.05</td>
</tr>
<tr>
<td>Al</td>
<td>0.00–8.21</td>
<td>3.39–4.42</td>
</tr>
<tr>
<td>Fe</td>
<td>0.00–0.00</td>
<td>0.00–0.20</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00–2.28</td>
<td>0.00–1.39</td>
</tr>
<tr>
<td>Ca</td>
<td>0.00–1.02</td>
<td>0.00–0.24</td>
</tr>
<tr>
<td>Na</td>
<td>0.00–0.50</td>
<td>0.00–0.20</td>
</tr>
<tr>
<td>K</td>
<td>0.00–3.26</td>
<td>2.15–2.61</td>
</tr>
<tr>
<td>Ti</td>
<td>0.00–0.61</td>
<td>0.00–0.00</td>
</tr>
<tr>
<td>P</td>
<td>0.00–4.18</td>
<td>0.00–1.48</td>
</tr>
</tbody>
</table>

*No. of analyses.

### Table 3. Carbon-14 dates of burnt layers from Theopetra cave and their sample location (square, unit)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Years before present (BP)</th>
<th>Square</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT2876</td>
<td>12,280 ± 100</td>
<td>I10</td>
<td>V (lower boundary)</td>
</tr>
<tr>
<td>RT2880</td>
<td>11,675 ± 165</td>
<td>H8</td>
<td>V (lower boundary)</td>
</tr>
<tr>
<td>RT2872</td>
<td>10,910 ± 170</td>
<td>E13</td>
<td>IV (upper boundary)</td>
</tr>
<tr>
<td>RT2879</td>
<td>25,625 ± 500</td>
<td>Z9</td>
<td>IIB</td>
</tr>
<tr>
<td>RT2870</td>
<td>26,470 ± 1,010</td>
<td>E13</td>
<td>IIB</td>
</tr>
<tr>
<td>RT2874</td>
<td>25,820 ± 270</td>
<td>I10</td>
<td>IIB</td>
</tr>
<tr>
<td>RT2878</td>
<td>36,550 ± 420</td>
<td>Z7</td>
<td>IIa (upper boundary)</td>
</tr>
</tbody>
</table>

> 37,590 ± 990 Independent repeat measurement
The upper part of this unit consists mainly of unaltered limestone fragments with some dahllite reaction rims present only in the lower portions. The lower part of the unit contains amorphous Ca,Al-phosphate phases together with dahllite. Crandallite was found occasionally, close to the more calcareous areas of the unit. The phosphate minerals are present either in the form of yellowish nodules or as thick masses that are aligned in the bedding plane.

Unit IV consists of loose redeposited sediment aggregates from the lower units, charcoal, phosphate nodule fragments and plant material. A very high percentage of voids is present. These sediments fill relatively deep troughs (Figure 2). This filling process is thought to be mostly of anthropogenic origin (Karkanas, 1999). In terms of authigenic minerals, taranakite and Ca,Al-phosphate fragments mixed with limestone clasts altered to dahllite characterize this unit.

An ash layer that caps the unit in another excavated area of the cave (E13) was dated to 10,910 BP (Table 3: RT2872), consistent with the lack of freeze–thaw activity in this unit.

Unit V is a stratified sequence of yellow sandy layers that covers the underlying units. Quartz, clay and other silicate minerals are the main constituents of this layer. These sediments were laid down under water. Some limestone fragments incorporated inside the unit have dahllite reaction rims. Thin charcoal-rich layers are present close to the upper and lower boundaries of this unit. Ash, however, is not preserved.

Presumably it was eroded and/or dissolved by the water action. Dating of the lower charcoal layer from two different parts of the cave gave ages of about 12,000 BP (Table 3: RT2876, RT2880).

Unit VI consists of stratified black charcoal-rich, greyish and white layers, alternating with unstratified layers containing a mixture of limestone pebbles and boulders, Neolithic-age sherds (dated to the 6th and 5th millennia), organic remains in a fine-grained quartz and clay matrix. The unit has the typical features of anthropogenic sediments. The greyish and white stratified layers consist of very fine-grained calcite and dahllite. Their presence, in association with the charcoal layers, is a clear indication of preserved ash.

