

Geochemistry of Egyptian Francolites

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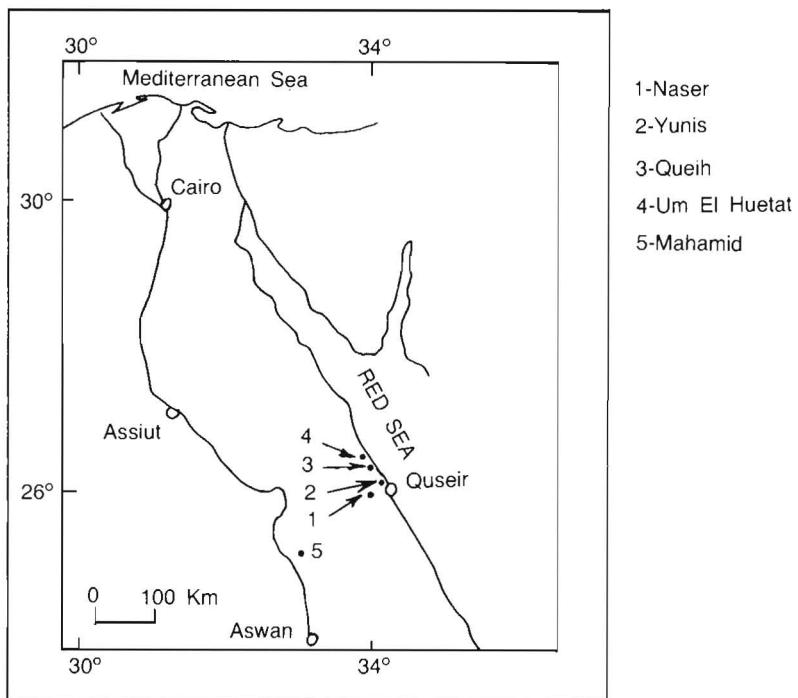
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ABSTRACT. The Cretaceous Duwi (phosphate) Formation of the Nile Valley (Mahamid area) and Red Sea (Nasser, Yunis, Queih and Um El Huetat areas) were studied. Ca, P, F, Na and Mg were determined quantitatively using the electron microprobe analyzer. Francolite is the principal phosphate mineral in the studied samples. It exhibits different isomorphous substitutions.

Red Sea francolites show relatively high cation substitutions. About 5% of the Ca ions can be replaced by Na and Mg. Maximum cation substitutions should take the form $\text{Ca}_{0.54} \text{Mg}_{0.10} \text{Na}_{0.36}$. The Nile valley francolites show relatively high anion substitutions. About 10% of the (PO_4) group is replaced by the (CO_3) group and/or (CO_3+F) group. Maximum anion substitutions should take the form $\text{Ca}_{0.54} \text{Mg}_{0.10} \text{Na}_{0.36}$. The Nile valley francolites show relatively high anion substitutions. About 10% of the (PO_4) group is replaced by the (CO_3) group and/or (CO_3+F) group. Maximum anion substitutions should take the form $(\text{PO}_4)_{0.39} (\text{CO}_3\text{F})_{0.61}$. Such variable substitutions are attributable to the effect of formational and secondary alteration environments.

Cretaceous sedimentary marine phosphorites of Egypt are confined to the Duwi Formation. The mineralogy of the Egyptian phosphorites has been discussed by El Tablawi (1966), Ghanem *et al.* (1971), Abdallah *et al.* (1972), El Kammar (1974), Phillobbos (1976), Abdel Gawad (1980), Ahmed (1983), Germann *et al.* (1984) and Soliman *et al.* (1986). Their main conclusion was that francolite is the principal phosphate mineral of Egyptian phosphorites.

The present work aims to study the mineralogy and the substitutional chemistry of the Egyptian francolites. Twenty seven representative phosphate samples were taken from Mahamid, Nasser, Yunis, Queih and Um El Huetat areas (Fig. 1). The samples were examined using X-ray diffraction, Infra-red and



electron microprobe analysis. The analyses were carried out at the technical University of Berlin, Western Germany.

Mineralogy

X-ray diffraction studies were undertaken to determine the mineralogical nature of the phosphate mineral phase. Phosphate samples were investigated using a Philips X-ray diffractometer with nickel filter and Cu K_α-radiation. X-ray data of the studied samples were found to match the results of carbonate - fluorapatite of Hoffman and Tridlicka (1967). The present samples show broad X-ray peaks which indicate a low degree of crystallinity. The peak-pair method of Gulbrandsen (1970) was used to determine the structural CO₂ content of the carbonate - fluorapatite (francolites). This method is based on the 2θ separation of the (004) and (410) apatite reflections (Fig. 2). Average weight percentages of the structural CO₂ were

