

The phosphate mineralogy of et-Tabun cave, Mount Carmel, Israel

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SUMMARY. Phosphates introduced into the et-Tabun cave as a result of human habitation, mainly as bone material, were partly dissolved by slightly acid solutions (organic acids derived from human or other animal activity). From these solutions, dahllite precipitated when the solutions came into contact with calcite. In the more weathered parts of the section, where little or no calcite occurs, the phosphate minerals formed are montgomeryite and crandallite.

THE cave of et-Tabun ($32^{\circ} 40' N$, $34^{\circ} 35' E$., Israel grid 1470 E/2306 N) is situated at the base of the western slope of Mount Carmel at the point where Nahal Me'arot (Wadi of the caves) enters the coastal plain. This cave is one of the most important Palaeolithic sites in the Near East (Garrod and Bate, 1937). As a result of this human habitation, appreciable quantities of phosphates have been introduced into the cave, mainly in the form of bone material (phosphate was also introduced in other forms, e.g. excreta). Partial dissolution of this phosphate and its subsequent redeposition as calcium and Ca-Al phosphates has produced a geochemical sequence that is readily understood, and which can shed some new light on the controversial subject of the phosphate cycle in nature including the genesis of phosphorites.

Description of et-Tabun and stratigraphic framework

Goldberg (1973), in an unpublished doctoral dissertation, studied the sedimentology, stratigraphy, and palaeoclimatology of et-Tabun cave. The cave basically consists of three chambers, an inner chamber (with chimney), an outer chamber, and an outermost chamber, each defined by bedrock constrictions.

Garrod and Bate (1937) divided the deposits of Tabun into 7 units (A to G). Layer A has subsequently been completely removed. Goldberg (1973) divided the Tabun section into three major geological units. Table I (after Goldberg, 1973) summarizes the stratigraphy and compares Goldberg's and Garrod and Bate's divisions.

The sediments of *Unit I* consist mostly of red clay, very similar to terra rossa soils found today on the Carmel. Within these soft sediments, large limestone fragments (10 to 25 cm long) are found. Almost without exception, these fragments have a rind generally 1 to 3 cm thick consisting mainly of dahllite with alternating black layers of diffuse amorphous MnO_2 . Similar coatings, much thicker, usually a few cm, can be found on the bedrock in the outer chamber. Fig. 1 shows a section through such a

coating. The upper part of Unit I contains abundant, poorly preserved, but identifiable bone fragments.

Unit II, now restricted to the inner chamber, consists of thin bands of fired clay, ash, and charcoal-rich sediment alternating in colour from white to pink to dark reddish brown to black. The sediments are for the most part clayey silts with about

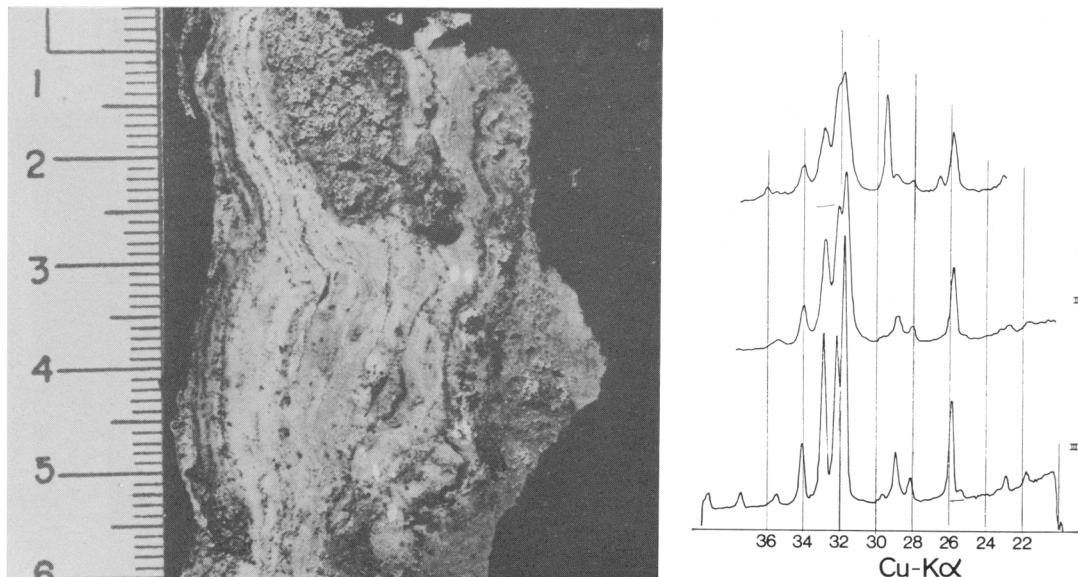
TABLE I. *General stratigraphy of the Tabun sediments (after Goldberg, 1973)*

