



Diagenesis in Prehistoric Caves: the Use of Minerals that Form *In Situ* to Assess the Completeness of the Archaeological Record

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An interpretation of the archaeological record, in particular that of a prehistoric cave site, is complicated by the diversity of depositional and post-depositional processes that affect the material deposited. Here we propose to use the authigenic minerals that form *in situ* within the cave sediments to reconstruct the ancient chemical environments in the sediments. This can be done by experimentally determining the conditions under which each of the authigenic minerals are stable. Although this information is not available to date for minerals formed in a prehistoric cave, we present calculated stability field data for the relevant minerals. The results clearly demonstrate the feasibility of this approach. This information, particularly if based on measurements of real authigenic cave minerals, will facilitate an assessment of the completeness of the cave archaeological record. This is particularly important for determining whether or not the distributions of archaeologically important materials, such as bones, teeth, plant phytoliths, charcoal and ash, reflect their original burial distributions or were altered as a result of secondary diagenetic processes.

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Introduction

The goal of an archaeological excavation is to reconstruct the comprehensive history of the site, taking into account the depositional and post-depositional processes. These may be geogenic, biogenic, anthropogenic or a combination of all three. Identifying these processes is crucial if we are to interpret the recorded contexts of human activities within a precise radiometric time scale. Behavioural interpretations of such well understood sites provide the building blocks for determining rates and trends of cultural changes over time. One of the major sources of

information for the study of human evolution during the Pleistocene is prehistoric caves in Africa and Eurasia. Since the early days of prehistoric research in Western Europe, archaeologists have paid particular attention to the residues of human activities in the form of fractured animal bones, lithics, ash and charcoal. At the same time, Quaternary geologists, working jointly with the excavators, have identified a suite of natural processes, which are responsible for accumulations in caves and rock-shelters. Summaries of these geogenic processes have been published (e.g. Bordes, 1972; Farrand, 1975; Davidson & Shackley, 1976; Colcutt, 1979; Laville *et al.*, 1980; Villa &

Courtin, 1983; Lowe & Walker, 1984; Goldberg *et al.*, 1993 and references therein). With the advance of geoarchaeological research, it also became clear that a better understanding of the chemical and biogenic processes occurring in the sediments is necessary, before proceeding with palaeoanthropological interpretations (e.g. Eidt, 1977; Sjöberg, 1976; Schiffer, 1987; Courty *et al.*, 1989; Dockrill *et al.*, 1994).

Biogenic processes occur in the form of burrows (terriers), which are typically circular to elliptical features about 6–10 cm across. They are generally filled with softer material than the surrounding matrix and micromorphologically are clearly characterised by a loose, aggregated fabric (Goldberg & Bar-Yosef, 1998). Additional bioturbation processes such as the activity of earthworms and insects have a more subtle appearance (Stein, 1983). Both are clearly responsible for microscale obliteration of original stratigraphic features, such as bedding and contacts between lithological units (Wood & Johnson, 1978; Courty *et al.*, 1989; Macphail *et al.*, 1990; Goldberg & Bar-Yosef, 1998). Carnivore contributions from hyaenas and their phosphatic coprolites are demonstrable in many cave-sites. The presence of hyenas is also reflected in bone gnawing. Their activities in the cave are another cause of bioturbation and a means of altering the sedimentary substrate (Horowitz & Goldberg, 1989).

Chemical transformation processes are often less obvious to the naked eye, but in many caves are major agents of destruction of the archaeological record. The chemical processes are driven by the water passing through the cave sediments, and the dissolved organic and inorganic constituents. Chemical processes may result in cementation and/or dissolution, depending upon the conditions. Of particular importance is the contribution of organic matter (guano) from bats and birds. This breaks down as a result of oxidation, and releases large quantities of phosphate into the water. Phosphate reacts readily with carbonates, setting off what is essentially a chain reaction (Weiner *et al.*, 1993). Evidence of the past presence of pigeons and birds survives as millimeter-sized, well-rounded and polished gizzard stones. At Tabun Cave, for example, such grains make up about 1% of the sediment by weight (Hoskin *et al.*, 1970; Goldberg, 1973, 1978). Chemical reactions can result in partial or total loss of bones, phytoliths, organic palaeobotanical remains, and in addition may radically alter the stratigraphy due to greater reduction of sediment volume in one location than in another. They may also influence the radioactive element distributions, and consequently the dates obtained by thermoluminescence and electron spin resonance (Mercier *et al.*, 1995a). Understanding these chemical processes and integrating them into an interpretation of the cave archaeological record is the major objective of this study.

Chemical cementation is volumetrically not very abundant in Levantine caves, but is more common in temperate European or tropical Asian cave sites (Ford

& Cullingford, 1976; Ford & Williams, 1989). It is usually represented by calcitic deposits of travertine, or stalactites and stalagmites, as well as more horizontal spéléothems or flowstones. These calcium carbonate accumulations, moreover, grade laterally into detrital sediments, which they cement, yielding what is known in the archaeological literature as “brecciated deposits” or just “breccia”. As such, they represent a form of water activity that can considerably obliterate the details of past events. Water, especially dripping from the ceiling, thus plays a major role in cementation processes, and by creating erosional features.

Ash was certainly a major component of the sediments in many prehistoric caves, and if preservation conditions are appropriate may still be a major component. The dissolution of ash is an important factor in assessing volume changes of the sediment (Schiegl *et al.*, 1996). The study of the microscopic structures and chemical compositions of prehistoric ash is still in its infancy. Several publications (reviewed by Courty *et al.*, 1989) produced some of the first analyses of campfires. Subsequent research in several Levantine caves has considerably added to our knowledge (e.g. Weiner *et al.*, 1995; Schiegl *et al.*, 1996).

All the processes that alter the archaeological record are collectively referred to as diagenesis. Here we will focus specifically on the post-depositional chemical changes. Interpreting the archaeological record correctly without reaching an understanding of diagenesis is usually impossible. This is certainly the case in many prehistoric caves, where the diagenetic processes are particularly aggressive, due essentially to the concentrations of large amounts of phosphate-rich guano and other organic refuse, as well as an active hydrologic regime. If, therefore, we are able to determine the processes and reconstruct the original depositional environment in each site, we could determine the original configurations of these components in the archaeological record. This would also make it possible to recognise environments where some of the primary anthropogenic constituents are absent because they were never incorporated in the archaeological record, as opposed to being absent or partially altered, because they were subject to diagenesis.

The Strategy

Here we propose to use the minerals that form within the sediments (the so-called authigenic minerals) to determine key chemical environmental parameters that prevailed in the sediments, such as calcium, phosphate and aluminum concentrations, acidity/alkalinity (pH), and oxidation conditions (Eh). These parameters can in turn be used to determine whether the primary anthropogenic constituents (such as bones, teeth, phytoliths, pollen, plant remains and charcoal) would have been affected by diagenesis irrespective of whether or not they are present in the sediments.

This approach has previously been proposed as a means of assessing the “completeness of the fossil record” in soils (Retallack, 1984). In soils and certainly in prehistoric caves, our knowledge of the formation and dissolution conditions (stability fields) of the relevant authigenic minerals, as well as for many of the primary constituents, is insufficient at present to readily apply this approach. Here we will review the current state of knowledge in this regard for prehistoric caves, list some of the more important archaeological implications of such an approach, and define some of the key studies that need to be undertaken to make this a reality.

An Important Premise

The use of authigenic minerals to reconstruct the chemical environmental conditions that prevailed in cave sediments is predicated on one major assumption, namely that the authigenic minerals under study formed under the same conditions that affected the primary archaeological constituents of interest. It is a straightforward matter to conceive that this may not be the case, especially if diagenetic reactions are ongoing and reflect changing conditions. For example, secondary calcite tends to form at locations where water drips from the cave ceiling onto the sediments, especially above the cave entrance. These sediments may originally have contained primary calcite, which has since dissolved. The fact that calcite is now forming secondarily provides no information about the earlier dissolution events. It provides some information about the possible effects that calcite formation may have on the remaining primary anthropogenic components.