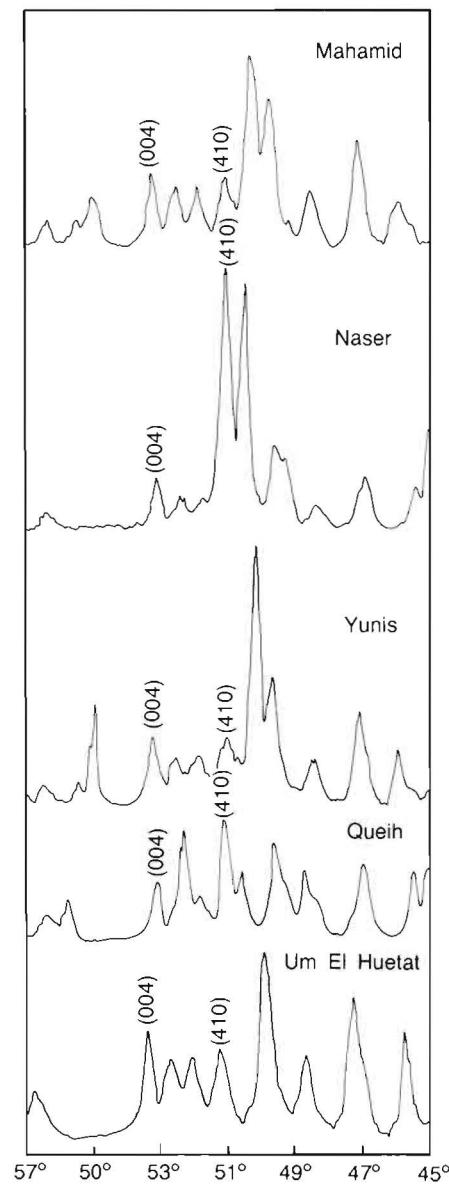


Fig. 2. X-ray diffractograms for phospharite samples.

found to be 2.2% for Mahamid area, 1.6% for Nasser area, 1.8% for Yunis area, 1.4% for Queih area and 1.8% for Um El Huetat area. The observed difference in the X-ray peaks of the apatite may be the result of its relative concentration and/or degree of crystallinity. Following the calculations carried out by McClellan and Lehr (1969), the a_0 - cell dimensions of the studied francolites are found to range between 9.3527 and 9.3610 \AA . According to Altschülar *et al.* (1952) these values belong to the carbonate - fluorapatite phase.

Infra-red spectrometry was used to study the phosphate samples using Perkin - Elmer apparatus with KBr in the reference cell. The spectra were recorded over the range 4000 to 2000 cm^{-1} (Fig. 3). The main peaks due to PO_4^{3-} (v_3 and v_4 mode peaks) are located at 1040 and $\approx 600 \text{ cm}^{-1}$ respectively and CO_3^{2-} (v_3 and V_2 mode peaks) are located at ≈ 1400 and 800 cm^{-1} respectively. According to Klee (1970) the resolution of the vibration bands reflects a composition of carbonate - fluorapatite containing OH groups. The CO_3^{2-} peaks appear as doublets. According to Adler and Kerr (1963) this indicates that the CO_3^{2-} groups occupy two distinct types of anion lattice site. The study reveals that the v_3 vibrational mode of the PO_4^{3-} groups is the most intense peak in the IR spectra and the doublet v_4 vibrational mode is weak. This agrees with the work of Pacey (1985). The magnitude of splitting of the doublet v_4 mode suggests a moderate degree of crystallinity (Termine and Ponser 1966). Comparing the IR spectra of the phosphorites revealed that the C-O/P-O ratios used by Lehr *et al.* (1967) are not similar in the different localities (Fig. 4). This is due to the different degrees of CO_3^{2-} substitutions. Substitution of PO_4^{3-} by CO_3^{2-} in the studied francolites led to a charge imbalance within the crystal lattice of the francolite.

Francolite Chemistry

Bone fragments, pelletal and intraclastic collophane grains were analyzed for Na_2O , F' , MgO , P_2O_5 and CaO (Tables 1, 2 and 3). A cambebam micro scanning electron X-ray microprobe analyzer was used. K_{α} lines were measured at 15 KV with a total beam current of 0.5×10^{-6} . To avoid the technical defects (*i.e.*, pitting or polishing defects) the measurements were carried out on homogeneous materials.

The average NaO content varies between 1.09 and 0.34%. The highest average value was recorded from the bone fragments of Um El Huetat area. The intraclastic collophane grains of Queih area show the lowest concentration of Na_2O (0.34%). Generally, the bone fragments and pelletal collophane grains have a higher concentration of $\text{Na}_2\text{O}\%$ than that of the intraclastic collophane grains (Fig. 5). The amount of Na_2O in marine apatite, as recorded by McClellan and Lehr (1969), reaches about 1.6% Na_2O , but is generally less than 1%. Using the