The above description is of the variations that occur in the vertical direction in the central profile. Lateral variations in each unit have been also observed (Figure 3). Unit IIA grades laterally from being predominantly siliceous in the central section to containing crandallite together with dahllite. In Unit IIB taranakite in the central section passes gradually to non-stoichiometric Ca,Al-phosphates and then to dahllite close to the east wall. The same lateral variation is observed in the central profile towards the entrance of the cave (Figure 2). Unit III is dominated by non-stoichiometric Ca,Al-phosphates in the central area, but these give way to dahllite towards the east wall (Figure 3). Leucophosphate, which was found only in burnt layers, grades laterally to dahllite in Unit IIA. In Unit IIB is laterally masked by the formation of high amounts of taranakite. In summary, the diagenetic sequence in Theopetra shows comparable patterns in the vertical as well as in the lateral directions.

Discussion

The analyses of authigenic minerals in Theopetra cave show a clear-cut sequence both vertically and laterally in order of increasing diagenetic severity, namely calcite, dahllite, Ca,Al-phosphates and taranakite. The layers rich in ash also vary spatially from containing abundant dahllite to comprising leucophosphate and silica-rich mineral phases. A similar sequence was noted in Kebara cave, Israel, with minor variations, as well as in Hayonim cave (Weiner et al., 1995; Schiegl et al., 1996). Thus there is a close similarity between the diagenetic processes occurring in all these caves. We also note that the studies of the calculated stability fields, solubility data and formation conditions of these minerals (Nriagu, 1976; Vieillard, Tardy & Nahon, 1979; Flicoteaux & Lucas, 1984; Vieillard & Tardy, 1984) are also essentially consistent with the cave observations. There is thus substantial evidence to support the notion that in these cave environments diagenesis proceeds along fairly specific common pathways. Furthermore, the existence of a theoretical basis for calculating relative stabilities in these and related minerals offers the exciting prospect of being able to predict diagenetic changes in other sites based on only partial information.

In Theopetra cave the sequence calcite–dahllite–Ca,Al-phosphates–taranakite has been observed in the lateral direction of the same unit as well as in the vertical direction of successive units. Furthermore, part of the diagenetic sequence repeats itself vertically even within a unit. Unit IIB is an example in which dahllite, Ca,Al-phosphates and taranakite are present in successive zones. Thus several successive diagenetic cycles are evident, altering each time the newly deposited units. In addition, the freeze–thaw activity, which affected this unit, did not influence the process of authigenic phosphate mineral formation in the same manner. In some layers the freeze–thaw activity pre-dates phosphate mineralization whereas in others it post-dates it. This means that diagenesis was interrupted by depositional as well as freeze–thaw episodes. We can thus infer that deposition, diagenesis and freeze–thaw activity were a continuous process. Consequently, much of the authigenic diagenetic process occurred relatively soon after deposition in order to be influenced by the new freeze–thaw cycle. Unfortunately we do not yet know what “soon” means in terms of absolute chronology. This conclusion can also be drawn from an analysis of other units, such as Unit III, which shows comparable diagenetic phenomena as in Unit IIB. Unit VI, which was deposited during the Holocene, contains calcite and dahllite, minerals that...
reflect relatively mild diagenetic conditions. This is probably due to a decrease in the influx of water in this unit, something inferred from the fact that the sediments are deposited above the level of the karstic aquifers at the back of the cave. Thus each layer has its own diagenetic imprint, which reflects conditions of sedimentation and the prevailing hydrological regime soon after sediment deposition. Furthermore, repetition of the diagenetic sequence in the vertical direction implies the existence of considerable stratigraphic gaps (hiatus) between the units. This can be seen also, when unit boundaries truncate successive mineralogical zones (e.g. IIA–IIB boundary). If stratigraphic gaps did not exist, the alteration sequence would have continued in the overlying units without changes in the mineralogy.

The distribution of bones in Theopetra sediments is directly related to the distribution of calcite and dahlite. In fact, bones were not found in the areas where dahlite and calcite are absent in the sediments. A similar distribution of bones vis-à-vis authigenic dahlite was observed in Kebara cave, Israel (Weiner, Goldberg & Bar-Yosef, 1993). The absence of bone in most areas of Theopetra cave is probably owing to the fact that they dissolved. It is interesting to note that the units which show evidence of freeze-thaw activity, namely Units I, IIB and III, also contain relatively large amounts of authigenic phosphate minerals. Asapatite is a lot more soluble at 0°C than at 25°C (Vieillard & Tardy, 1984), it is conceivable that more bone dissolution took place during these cold periods as compared to warmer periods. This possibility needs to be carefully evaluated at other sites which have been subjected to low temperature regimes.