There is, however, strong evidence to support the notion that many authigenic minerals do form at the same time and under the conditions that also affect the primary anthropogenic constituents. The evidence is derived as a “by-product” of thermoluminescence (TL) dating of burned flints in prehistoric caves. It indirectly provides information on the progress of diagenesis over time. For our purposes, the important results are not the dates, but the comparisons of the calculated environmental radiation doses using the TL isochron analysis (see Aitken & Valladas, 1992), and the measured values in the field. If the calculated and the measured values are the same, it implies that the amount of radioactivity emanating from the sediments today is the same as the radioactivity emanating over the whole period of time since the accumulation of the sediments on the surface. If the values are different, then diagenesis has subsequently altered the sediments in terms of the components that contain the radioactive elements.

The isochron analysis has only been performed in four caves to date. The result from the cave of Qafzeh is that the isochron age is 88 ± 9 ka and the measured age is 92 ± 5 ka (Aitken & Valladas, 1992). In Kebara

Cave the isochron age is 57 ± 8 ka and the measured age is 60 ± 3.5 ka (Valladas *et al.*, 1998). In Tabun Cave the isochron age is 287 ± 20 ka and the measured age is 306 ± 33 ka (Mercier *et al.*, 1995b). In Hayonim Cave the two values are indistinguishable (Mercier & Valladas, pers. comm.). As the major radioactive elements are constituents of authigenic and primary minerals in cave sediments, this supports the notion that most diagenesis took place at the surface or soon after burial. “Soon” can be roughly estimated from the TL data as being within the statistical error of the measurement, namely 10% or less of the time elapsed since deposition.

The fact that diagenesis for the most part tends to occur at or near the surface, and then slows down significantly after deeper burial, implies that each stratigraphic layer may take on a characteristic diagenetic “fingerprint”. The fingerprint reflects the conditions of accumulation at the surface, rate of sedimentation, temperature and so on. This trend can in turn explain, for example, how preservation conditions can improve with depth. This situation occurs in Hayonim Cave, even though the deeper layers have obviously been buried for a longer time than the upper layers. Another consequence of this phenomenon is observed in Theopetra Cave in central Greece (Karkanas *et al.*, 1999). Each layer has a different assemblage of authigenic minerals that formed *in situ* under different conditions. The diagenetic fingerprint of each layer presumably reflects the unique conditions that prevailed at the surface and soon after burial for each layer, rather than the accumulated diagenetic change that might have occurred since burial.

The Authigenic Minerals

Authigenic minerals form *in situ* within the sediments, as opposed to those that are transported into the cave. They are known to form in many caves that were occupied by ancient hominids, as well as caves that were not occupied (White, 1976, 1982; Martini & Kavalieris, 1978; Hill & Forti, 1997). Each mineral forms under a specific set of conditions, and hence its presence is indicative of the conditions that prevailed at the time of formation. As many of the authigenic minerals are phosphates that have relatively poor order at the atomic level, and/or very small crystal sizes, they are not easily detected by the most commonly used method for mineral identification, namely X-ray diffraction. A more reliable and much more convenient method for identifying these minerals is infra-red spectroscopy, especially when it is combined, where necessary, with X-ray diffraction, back scattered electron microscopy and elemental analyses using either a microprobe or an energy dispersive spectrometer attached to a scanning electron microscope. Infra-red spectroscopy can also be used on-site; an added convenience and a great improvement in

Table 1. The authigenic minerals noted in the text, their abbreviations, and chemical formulae

Mineral	Formula
Calcite (C)	CaCO_3
Hydroxyapatite (HA)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
Fluor-carbonated apatite (FCA) (Francolite)	$\text{Ca}_{10}(\text{PO}_4)_5(\text{CO})_3\text{F}_3$
Dahllite (D) (carbonated apatite)	$\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6(\text{OH})_2$
Ca, Al-phosphate amorphous (N)	Ca, Al, P-phase, non-stoichiometric
Crandallite (R)	$\text{CaAl}_3(\text{OH})_6[\text{PO}_3(\text{O}_{1/2}(\text{OH})_{1/2})_2]^{(1)}$
Taranakite (T)	$\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}^{(2)}$ or $\text{K}_x[\text{Al}_{2-y}(\text{H}_3)_y](\text{OH})_2[\text{Al}_x\text{P}_{4-x-z}(\text{H}_3)_z\text{O}_{10}]^{(3)}$
Leucophosphate (L)	$\text{K}_2[\text{Fe}^{3+}(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_4] \cdot 2\text{H}_2\text{O}^{(4)}$
Montgomeryite (M)	$\text{Ca}_4\text{Mg}(\text{H}_2\text{O})_{12}[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]^{(5)}$

⁽¹⁾Blount (1974); ⁽²⁾Smith & Brown (1959); ⁽³⁾McConnell (1976); ⁽⁴⁾Moore (1972); ⁽⁵⁾Moore & Araki (1974).

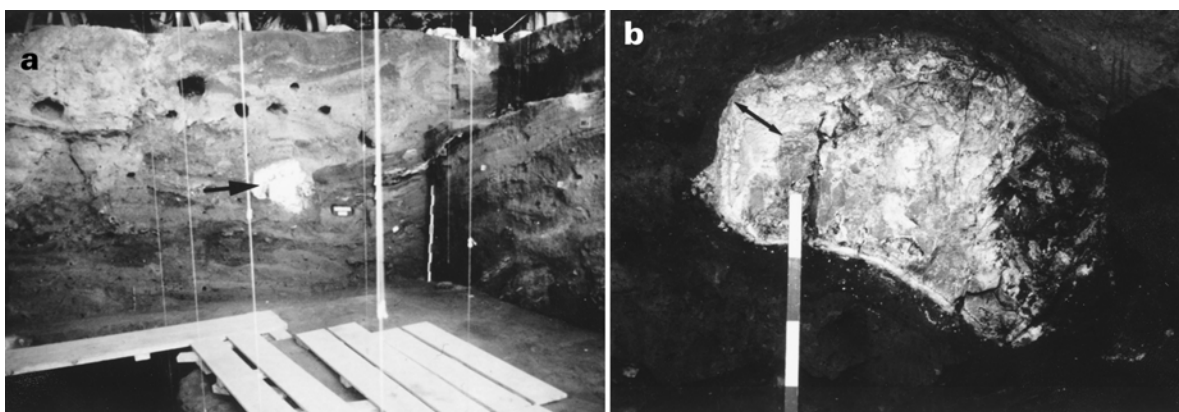


Figure 1. (a) Photograph of the eastern section of Kebara Cave showing the presence of a large boulder (arrow) buried in the Upper Palaeolithic sediments. (b) Photograph of the boulder. The arrow spans the thickness of the reaction rim. Scale bar: 10 cm.

problem-solving efficiency (Weiner *et al.*, 1993). The current state of our knowledge therefore is that relatively few prehistoric caves have been well studied in terms of their authigenic mineral assemblages. We note that one of the first, if not the first, study of this type was that of Goldberg & Nathan (1975) in Tabun Cave, Israel. (See Table 1 for the chemical formulae of the authigenic minerals mentioned in the text.)

The information needed to reconstruct the palaeo-environmental conditions of mineral formation is not only the identification of the authigenic minerals, but also their specific associations with other mineral phases in the field and at the microscopic level, if indeed such associations exist. These associations may indicate that a less stable mineral phase has dissolved and then reprecipitated in the form of a more stable mineral. Such transformations occur under specific chemical conditions. Thus knowing the mineral that is being replaced, as well as the mineral replacing it, allows us to also reconstruct the trends in changing palaeoenvironmental conditions.