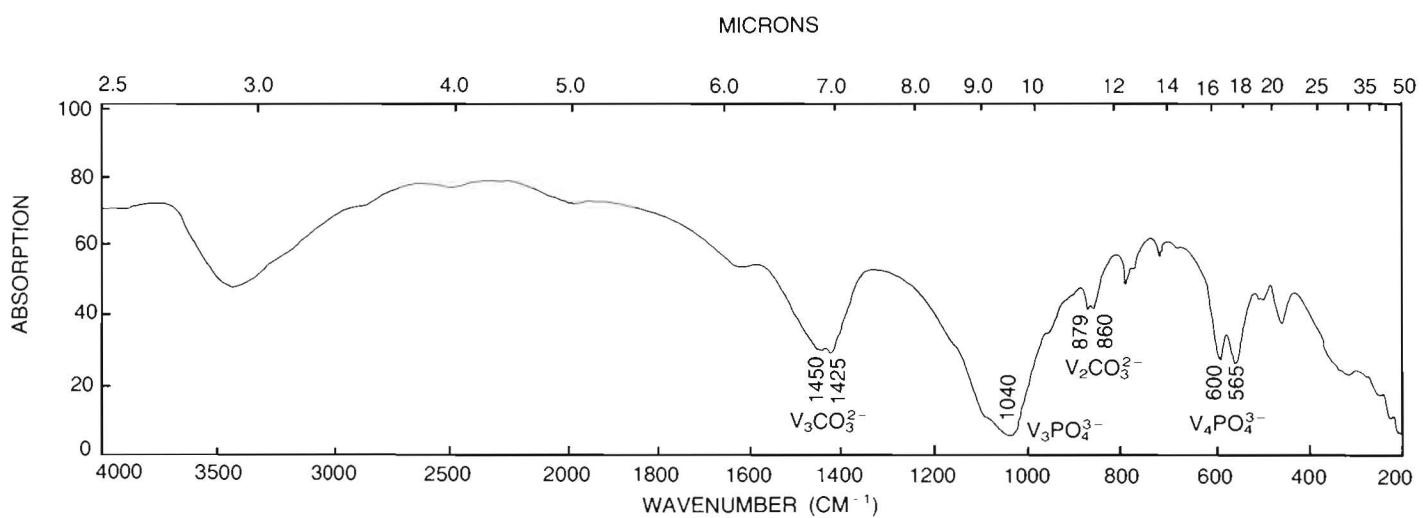


Fig. 3. Infra-red absorption spectrum of phosphorites

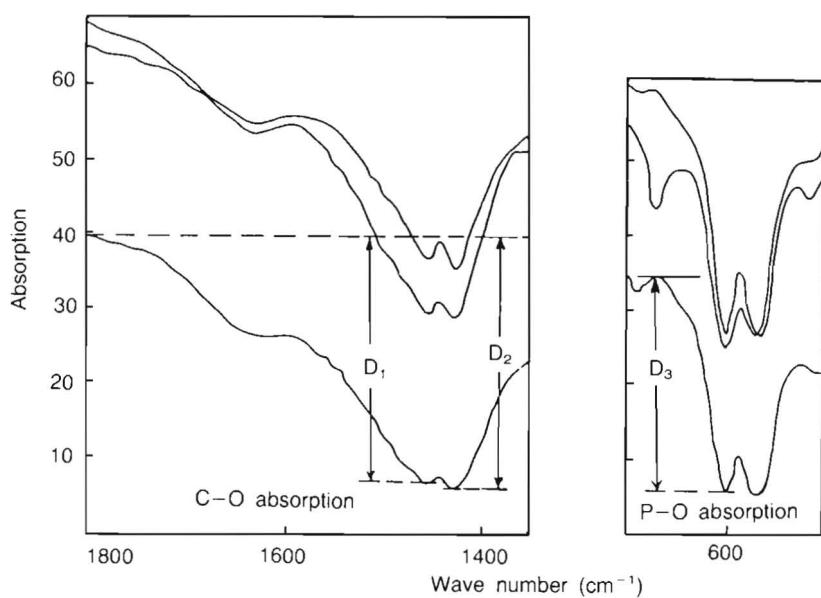


Fig. 4. Variation of intensities of C–O and P–O absorptions

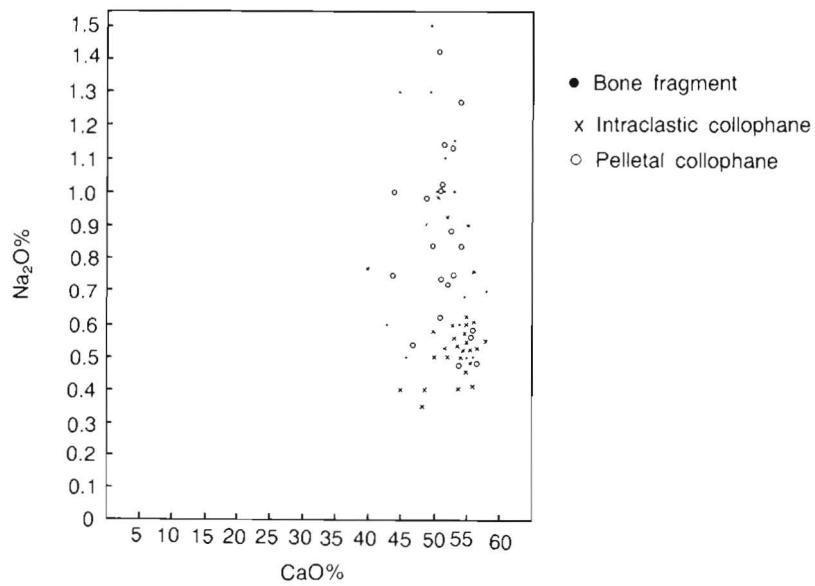


Fig. 5 Relationship between CaO and NaO in the apatite crystallites

$\text{Na}_2\text{O}\%$, McArthur (1978) differentiates between the highly substituted francolites ($\approx 1.6 \text{ Na}_2\text{O}\%$) and poorly substituted francolites ($\approx 0.5 \text{ Na}_2\text{O}\%$).

The average MgO content ranges between 0.37 and 0.10%. The maximum value of MgO content was observed from the bone fragments of Um El Huemat area, whereas the minimum value was encountered in the intraclastic collophane grains of Mahamid and Queih areas. MgO concentrations in bone fragments, pelletal and intraclastic collophane grains are illustrated in Fig. 6.

