Formation Processes of Cemented Features in Karstic Cave Sites Revealed Using Stable Oxygen and Carbon Isotopic Analyses: A Case Study at Middle Paleolithic Amud Cave, Israel

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Hearths are important archaeological features, serving to infer past practices related to hominin subsistence and social behaviors. The identification of hearths is not always straightforward due to post-depositional processes. In karstic cave environments in particular it is not always easy to distinguish, in the field or in the laboratory, between geogenic and anthropogenic cemented features because both are composed of calcite. Here we present a novel study in which bulk oxygen and carbon isotopic analyses were used in order to unequivocally identify anthropogenic calcite derived from hearths in the Neanderthal site of Amud Cave (Israel). We demonstrate that the isotopic composition of wood ash is distinctively different from that of geogenic calcite. The linear relationship observed between carbon and oxygen isotopic compositions of the various sediment types in Amud Cave is interpreted as a mixing line between wood ash and geogenic calcite, thus enhancing our understanding of the origins of sedimentological variability at the site and showing that not all of the cemented sediments in Amud Cave should be regarded as hearths. Our study suggests that the relative abundance of validated hearths in the various areas of the cave may be associated with Neanderthal use of space in Amud Cave. © 2008 Wiley Periodicals, Inc.

INTRODUCTION

Identifying prehistoric hearths and understanding the processes that have affected their formation and modification is crucial for paleoanthropologists' reconstructions of (among others) fire-associated subsistence practices, spatial behaviors, and social

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relations of the groups that inhabited the sites (e.g., Clark and Harris, 1985; Gamble, 1999; Rolland, 2004). Recent studies of hearths and hearth-related features in prehistoric sites, located primarily in the Mediterranean ecological zone, centered on the depositional processes that influence their preservation and visibility in the archaeological record. These studies have focused on the process of dissolution of wood ash, composed primarily of the mineral calcite ($CaCO_3$), which is the main component of prehistoric fires in the circum-Mediterranean region (e.g., Weiner et al., 1993; Schiegl et al., 1996; Karkanas, 2001; Karkanas et al., 2002). Using Fourier Transform Infrared spectroscopy (FTIR), micromorphology, and phytolith analyses, these studies highlighted a process in which the calcitic ash reacted with phosphate-rich solutions deriving from degradation of bat guano. The outcome of this process was either the replacement of calcitic wood ash by authigenic phosphate minerals or, in extreme cases, complete dissolution of the wood ash. These studies, however, did not focus on the processes occurring in hearths composed of calcitic ash.

Many karstic cave sites in the east Mediterranean region that include cultural remains have developed in Cretaceous and Eocene limestone and/or dolomite rocks. They include deposits that span the late Lower Paleolithic through the Epipaleolithic and sometimes also preserve historical cultural remains. The current working hypothesis for karstic caves in the circum-Mediterranean region, and possibly in other regions (cf. Schiegl et al., 2004 for South Africa), is that the presence of preserved calcitic ash indicates minimal chemical diagenesis (Karkanas et al., 2000; Shahack-Gross et al., 2004). This further implies that the paleo-chemistry of the sediments associated with preserved calcitic ash did not change much with time and therefore bones are expected to be preserved as well. Yet ash deposits in the archaeological record appear as either loose or cemented sediments. In cases where cementation has occurred, mostly in karstic caves, the excavated hearth material may be composed of pristine calcitic ash and/or re-crystallized calcitic ash and/or geogenic calcite (i.e., speleothems). Re-crystallized ash and geogenic calcite presumably result from the presence of percolating water rich in bicarbonate. Thus, the mere presence of calcite identified using mineralogical analyses (e.g., infrared spectroscopy or X ray diffraction) of bulk samples cannot reveal whether it derives from wood ash or is geogenic. Additionally, in those cases where both anthropogenic and geogenic processes affected the archaeological sediments, these analyses are insufficient to determine the degree of mixing of the two components. The distinction between the two processes is also not easy at the microscopic level, because both re-crystallized ash and geogenic calcite may be composed of micritic (i.e., smaller than 4 micrometers) crystals in thin section. Experienced micromorphologists may be able to identify re-crystallized micritic ash as such, but are less likely to be able to quantitatively determine the extent of mixing of calcitic sources. Previous studies also dealt with the phytolith assemblages that are expected to occur in wood ash (Albert et al., 1999, Albert and Weiner, 2001) and thus serve as markers for these anthropogenic features. However, not all tree species produce phytoliths (Tsartsidou et al., 2007). Moreover, ash-derived phytoliths in karstic caves with an active hydrological system may well have been dissolved due to the high alkalinity of the sediments (Karkanas et al., 2007).

Thus, before any implications are made about spatial patterning, subsistence and social behaviors related to hearths, it is extremely important to be able to first determine whether cemented sediments in prehistoric karstic caves are indeed composed of ash and second, what were the taphonomic processes that affected calcitic hearths. Here we present a case study of cemented calcitic sediments from the Neanderthal site of Amud Cave, Israel, in which calcitic sources and the degree of their mixing were identified and semi-quantified.

Amud Cave is located on the eastern flanks of the Upper Galilee Mountains, on the margins of the Dead Sea Rift. The cave is a karstic feature that developed in Middle Eocene limestone of the Bar-Kokhba formation (Zaltsman, 1964). The vegetation above the cave and in the surrounding area is primarily of C3 type (trees, shrubs, and grasses of temperate climates). Average annual rainfall is 500 mm, occurring only during the winter season (December to May), and average yearly temperatures are 16–17°C. Recent excavations at Amud Cave exposed locally cemented features composed mostly of calcite (Figure 1), and initiated the need to understand the formation processes associated with these calcitic features. The stratigraphy of Amud Cave, identified by Chinzei (1970) and corroborated during the 1990s excavations at the site (Hovers et al., 1991), consists of units A and B. The latter, which contains the Middle Paleolithic sediments, was divided into sub-units B1 through B4 (from top to bottom). Sub-unit B1, which had been subjected to severe erosion in the central part of the cave, was encountered in Area A next to the cave's northern wall (see Figure 2 for excavation areas). Sub-units B2 and B4 have been encountered throughout the cave. Sub-unit B3, an archaeologically sterile layer mainly composed of gravel from the roof and wall collapse (*éboulis sec*), runs across all the excavation areas and served as a stratigraphic marker bed (Hovers et al., 1991; Valladas et al., 1999; Hovers, 2004). The anthropogenic sediments in all the excavation areas are grayish in color, while in the sterile sub-unit B3 the sediment is yellowish.