Stratigraphy		Sediment type	Approx. average thickness
Goldberg (1973)	Garrod and Bate (1937)		
I	A—mixed (now removed)	Mixed red clay, limestone fragments	0·8 m
	B—Up. Levalloiso-Mousterian	Red clay with large limestone fragments and local bone breccias	3·0 m
II	C—Low. Levalloiso-Mousterian	Thinly bedded red, pink, white and black sediment, including ash and charcoal	
III	D—Low. Levalloiso-Mousterian	Silty sand, mostly pale yellowish brown, but some darker layers; numerous vugs, lenses and stringers of collophane and calcite	2·4 m
	E—Up. Acheul. (Micoq.)		
	F—Up. Acheulean	Similar to above but more sandy and better stratification; numerous cemented layers	2·1 m
	G—Tayacian	Clayey to silty sand with several dark-brown layers	1·5 m

50 to 65 % silt. Sand content averages 10 %. Here as in Unit I numerous limestone blocks with rinds of dahllite and MnO_2 occur throughout. Bones are relatively rare.

Unit III constitutes well over half the estimated total volume of the original sedimentary fill in Tabun. The sediments vary from silty sands in the lower part to sandy silts in the upper part. In marked contrast to Units I and II limestone fragments are extremely rare and confined only to certain portions especially near the rock walls. An interesting phenomenon is the occurrence of well-crystallized hydroxy-apatite (almost devoid of carbonate) in many of the vugs and veins of the sediments. It also occurs finely disseminated throughout much of the sediments, commonly cementing them to the point where hammer and chisel are necessary to excavate them. Related to this occurrence is the almost complete absence of bone in Unit III. Green patches that occur in clayey sediments were found to contain crandallite and montgomeryite. Montgomeryite was also found finely disseminated throughout the Unit III sediments (first identified by H. Paquet from diffraction patterns).

Thin bands of white flecks, about 3 mm long and 1 mm thick occur in several samples mainly in Layer E (Garrod and Bate) and are very probably what they called millipedes. Close examination of specimens under the microscope reveals a micro-porous structure. X-ray diffraction gives a spectrum of quartz.



FIGS. 1 and 2: FIG. 1 (left). Photograph of a section through a wall coating. Note alternating bands. FIG. 2 (right). Diffraction patterns of apatites from Tabun and Kebara. I: Rind from Kebara (on dolomite). II: Rind from Tabun (on calcite). III: Hydroxyapatite from vug, Tabun.

Chemistry and mineralogy—methods and results

Two types of phosphorus analyses were performed: analysis of principally aluminium phosphates and analysis of total P.

The *aluminium phosphate* analyses were done for all Tabun samples at the Soil Science Laboratory of Michigan State University. Their method (a modification of Bray and Kurtz, 1945) is a dilute acid fluoride extraction, which primarily measures the phosphates more or less available to plants, i.e. aluminium and iron phosphates. In Tabun, however, no iron phosphates were found. This method does not measure (or only to a very limited extent) the calcium phosphates (apatites). The results are given in Table II.