A key observation in this regard is the suite of diagenetic minerals that developed on the surface of a large rock that fell from the ceiling of Kebara Cave, Israel, in the Upper Palaeolithic (Figure 1). The rock

was subsequently buried in sediments. A major component of these sediments is derived from wood ash, namely an aggregate of soil minerals cemented by an amorphous matrix rich in silicon, iron, aluminum and potassium, so-called siliceous aggregates (Schiegl *et al.*, 1994). These were derived from the wood and bark of trees of this region, but may also be present in other plants. A second component is the clays, e.g. kaolinite and montmorillonite, that are common in the soils of this area (Singer & Ravikovich, 1980). Weiner *et al.* (1993) analysed this rock reaction rim in detail (Figure 2(a)) and the results are shown in Figure 2(b). The rock itself is composed of dolomite, a calcium–magnesium carbonate mineral. The fact that authigenic minerals on the rim of the rock developed at the expense of the outer layers of the rock indicates that dolomite was not stable under these conditions, and reacted with the water in the sediments. The first authigenic mineral product of this reaction was pseudomorphic dahllite (also known as carbonated apatite) which precipitated in rhomb-shaped cavities formed as a result of dolomite dissolution. Dahllite is the same calcium phosphate mineral present in bones and teeth. The phosphate must also have been present in the sediment water. Its source is not known for sure, but is

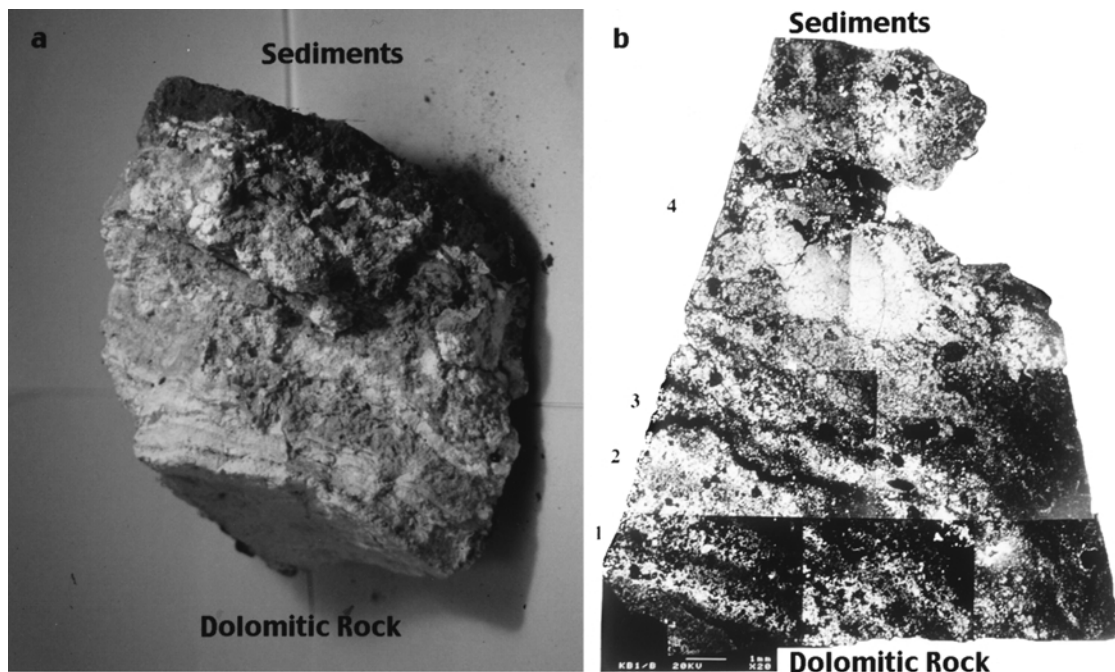


Figure 2. Photographs of a portion of the reaction rim removed from the surface of the rock in Figure 1. (a) A light micrograph. The thickness of the specimen from the rock surface to the sediments is 10 cm. (b) A scanning electron micrograph of about 4 cm of the central portion of the rim specimen shown in (a) using back scattered electrons. The major mineral phases and their locations are shown. 1: Carbonated apatite; 2: calcium aluminum phosphate (non-stoichiometric); 3: crandallite; 4: leucophosphite and montgomeryite. Scale bar: 1 mm.

most likely the phosphate-rich guano of bats and birds that is released upon oxidation of the organic matter (Martini & Kavallieris, 1978), and possibly the original wood ash itself which can contain up to 24% phosphate (Wattez & Courty, 1987). Dissolving bones may be another important source of phosphorous. During the dissolution and reprecipitation reaction the magnesium present in the rock was lost, as was most of the carbonate. The dahllite itself was not stable with time and was replaced by crystals of a calcium aluminum-rich phosphate mineral, whose elemental composition varied. The variability is an indication that this mineral did not reach its most stable form. In its most stable form the proportions of elements would be constant (the so-called “chemical formula” of the mineral). It does reach its most stable form in a thin layer at the border between this zone and the next. The mineral of this thin layer is called crandallite. The mineral phases of the outermost layer that today is in contact with the sediments is most complex. It is an intimate mixture of two minerals, montgomeryite, a calcium aluminum phosphate mineral that may or may not contain magnesium (Fanfani *et al.*, 1976), as well as leucophosphite, a potassium iron-rich phosphate mineral. These should be the most stable or least soluble of all the minerals in this reaction rim.

The replacement features of the minerals in the reaction rim show that a cascade of reactions occurred over time. The cascade reflects the fact that the rock itself is rich in calcium, hence the proportion of calcium decreases in the minerals with increasing distance

outward from the present day dolomite rock–rim boundary. In contrast the proportion of aluminum in the various minerals in the reaction rim increases with increasing distance from the rock surface, as its source is in the sediments in which the rock is buried. The cascade should also reflect the different stabilities of the minerals, with the most stable minerals adjacent to the sediment being those that formed last. The presence of leucophosphite is enigmatic. It does not contain calcium, but does contain potassium, aluminum and iron. These elements are present in relatively large amounts in siliceous aggregates present in wood ash, as well as in many clays. We have noted in Kebara and Theopetra Caves an intimate association between leucophosphite and siliceous aggregates, raising the interesting possibility that its presence may often reflect an association with ash (see Discussion).

The reaction cascade described above occurs over a scale of centimetres. In Theopetra Cave, Greece, we have observed another reaction cascade that occurs over a distance of metres in one specific stratigraphic horizon (Karkanas *et al.*, 1999). Figure 3 shows the distribution of the authigenic minerals in unit IIB dated by radiocarbon to between 25,000 and 38,000 years BP. The reaction cascade observed is calcite, dahllite, crandallite or montgomeryite, and finally the mineral called taranakite, a potassium aluminum phosphate mineral. The same trends of decreasing calcium and increasing aluminum are also present here, but over much larger distances than in the reaction rim of the rock in Kebara Cave. The sequence of mineral changes