Three types of sediments have been encountered in the anthropogenic stratigraphic units during the excavation, differing in their color and hardness: gray-brown loose sediments, slightly cemented gray-white sediments (henceforth "soft concretions"), and highly cemented gray-white sediments (henceforth "hard concretions"). Note that the term "concretion" as used here describes cemented sediments and does not conform to typical geological or pedological nodules and/or crusts that include distinctive internal laminations. As a rule, the extent of cementation is higher in Area A for both sub-units B1 and B2. (Sub-unit B4 has not been reached in this area during the recent excavations.) Variability in the sizes and shapes of the cemented features, however, cross-cuts excavation areas and stratigraphic boundaries. The highly cemented features in Area A tend to be small (ca. 3–30 cm in maximum dimension), and many of them (though not all) are flat (3–10 cm thick) (Figure 1a). Similar features were found near the top of sub-unit B2 in Area B (Figure 1). In Area A, a few larger flat features also occurred; they measured ca. 50 cm in maximum dimension, were mildly cemented, and possibly filled shallow basins (Figure 1b). Highly cemented sediments were encountered as a massive feature (ca. 30 cm thick and 170 cm in maximum dimension) also at the truncated top of sub-unit B2 in Area C. Cemented features in sub-unit B4, in both areas B and C, consist mostly of slightly cemented,

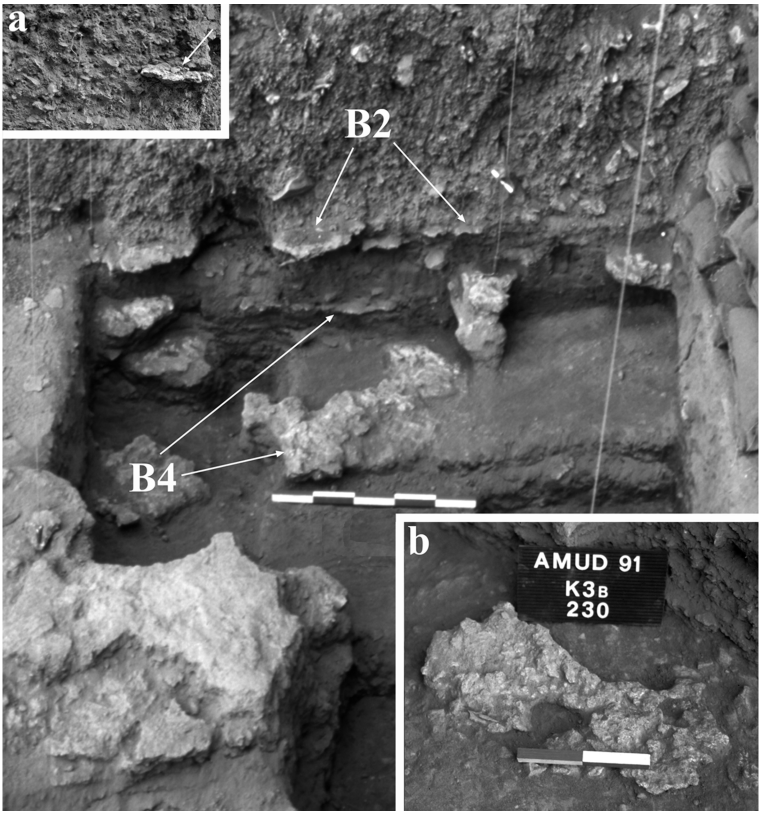

Figure 1. Photographs of typical cemented sediments encountered during the 1990's excavations. The main photograph is from excavation area B showing light-colored cemented sediments (i.e., "concretions") in section and in plan view, from sub-units B2 and B4. The scale is 50cm. Note the large size and flat form of the concretions from sub-unit B4 compared to the concretions from sub-unit B2. Inset (a) shows a typical, small-sized concretion from area A sub-unit B1 (same scale as in the main photograph). Note the similarity in size between the concretions from area A to those of sub-unit B2 in area B. Inset (b) shows an atypical large concretion in area A. Scale is 20cm. Note the similarity in size and shape to the large concretions of sub-unit B4 in area B.

white-gray sediments. They tend to be rather large (ca. 50 cm in maximum dimension; a single feature in Area B is ca. 150 cm in maximum dimension) and generally flat (up to 7 cm thick) (Figure 1).

Fire-damaged lithics and burned animal bones are abundant throughout the various anthropogenic sub-units and in all the depositional microenvironments (Hovers et al., 1991; Valladas et al., 1999; Hovers, 2004; Rabinovich & Hovers, 2004). The presence of bones and bone fragments in the three sediment types suggested that chemical diagenesis was minimal. This notion was corroborated by infrared spectroscopy (S. Weiner, personal communication, 1994, and see below) and by an initial series of micromorphological analyses (Madella et al., 2002; and see below). The latter indicated that ash was preserved in both the soft sediments and the concretions. The identification

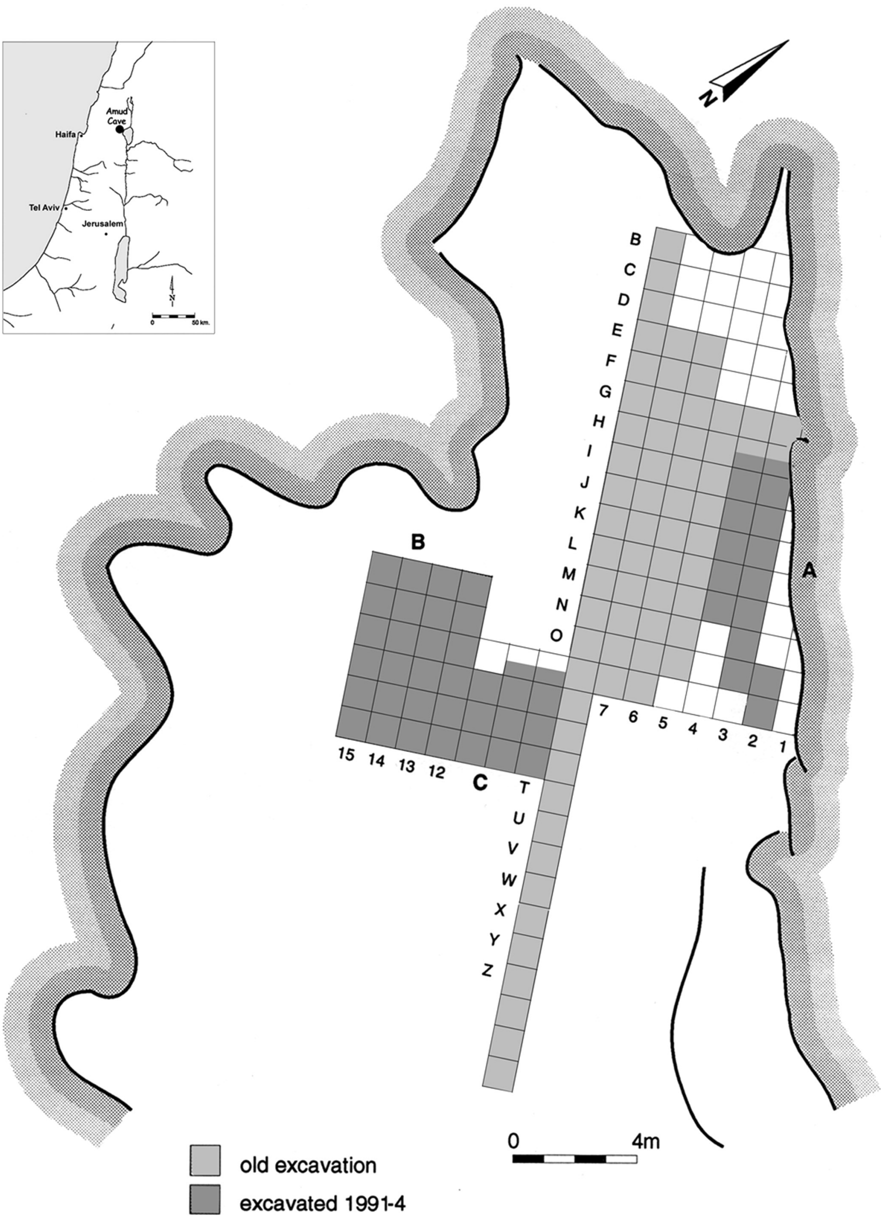

Figure 2. Detailed map of the excavation areas within Amud Cave. The inset shows the location of Amud Cave in Israel. Sampling for the current study was conducted on cleaned profiles left after the 1990s excavation (squares marked by dark gray). The squares marked by light gray were excavated in the 1960s.

