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Original scientific paper

EARTHY–CRYPTOCRYSTALLINE VIVIANITE FROM THE TREPEL DEPOSITS NEAR THE SUVODOL VILLAGE, BITOLA, MACEDONIA

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A b s t r a c t: Within the frame of the trepel deposits (Fig. 1) near Suvodol village, Bitola city it was discovered (Lj. Petreski) an earthy-cryptocrystalline vivianite occurrence. The examined vivianite sample was confirmed by X-ray powder diffraction, chemical, SEM, DTA/TG, infra-red analyses. The treated vivianite sample actually represents a typical earthy-cryptocrystalline variety (Fig. 2) with a peculiar progressive oxidation state of Fe_2^+ to Fe_3^+ (FeO/Fe_2O_3 contents nearly 1:1). X-ray powder diffraction, DTA/TG-data are in quite good concordance with literature data.

Key words: earthy; cryptocrystalline vivianite

INTRODUCTION

According to the earlier examinations (Jelena D. Marković-Marjanović, 1956) vivianite (coarsely grained sample) was discovered in the area of the city brickkiln, Bitola. This vivianite occurrence was determined and elaborated only by means of the macroscopic characteristics of the treated mineral and description of it's geological environment. The new-discovered earthy-cryptocrystalline vivianite occurrence deserves a more complex elaboration by X-ray powder, SEM, chemical, DTA/TG, infra-red data.

EXPERIMENTS

Geological setting

The terrains around Bitola city, Suvodol village and the wider area belong to the Pelagonian depression composed of alluvial-delluvial as well as sediments of miocene-pliocene age which are superposed over the gneisses, micaschists (upper Precambrian age) of the Selečka mountain.

At the Suvodol village and the wider area there is an opened vertical cross section (starting from the surface to 150 m in depth) – daily excavation miner works according to the very intensive coal deposits exploitation. The mentioned vertical cross section actually represents a profile-line performed through a peculiar biogenetic-sedimentary formation composed as follows:

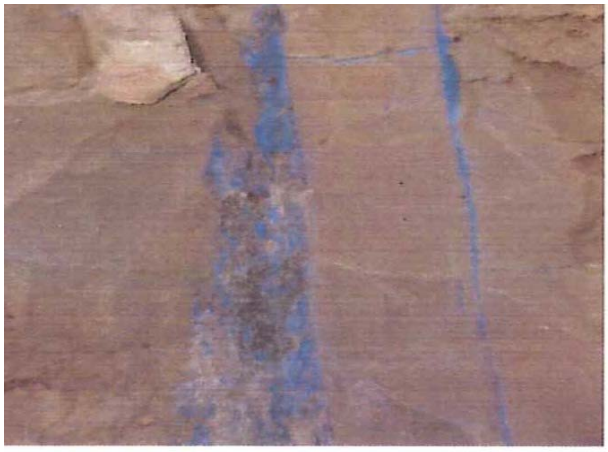


Fig. 1 Dark bluish earthy-cryptocrystalline vivianite enclosed in the surrounding trepel mass

The deepest part of the vertical cross section is composed of an alternating complex of coal layers (cca 1.0–39.0 m in thickness), sands, gravel etc.

The upper coal layer is about 1.5 m to 61.4 m in thickness.

The further layers of cca 10 m to cca 80 m in thickness belong to a typical biogenetic formation consisted of trepel sedimentary rocks.

The uppermost layers of cca 0.5–1.0 m in thickness belong to the redish-yelowish sands, gravels of alluvial-deluvial age.

In the frame of certain open fissures in the biogenetic trepel formation at Vranjevski part – microlocality 7 (Fig. 1) were discovered (Lj. Petreski) bluish earthy-cryptocrystalline masses of vivianite representing a subject of our examination the results of which are given in this paper.

MINERALOGY

The examined vivianite actually represents very soft, earthy-cryptocrystalline sample with dark blue even marine bluish color (Fig. 1).

SEM–pictures (Fig. 2AB) show that vivianite crystals have plate-like forms (0.10) to cca 0.02 – 0.03 mm long and very intimately associated-enclosed in the typical micromass of the surrounding trepels sediments composed of micro fossils (alga Diatomeae).