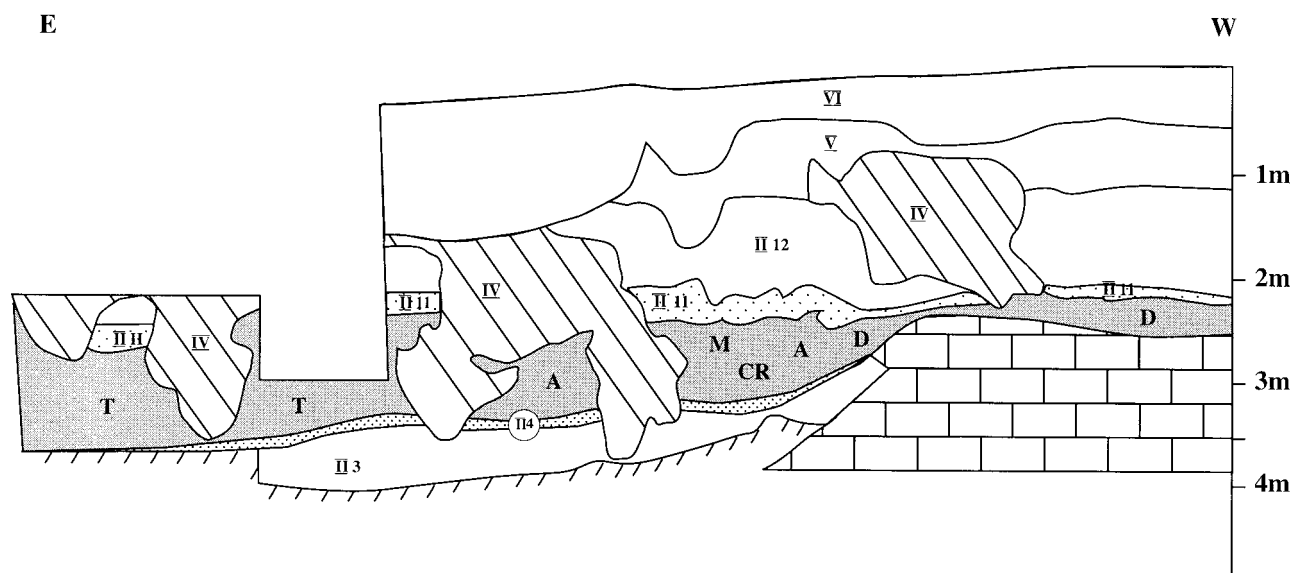


Figure 3. Northern section of excavation squares Z10–L10 in Theopetra Cave, Greece. Note how the mineralogy changes from east to west in layers between II4 and II1. D: dahlite; CR: crandallite; M: montgomeryite; A: non-stoichiometric Ca–Al phosphates; T: taranakite. Micromorphological evidence showed that the alteration did not proceed from a single front but continued with ongoing sedimentation.

Table 2. Distribution of major authigenic minerals in caves studied to date by the authors

Caves	Qumran 24	Ortvale Klde	Zhoukoudian	Tabun	Hayonim	Kebara	Theopetra
Minerals							
None	+						
Calcite		+	+		+	+	+
Dahlite		Small amount	+	+	+	+	+
Crandallite					+	+	+
Montgomeryite				+	+	+	+
Leucophosphate				+	+	+	+
Taranakite						+	+

is thus similar but not identical to that observed in the reaction rim. Taranakite was also observed in Kebara Cave, but not in direct association with this specific rock. In Hayonim Cave, dahlite, crandallite, montgomeryite and leucophosphate have been identified, whereas in localities 1 and 4 at Zhoukoudian, as well as in Ortvale Klde Cave, Georgia, only dahlite was found (Table 2). Table 2 shows that at least with respect to authigenic phosphate minerals, caves in a very wide geographic range exhibit common properties that can be understood in terms of the diagenetic reaction cascade. Note too that authigenic phosphate minerals may not form in prehistoric caves at all. This probably occurs only under exceptional circumstances. In Qumran Cave 24, Israel (Table 2), which is located in a very dry area adjacent to the Dead Sea, no authigenic phosphates were noted. This is likely due to the lack of available moisture.

Iron-containing authigenic minerals are of particular interest, because iron can exist in the non-oxidised

state, the so-called reduced ferrous form, when oxidation conditions are minimal or absent, or in a ferric state when oxidation conditions prevail. They can, therefore, in principle, be used to reconstruct the past oxidation conditions. This is of great interest because many of the primary constituents of the sediments that are most important archaeologically are composed of organic matter (pollen, charcoal and other botanical remains) that may be destroyed under oxidising conditions. Another helpful property of one of the most common groups of iron containing minerals, the iron oxides, is that they are very insoluble under oxidation conditions, but when very little or no oxygen is present will readily dissolve. Thus observations that iron oxide minerals have been redistributed is also an indication (but not a proof) of past reducing or minimally oxidising conditions. Solubility of iron minerals also increases with decreasing pH. The same situation exists for manganese-containing minerals. The base of layer 4 in locality 1 of Zhoukoudian has a very distinct red

colour. The mineral mainly responsible for this colour is the iron oxide haematite. It was observed to be present as coatings on quartz grains. The haematite zone is found in a cultural horizon containing relatively abundant stone artefacts and bones, some of which were burned (Weiner *et al.*, 1998). Even though we did not observe organic matter in this layer, it is likely that in the past organic matter was present. The reasoning is that organic matter is generally destroyed by oxidation and therefore while it is being destroyed little or no oxygen is present. This in turn leads to conditions under which the iron minerals became soluble and redistribute themselves for distances of centimetres to decimetres from the breaking-down organic material, where oxidation conditions prevail. We have noted a similar phenomenon in Theopetra (unpublished observation). In general little is known to date about the suites of authigenic iron and manganese minerals in prehistoric caves. We also note that haematite and other iron oxides may form directly from the breakdown of certain silicate minerals, such as biotite, which are common in many igneous rocks (Righi & Meunier, 1995).

What can be Deduced from the Authigenic Minerals?

In general chemical diagenetic changes reflect the tendency of sedimentary materials to achieve chemical equilibrium when new environmental conditions are imposed (Taylor, 1964). Thus the formation of an authigenic mineral can be regarded as the product resulting from changes of specific environmental parameters. These parameters define the stability field of the authigenic mineral under consideration. The stability field can therefore provide information on the limits of the chemical element concentrations that are required for the formation of the mineral, the acidity or alkalinity of the formation waters, and even the oxidation conditions that prevailed if the formation of the mineral is related to changes in oxidation state.

A convenient way to display the relationships between minerals is a diagram in which the stability fields of different minerals are plotted as a function of two variables (e.g. pH and aluminum concentration in the circulating waters). From such diagrams we can define the range of water chemical compositions in which the mineral is stable. Lines define the equilibrium conditions under which two minerals can coexist and they separate different mineral stability fields. We can also use these diagrams to deduce what will happen if a shift in a chemical condition, such as pH, occurs. The diagrams are constructed using experimentally estimated thermodynamic and solubility data of the minerals. The relevance of these data can be evaluated and/or verified from the observed relationships of the minerals in the field. In our case most of the data for the authigenic minerals in prehistoric caves were

determined by Nriagu (1976) based on calculations, and not by direct measurements. Their relevance to natural cave environments needs to be verified. Our empirical observations in eight different prehistoric caves are generally consistent with the calculated relationships of the stability fields produced by Nriagu (1976). This strongly suggests that they are at least a reliable first estimation for assessing preservation conditions. They therefore provide an invaluable means of determining the chemical palaeoenvironment during the formation of the authigenic minerals observed in the field, of deducing information about the changes in the chemical palaeoenvironment, and for assessing the completeness of the assemblage of primary anthropogenic minerals that are preserved in a particular environment. The latter is of much archaeological importance.

One particularly important environmental parameter is pH, as it reflects the acidity or alkalinity of the water in the sediments. This in turn affects the chemical reactions that occur during the formation and dissolution of authigenic minerals. Thus one of the variables of the stability field diagrams presented here is pH. Water entering a limestone cave contains the products of dissolved calcite and its pH is controlled by the dissolved CO₂ content. Generally this water is neutral to alkaline (pH 7–8.5). It is well known that the more CO₂ that is dissolved, the lower is the pH (Krauskopf, 1979). The CO₂ content increases when the water passes through an organic-rich soil cover above the cave, or when the temperature decreases (Palmer, 1991).

When water passes through guano it becomes rich in phosphate and more acidic. The pH of bat guano is reported to be between 2 and 3 (Martini & Kavalieris, 1978). This is due to the fact that guano, particularly bird and bat guano, is particularly rich in phosphorous (Martini & Kavalieris, 1978), and that when the organic matter reacts with the dissolved oxygen in the water, it releases CO₂ which lowers the pH and liberates the phosphate. This water is capable of reacting with calcite (or dolomite) and altering it to dahllite. The reaction uses acid and therefore the remaining solution becomes more alkaline, favouring the stabilisation of carbonates. This means that as long as calcite is present in the sediments the pH is controlled by the pH of the waters entering the cave. This in turn prevents the associated dahllite from being dissolved. Thus sediments such as loess, that can often comprise up to 30% calcite (Pye, 1987), essentially prevent the diagenetic cascade of reactions from continuing beyond the dahllite stage. This may be the reason why only authigenic apatite is present in Zhoukoudian and Ortvale Klde (Table 2), both of which contain a major component of loess in the sediments.