Unit IIA is clearly associated with large amounts of ash and charcoal, which were subjected to severe diagenesis. This resulted in the formation of authigenic opal and some leucophosphite. The major insoluble components of wood ash are siliceous aggregates, and to a lesser extent phytoliths and burnt clay that adheres to the wood (Schiegl et al., 1994). Siliceous aggregates are themselves composed of fine-grained silicate minerals embedded in an amorphous Si, Al, Fe and K-rich matrix. In Theopetra, as well as in Kebara, they are closely associated with leucophosphate (Schiegl et al., 1996). In Theopetra, however, the ash insoluble fraction has undergone even more severe diagenesis than in Kebara cave, and has decomposed mainly into opal. The presence of appreciable amounts of aluminium and potassium in some of the analyses of opal presumably reflects the chemistry of the precursor material. In fact the elemental composition of opal range from pure Si, to Al and K-richopal (Table 2). Leucophosphate is an iron and potassium containing phosphate mineral and its association with the ash insoluble fraction probably reflects the fact that this fraction is also rich in iron and potassium. Tinsleyite is actually an AI-rich leucophosphite but still contains appreciable amounts of iron. Its mode of appearance indicates that it plays a part in the initial diagenetic fixation of iron and is a precursor of leucophosphite. Thus the presence of concentrations of opal, especially in association with leucophosphite, or tinsleyite and leucophosphite could be used as an indicator of ash-rich layers having undergone severe diagenetic alteration in other caves.

It is of much interest to ascertain whether or not Unit IIA with its high ash component represents a period of relative intensive occupation in the cave, whereas Unit IIB represents a period of relative non-occupation. In general more lithics are present in IIA as compared to IIB. This could also, however, be an artefact of preservation due to volume reduction of the ash “soluble” fraction when subjected to severe diagenesis. Such volume reduction was observed in Kebara cave (Schiegl et al., 1996). Volume reduction of Unit IIA was more severe in the central and southern parts of the cave compared to the peripheries, judging from the observed lateral variations in authigenic minerals. Thus, Unit IIB was deposited in the depression made in the underlying Unit IIA. This could have led to higher sedimentation rates and consequently to a “dilution” effect on the concentration of lithics in this particular area. Clearly, any interpretations of distribution and concentration patterns of lithic artefacts or bones, if preserved, in such archaeological environments must take into account volume changes associated with diagenesis. These will be particularly pronounced in sediments containing large proportions of ash. Note too that carbon-14 dating of the charcoal in these layers could also be affected by severe dissolution, as originally separated layers are probably now superimposed. Because of all the above complication nothing, as yet, can be concluded with regard to the extents of occupation in Unit II.

The diagenesis of Theopetra cave sediments must be taken into account when the older units are dated by either thermoluminescence (TL) or electron spin resonance (ESR) techniques. Both methods depend on an estimation of the amount of gamma radiation in the sediments around the tools or teeth being analysed. This reflects the external radiation dose to which they were exposed during their burial. If after prolonged burial the sediments have been affected by diagenetic alteration and new minerals with different radioisotopic contents have formed, then the amount of radiation measured in the present may not reflect the amount prevailing in the past. If however diagenesis was complete soon after deposition then the measurements made in the present will reflect the radioactivity produced during most of the period following deposition. This study shows that much of the diagenesis occurred “soon” after the sediments were deposited. In the case of Theopetra “soon” may represent an appreciable portion of the time elapsed since burial of even the older units, and hence the changing mineral assemblage with time could affect the dating. Furthermore, the vertical and lateral variations in mineralogy can
occur over distances of a few tens of centimetres or less, and hence care must be taken to avoid such gradients when estimating environmental radiation doses.

Concluding Comment

Sedimentation, anthropogenic activities and diagenesis are three parameters which interact and overlap to produce a very complex record in Theopetra cave. A detailed study of the mineral distribution, and in particular the authigenic minerals, provides the means of sorting out some of these processes in order to better understand the archaeological record. Many of the phenomena observed in Theopetra are reminiscent of the caves in Israel, which have been studied in this way, suggesting that common diagenetic processes may occur. Differences were also, however, observed, and these relate particularly to the severity of diagenetic events in Theopetra cave.

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