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MANGANIFEROUS CONCRETIONS BEARING LUMINESCENT FLUORAPATITE IN JURASSIC RED CHERTS OF PILLOW-LAVAS OPHIOLITE UNIT (ANGELOKASTRO, ARGOLIS)

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ABSTRACT

Manganiferous concretions derived from the footwall chert slivers of pillow-lavas ophiolite unit (Angelokastro, northern Argolis), have been studied under optical mineragraphic, infra-red spectroscopy, cathodoluminescence and electron probe microanalysis techniques.

The results reveal that the black manganiferous concretions formed by highly luminescent carbonate-fluorapatite which replaces and cross-cuts the radiolarian Jurassic cherts. Though, the transformation of carbonate-fluorapatite into Ca-rich cryptomelane, associated with pyrolusite, is connected with subsequent more oxidized conditions.

The occurrence of carbonate-fluorapatite indicating several hydrothermal processes, took place after the deposition of Jurassic red cherts on pillow-basalts.

KEY WORDS: Mn-concretions;fluorapatite; cathodoluminescence; cryptomelane; pyrolusite;MORB; Argolis; Greece.

1. INTRODUCTION

In this paper, we describe the mineralogy of some manganiferous concretions, which were found on the ophiolitic formations of Angelokastro area (with samples locality placed at x=37°47'92" and y=23°01'38") from northern Argolis.

The ophiolitic formations of Angelokastro include a volcano-sedimentary "melange" with boninitic affinity (CAPEDRI et al. 1996) and locally, on their upper parts develop tectonically an imbricated structure of Jurassic radiolarian chert slices bearing manganiferous concretions. These slices associated with thin sheared serpentinite slivers were thrust over the volcano-sedimentary sequence during the post-Early Jurassic compressive phase (PHOTIADES, 1986). But, their primary sedimentary cover within the underlying pillow-lavas ophiolite unit of MORB affinity (DOSTAL et al. 1991) have been disrupted.

Therefore, the imbricated Jurassic cherts are metre-scale in size and consist of red-brown ribbon cherts, often deformed into recumbent folds. Along the basal contact, sheared chert and serpentinite, host centimetre-scale manganiferous concretions and various lens-like clasts of jasper and basalt of MORB affinity (CAPEDRI et al. 1996). Manganiferous concretions with Ni-rich todorokite were also found in this locality and have already been studied by PHOTIADES et al. (1995).

2. MINERALOGY

Black concretions of manganese oxides associated with very fine chalcedony-quartz reveal a progressive replacement of fluorapatite areas. The Mn-oxides consist of an intimate association of

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pyrolusite and cryptomelane. A progressive replacement of fluorapatite is responsible for its residual texture. Fluorapatite islet structures can still be seen in the Mn oxide areas. Thus the fluorapatite has been the precursor of the Mn-oxides. Many radiolarian microfossils are epigenetically transformed into fluorapatite (Fig. 1) and display a luminescence under cathodoluminescence process. We should like to point out that we have also found within the same deposits fine veins (few mm)

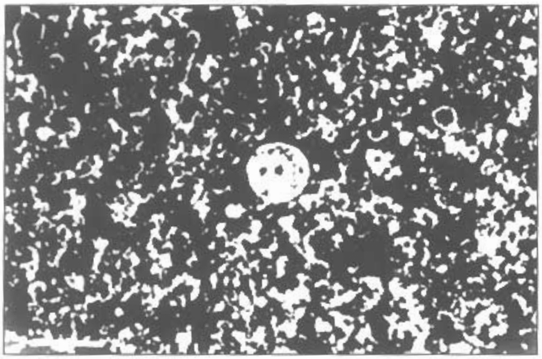

Fig.1: Luminescence of fluorapatite (bright) in cathodoluminescence, showing residual material. The first replacement of radiolaria by fluorapatite (bar is 100μ)can be seen.