Fresh wood ash has a pH of 9–13 (Etiegni & Campbell, 1991). During combustion of wood CaO is formed, most probably from the oxidation of calcium oxalate crystals that are commonly found in wood

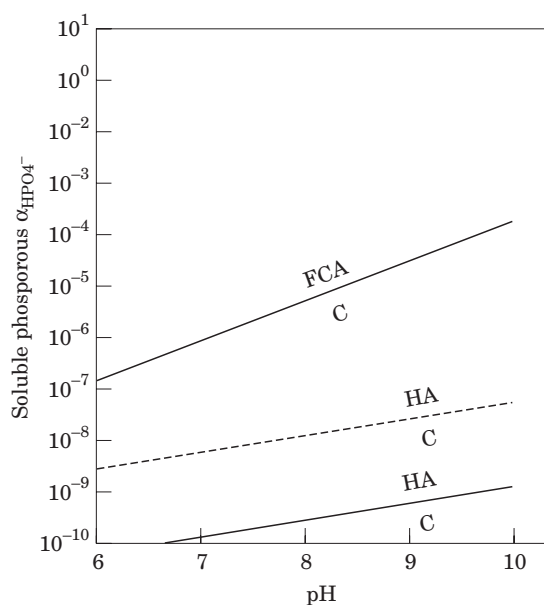


Figure 4. Limiting conditions for the alteration of calcite (C) to hydroxyapatite (HA) and fluor-carbonate apatite (FCA) following Nriagu (1976) and Vieillard *et al.* (1979), respectively. Solid lines for fixed activity of bicarbonates $\alpha_{\text{HCO}_3^-} = 10^{-3.7}$ and dashed line for $\alpha_{\text{HCO}_3^-} = 10^{-2.7}$ assuming saturation with calcite for $\alpha_{\text{Ca}^{2+}} = 10^{-4}$ and 10^{-3} , respectively.

(Kennedy *et al.*, 1968; Scurfield *et al.*, 1973). The amount of CaO formed increases with increasing combustion temperature. Upon cooling the CaO readily reacts with water (or water vapour) to form $\text{Ca}(\text{OH})_2$. As calcium hydroxide is very soluble, it may be removed from the ash if sufficient water is available, or in the “dry” state it will absorb CO_2 from the atmosphere and react to form CaCO_3 in the form of calcite. The latter is the major mineral component of ash (Humphreys *et al.*, 1987), even a few hours after cooling. When this ash is moistened by water, its pH will be buffered to about 8.2 by the CaCO_3 . If the ash contains a large proportion of K and Na, their presence in the form of hydroxides may raise the pH even higher. As both these compounds are very soluble, this effect may only be transient until such time as they are washed out of the ash (Wattez & Courty, 1987; Etiegni & Campbell, 1991).

The pH of the water in equilibrium with dahllite in a cave environment will remain between 7 and 8.5. The reaction of calcite to dahllite is strongly related to the concentration of phosphorus in the form of phosphate in the water and the carbonate concentration. From Figure 4 it can be seen that the concentration of phosphate required for converting calcite to apatite is relatively low irrespective of the pH. It can also be seen that very low amounts of phosphorous can react with calcite to form apatite, but in order for the reaction to continue, dissolved phosphorous needs to be supplied at concentrations above the equilibrium line in Figure 4. Note that in these calculations and the ones

presented below, we refer to this mineral phase as apatite (or hydroxyapatite) and not the carbonated form of apatite, dahllite, found in caves (and bones). The reason is that the appropriate solubility parameters of cave dahllite are not, as yet, available. The manner in which this plot, and the ones presented below is calculated is shown in the Appendix.

Figure 5 illustrates plots of the phosphate or aluminum concentration against pH for various concentrations of aluminum, calcium, phosphate and potassium. The calculated stability fields are shown for the four most common phosphate minerals found in the prehistoric caves we have examined. The aluminum, calcium and potassium concentrations used for calculating the stability fields are “educated guesses” for the natural concentrations. If, for example, the aluminum concentration is decreased, then the stability field of montgomeryite increases (compare Figure 5(a), (b)).

These diagrams show that pH is an important environmental parameter in determining the stability of these authigenic minerals. In general, apatite is stable when the pH is greater than 7, montgomeryite and crandallite for pH values between 6 and 7, and taranakite for more acidic pH conditions. The aluminum concentration is clearly an important environmental parameter. In Figure 5(c), the aluminum concentration is plotted against pH and the appropriate stability fields are depicted. Clearly, higher aluminum concentrations will result in crandallite rather than montgomeryite forming at approximately the same pH conditions.

These diagrams provide us with interesting insights into possible past diagenetic chemical processes that resulted in the formation of the observed authigenic minerals. For example, the stability field of montgomeryite is most restricted. Its presence in the sediments implies that the prevailing pH conditions were between 6 and 7, the aluminum concentrations were low (Figure 5(c)) and the phosphate concentrations moderately high (Figure 5(a), (b)). The major likely sources of phosphate are breaking down (oxidising) bird and bat guano and wood ash, and the major source of aluminum is from clays, and possibly other sources such as siliceous aggregates. We can conclude that montgomeryite will form when the clays are relatively stable, but guano is breaking down. Crandallite will be preferred if a source of aluminum is present and the phosphate concentration is low. Taranakite on the other hand will form in place of montgomeryite or crandallite under more acidic conditions. However under conditions of high phosphate concentration and close to neutral pH conditions, taranakite will form directly from apatite. The latter is known to commonly occur in direct association with guano in open air deposits (Hutchinson, 1950), and in caves unoccupied by humans (Sakae & Sudo, 1975; Fiore & Laviano, 1991). Taranakite also forms in prehistoric caves (Schiegl *et al.*, 1996; Karkanis *et al.*,