The most noticeable aspect of these Al-P results is the distinct change from generally high P values in Unit III (usually more than 100 ppm) to relatively low ones in Units I and II (usually less than 100 ppm). These low values may simply represent some P dissolved from calcium phosphates. The higher values in Unit III agree with the X-ray analyses, which show the appearance of Al-phosphate minerals only below the contact between Units II and III. The sudden change in P at this contact coincides stratigraphically not only with changes in heavy minerals (Goldberg, 1973) but also

with the disappearance of vug-type collophane and simultaneous appearance of bone and limestone fragments in Units I and II. All of these circumstances lead to the conclusion that the Unit III sediments have been subjected to substantially more chemical alteration than those of I and II.

Analysis of *total phosphorus* was done by wet-chemical procedures on 26 samples from the main excavation at three different laboratories (Table II); it is immediately apparent that the total P results are quite variable and show no correlation with the Al-P results. Similarly, there is no break in the total P values between Units II and III as there was in the Al-P results. In fact, the mean percentage of total P in Units I and II combined equals 2.60% and is almost identical to the mean percentage of

TABLE II. *Phosphorus analyses*

Sample	Total P	Al-P ppm	Sample	Total P	Al-P ppm	Sample	Total P	Al-P ppm	Sample	Total P	Al-P ppm
<i>Unit I</i>			<i>Unit III</i>			<i>Unit III (contd.)</i>			<i>Unit III (contd.)</i>		
1-6	1.10%*	17.0	2-1	3.87%‡	282.6	14-17	1.23%‡	157.5	16-8	1.06%†	151.5
<i>Unit II</i>			2-11	1.64*	402.0	14-19	2.82†	315.0	16-9	2.51†	199.5
3-1	1.23†	15.3	2-14	4.80‡	315.0	14-25	1.50‡	234.0	16-13	6.03†	329.5
4-4	6.03†	114.0	2-18	2.33‡	475.0	16-1	1.32†	4.0	16-15	1.58‡	311.0
5-15	3.08‡	87.0	14-2	2.11‡	8.5	16-2	0.97‡	—	16-19	2.42‡	230.0
5-17	2.68†	30.5	14-7	1.58‡	16.0	16-4	2.51‡	398.5	16-26	0.57‡	58.5
5-18	1.58†	67.0	14-11	8.54†	282.0	16-7	3.04‡	160.0			

Analysts: Al-P determinations, Michigan State University Soil Science Laboratory. Total P determinations: * Dr. B. G. Ellis, Michigan State University; † Laboratory of Geology, University of Strasbourg; ‡ Mrs. Irene Gal, Geochemical Laboratory, Geological Survey of Israel.

total P for Unit III which is 2.62%. Since the amount of P in Al-P constitutes such a small part of total P in the sediments it seems probable that the amount of total P represents the amount of dahllite and hydroxy-apatite in the samples. The great variability in the total P results is indicative of the very localized nature of dahllite in Units I and II (bones and limestone rinds) and hydroxy-apatite in Unit III (vug-filling and disseminated).

Phosphate minerals

Units I and II. Dahllite is the main phosphate mineral occurring either as rinds surrounding limestone blocks or in the form of bone material. There is one doubtful occurrence of montgomeryite. Dahllite was found to contain 2.4% CO₂; the analysis was carried out after dissolving the calcite in Silverman's solution (1969).

Unit III. Hydroxy-apatite (almost devoid of CO₂), much better crystallized than dahllite, occurs in vugs and veins. Near the bedrock walls some bones can be found generally well preserved; elsewhere in the rest of Unit III bones are completely absent. Montgomeryite is relatively abundant and is usually in a finely disseminated form. Crandallite occurs too and can be recognized in the outcrop by its typical green colour.