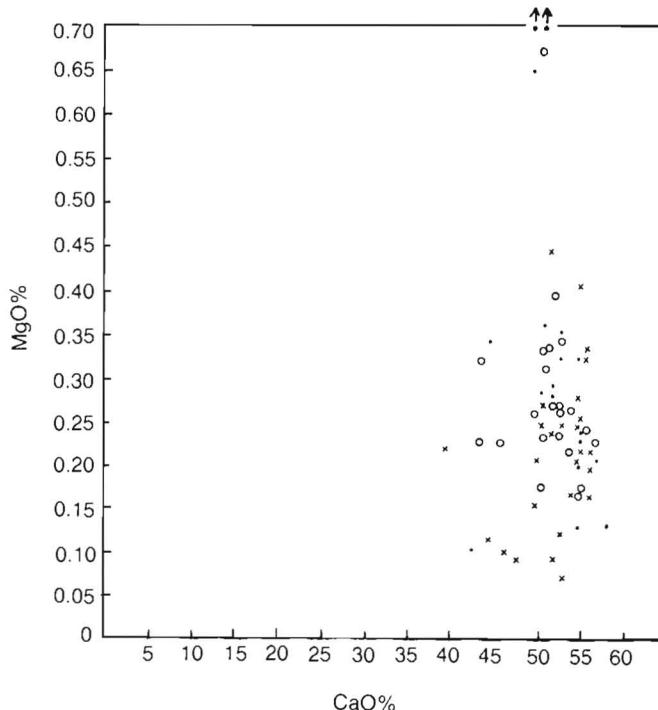


Fig. 6. Relationship between CaO and MgO in the apatite crystallites

The high average concentration of F' (5.02%) was recorded from the intraclastic collophane grains of Mahamid area, whereas the minimum value (1.35%) was recorded from the intraclastic collophane grains of the Queih area. The francolite model of McClellan and Lehr (1969) predicts that the maximum fluorine substitution is 3.78 mol/formula weight. Intraclastic collophane grains of

Mahamid area show a maximum fluorine substitution (3.2 mol/formula weight). McClellan (1980) reported that the mineral francolite has a_o -values smaller than 9.370 °A and fluorine contents of 3.5-4% F. According to McClellan (1980) carbonate apatites with other compositions may not actually be francolites.

The maximum average concentration of P_2O_5 (35.46%) was recorded from the pelletal collophane grains, while the minimum value (29.49%) was obtained from the intraclastic collophane grains of Queih area. The F/P_2O_5 ratios for the samples vary between 0.20 and 0.04. Mahamid, Yunis and Um El Huetat areas have a relatively higher F/P_2O_5 ratios than Nasser and Queih areas. McClellan (1980) reported that F/P_2O_5 ratio increases from 0.089 for fluorapatite to a maximum of about 0.148 in the highly substituted francolites.

The CaO concentration varies between 40.57 and 58.44%. The anomalous low value (40.57%) was observed from the intraclastic collophane grains, of Um El Huetat area. The maximum value was recorded from the bone fragment of Um El Huetat area.

Discussion and Conclusions

Phosphate minerals of the studied areas (Nile Valley and Red Sea) are characteristically carbonate-fluorapatite (francolite) with a tendency to be poorer in carbonate content. The Red Sea francolites show relatively high cation substitutions. On the other hand, the Nile Valley francolites display relatively high anion substitution (Fig. 7 and Table 4). McClellan (1980) reported that about 5% of Ca ions in the Red Sea francolites and those of Um El Huetat area, in particular, are replaced by Na and Mg. This may indicate a formational environment of high salinity (Russell and Trueman 1971). Such enrichment of Mg and Na in the francolites of Um El Huetat relative to the adjacent areas (Nasser, Yunis and Queih) may be connected with the changes in the chemical composition of sea water due to the position of the sedimentation site relatively to the land/or open sea (c.f. Axelrod and Röhrlich 1982). The Nile Valley francolites show that about 10% of (PO_4) group is replaced by (CO_3) and/or (CO_3+F) group. The variable substitutional (CO_3) contents of the studied francolites may be attributed to the temperature of its formation (Gulbrandsen 1970) or to pH control (McArthur 1985).

Based on the substitutional chemistry of the francolites induced by the formational and secondary alteration environments, the studied samples can be grouped into:

1. High mature francolites (Mahamid area).
2. Mature francolites (Um El Heutat and Yunis areas).
3. Altered francolites (Nasser and Queih areas).