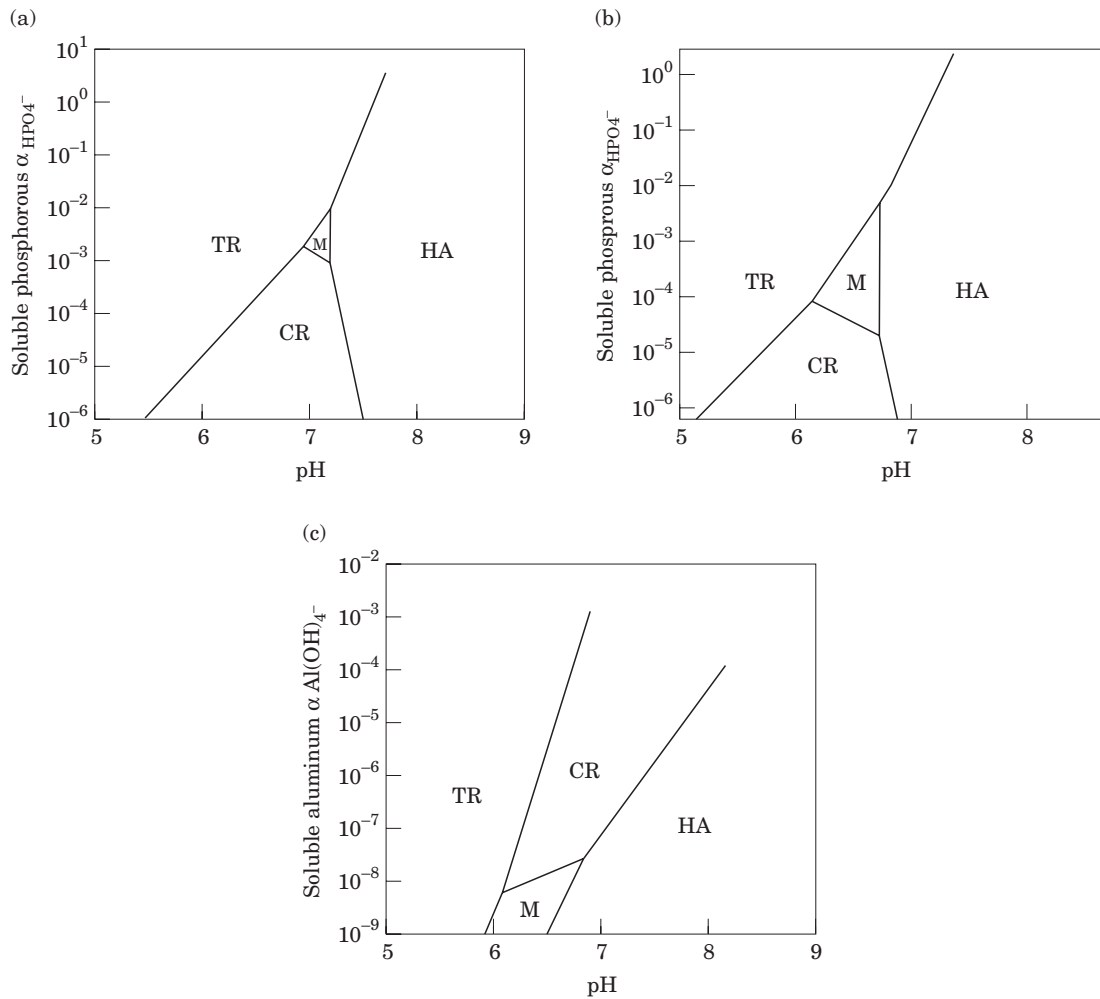


Figure 5. Stability relations for hydroxyapatite (HA), montgomeryite (M), crandallite (CR) and taranakite (TR) following Nriagu (1976). (a) The activities of Al(OH)_4^- , Ca^{2+} and K^+ are fixed at 10^{-6} , 10^{-4} and 10^{-4} , respectively. (b) The activities of Al(OH)_4^- , Ca^{2+} and K^+ are fixed at 10^{-8} , 10^{-4} and 10^{-4} , respectively. (c) The activities of HPO_4^- , Ca^{2+} and K^+ are fixed at 10^{-4} . These activity values are considered normal for pore fluids in contact with soil and sediments. Variations in the activities of dissolved Al^{3+} , Ca^{2+} and K^+ are usually small compared to the variations of H^+ and PO_4^{3-} (see Nriagu, 1976). Furthermore, the activity of dissolved Ca^{2+} is limited by the carbonate equilibria of the limestone rock.

1999), and in Theopetra Cave it is clearly an end product of a reaction cascade (Karkanis *et al.*, 1999).

Implications for Archaeological Site Formation Processes

We now discuss the implications of the recognised diagenetic processes. Field observations in Kebara Cave and in Theopetra Cave show that the transformation pathway of apatite to montgomeryite is common (Schiegl *et al.*, 1996; unpublished observations). In Figure 6, the line A–A' more or less depicts this situation. We can thus infer that when montgomeryite formed, the prevailing pH conditions were between 6 and 7, and in general for this pathway the phosphate concentrations are moderately high. In Theopetra Cave the reaction cascade continues until the for-

mation of taranakite (line A–A'–A'' in Figure 6). In Theopetra Cave there is also a sedimentary layer in which the pathway is from apatite to crandallite to taranakite (line B–B'' in Figure 6), implying that the environmental conditions that prevailed when these authigenic minerals formed included higher aluminum concentrations and lower phosphate concentrations. The path E–E''' best describes the situation of the Kebara Cave boulder (Figure 1), namely a continuous increase in phosphorous concentration and a decrease in pH. These are in fact common geochemical processes. What is rarely observed in the prehistoric caves that we have studied to date is apatite in direct association with taranakite even at the mesoscopic level. This may imply that in the past very large accumulations of guano were not buried, because only under such conditions of massive oxidation of organic matter will the high phosphate concentrations

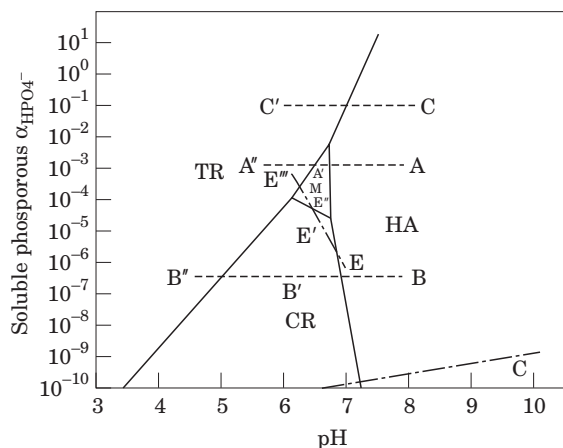


Figure 6. Diagram of Figure 5(b), with the stability field of calcite with respect to hydroxyapatite from Figure 4. The paths A–A'–A'', B–B'–B'', C–C' and E–E'–E''–E''' illustrate the mineralogical changes in constant and changing soluble phosphorus concentrations. The path E–E''' represents the possible chemical changes in the case of the Kebara boulder (continuous increase of soluble phosphorous and decrease of pH). The path can be extrapolated down to calcite although the starting material was dolomite.

necessary for this reaction occur. Thus the stability field diagram shown in Figure 6 enables us to define the approximate conditions that prevailed during the period that the sediments initially accumulated and were buried, and when the authigenic minerals formed.

With this information in hand, we can deduce whether or not other minerals are stable, and in particular those of archaeological interest. One important example is amorphous silica (opal), the mineral that comprises phytoliths. Figure 7 shows the stability fields of silica and its common crystalline form, quartz. It can be observed that at pH 6 to 7, silica is practically insoluble and therefore when montgomeryite is forming, phytoliths should be well preserved. Figure 7 also shows that the solubility of silica starts increasing significantly only above pH 8.5. Such alkaline conditions are generally rare, but when calcite is the dominant mineral component in the sediments or when calcite is transforming into apatite, it is conceivable that the pH could approach 8.5 or even higher. Thus given sufficient time and water throughput, silica phytoliths may begin to etch and even dissolve. In fact we have observed in Kebara Cave that the phytoliths that are present in a hearth composed today of calcite show severe signs of etching, whereas those in hearths composed of dahllite and montgomeryite show much less indication of etching (Albert *et al.*, 2000). The latter, of course, were originally composed of calcite.

We also note that occasionally flint artefacts partially dissolve or are replaced in part by phosphate minerals or oxide minerals (e.g. Kuhn *et al.*, 1996). Flint is composed of microcrystalline quartz, which is more soluble than quartz from igneous rocks (Sheppard & Pavlish, 1992). Apparently pH conditions even more alkaline than 8.5 may exist under certain

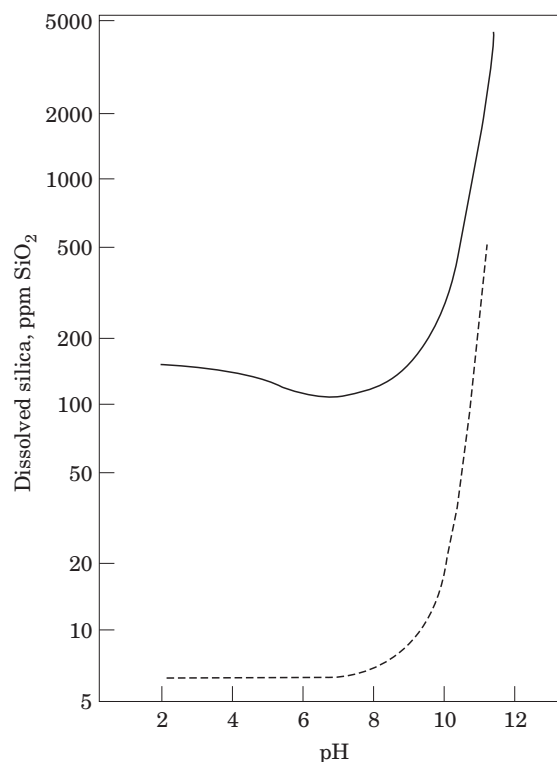


Figure 7. Variation of solubility of silica at 25°C with pH. The solid line is the solubility of amorphous silica (opal) as determined experimentally. The dashed line is the calculated solubility of quartz (adapted from Krauskopf, 1979).

conditions. This is known to occur in water that fills deep-seated cavities within limestone rocks (Palmer, 1991).