Discussion

The formation of dahllite in the rinds in Units I and II seems to be a relatively straightforward process: bone material was dissolved by slightly acid solutions (organic acids derived from human or animal activity, e.g. uric acid, bat guano, plant decay, humic acid). When these phosphatic solutions came into contact with limestone, dahllite precipitated. As a matter of fact we have here a natural laboratory where the so-called 'replacement' of calcite by apatite is realized. However, we can see that this process is not plausible as a possible genesis of phosphorites (Ames, 1959; Degens, 1965), since the apatite formed in this manner has either the original carbonate texture or the laminated 'travertine' texture (fig. 1) and never has one of the typical phosphorite textures (Cayeux, 1955).

In any case this process seems to be widespread in prehistoric caves in Israel and has been found at Qafzeh, near Nazareth, and at Oumm Qatafa, near Bethlehem (Bentor, in Neuville, 1951). A similar interesting occurrence has been found very near et-Tabun, at the Kebara cave where a dahllite rind was found surrounding a dolomite block. Although this dahllite is very poorly crystallized it nevertheless shows that we cannot automatically transfer our knowledge from the laboratory to the field (Simpson, 1966).

The genesis of the calcium aluminium phosphates in Unit III (crandallite and montgomeryite) is probably very similar to their formation in soils, as a reaction between aluminium derived from the clays and the phosphate solutions (Coleman, 1944; Low and Black, 1947; Ellis and Truog, 1955; and Hemwall, 1957).

The genesis of the well-crystallized hydroxy-apatite in the vugs and veins of Unit III is more of a problem, since it might have been formed either by a reduction of acidity (in the phosphate solutions) due to a drop in the partial pressure of CO₂, or very slowly, after the precipitation of montgomeryite. The second possibility is strongly supported by Lindsay and Moreno (1960) who studied phosphate phase equilibria in soils. Obviously, both possibilities may occur side by side since they are not exclusive. However, in our opinion, since we are dealing with a leaching environment, leaching the Si from the clays and Ca from the carbonates, the first possibility seems more plausible. It is true that montgomeryite is metastable but it goes to crandallite (less Ca) and eventually both might go to variscite (no Ca) if the leaching process continued.

As a further confirmation we may point out that while montgomeryite and crandallite occur together, they do not occur in the same sample with dahllite, which would be expected in the event of the second possibility.

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REFERENCES

- AMES (L. L., Jr.), 1959. *Econ. Geol.* **54**, 829-41.
BRAY (R. H.) and KURTZ (L. T.), 1945. *Soil Sci.* **59**, 39-45.

- CAYEUX (L.), 1955. *Études des gites minéraux de France. Les phosphates de chaux sédimentaires de France (France Métropolitaine et d'Outre Mer)* Imprimerie Nationale, Paris.
- COLEMAN (P.), 1944. *Soil Sci.* **58**, 71-7.
- DEGENS (E. T.), 1965. *Geochemistry of Sediments*. Prentice Hall, N.J.
- ELLIS (R., Jr.) and TRUOG (E.), 1955. *Proc. Soil Sci. Soc. Amer.* **19**, 451-4.
- GARROD (D. A. E.) and BATE (D.), 1937. *The Stone Age of Mount Carmel*, **1**. Clarendon Press, Oxford.
- GOLDBERG (P.), 1973. *Sedimentology, Stratigraphy and Paleoclimatology of et-Tabun Cave, Israel*. Unpublished Ph.D. thesis (Geology), University of Michigan.
- HEMWALL (J. B.), 1957. *Soil Sci.* **83**, 101-8.
- LINDSAY (W. L.) and MORENO (E. C.), 1960. *Proc. Soil Sci. Soc. Amer.* **34**, 177-82.
- LOW (P. F.) and BLACK (C. A.), 1947. *Ibid.* **24**, 177-82.
- NEUVILLE (R.), 1951. Le Paléolithique et le Mésolithique du Désert de Judée. *Archives de l'Institut de Paléontologie Humaine, Mém.* **24**.
- SILVERMAN (S. R.), FUYAT (R. K.), and WEISER (J. D.), 1952. *Amer. Min.* **37**, 211-22.
- SIMPSON (D. R.), 1966. *Ibid.* **51**, 205-9.

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