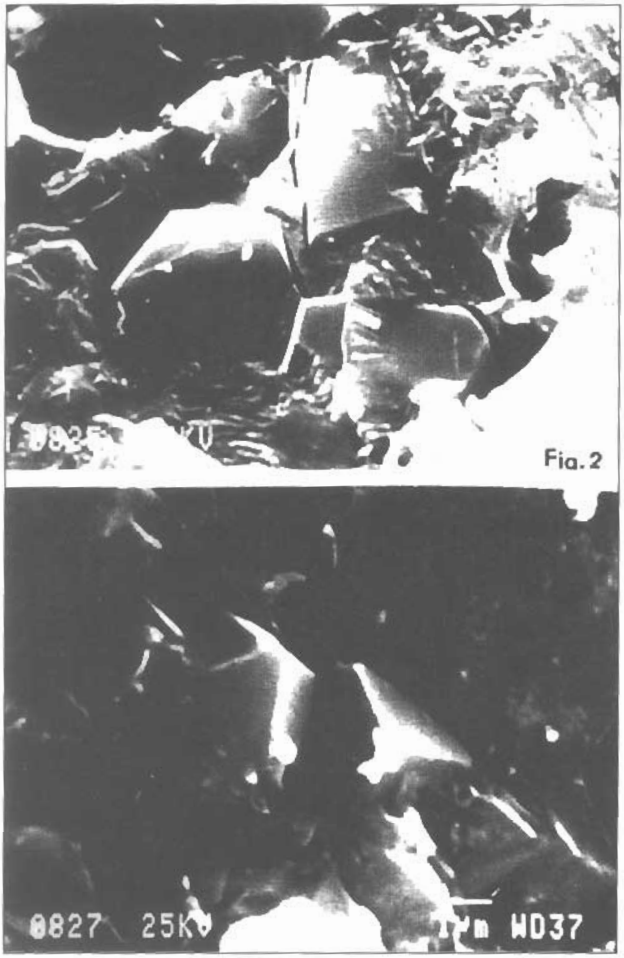

Fig. 2

Fig.2: Fluorapatite, well-crystallized, in a fine vein is cross-cutting the concretions (SEM micrograph)(scale bar is 1μ).

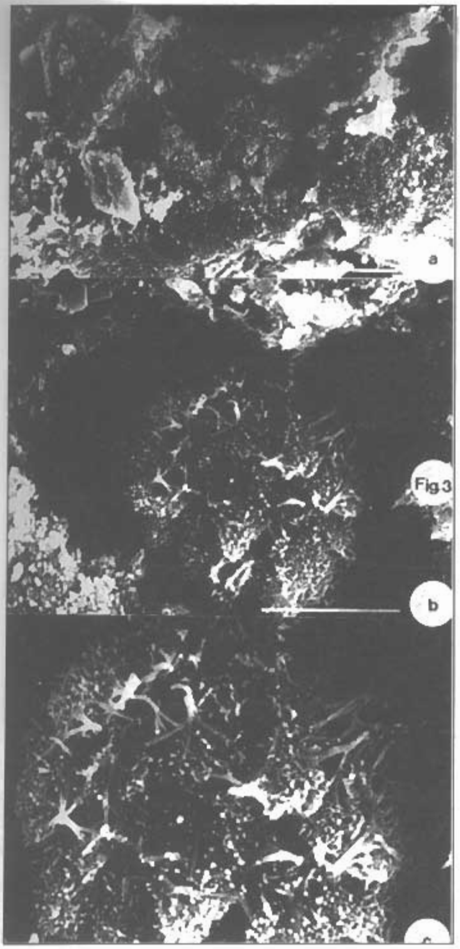

Fig.3: Dissolution of fluorapatite and formation of cryptomelane concretions in the neighbourhood of a thin fissure (SEM micrographs with bars representing 100μ for a, 150μ for b and 2μ for c).

of well-crystallized fluorapatite (Fig. 2), which cross-cut the concretions; hence, these veins have been formed later than all other constituents of these concretions.