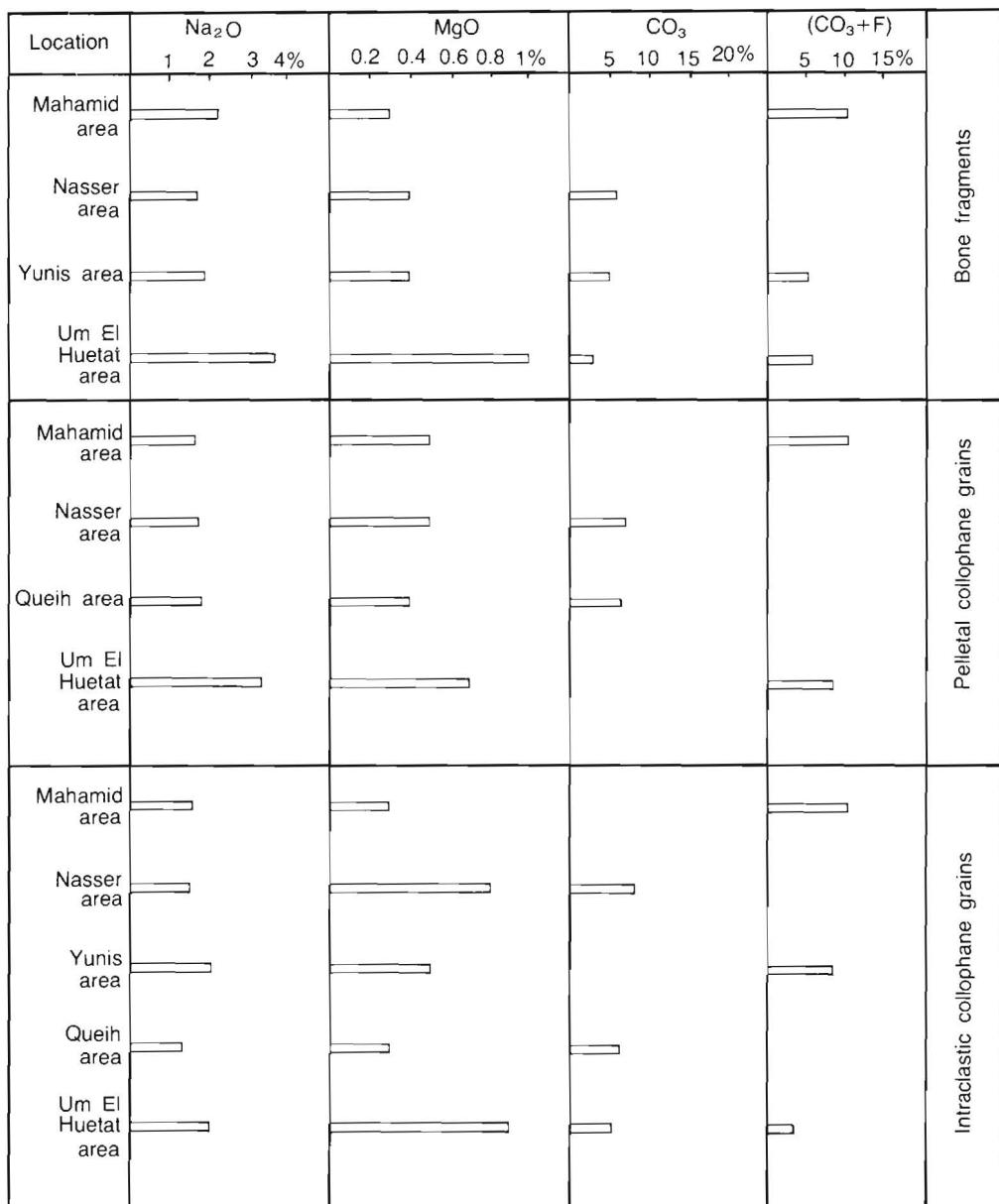


Fig. 7. Percentage of cation and anion substitutions of the studied francolites (expressed as moles/formula weight)

The characteristic features of each mineralogic environment are given in Table 5. Francolites of Nasser and Queih areas have a lower amount of F' and CO₂ than that of other areas. This is due to alteration of francolites towards fluorapatite compositions as a result of the effect of diagenesis and/or chemical weathering. Mathews and Nathan (1977) pointed out that the possible ways of achieving such deficiency in F' and CO₂ are the result of the relatively high energy conditions which are required to expel CO₂ from the apatite lattice. The decarbonation being accompanied by partial loss of F'.

Petrographic examination of the studied phosphorites demonstrates a progressive alteration of phosphatic components (Fig. 8) which are due to the effect of diagenesis and/or chemical weathering. Chemical weathering imparts brownish alteration hues to the surface exposures of phosphorites (El Kammar and Basta 1982) and may be related to Tertiary and Quaternary fluvial periods in North Africa (Valeton 1983).

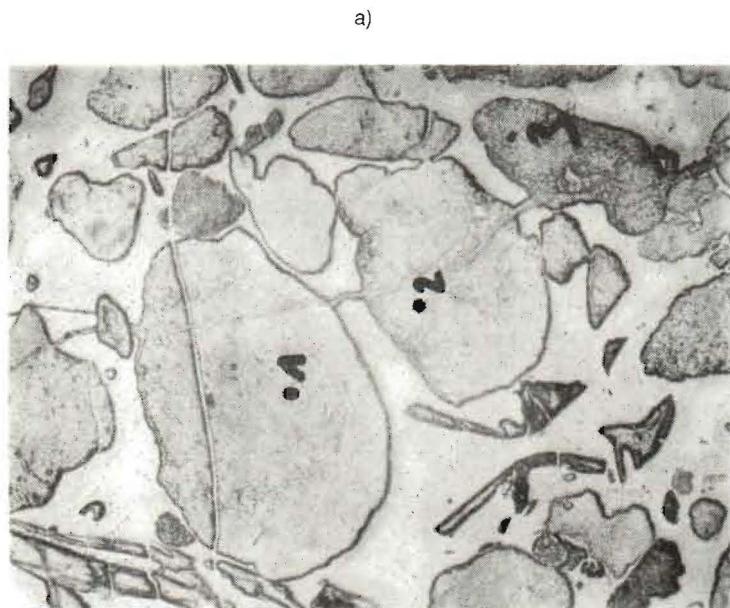
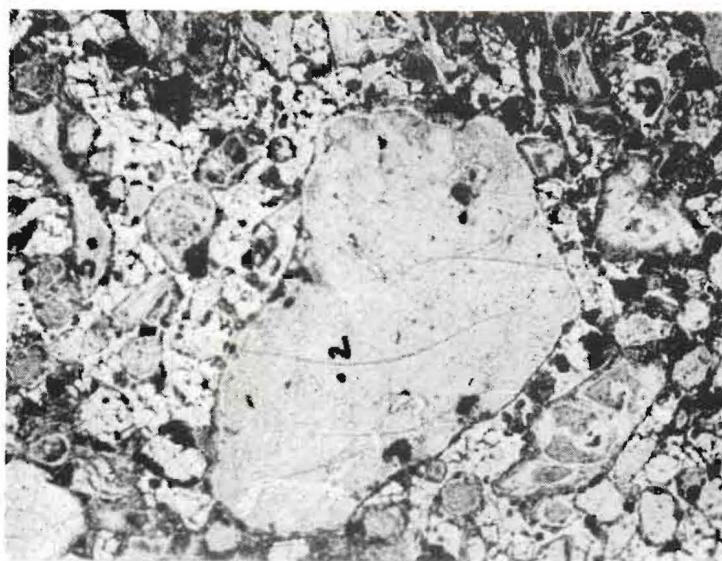