of calcitic ash in some of the concretions led to the hypothesis that these features were hearths that were cemented rapidly after they had been used (Madella et al., 2002). This inference in turn indicated that the concretions referred to the original locations of fireplaces used by hominins at the site. Yet the proximal occurrence of burned and non-burned elements, sometimes lumped together in the cemented calcitic sediments, coupled with the presence of geogenic calcite in some of the highly cemented concretions and the bioturbated state of the soft sediments (Goren and Goldberg, n.d.), indicated that complex depositional processes had been at work (Hovers et al., 1991; Madella et al., 2002; Hovers, 2004; Rabinovich & Hovers, 2004). In the current study we focused specifically on understanding the sources of calcite and on determining the extent of mixing between pristine wood ash, re-crystallized wood ash, and geogenic calcite, as well as the mechanism/s that operated in the formation of the cemented sediments in Amud Cave. In order to address these questions, we carried out a geoarchaeological study that included measurements of the isotopic composition of carbon and oxygen from the calcitic component of the sediments from Amud Cave.

Oxygen and Carbon Isotopes in Burned Materials

The stable isotopes of oxygen and carbon are routinely used in archaeological research in the framework of climatic and dietary studies. However, it is the isotopic fractionation of oxygen and carbon in lime mortar that is of direct relevance to the problem at hand, because the production of lime mortar is analogous, in part, to the formation of wood ash. The chemical reactions leading to lime mortar formation involve calcination of limestone rocks at high temperature to form quicklime (calcium oxide, CaO) followed by hydration of the quicklime to slaked lime ($Ca(OH)_2$), which is used in construction. Upon drying, the slaked lime absorbs atmospheric CO_2 and re-crystallizes as calcite. It is in this stage of mortar formation that the isotopic fractionation between the atmospheric CO_2 and calcium oxide occurs. The absorbance of CO_2 by the CaO is rapid and kinetically determined, resulting in calcite that is enriched in the light isotopes, ^{12}C and ^{16}O. The isotopic values of dry fresh lime mortar are therefore extremely low relative to the atmosphere, i.e., range between −15.3 and −18.4‰ for carbon and between −19.1 and −22.2‰ for oxygen (Van Strydonck et al., 1989), while the isotopic values of atmospheric CO_2 are in the order of −6.5 to −8‰ for carbon and +41‰ for oxygen (Faure, 1986; Friedli et al., 1986).

The process of ash formation due to burning of woody tissues is similar to the formation of lime, except for the raw material being burned and the steps of thermal degradation. In the case of woody tissues, the biogenic mineral whewhellite (calcium oxalate monohydrate, $CaC_2O_4{\cdot}H_2O$; Arnott and Pautard, 1970), found in wood in large quantities, disintegrates in two steps; the first occurs at 425°C where CO is released, resulting in pseudomorphs of calcite after calcium oxalate crystals, and the second occurs at 600°C with the release of CO_2 resulting in formation of CaO (Brochier and Thinon, 2003; Kloprogge et al., 2004). Here, similar to formation of lime, calcium oxide absorbs atmospheric CO_2 upon cooling and reforms as micritic calcite crystals (Wattez and Courty, 1987; Karkanas et al., 2000; Karkanas, 2007). It is therefore expected that the carbon and oxygen isotopic values of wood ash from formal hearths where burning occurred at high temperatures will be enriched in the light isotopes.

Geogenic calcite is enriched in the heavy isotopes relative to calcite from lime mortar. The average value of limestone and dolomite rocks in Israel is 0±4‰ for carbon and 0±2‰ for oxygen (Magaritz, 1973). Altered carbonate rocks may have lower $\delta^{18}O$ values. Most relevant to our study is the isotopic composition of speleothems that form in cave environments. In the Mediterranean zone of Israel such speleothems have isotopic values averaging −11‰ for carbon and −5‰ for oxygen (e.g., Bar-Matthews et al., 2003). We thus hypothesized that the isotopic composition of carbon and oxygen in wood ash should be within the range of values known for calcite from lime mortar, and distinctively different from the values of geogenic calcite in karstic cave settings. Thus, if the cemented sediments in Amud Cave are wood ash from hearths, they should have an isotopic signature similar to that of calcitic lime mortar (i.e., enriched in the light isotopes), whereas geogenic calcite will be recognized by an isotopic signature similar to that of local speleothems deposited in isotopic equilibrium conditions, characterized by relatively higher $\delta^{18}O$ and $\delta^{13}C$ values. Moreover, it was expected that the isotopic signal would also reflect cases where mixing of the two "end members" (i.e., pristine ash and geogenic calcite) had occurred and/or reflect the presence of re-crystallized ash, by showing intermediate values between the two "end members."

We determined the isotopic values for modern calcitic wood ash in order to estimate the range of values for fresh ash (see below). Similarly, because the Middle Paleolithic deposits at Amud Cave are dated between 70,000 and 55,000 years ago (Valladas et al., 1999; Rink et al., 2001), we used the isotopic composition of the contemporaneous speleothem record of northern Israel to set the expected value range of geogenic features. This range is between −4‰ and −5‰ for oxygen, and −10‰ and −12.5‰ for carbon (Bar-Matthews et al., 2003). Note that variations in the $\delta^{13}C$ values of speleothems mainly reflect changes of the vegetation type in the vicinity of the cave. In the Mediterranean region, $\delta^{13}C$ values ranging between ca. −13 and −10‰ are associated with the dominance of C3-type vegetation while higher values indicate an increased contribution of C4-type vegetation (Bar-Matthews and Ayalon, 2003; Bar-Matthews et al., 2003). The $\delta^{18}O$ values of speleothems mainly reflect changes in meteoric water composition, related to climatic factors such as mean air temperature and humidity, and temperature of deposition within the cave. Overall, the carbon isotopic composition of speleothems is determined by the isotopic composition of the soil-CO_2 and of the host rock.