We observe on a fresh broken surface under the scanning electron microscope (SEM), the dissolution of fluorapatite areas in the neighbourhood of fine fissures; there, in the remaining voids, the formation it takes place of Mn-oxide concretions (Fig. 3). The predominant features of this newly formed material, under more oxidized conditions, are needle-shaped structures, which are fairly characteristic to cryptomelane.

In reflected light, the Mn-oxide concretions show an intimate association of cryptomelane and pyrolusite (Fig. 4). These concretions frequently remind the former automorphic crystal of fluorapatite of which only islet structures remain intact.

Besides,the Mn-oxide concretions are cross-cut by numerous veinlets of cryptomelane (Fig.4).

The presence of residual fluorapatite as islet structures within the Mn-oxide concretion areas, explains the remarkable luminescence of microscopic preparations (Fig. 5).

Cathodoluminescence reveals a slight zonation of the fluorapatite which indicates replacement of phosphorus by silica and alumina. The spectrum indicates two major luminescence bands, one at l = 565nm and the other one, is the intrinsic luminescence at l =340 nm testifying respectively the presence of manganese (Mn^{2+}) in apatite structure.

Furthermore, electron microprobe analyses (Tab.1) and backscattered scanning electron (BSE) image (Fig. 6) on fluorapatite, point that the replacement of phosphorus by silica is initially very slight but then becomes rather important. This suggests that there is a composition limit rich in silica corresponding to a value near 3 in the structural formula, while phosphorus in fluorapatite is 6. Besides, the low amount on fluorapatite analyses is due to the absence of 3 to 4% of CO_2+H_2O after DEER et al. (1982).

Moreover, X-ray diffraction patterns on this fluorapatite, show the absence of an important reflection near 1,84 Angstrom which suggests that we are facing here with carbonate-fluorapatite. Microprobe investigations have indeed shown the presence of C (carbon) in fluorapatite areas. The enrichment in carbon in these areas is most important, principally in the neighbourhood of fissures. This also suggests a late transformation of the initial fluorapatite. The presence of water and carbonate (CO_3^{-2})groups can be shown by infrared (IR) spectroscopy.

IR analysis in the transmission microscope (Nicolet 740/I.R., plane II) of areas previously analyzed by electron microprobe gives two absorption bands. One near 3566 cm-1 and the other near 633cm-1,that can be attributed to OH- vibrations. There are also 867 cm-1 and 1455 to 1425 cm-1 absorption bands which are generally attributed by FARMER (1974) to a substitution of PO_4^{-3} by CO_3^{-2} or by CO_3OH groups.

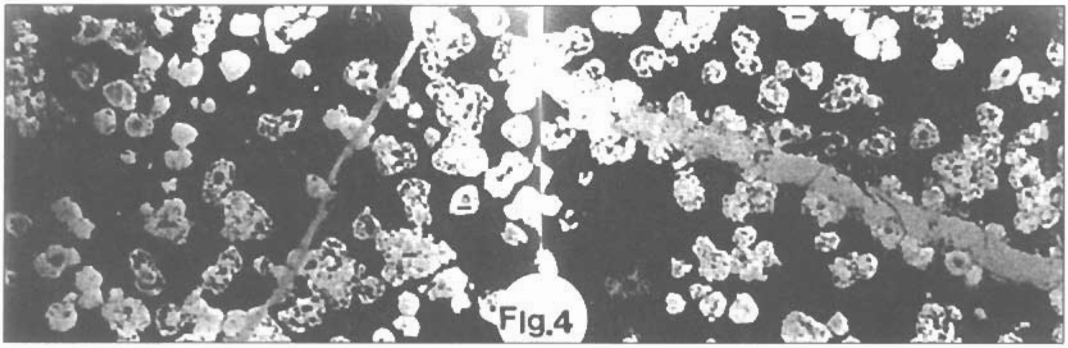

Fig.4

Fig.4: Cryptomelane concretion (grey) and pyrolusite (bright) in intimate association, with thin veins of cryptomelane (Reflected natural light; bar represents 50μ).