Fig. 8. Effect of diagenesis and/or chemical weathering on the collophane grains:
a) High mature b) Mature and c) Altered.

b)



c)

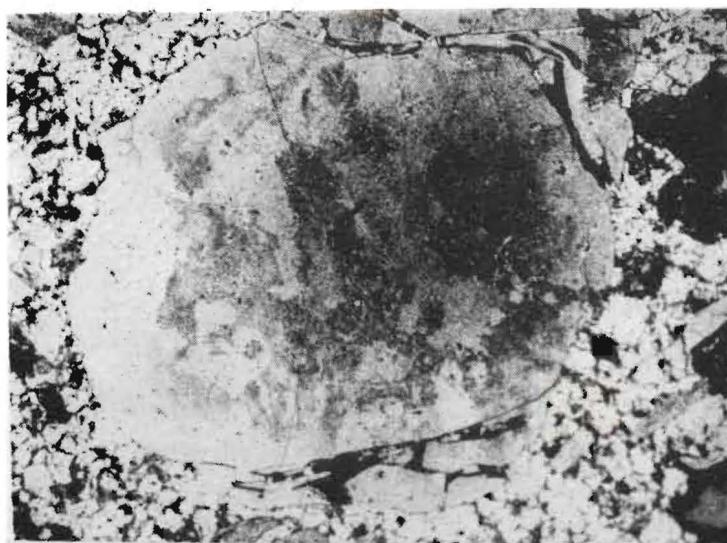


Table 1. Microprobe analyses of bone fragments

Sample	Na ₂ O	F'	P ₂ O ₅	MgO	CaO	$\frac{\text{CaO}}{\text{P}_2\text{O}_5}$	$\frac{\text{F}}{\text{P}_2\text{O}_5}$	Location
1	0.50	5.92	29.94	0.18	57.03	1.90	0.20	Mahamid area Nile Valley
2	0.64	4.60	31.90	0.08	43.64	1.37	0.14	
3	0.71	4.40	36.30	0.14	58.54	1.45	0.12	
Av	0.62	4.97	32.71	0.13	51.07	1.57	0.15	
4	0.50	3.89	35.99	0.13	55.48	1.54	0.11	Nasser area
5	0.54	1.60	34.65	0.21	55.20	1.59	0.05	
Av	0.52	2.75	35.32	0.17	55.34	1.57	0.08	
6	0.58	3.92	35.08	0.18	54.66	1.56	0.11	Yunis area
7	1.33	3.86	34.00	0.66	49.84	1.47	0.11	REDSEA Um El Huetat Area
8	1.47	3.63	34.17	0.84	49.76	1.46	0.11	
9	1.00	4.80	34.87	0.30	53.43	1.53	0.14	
10	1.26	3.44	28.72	0.32	45.06	1.57	0.12	
11	1.00	3.33	34.61	0.26	52.70	1.52	0.10	
12	1.00	3.46	36.31	0.26	51.55	1.42	0.10	
13	1.15	4.60	34.35	0.33	53.31	1.55	0.13	
14	0.67	4.28	31.84	0.22	54.99	1.73	0.13	
15	1.05	2.45	28.03	0.34	51.53	1.84	0.09	
16	0.92	2.74	35.91	0.30	55.37	1.54	0.10	
17	0.12	2.59	34.57	0.27	52.73	1.53	0.07	
Av	1.09	3.65	33.40	0.37	51.84	1.56	0.77	

Table 2. Microprobe analyses of pelletal collophane grains

Sample	Na ₂ O	F'	P ₂ O ₅	MgO	CaO	CaO	F	Location
						P ₂ O ₅	P ₂ O ₅	
1	0.48	4.25	32.00	0.20	54.55	1.70	0.13	Mahamid area Valley Nile
2	0.54	4.75	31.22	0.21	56.64	1.53	0.15	
Av	0.51	4.50	31.61	0.21	55.60	1.62	0.14	
3	0.49	2.12	35.52	0.21	56.10	1.58	0.06	Nasser area
4	0.54	1.56	34.92	0.23	54.91	1.57	0.04	
Av	0.52	1.84	35.22	0.22	55.51	1.58	0.05	
5	0.58	1.38	35.16	0.15	55.76	1.59	0.04	Queih area
6	0.56	1.55	35.76	0.15	55.51	1.55	0.04	
Av	0.57	1.47	35.46	0.15	55.64	1.57	0.04	
7	1.26	3.76	32.91	0.37	52.54	1.60	0.11	R E D S E A Um El Huata Area
8	0.74	2.46	32.13	0.31	51.39	1.60	0.08	
9	0.62	3.67	30.91	0.16	51.56	1.67	0.12	
10	1.14	4.10	33.90	0.31	52.66	1.55	0.12	
11	0.84	4.64	37.57	0.24	54.00	1.44	0.12	
12	0.98	5.00	34.87	0.25	53.90	1.55	0.14	
13	1.41	3.62	34.22	0.68	51.76	1.51	0.11	
14	0.82	4.63	35.15	0.22	52.28	1.49	0.13	
15	0.75	3.67	31.54	0.21	44.13	1.40	0.12	
16	1.02	3.58	28.10	0.30	44.08	1.57	0.13	
17	0.13	3.59	34.69	0.32	53.22	1.53	0.10	
18	0.75	3.63	37.50	0.25	52.97	1.41	0.10	
19	0.84	3.11	30.61	0.24	49.96	1.63	0.10	
20	0.89	2.47	27.44	0.24	53.69	1.96	0.09	
21	1.02	1.61	24.50	0.29	51.36	2.10	0.07	
22	1.04	2.32	32.10	0.22	51.35	1.60	0.07	
Av	0.95	3.49	32.38	0.29	51.30	1.60	0.11	