MATERIALS AND METHODS

We analyzed two samples of modern wood ash produced in an open camp fire (from oak [*Quercus calliprinos*] and carob [*Ceratonia siliqua*] trees growing in the Mediterranean region), one sample of geological calcite (limestone from the bedrock of Amud Cave), and 21 samples of archaeological sediments derived from the three anthropogenic sub-units (i.e., B1, B2, B4). The analyses include soft powdery sediments as well as concretions. One soft concretion from sub-unit B4 (sample 94-14)

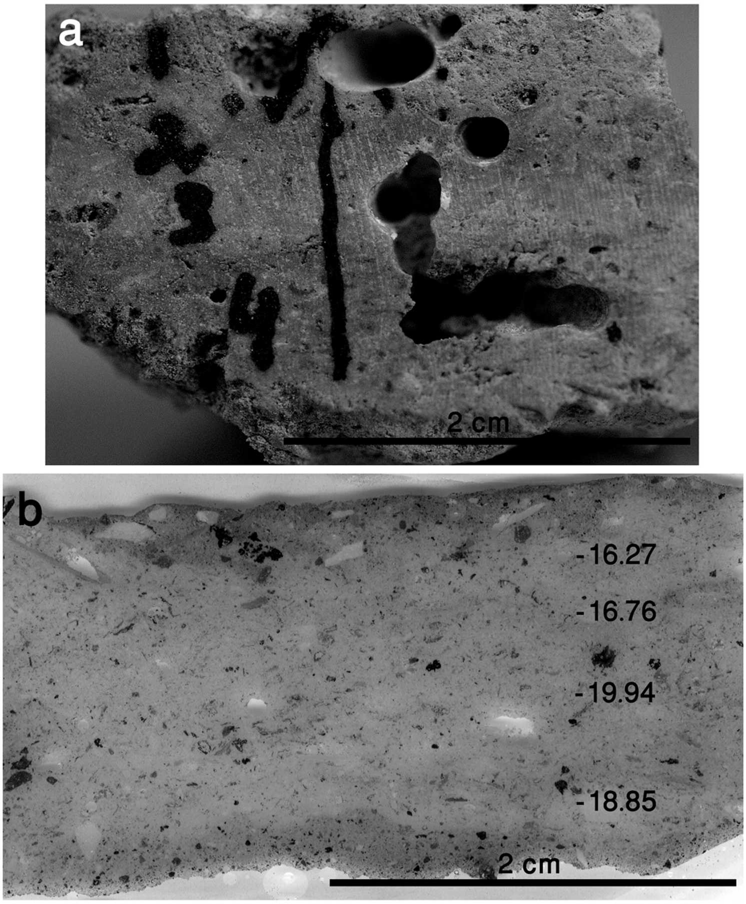

Figure 3. (a) Photograph of a part of concretion 94-14 that was sawed diagonally in order to observe laminations. Note the drill holes at the right half of the photograph (marked 1 through 4 on the left half of the photograph). Material for isotopic analysis was obtained from what appeared macroscopically to be different laminae based primarily on color. (b) A scan of the corresponding thin section prepared from the same concretion. The carbon isotopic values obtained from the drilled material are indicated. Note the enrichment in ^{13}C in the upper two laminae compared to the lower two laminae. This enrichment is due to re-crystallization and thus addition of geogenic calcite to the upper two laminae.

was cut diagonally where various sub-horizontal laminae were observed. A sequence of four samples was drilled out of these various laminae for isotopic determination (Figure 3a). The soft archaeological sediments and concretions were lightly ground using mortar and pestle and sieved through a 0.25mm screen. This process eliminated from the samples the large particles (e.g., limestone fragments, flint implements, and bones). The mineralogical composition of the samples was determined using Fourier Transform Infrared Spectroscopy following Weiner et al. (1993). Stable isotopic analyses were performed at the Geological Survey of Israel. The CO_2 gas was liberated from ~0.5 mg samples by phosphoric acid digestion at 90°C and introduced into the mass spectrometer and analyzed for $\delta^{18}O$ and $\delta^{13}C$ values using a VG

Isocarb system attached to a SIRA-II mass-spectrometer. All $\delta^{18}O$ and $\delta^{13}C$ values were calibrated against the international standard NBS-19, and are reported in permil (‰), relative to the Pee Dee Belemnite standard.

As this study has been part of a wider and systematic geoarchaeological study in Amud Cave, most of the archaeological samples reported here have embedded counterparts that were studied micromorphologically (following Bullock et al., 1985; Courty et al., 1989). In addition, quantitative phytolith analyses (based on the method of Albert et al., 1999) were performed on ten sediment samples from concretions as well as soft sediments from excavation areas A and B and covering all three archaeological sub-units as well as the sterile sub-unit B3. Seven of the sediment samples analyzed for phytoliths have also been analyzed isotopically.

RESULTS

Mineralogical Identifications

The mineral components as identified by FTIR in the cave sediments are mostly calcite and clay, with minor amounts of quartz, opal, and dahllite. Representative FTIR spectra from soft and cemented sediments are presented in Figure 4. The relative

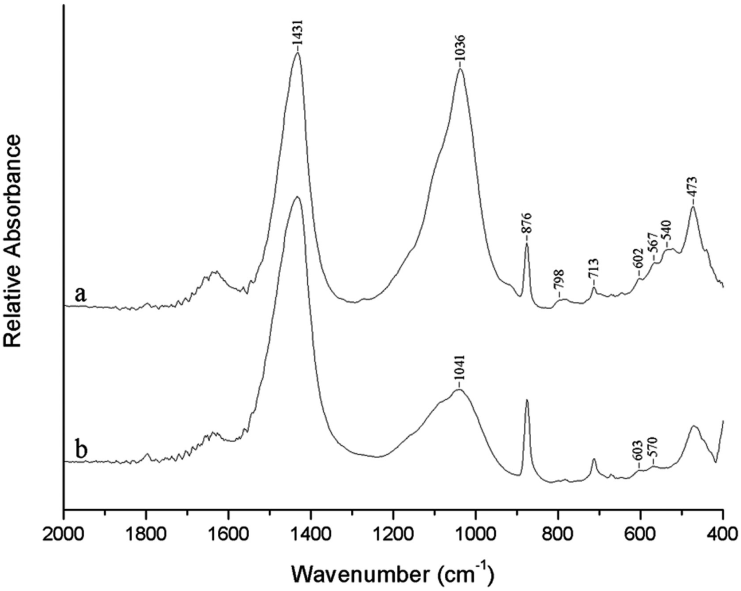

Figure 4. FTIR spectra of (a) soft gray sediment and (b) soft concretion, both from Area B, sub-unit B4. These spectra show the general mineralogical composition of the sediments in Amud Cave. The absorbance bands at 1431, 876, and 713 cm^{-1} are from calcite, the absorbance bands at 1036, 540, and 473 cm^{-1} are from clay, and the absorbance bands at 602 and 576 cm^{-1} are from dahllite. Note that soft sediments are richer in clay relative to concretions. Both types of sediments include a small amount of dahllite, mostly due to presence of microscopic bone fragments. The absorbance at 1041 cm^{-1} in spectrum (b) coupled with the absorbance bands at 603 and 570 cm^{-1} are from dahllite and only little amounts of clay. The shoulders apparent around 1100 cm^{-1} coupled with the lack of splitting around 800 cm^{-1} indicates the presence of opal that, based on microscopic observations, is in the form of phytoliths.

amounts of the mineral components are variable. Phosphate minerals that form in acidic conditions (e.g., taranakite, montgomeryite, leucophosphite; see Karkanas et al., 2000; Shahack-Gross et al., 2004), which were identified in other Middle Paleolithic cave sites in the Mediterranean region, have not been identified in Amud Cave. Moreover, based on the micromorphological observations of the current study, the sediments of Amud Cave include large amounts (usually between 5 and 10% by area) of microscopic bone fragments and no indications for authigenic phosphate nodules. The presence of dahllite in the FTIR spectra thus reflects the occurrence of such bone fragments. These results, and the mostly powdery nature of the sediments, indicate that minimal chemical diagenesis took place in Amud Cave under neutral to alkaline conditions (verified by 2 determinations of pH, 7.1 and 7.5, conducted on sediments from sub-unit B1). These are the chemical conditions that promote ash and bone preservation and are also conducive for the formation of geogenic calcite.