Bones are composed of carbonated apatite (dahllite) (McConnell, 1952). The crystals in fresh bone are exceedingly small (about $50 \times 25 \times 2\text{--}3$ nm) and have a very large surface area rather similar to that of clay (Weiner & Price, 1986). They are therefore expected to dissolve more readily as compared to authigenic dahllite formed in cave sediments, although to our knowledge the solubility of the latter has never been measured. Assuming this to be the case, then under conditions that authigenic dahllite forms in the sediments, bone dahllite should not be stable but will undergo recrystallisation or conceivably even dissolution. However when authigenic dahllite dissolves and reprecipitates as crandallite or montgomeryite, bones will almost certainly dissolve. This was first documented in Kebara Cave (Weiner *et al.*, 1993) and has since been observed in Hayonim (unpublished observation) and Theopetra Caves (Karkanas *et al.*, 1999). We could also infer that at one location in Kebara Cave where no bones were present, but authigenic calcite and dahllite were present in the sediments, there were probably never any bones (Weiner *et al.*, 1993). Observations of this type are clearly very important when interpreting the archaeozoological record.

We have also noted several enigmatic phenomena related to bone preservation. We have seldom, if ever, noted bone pseudomorphs preserved in the archaeological record, whereas we have observed pseudomorphs of, for example, aragonitic land snail shells. We also noted that in Kebara Cave bones that are apparently right on the border of the *in situ* stability field between apatite and montgomeryite transformed into an aluminum phosphate mineral called variscite. Variscite is rare in this and the other caves we have studied, although it is relatively common in other caves (Hill & Forti, 1997). We do not understand why variscite forms, apparently transiently, under these conditions. It is also of interest to note that the solubility of dahllite increases with decreasing temperature (Vieillard & Tardy, 1984), as this might have implications on certain archaeological sites for relative bone preservation during glacial periods as opposed to inter-glacial periods.

Leucophosphite is an authigenic mineral that is as common as montgomeryite in the caves we have studied. It contains iron in the oxidized ferric form, as well as potassium, and is therefore not conveniently plotted in the stability field diagrams we presented. It is however often closely associated with montgomeryite, for example in the reaction rim of the large rock in Kebara Cave (Figure 1). In Theopetra, Hayonim and Kebara Caves it is also clearly associated with ash layers that have been subjected to severe chemical diagenesis. This raises the interesting possibility that the source of the iron and the potassium is the ash itself, possibly from the siliceous aggregates that are known to contain relatively high concentrations of both these elements. For the iron to dissolve and relocate, the conditions must exclude oxygen and be reducing, as only in the ferrous form is iron oxide soluble. Thus another reason why leucophosphite may be closely associated with ash is the presence in ash of relatively large amounts of organic matter. As the latter undergoes oxidation, reducing conditions are produced. If this association is indeed widespread, it could prove to be an invaluable parameter for recognizing diagenetically-altered wood ash. We do note however that some clays contain both potassium and iron, and if they break down in a phosphate-rich environment, leucophosphite may also form. Hence the presence of leucophosphite in a prehistoric cave may also be unrelated to ash.

Iron and manganese containing minerals probably provide the key to addressing another important aspect of preservation in prehistoric archaeological sites, namely whether or not conditions for preserving organic matter prevailed. This has direct bearing on the preservation of pollen, wood, charcoal, seeds etc. Some of the authigenic minerals contain iron or manganese in the oxidized or the reduced state. By identifying these minerals, we can deduce whether organic matter was or was not breaking down. We have noted above the association of red-coloured iron

containing minerals in Theopetra and Zhoukoudian with cultural horizons, probably because they were rich in organic matter. This too could be an interesting application to certain archaeological problems. Caution however is in order, as iron oxide minerals may also form directly from certain silicate minerals (Righi & Meunier, 1995).

A Proposal

In Figure 4 it can be seen that different types of apatite have different stability fields relative to calcite. This reflects the different solubilities of these phases, which are actually different minerals. We have already noted that the appropriate solubility data of the apatites found in the studied caves are lacking. Their stability fields will be different if we calculate them using the “real” solubility data of the cave apatite. These differences may be small and will not alter our general view. However, accurate and reliable estimations of the chemical conditions prevailing after burial cannot be made until the appropriate solubility data of the various forms of apatite are known. This is also the case for the other authigenic cave minerals. Minerals such as montgomeryite or leucophosphite can have different contents of certain elements in their structure, and this will affect their solubilities. Even more important, some of the cave phosphate minerals have chemical compositions that are very different from any of the ideal known mineralogical phases. They may also be more or less ordered at the atomic level, and be intimately associated with another mineral phase. Clearly, the solubilities of the actual authigenic cave minerals need to be experimentally determined. Although measurements of the relative solubility data are difficult and time-consuming, they are important in order to establish a reliable basis for this program.

Invaluable information can be gained from the study of the iron and manganese bearing minerals in the cave environment with respect to the preservation of the organic matter. Organic material is generally not well preserved in the archaeological record and predicting localities in a cave with the best preservation conditions will be very useful. The iron and manganese minerals are often only present in very small amounts, and therefore difficult to characterise. In some cases these minerals are insoluble in hydrofluoric acid, whereas silicate minerals are not. This difference can be exploited in order to concentrate the oxides of iron and manganese, as was done by Shahack-Gross *et al.* (1997). The oxidation state of the iron and manganese may be conveniently determined by Mössbauer spectroscopy. The data obtained may be very interesting.

Except for the case of bone preservation (Weiner *et al.*, 1993) there are no direct field correlations between preserved primary archaeological constituents and the distribution of related authigenic minerals. Field studies in different cave environments should be

continued to provide additional correlations between the preservation states of the primary anthropogenic constituents and the chemical conditions inferred from the authigenic mineralogical studies. The ultimate goal of this approach will be to construct a diagram where the stability fields of the primary constituents will be plotted against the stability field of the real authigenic minerals produced in prehistoric caves.

Much information may also be obtained by the study of the surface and near-surface diagenetic processes in both prehistorically-occupied caves and non-occupied caves. Clearly this is a crucial environment that greatly influences the grade of diagenesis that will characterise the forming sedimentary layer, and in turn determine what proportion of the components of archaeological interest will be preserved.

Broader Archaeological Implications of Authigenic Mineral Analysis

We have noted that much of the chemical diagenesis takes place at the surface or soon after burial of the sediments, probably within a few tens of centimetres or less of the surface. The chemical environment in this zone will therefore “fingerprint” the sediments diagenetically. The main factors that determine the extent and nature of diagenesis are, we suspect, the rate of water throughput, the chemical composition of that water, the rate of sedimentation and the organic content of the sediment. This in turn raises the interesting possibility of whether or not the “fingerprint” will be different for sediments produced during the periods that the cave was occupied as compared to when it was not occupied. During occupation periods the rate of sedimentation is relatively high due to the large amounts of wood ash that is produced by fires. On the other hand the organic content of the sediments is probably lower and the organic matter itself contains less phosphate, as compared to periods of non-occupation when bird and bat guano accumulates. It is premature to try to predict the implications of these differences based on the theoretical calculated stability field diagrams in the previous section, as these could be quite different from those of a real cave environment. Conceptually, however, this may be feasible in the future.