Table 3. Microprobe analyses of intraclastic collophane grains

Sample	Na ₂ O	F'	P ₂ O ₅	MgO	CaO	CaO P ₂ O ₅	F P ₂ O ₅	Location
1	0.41	4.30	23.95	0.08	48.04	2.01	0.18	Mahamid area Nile Valley
2	0.45	5.12	27.91	0.15	53.96	1.93	0.18	
3	0.51	5.87	30.25	0.08	52.51	1.74	0.19	
4	0.40	5.01	37.56	0.06	53.77	1.43	0.13	
5	0.61	4.82	36.65	0.11	53.14	1.45	0.13	
Av	0.48	5.02	31.26	0.10	52.28	1.71	0.16	
6	0.48	1.74	32.97	0.24	55.53	1.68	0.05	
7	0.49	2.21	31.83	0.30	55.31	1.74	0.07	
8	0.46	1.36	31.02	0.38	54.94	1.77	0.04	
Av	0.48	1.77	31.94	0.31	55.26	1.73	0.05	
9	0.62	4.31	35.30	0.20	54.94	1.56	0.12	Yunis area
10	0.62	4.48	34.86	0.23	55.29	1.59	0.12	
Av	0.62	4.40	35.08	0.22	55.12	1.58	0.12	
11	0.35	1.22	27.46	0.09	47.31	1.61	0.04	Queih area
12	0.32	1.48	31.52	0.11	45.57	1.29	0.05	
Av	0.34	1.35	29.49	0.10	46.44	1.45	0.05	
13	0.78	2.52	24.44	0.20	40.57	1.66	0.10	RED SEA Um El Huetat Area
14	0.40	2.64	27.68	0.10	45.44	1.64	0.10	
15	0.54	4.15	35.05	0.19	55.39	1.58	0.12	
16	0.41	4.13	34.29	0.15	56.17	1.64	0.12	
17	0.46	3.94	32.25	0.20	55.28	1.71	0.12	
18	0.62	4.55	35.42	0.31	55.88	1.58	0.13	
19	0.55	3.60	32.44	0.42	52.75	1.63	0.11	
20	0.53	4.13	31.82	2.33	52.47	1.65	0.13	
21	0.56	3.91	33.49	0.23	53.41	1.59	0.01	
22	0.54	3.25	28.09	0.22	55.72	1.98	0.12	
23	0.54	2.55	33.71	0.18	56.48	1.68	0.08	
24	0.76	1.88	24.30	0.23	51.04	2.10	0.08	
25	0.92	2.82	31.54	0.27	52.39	1.66	0.09	
26	0.58	2.68	32.72	0.19	50.72	1.55	0.08	
27	0.50	3.48	32.18	0.14	50.09	1.56	0.11	
Av	0.58	3.35	31.29	0.36	52.25	1.90	0.10	

Table 4. Average weight percentages and structural formulae of bone fragments, pelletal collophane grains and intraclastic collophane grains