Oxygen and Carbon Isotopic Compositions

The isotopic analyses (Table I) played an important role in identifying the diagenetic processes that had affected the anthropogenic deposits in the neutral to alkaline chemical environment of Amud Cave. The $\delta^{13}C$ and $\delta^{18}O$ obtained from the modern oak ash are $-22.37‰$ and $-16.44‰$ respectively, and those from the modern carob ash are $-24.54‰$ and $-17.33‰$ respectively. As expected, these values are enriched in the light isotopes.

The isotopic values of the cave limestone bedrock are $-2.39‰$ for the carbon and $-5.16‰$ for the oxygen. These values are within the expected range of marine limestone and are distinctively different from the ones obtained from the modern wood ashes. The carbon isotopic composition of the bedrock is distinctively different from that of the speleothems (i.e., enriched in ^{13}C).

Isotopic compositions of the archaeological sediments encompass the whole range between the speleothem and modern ash values irrespective of sediment type (Figure 5). All the sediment samples included in this study have lower isotopic values than the local speleothems. These results indicate that all the sediment types in Amud Cave are composed from chemically preserved wood ash variably mixed with geogenic calcite. The sediment samples with isotopic values approaching those of modern wood ash (Figure 5, lower left part of the plot, $n = 12$) are exclusively from the central part of the cave (Areas B and C) and include both cemented and soft sediments (from sub-units B4 and B2). The sediment samples that have isotopic values approaching those of speleothems (Figure 5, upper right part of the plot) are mostly from area A of the excavation and include both cemented and soft sediments (from sub-units B1 and B2). Only three samples from areas B and C (sub-units B2 and B4), all of them cemented sediments, belong to this group, having "speleothem-like" isotopic values.

Micromorphology, and Mineral and Phytolith Quantities

Micromorphological analyses show that the soft gray sediments from Amud Cave include pseudomorphs of calcite after calcium oxalate crystals, microscopic charcoal,

Table I. List of samples from Amud Cave with field description, carbon and oxygen isotopic compositions (in permil [‰] relative to PDB standard), and the micromorphological blocks that correspond to these samples.

Sample	Context	Sediment type	$\delta^{13}C$	$\delta^{18}O$	Counterpart micromorphological sample
RAM-1	Area B, Layer B4	Soft gray sediment	−22.18	−15.04	RAMB-1
RAM-3	Area B, Layer B4	Soft gray sediment	−20.15	−13.63	
RAM-5	Area B, Layer B4	Top of white concretion	−12.7	−7.48	RAMB-1
RAM-9	Area B, Layer B2	Soft gray sediment	−19.72	−12.47	
RAM-17	Area B, Layer B2	Soft gray sediment	−19.09	−12.38	RAMB-2
RAM-18	Area B, Layer B4	Top of gray concretion	−13.42	−12.59	
RAM-20	Area B, Layer B2	White concretion	−19.7	−12.92	RAMB-2
RAM-22	Area B, Layer B2	Brown concretion	−13.07	−6.1	
RAM-24	Area C, Layer B4	Light gray slightly hard sediment	−13.95	−16.71	RAMB-4
RAM-25	Area C, Layer B4	Soft brown sediment	−18.86	−14.71	RAMB-4
RAM-29	Area C, Layer B2	Soft gray sediment	−11.14	−8.43	
RAM-33	Area A, Layer B2	Hard gray sediment	−15.32	−8.38	RAMB-8
RAM-34	Area A, Layer B2	Soft gray sediment	−13.42	−8.65	RAMB-8
RAM-36	Area A, Layer B2	Soft white concretion	−8.25	−7.14	
RAM-38	Area A, Layer B2	Hard white concretion	−8.22	−4.59	RAMB-5
RAM-39	Area A, Layer B2	Concretion	−9.47	−6.16	RAMB-6
RAM-42	Area A	Limestone bedrock	−2.39	−5.16	
RAM-44	Area A, Layer B1/7	Soft gray sediment	−11.02	−7.08	RAMB-10
94-14a	Area B, Layer B4	Top white part of concretion	−16.27	−11.9	94-14
94-14b	Area B, Layer B4	Upper middle of concretion	−16.76	−12.79	94-14
94-14c	Area B, Layer B4	Lower middle of concretion	−19.94	−13.8	94-14
94-14d	Area B, Layer B4	Bottom gray part of concretion	−18.85	−13.81	94-14

and burned bones (Figure 6a), as well as microscopic specs of reddened, possibly burned, clay. The presence of burned clay in some but not all of the soft gray sediments was confirmed by FTIR spectroscopy (following Berna et al., 2007). When compared to the data given in Berna et al. (2007), spectral changes in the clay component from the soft sediments in Amud Cave suggest that, where present, the clay was burned at temperatures between 400 and 600°C (Table II). The frequencies of the mineral components in the soft gray sediments are 60±10% of calcite, 30±8% clay and 6±2% of quartz (Table II), irrespective of spatial location in the cave or stratigraphic assignation. The average phytoliths concentration in the soft gray sediments is ca. 1,800,000 phytoliths in 1 g of acid insoluble fraction (Table II). The overall microstructure of the soft gray sediments is granular, indicative of bioturbation. The soft gray sediments thus represent bioturbated ash formed in relatively low