The diagenetic cascade of reactions documented in the field and predicted from the stability field diagrams clearly involves volume changes. These are of two types. During the transformation of one mineral type to another the volume can increase or decrease depending upon the specific transformation, and the amount of volume change based on theoretical calculations can be up to 90%. The more important volume change is, however, probably due to loss of material during the dissolution stage of the transformation and prior to the reprecipitation stage. The extent of the volume change will depend first and foremost on the proportion of

relatively soluble minerals in the primary sediment. In the case of wood ash from trees in northern Israel which on average contain about 98% volume calcite, which is relatively soluble, and 2% volume phytoliths and siliceous aggregates, the volume decrease if all the calcite is lost could be 50 times. This can be monitored by measuring the coincident increase in the proportion of the relatively insoluble fraction. Observations of this kind in Kebara Cave have documented major volume changes of ash volume both indirectly and by direct observation of the stratigraphic section (Schiegl *et al.*, 1996). Clearly sediments which contain less calcite (as compared to ash), such as airborne dust or soils, will potentially be subject to smaller volume changes due to diagenesis. Dissolution of mineral phases may not necessarily result in a volume change, but only in an increase in porosity. In the southwest corner of Kebara Cave the sediments have an extremely high porosity. Micromorphological observations show that nodules are etched and large void spaces occur in their immediate proximity. This may be due to the dissolution of taranakite.

Volume changes due to diagenesis affect calculations of bone and lithic artefact densities, which are often used to assess “intensity” of occupation. Volume changes also sometimes result in serious stratigraphic problems, as dissolution is not likely to be uniform over the whole sedimentary layer, and thinning occurs in some areas and not in others. If, as we expect, much of this occurs when the sediment is close to the surface, then a depression will form on the surface and the rate of sedimentation there will be higher than on the flanks. This has apparently occurred in Tautavel Cave, southwestern France, as well as in Theopetra Cave (Karkanas *et al.*, 1999). Volume changes are also accompanied by changes in the mineral assemblages. The differing assemblages in turn have different contents of the elements uranium, thorium and potassium, which are the major sources of the radiation that affects dating by thermoluminescence and electron spin resonance (Mercier *et al.*, 1995a). All the above factors may seriously affect the interpretation of the archaeological record of a prehistoric cave.

Concluding Comments

Assessing the nature of the archaeological record is essential for the interpretation of the behaviour of the human occupants of a prehistoric cave. Here we propose that the properties of the authigenic minerals that form in a prehistoric cave can be used to reconstruct ancient palaeoenvironmental chemical conditions. From this information we can deduce whether or not materials of anthropogenic origin are absent because they were never deposited, or because they were not preserved. In order to achieve this objective, a better understanding of the properties of naturally formed authigenic minerals needs to be obtained. This

information can then be used in a predictive manner, together with knowledge of the site formation processes, to better interpret the archaeology of a prehistoric cave site.

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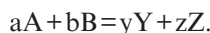
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Appendix

Calculation of mineral equilibrium relations

The first and most important step is to formulate a suitable equation for the reaction. A general equation for a chemical reaction is



The corresponding equilibrium is

$$K_{\text{reaction}} = \frac{[Y]^y [Z]^z}{[A]^a [B]^b}$$

and

$$\log K_{\text{reaction}} = y \log[Y] + z \log[Z] - a \log[A] - b \log[B] \quad (\text{i})$$

where $[A]$, $[B]$, $[Y]$, $[Z]$ are the concentrations of A, B, Y, and Z substances. In dilute solutions concentrations are generally equal to activities of the dissolved substances.

We can estimate the logK of the reaction by calculating the change of the standard free energy of the reaction ΔG . To find the standard free energy of a reaction we subtract the sum of ΔG values for the reactants from the sum of ΔG of the products. ΔG of the substances are derived from the literature, measured experimentally, or calculated. Therefore

$$\Delta G_{\text{reaction}} = y\Delta G_Y + z\Delta G_Z - a\Delta G_A - b\Delta G_B$$

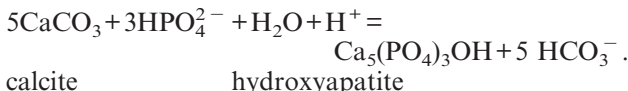
and

$$\log K = -\Delta G/1.364.$$

We substitute in (i) and solve for a certain variable. Concentration of solids is set to 1. The equation can be represented graphically, but graphs can conveniently display only two variables. Therefore we eliminate some of the variables by fixing them at a reasonable value. We can calculate a series of graphs from the same equation introducing each time different variables as constants.

The reactions for the calculation of the stability fields of the related minerals

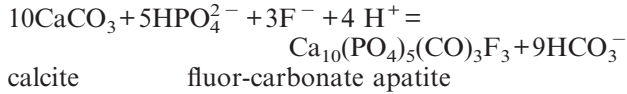
The equilibria are calculated from standard free energy data at 25°C and 1 bar. For hydroxyapatite formation the reaction is:



The equilibrium constant K of the reaction is $10^{18.12}$ and

$$\log K = 5\log(\alpha\text{HCO}_3^-) - 3\log(\alpha\text{HPO}_4^{2-}) + \text{pH} = 18.12.$$

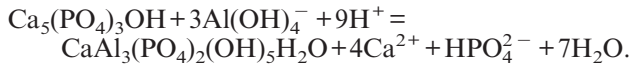
For fluor-carbonate apatite (francolite) the reaction is:



and

$$\log K = 9\log(\alpha\text{HCO}_3^-) - 5\log(\alpha\text{HPO}_4^{2-}) - 3\log(\alpha\text{F}^-) + 4\text{pH} = 33.81.$$

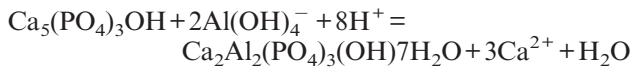
For hydroxyapatite to crandallite



The equilibrium constant K of this reaction is $10^{63.90}$ and

$$\log K = 4\log(\alpha\text{Ca}^{2+}) + \log(\alpha\text{HPO}_4^{2-}) - 3\log(\alpha\text{Al}(\text{OH})_4^-) + 9\text{pH} = 63.90.$$

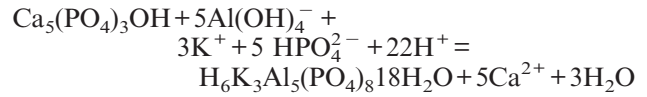
For hydroxyapatite to montgomeryite



and

$$\log K = 3\log(\alpha\text{Ca}^{2+}) - 2\log(\alpha\text{Al}(\text{OH})_4^-) + 8\text{pH} = 57.70.$$

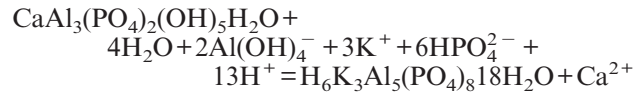
For apatite to taranakite



and

$$\log K = 5\log(\alpha\text{Ca}^{2+}) - 5\log(\alpha\text{Al}(\text{OH})_4^-) - 3\log(\alpha\text{K}^+) - \log(\alpha\text{HPO}_4^{2-}) + 22\text{pH} = 190.50.$$

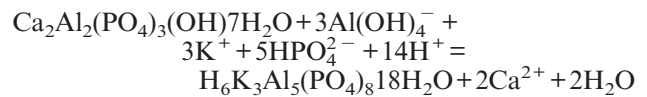
For crandallite to taranakite



and

$$\log K = \log(\alpha\text{Ca}^{2+}) - 2\log(\alpha\text{Al}(\text{OH})_4^-) - 3\log(\alpha\text{K}^+) - 6\log(\alpha\text{HPO}_4^{2-}) + 13\text{pH} = 126.60.$$

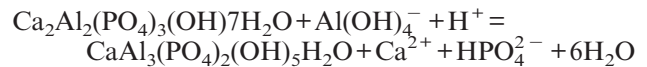
For montgomeryite to taranakite



and

$$\log K = 2\log(\alpha\text{Ca}^{2+}) - 3\log(\alpha\text{Al}(\text{OH})_4^-) - 3\log(\alpha\text{K}^+) - 5\log(\alpha\text{HPO}_4^{2-}) + 14\text{pH} = 132.80.$$

For montgomeryite to crandallite



and

$$\log K = \log(\alpha\text{Ca}^{2+}) + \log(\alpha\text{HPO}_4^{2-}) - \log(\alpha\text{Al}(\text{OH})_4^-) + \text{pH} = 6.20.$$