Location	CaO	MgO	Na ₂ O	P ₂ O ₅	CO ₂ *	F	Structural formula		F anions	Total Charges	Unit cell a(A°)
							10 cations	6 anion groups			
A. Bone fragments											
Mahamid area	51.07	0.13	0.62	32.71	2.2	4.97	Ca _{9.75} Mg _{0.03} Na _{0.22}	(PO ₄) _{5.41} (CO ₃ F) _{0.6}	F _{2.4}	+19.8(-20.5)	9.3527
Nasser area	55.34	0.17	0.52	35.32	1.6	2.75	Ca _{9.79} Mg _{0.04} Na _{0.17}	(PO ₄) _{5.59} (CO ₃) _{0.4}	F _{1.6}	+19.8(-19.2)	9.3537-9.3601
Yunis area	54.66	0.18	0.58	35.08	2.2	3.92	Ca _{9.77} Mg _{0.04} Na _{0.19}	(PO ₄) _{5.44} (CO ₃) _{0.3} (CO ₃ F) _{0.3}	F ₂	+19.8(-19.7)	9.3527-9.3537
Um El Huetat area	51.84	0.37	1.09	33.40	1.8	3.65	Ca _{9.54} Mg _{0.10} Na _{0.36}	(PO ₄) _{5.52} (CO ₃) _{0.2} (CO ₃ F) _{0.3}	F ₂	+19.6(-19.8)	9.3527-9.3610
B. Pelletal collophane grains											
Mahamid area	55.60	0.21	0.51	31.61	2.2	4.50	Ca _{9.79} Mg _{0.05} Na _{0.16}	(PO ₄) _{5.39} (CO ₃ F) _{0.6}	F _{2.3}	+19.8(-20.2)	9.3527
Nasser area	55.51	0.22	0.52	35.22	1.6	1.84	Ca _{9.79} Mg _{0.05} Na _{0.17}	(PO ₄) _{5.59} (CO ₃) _{0.41}	F _{1.4}	+19.8(-18.7)	9.3537-9.3601
Queih area	55.64	0.15	0.57	35.46	1.4	1.47	Ca _{9.78} Mg _{0.04} Na _{0.18}	(PO ₄) _{5.64} (CO ₃) _{0.36}	F _{0.9}	+19.8(-18.5)	9.3601-9.3610
Um El Huetat area	51.30	0.29	0.95	32.38	1.8	3.49	Ca _{9.60} Mg _{0.07} Na _{0.33}	(PO ₄) _{5.51} (CO ₃ F) _{0.49}	F ₂	+19.7(-19.7)	9.3527-9.3610
C. Intraclastic collophane grains											
Mahamid area	52.28	0.10	0.48	31.26	2.2	5.02	Ca _{9.81} Mg _{0.03} Na _{0.16}	(PO ₄) _{5.39} (CO ₃ F) _{0.6}	F _{2.6}	+19.8(-20.6)	9.3527
Nasser area	55.26	0.31	0.48	31.94	1.6	1.77	Ca _{9.77} Mg _{0.08} Na _{0.15}	(PO ₄) _{5.55} (CO ₃) _{0.45}	F _{1.1}	+19.8(-18.7)	9.3537-9.3601
Yunis area	55.12	0.22	0.62	35.08	2.2	4.40	Ca _{9.75} Mg _{0.05} Na _{0.20}	(PO ₄) _{5.45} (CO ₃ F) _{0.55}	F ₂	+19.8(-18.9)	9.3527-9.3537
Queih area	46.44	0.10	0.34	29.49	1.4	1.35	Ca _{9.84} Mg _{0.03} Na _{0.13}	(PO ₄) _{5.57} (CO ₃) _{0.42}	F ₁	+19.9(-19.5)	9.3601-9.3610
Um El Huetat area	51.25	0.36	0.58	31.29	1.8	3.35	Ca _{9.7} Mg _{0.09} Na _{0.20}	(PO ₄) _{5.59} (CO ₃) _{0.3} (CO ₃ F) _{0.2}	F ₂	+19.9(-19.7)	9.3527-9.3610

* Structural CO₂

+ Total cation charges

- Total anion charges

Table 5. Characteristics of the studied francolites

Location	Naturity	CaO	F	Structural CO₂%	a (Å)	Formula
		P₂O₅	P₂O₅			
Mahamid area	High mature	1.63	0.15	2.2	9.3527	Ca _{9.78} Mg _{0.04} Na _{0.18} / (PO ₄) _{5.40} (CO ₃ F) _{0.6} F _{2.5}
Yunis area Um El Huetat area	Mature	1.57	0.12	2.2	9.3527–9.3537	Ca _{9.76} Mg _{0.05} Na _{0.19} / (PO ₄) _{4.45} (CO ₃) _{0.14} (CO ₃ F) _{0.41} F ₂
		1.69	0.11	1.8	9.3527–9.3610	Ca _{9.62} Mg _{0.09} Na _{0.29} / (PO ₄) _{5.51} (CO ₃) _{0.27} (CO ₃ F) _{0.22} F ₂
Nasser area	Altered	1.63	0.06	1.6	9.3537–9.3610	Ca _{9.78} Mg _{0.06} Na _{0.16} / (PO ₄) _{5.57} (CO ₃) _{0.43} F _{1.3}
Queih area		1.51	0.05	1.4	9.3601–9.3610	Ca _{9.81} Mg _{0.03} Na _{0.16} / (PO ₄) _{5.61} (CO ₃) _{0.39} F _{0.9}

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جيـو كـيمـيـاء الفـرانـكـولـاـيت المـصـرى

عزـت عـبـدـالـه أـحـمـد

قـسـم الـجيـلـوـجـياـ - كـلـيـةـ الـعـلـومـ - جـامـعـةـ أـسيـوطـ - مـصـرـ

درست فوسفات الكريتاوي العلوي في وادي النيل (منطقة المحاميد) والبحر الأحمر (مناطق ناصر ويونس والقويع وأم الحويطات) من الناحية المعدنية، حيث حللت عناصر Ca, P, F, Na, Mg باستخدام جهاز التحليل الدقيق (electron microprobe). ودللت الدراسات على أن معدن الفرانكولait هو المعدن الأساسي المكون لرواسب الفوسفات وأنه يعكس اختلافاً في الإحلال الأيوني. حيث وجد أن فرانكولait البحر الأحمر يوضح إحلال كاتيوني أعلى من نظيره في وادي النيل، فحوالي ٥٪ من كاتيون الكالسيوم تحل بوساطة الصوديوم والمغنيسيوم، ووجد أن أعلى إحلال كاتيوني هو $(Ca_{9.54} Mg_{0.10} Na_{0.36})$.

أما فرانكولait وادي النيل فيوضح إحلال أنيوني أعلى من نظيره في البحر الأحمر حيث وجد أن حوالي ١٠٪ من مجموعة الفوسفات (PO_4) تحل إما بوساطة مجموعة الكربونات (CO_3) أو مجموعة الكربونات + الفلورين (CO_3+F) وأن أعلى إحلال أنيوني هو $(FO_4)_{0.61}$ ($CO_3F)_{5.39}$) ويعزى اختلاف الإحلال الأيوني في معدن الفرانكولait إلى تأثير كلٍ من بيئتي التكوين والتحلل الثانوية.