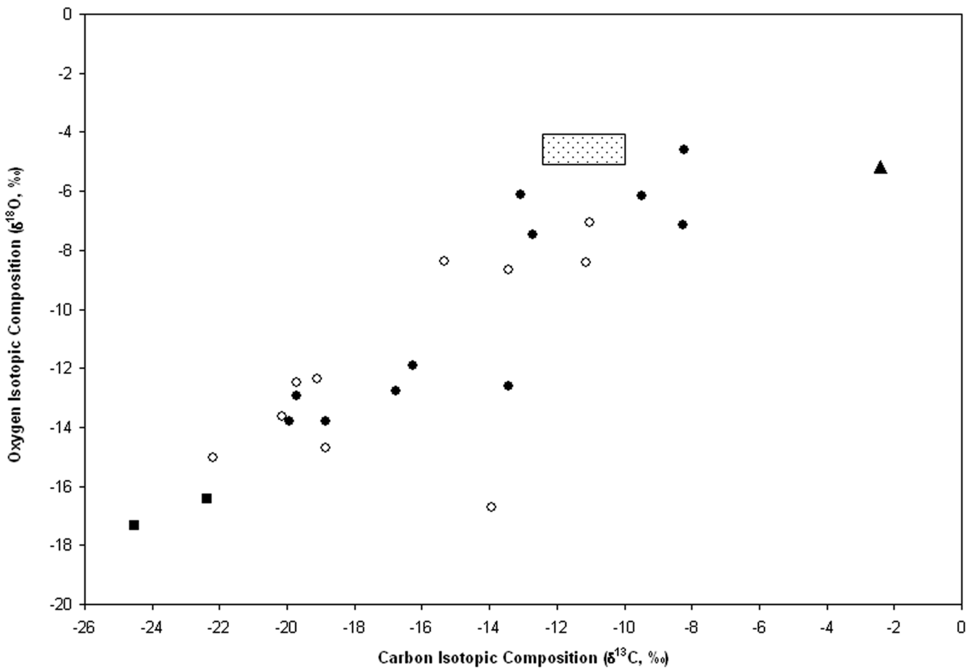

Figure 5. A plot of the carbon and oxygen isotopic values obtained from modern wood ash (closed squares), cave limestone bedrock (closed triangle), local speleothems (dotted rectangle), Amud Cave soft gray sediments (open circles), and Amud Cave soft and hard concretions (closed circles). Note the sharp difference in isotopic values between wood ash (lower left part of the plot) and geogenic calcite (upper right part of the plot). The isotopic compositions of sediments from Amud Cave cover the range between wood ash and geogenic calcite.

temperature (400–600°) based on both the presence of calcite pseudomorphs after calcium oxalate crystals and the infrared spectra of clays.

Ash crystals, charcoal specs, and burned and un-burned bones were previously identified micromorphologically in the cemented sediments from Amud Cave in either laminated or un-oriented microstructures (Madella et al., 2002). These two facies were interpreted as *in situ* intact hearths and disturbed hearth material, respectively (Madella et al., 2002). In the current study, we noted, upon mesoscopic observations (i.e., intermediate between the macro and the micro levels) on freshly cut consolidated blocks from both the soft and hard concretions, that the massive, un-oriented microstructure is mostly prevalent in the hard and small-sized concretions typical of excavation area A and sub-unit B2 in excavation area B. Only a few hard concretions from excavation area A that are typically flat (ca. 3 cm thick) show laminated structure. The softer concretions typical of excavation areas B and C, and notably the flat concretions from sub-unit B4, invariably possess a laminated structure.

A closer, microscopic, examination of each lamina in the soft concretions from sub-unit B4 shows that the lower laminae are gray, and their fabric and composition are similar to those of the soft gray sediments. Such laminae contain 71% calcite, 23% clay, 2% quartz, and ca. 4,500,000 phytoliths in 1 g of AIF (see sample 94-14 bottom in

Table II). The lower gray laminae in soft concretions from sub-unit B4 (in areas B and C) thus represent local cementation of bioturbated ash (i.e., cementation of the soft gray sediment discussed above). Microscopically, the uppermost white lamina in the soft concretions is composed of micritic calcite with almost no indications for calcitic pseudomorphs after calcium oxalate crystals (Figure 6b). It contains

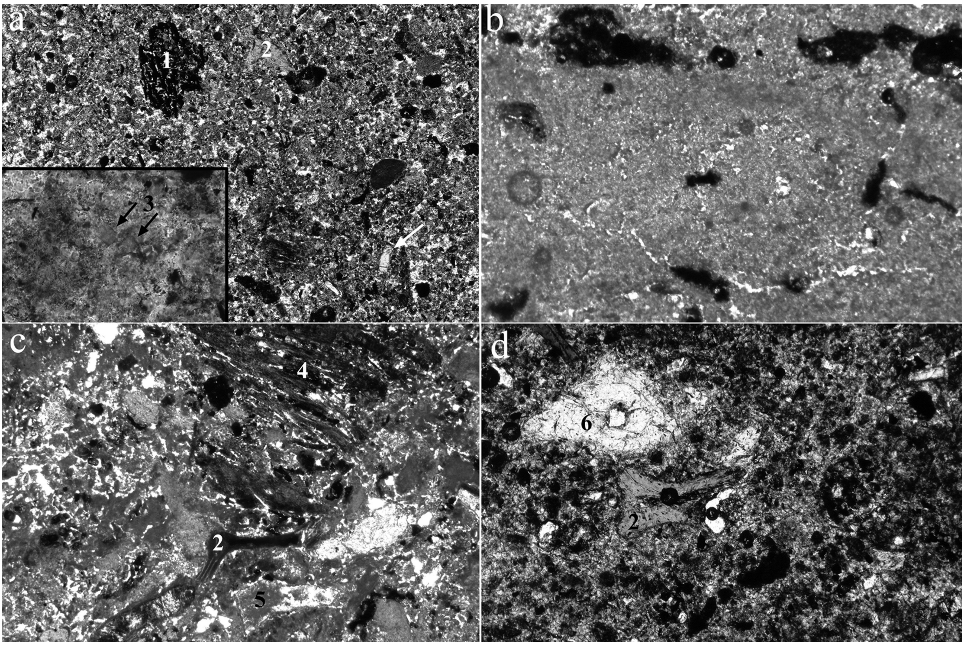

Figure 6. Photomicrographs of the typical appearance of the three major sediment types at Amud Cave. (a) Soft gray sediment (Area B, sub-unit B2, sample RAMB-2) showing a clayey calcitic groundmass including charcoal (1), burned bones (2), unburned bones (white arrow), and reddened clay fragments. The width of frame is 2.2 mm. The inset shows typical ash crystals that are incorporated in the clayey calcitic groundmass (3; inset frame width is 0.22 mm). The δ^{13}C value corresponding to this sample is −19.09‰, a value that is close to values of modern wood ash. (b) Cemented micritic calcite at top of soft concretion (Area B, sub-unit B4, sample RAMB-3). The width of frame is 2.2 mm. Note the absence of bones, charcoal, and reddened clay, and the presence of manganese-oxide stains (i.e., the black features in the photograph). The latter indicates formation in a humid sedimentary environment. The δ^{13}C value corresponding to this sample is −12.70‰, a value that is closer to values of geogenic calcite, indicating that this sub-layer is a mixture of geogenic calcite and ash, possibly re-crystallized ash. (c) Micritic calcite associated with burned bones (2), pseudomorphic cellular structures after woody tissues (4), and burned flint fragments (5). Most bone fragments in this sample are calcined. This photograph was taken from a sub-layer in concretion RAMB-3 that is found immediately below the top layer of the concretion shown in (b). The width of frame is 2.2 mm. Note the difference between the two sub-layers in this concretion, indicating that the calcitic ash and burned remains in (c) were cemented by geogenic calcite as seen in (b). (d) Cemented sediment from a hard concretion (Area A, sub-unit B2, sample RAMB-6). Note the clayey nature of the sediment with remains of burned (2) and unburned (6) bones, black managanese-oxide speckles, and sparitic calcite indicative of a geogenic origin in humid conditions. The width of frame is 2.2 mm. The δ^{13}C value corresponding to this sample is −9.47‰, a value that is very close to that of geogenic calcite indicating that most of the calcite in this concretion is geogenic.