The Ca content of cryptomelane as shown in microprobe analyses (Tab. 2) is due to a crystallochemical peculiarity, Ca is clearly inherited from the replaced fluorapatite. Besides, cryptomelane has a tunnel structure into which the Ca-ion can be inserted, similarly to K, Na, Ba, Pb and Sr; and the amount of water in its crystal structure, is 1 to 2% after FLEISCHER (1964).

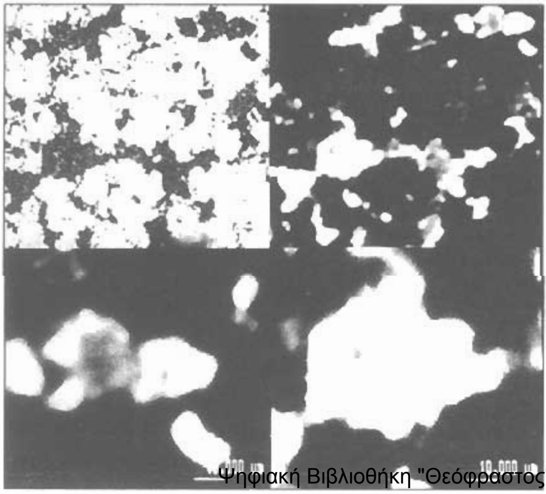

Fig.5: Luminescence of residual carbonate fluorapatite as islet structures.

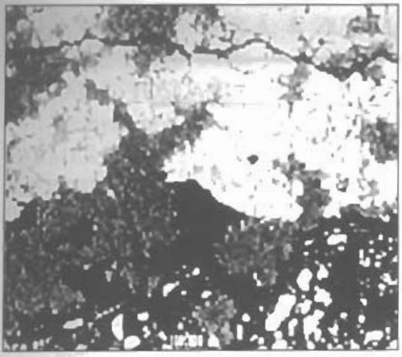

Fig. 6: BSE image of an area with residual carbonate fluorapatite as islet structures in cryptomelane-pyrolusite concretions and element mapping (P and Ca) of the same area.