Table II. Sediment samples from Amud Cave showing archaeological context, percentages of minerals (by weight) of the total sediment, the presence/absence of burned clay and its estimated burning temperature following Berna et al. (2007), and phytolith concentrations in the total sediment and the Acid Insoluble Fraction (AIF, in parentheses) for each sample. The percentage of calcite/dahllite was determined after acid dissolution of the total sediment. The percentages of quartz and clay were determined after heavy liquid separation procedure (following the procedure developed by Albert et al., 1999) in which the first two fractions are composed of quartz (and minor amounts of heavy minerals), and the third and fourth fractions are composed primarily of clay. The fifth and sixth fractions usually contain the phytoliths. FTIR analyses of the six fractions from all of the samples were done in order to verify which minerals were present in each fraction.

Sample	Sample information	% Quartz	% Clay	Altered clay (°C)	% calcite/ dahllite	Phytolith concentration in sediment (AIF)
Loose sediments						
RAM-1	Area B, sub-unit B4	7.8	37.7	Yes (5–600)	47.8	2,484,073 (4,755,832)
RAM-7	Area B, sub-unit B3	6.4	39.3	No	51.5	569,195 (1,172,926)
RAM-17	Area B, sub-unit B2	3.8	23.0	Yes (4–600)	67.5	627,206 (1,930,873)
RAM-34	Area A, sub-unit B2	5.4	25.8	No	67.5	226,131 (695,045)
RAM-44	Area A, sub-unit B1/7	6.3	23.7	No	68.9	114,641 (368,065)
Concretions						
94-14 top	Area B, sub-unit B4	0.3	3.4	Yes (>600)	93.0	90,865 (1,305,652)
94-14 bottom	Area B, sub-unit B4	2.0	23.1	Yes (>600)	71.2	1,311,740 (4,559,643)
RAM-14	Area B, sub-unit B2	0.2	0.6	Yes (>600)	97.6	142,552 (5,994,153)
RAM-39	Area A, sub-unit B2	2.3	10.0	No	87.1	5,009 (38,807)
RAM-43	Area A, sub-unit B1/6	1.9	7.0	Yes (4–600)	90.3	227,088 (2,331,294)

93% calcite, only 3% clay that has been burned at temperatures above 600°C based on its infrared spectrum, and 0.3% quartz. Its phytoliths concentration is low relative to the gray sediments, either soft or cemented (see sample 94-14 top in Table II). Charcoal, reddened clay specs, and fragments of calcined bones are present in white laminae that are slightly below the top part of the soft concretion (Figure 6c). The high amount of calcite in the white topmost lamina relative to the gray lamina, the small amount of preserved wood ash crystals, and the lower amounts of clay and quartz suggest that this upper lamina represents a mixture of ash that formed after complete calcination at high temperature and geogenic calcite (thus "diluting" the siliceous components, namely phytoliths, clay, and quartz). This type of sediment seems to have been formed through re-crystallization of wood ash and/or impregnation of wood ash by geogenic calcite.

We explored this possibility through isotope sampling of a diagonal section along one soft concretion (sample 94-14). The isotopic analysis indicates that the bottom grayish lamina is composed of large amounts of wood ash (−18.85‰ and −13.81‰ for carbon and oxygen, respectively), whereas the uppermost white lamina is more enriched in the heavier isotopes (−16.27‰ for carbon and −11.9‰ for oxygen). The two laminae between the lowermost and uppermost laminae of sample 94-14 show a gradual change in color from gray to white (from bottom to top) that is accompanied with higher amounts of micritic calcite relative to preserved ash pseudomorphs and with intermediate isotopic values between the lower and upper laminae (Figure 3b). The uppermost lamina shows values that are too low to be attributed solely to geogenic calcite. Moreover, the paucity of preserved wood ash crystals combined with the relatively low isotopic values indicates that the uppermost white lamina is composed mostly from re-crystallized wood ash. Therefore, re-crystallized ash can most probably be differentiated from geogenic calcite because it retains relatively low isotopic values.

The micromorphological features typical of the hard concretions include clear sparitic calcite crystals indicative of precipitation from a sediment solution rich in bicarbonate. The groundmass is mostly clayey including burned and unburned bone fragments (Figure 6d). The phytolith concentration is relatively low and the clay component is not always burned (Table II).

DISCUSSION

The stable isotopes of carbon and oxygen are clearly useful for elucidating the formation processes of cemented features in karstic cave sites. Our initial assumption that the similarity in formation of high temperature wood ash and lime mortar, through the absorbance of atmospheric CO_2 by calcium oxide, should result in a similar range of isotopic values was confirmed. We note that the range of isotopic values obtained experimentally for lime is large, with $\delta^{13}C$ values ranging from −8‰ to −26‰ and $\delta^{18}O$ values ranging from −14‰ to −26‰ (Ambers, 1987; Van Strydonck et al., 1989; Nissenbaum and Killebrew, 1995; Goren et al., 2005). This range has been explained previously by several factors: it may be related to the burning temperature and its duration (Kolodny and Gross, 1974; Nissenbaum and Killebrew, 1995), affected by the isotopic composition of the atmosphere in which the material reforms (Kolodny & Gross, 1974; Ambers, 1987) and by mixing with partially combusted calcareous materials and geogenic carbonates. Although we do not have direct evidence for the burning atmosphere in the cave, we assume that conditions were similar to current ones, because the cave most probably had a large opening in antiquity that would have promoted air circulation. Based on the mineralogical transformations observed in the clay minerals from Amud Cave, we deduce that burning temperatures were similar to those produced in modern camp fires, and based on micromorphology we deduce that the wood in the Neanderthal camp fires was fully combusted as in modern camp fires, such as the ones from which the reference wood ash was sampled.

The variability in isotopic compositions seen in the sediments from Amud Cave (Figure 5) may suggest any one of the following formation processes: a) the sediments with ash-like isotopic values are composed of large amounts of preserved ash and small amounts of geogenic calcite, while the sediments with more speleothem-like values are composed of small amounts of preserved ash and large amounts of geogenic calcite; b) the sediments with ash-like values are composed exclusively of ash that had undergone minimal re-crystallization, while the sediments with more speleothem-like values were composed exclusively of ash that has undergone severe re-crystallization; c) a combination of the above. Based on our micromorphological, mineralogical, and phytoliths analyses, it seems likely that the variability seen in Amud Cave is mostly attributed to the mixture of ash with geogenic calcite. We thus interpret the close to linear relationship seen in Figure 5 as a mixing curve between pure soft ash and speleothem end members. Using the average isotopic values from the modern ash and from the speleothem range as the values of the "end members," we have calculated an estimate of the percentage of ash in the analyzed sediment samples (Figure 7).