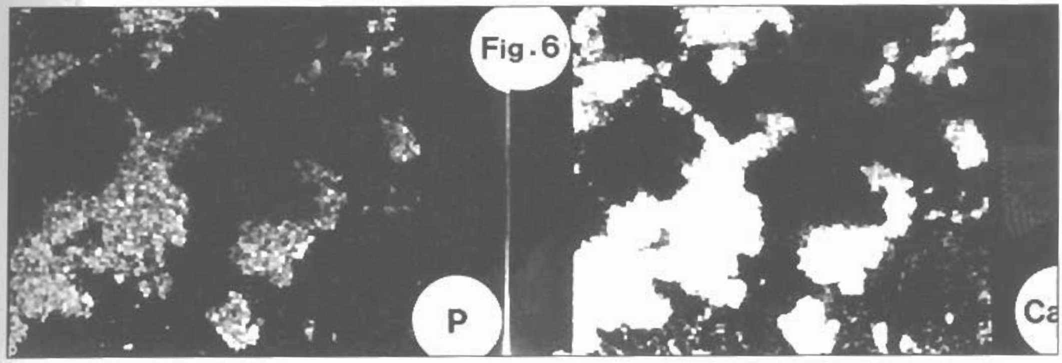

Table 1: EMP analyses of carbonate-fluorapatite from Angelokastro

	1	2	3	4	5	6
FeO	0.60	1.07	0.59	0.30	1.08	0.78
TiO_2	0.02	0.01	0.03	0.02	0.00	0.05
Al_2O_3	0.06	0.19	0.26	0.07	0.07	0.75
MnO	1.98	1.03	0.79	0.96	0.87	0.71
CaO	53.51	53.55	53.82	52.37	54.20	51.50
SrO	0.12	0.14	0.12	0.12	0.16	0.09
P_2O_5	35.72	35.08	35.51	34.97	34.43	33.84
V_2O_5	0.01	0.00	0.09	0.00	0.00	0.00
SiO_2	0.92	0.70	1.44	3.06	0.41	4.38
F	3.43	3.71	3.83	3.43	3.72	3.44
Cl	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.37	95.48	96.48	95.30	94.94	95.54
- O = F.Cl	1.45	1.56	1.61	1.44	1.57	1.45
Total	94.92	93.92	94.87	93.86	93.37	94.09
P^{5+}	5.102	5.046	5.015	4.983	5.008	4.794
V^{5+}	0.001	0.000	0.010	0.000	0.000	0.000
Fe^{2+}	0.087	0.152	0.083	0.041	0.156	0.109
Ti^{4+}	0.002	0.001	0.003	0.000	0.000	0.006
Al^{3+}	0.011	0.039	0.050	0.014	0.014	0.149
Mn^{2+}	0.282	0.148	0.112	0.136	0.126	0.101
Ca	9.674	9.750	9.621	9.443	9.976	9.235
Sr	0.012	0.014	0.011	0.011	0.016	0.009
Si^{4+}	0.155	0.119	0.240	0.314	0.070	0.732

Table 2: EMP analyses of Ca cryptomelane(A8).

	1	2	3	4	5	6
MnO_2	90.47	88.64	87.66	86.90	86.03	81.55
Fe_2O_3	1.32	2.28	1.97	0.84	0.64	9.85
K_2O	0.62	0.67	0.77	0.72	0.75	0.71
Na_2O	0.09	0.15	0.17	0.21	0.19	0.22
BaO	0.14	0.13	0.00	0.11	0.21	0.13
SrO	0.12	0.06	0.06	0.00	0.07	0.12
CaO	5.14	5.86	6.68	6.78	7.58	6.21
Σ	97.90	97.79	97.31	95.56	95.47	98.79
Formula per 16 oxygens						
Mn4+	7.525	7.351	7.317	7.382	7.369	6.850
Fe3+	0.120	0.206	0.179	0.077	0.060	0.900
K	0.095	0.103	0.118	0.112	0.119	0.110
Na	0.021	0.034	0.040	0.049	0.046	0.052
Ba	0.007	0.006	0.000	0.005	0.010	0.006
Sr	0.009	0.004	0.004	0.000	0.005	0.002
Ca	0.663	0.753	0.863	0.892	1.006	0.808
Σ	**0.795**	**0.900**	**1.025**	**1.058**	**1.186**	**0.978**

3. CONCLUSIONS

Manganiferous concretions from Angelokastro occur in tectonically disrupted slices of Jurassic cherts, detached from the pillow-lava ophiolite unit (PHOTIADES 1986) with MORB affinity (DOSTAL et al. 1991).

The presence of highly luminescent carbonate-fluorapatite which replaces and cross-cuts the radiolarian chert, has made possible the establishment of its accumulation after the deposition of radiolarian Jurassic chert.

Furthermore, the presence of the mineral above, can be interpreted as an important portion of fluor and phosphorus might be scavenged from pillow-basaltic lavas, through interaction of hydrothermal water and might be discharged with fumarolic activity. This hydrothermal contribution is also indicated by veinlets of Ni-rich todorokite (PHOTIADES et al. 1995).

Additionaly, the replacement of automorphic carbonate fluorapatite minerals by Ca-rich cryptomelane and pyrolusite can be seen as subsequent more oxidized conditions which activated during the pre-emplacement period of the subpelagonian back-arc ophiolite (DOSTAL et al. 1991; CAPEDRI et al. 1996).

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