The group of samples at the lower left part of Figure 7 probably contains about 60–85% ash while the group of samples at the upper right part of the plot contains 0–32% ash. As noted above, the group of samples at the lower left part of the plot is exclusively from excavation areas B and C (i.e., the central part of the cave) while the group of samples at the upper right part of the plot are mostly from excavation area A. Clearly, geogenic processes were more pronounced in area A whose proximity to the cave wall, and thus to larger amounts of dripping water, is probably the cause for the higher degree of sediment cementation and to the greater mixing of geogenic calcite with the ash component of the sediment in this area. For example, sample RAM-39 (Table II) is composed of a large amount of calcite, some clay and quartz, but almost no phytoliths (ca. 38,000 in 1 g of AIF), and does not contain burned clay (Table II). Clearly sample RAM-39 is an example of a concretion that is almost entirely geogenic. This assertion is supported by the micromorphological identification of sparitic (i.e., more than 4 micrometer) calcite in this concretion. On the other hand, another concretion from area A (sample RAM-43 in Table II) does seem to be composed of re-crystallized ash and geogenic calcite based on the criteria outlined above. Overall, it appears that most of the small and hard concretions in excavation area A do not represent hearths except for the few thin concretions that are larger than 30 cm in diameter and possess a laminated structure. This may further indicate that area A may have been used infrequently for activities that centered around hearths compared to other areas of the cave. Our data thus support and amplify the results presented by Alperson-Afil and Hovers (2005). These authors suggested that during the time of deposition of sub-unit B2, area A was used by the Neanderthal occupants for both initial core modification (possibly around hearths; Ekshtain and Hovers, 2005) as well as a discard zone for rejected and exhausted lithic artifacts.

The generally softer concretions from areas B and C are mostly composed of ash. The soft concretions from sub-unit B4 are of special interest. These concretions show the gradual impregnation of the calcitic ash by geogenic calcite accompanied by ash re-crystallization and usually have a flat circular form. We therefore suggest

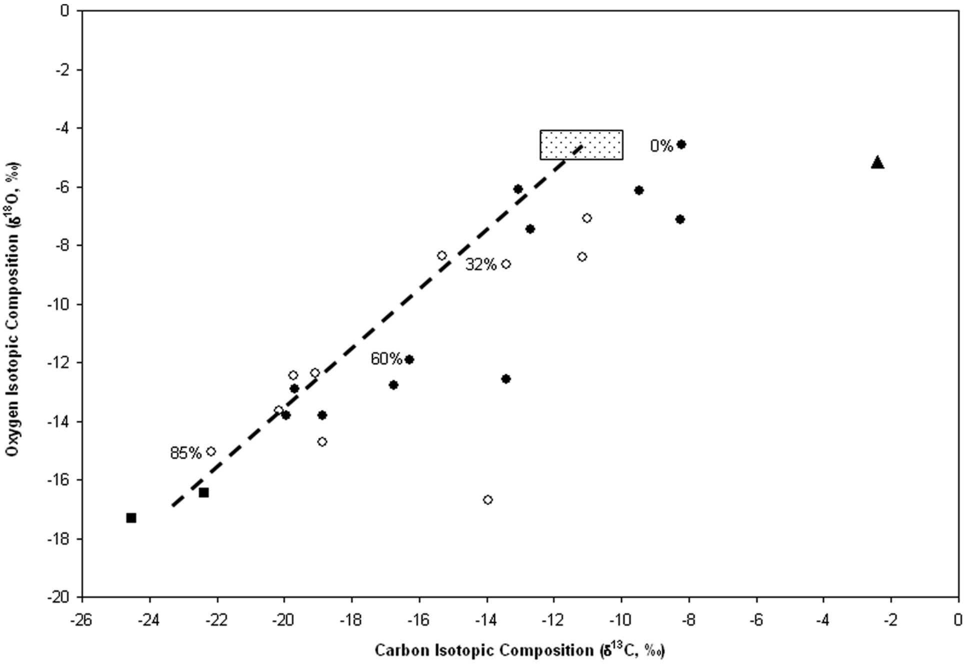

Figure 7: A plot of the carbon and oxygen isotopic values obtained from modern wood ash (closed squares), cave limestone bedrock (closed triangle), local speleothems (dotted rectangle), Amud Cave soft gray sediments (open circles), and Amud Cave concretions (closed circles), as in Figure 5. The dashed line indicates a mixing line between wood ash and geogenic calcite that derives from speleothems. Calculations of the percentage of ash in 4 samples are given as an example for interpreting the formation processes of these sediments. Note that the examples show that some concretions are almost entirely composed of ash and these are mostly prevalent in excavation areas B and C, while others are almost entirely composed of geogenic calcite and these are mostly prevalent in excavation area A. See text for discussion of these phenomena.

that these laminated features should be regarded as well-preserved *in situ* hearths and may serve for further spatial analyses. The few concretions from areas B and C, usually from sub-unit B2, which possess an un-oriented structure and are usually not flat-shaped, probably represent disturbed hearth material. Overall, it appears that the central part of the cave (i.e., excavation areas B and C) was used in antiquity for activities that centered on hearths, and this is especially evident in sub-unit B4. We suggest that future analysis of the lithic assemblage associated with these hearths may reveal the types of activities that were conducted around hearths (and see Ekshtain & Hovers, 2005). We note that the gray sediment surrounding these hearths is bioturbated and thus the association of lithics with specific hearths may not be straightforward. However, the effect of bioturbation is localized (e.g., bone fragments are not rounded due to transport), indicating that spatial analysis will be meaningful in at least some stratigraphic units.

We also note that several archaeological sediment samples are enriched in ^{13}C, appearing as outliers relative to the overall mixing line. We attribute this phenomenon to the presence of large amounts of microscopic bedrock particles in these samples, because the bedrock limestone is enriched in ^{13}C relative to the local speleothems (Figure 7). This hypothesis was verified through micromorphology.

CONCLUSIONS

The stable isotopes of oxygen and carbon show distinctive values indicative of wood ash that are significantly different from the isotopic values of geogenic calcite. It is thus possible to use this technique alone to determine the presence of wood ash in archaeological sediments. Moreover, this technique enables us to determine the degree of mixing between wood ash and geogenic calcite. When coupled with micromorphology, it also permits us to determine the degree of wood ash re-crystallization.

Based on our data, the sediments in Amud Cave invariably contain wood ash and may be generally divided spatially within the cave according to the amounts of ash and geogenic calcite contained in them. The sediments in excavation area A show a greater mixing of ash with geogenic calcite due to proximity to the cave wall. On the other hand, the sediments from the central part of the cave (areas B and C) generally show less mixing of ash with geogenic calcite. The highest amounts of ash were identified in flat concretions with laminated structure whose diameter is mostly larger than 30 cm, features that are especially evident in sub-unit B4. They are composed largely of re-crystallized micritic wood ash and were cemented by small amounts of geogenic calcite deriving from drip water. Except for burrowing activities (mostly by land snails and earth worms), these soft concretions are virtually undisturbed, and they can safely be interpreted as *in situ* well preserved hearths. Other concretions from excavation area B that are smaller, have un-oriented structure, and are not flat-shaped are interpreted as disturbed hearths.

The technique presented here may be useful for initial identification of calcite sources in karstic cave sites, and possibly also in open-air sites, where cemented sediments are prevalent. The method is relatively simple and inexpensive. Used in combination with micromorphology, mineralogy, and phytolith studies, this isotopic method enhances our understanding of the formation processes of cemented sediments and provides a secure starting point for hearth-related spatial studies. Furthermore, oxygen and carbon isotopic analyses can be used in other archaeological contexts to identify burning of calcitic remains originally formed in ambient temperatures (e.g., mollusk and crab shells). The technique can also establish quantitative parameters to the preservation of lime mortar/plaster.

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