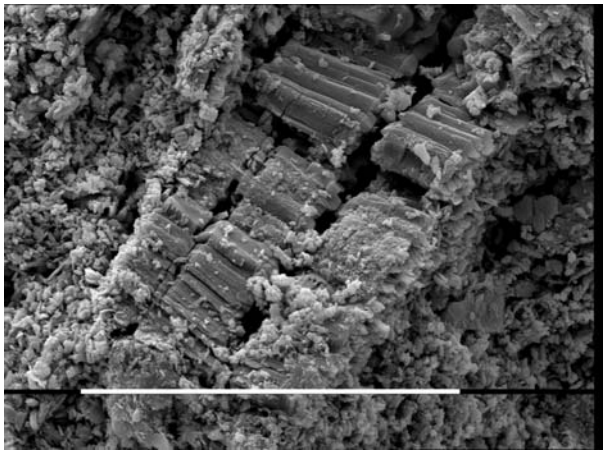


Fig. 2A. Superfine grained (0.02–0.03 mm) plate-like forms (010 of vivanite) in the surrounding trepel mass

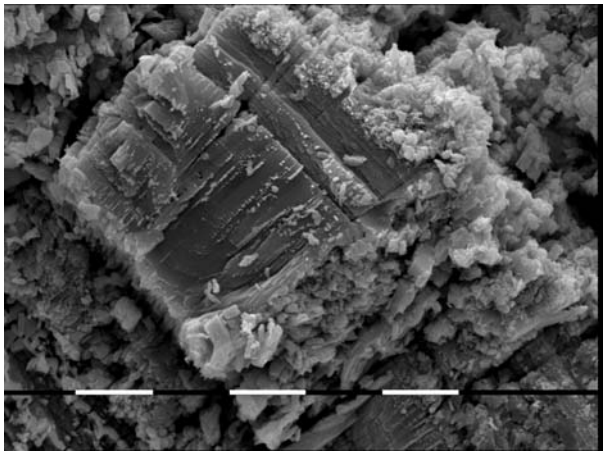


Fig. 2B. Superfine grained (cca 0.05 mm) plate-like forms (010 of vivanite) in the surrounding trepel mass

Recent X-ray powder diffraction examinations (CuKα/Ni; 36 kV; 18 mA) show that X-ray powder data of the treated vivianite sample are in quite good correlation (Tab. 1 and Fig. 3) with the compared earthy-cryptocrystalline vivianite samples from literature data.

Table 1

X-ray powder data of the treated earthy-cryptocrystalline vivianite sample compared with other cryptocrystalline vivianites from different microlocalities in the world (d – Å; I – intensities)

1	2	3	4	5	I
110	7,92	7,84	7,89	7,93	37
020	6,73	6,72	6,71	6,71	100
200	4,93	4,91	4,90	4,906	40
101	4,562	4,55	4,60	4,535	7
011	4,342	4,34	4,40	4,353	2
130	4,073	4,08	4,10	4,073	10
101	3,860	3,85	3,88	3,857	14
	–	–	–	3,636	5
	3,211	–	–	3,202	26
301	2,978	2,98	2,99	2,978	40
211	–	–	2,90	–	
240	–	–	2,83	–	
	2,773	–	–	2,768	4
231	2,728	2,72	2,73	2,718	19
141	2,716	–	2,68	2,700	17
330	2,634	2,64	–	2,639	10
141	2,586	2,54	2,54	2,592	2
	–	–	–	2,524	11
400	2,433	2,44	2,44	2,431	13
051	2,313	2,33	2,36	–	
002	–	2,30	2,33	–	
341	–	2,25	2,25	–	
251	2,194	2,20	2,20	–	
431;112	2,149	–	2,15	–	

1 – hkl values for vivianite (ASTM card – 30 – 0662).
2 – d-values for earthy-cryptocrystalline vivianite from Suvodol village.
3 – Earthy-cryptocrystalline vivianite, Wafotu, New Zealand. AU: 2473.
4 – Cryptocrystalline vivianite, Leadville, Colorado, USA, BM (NH): 1907, 115.
5 – Earthy (cryptocrystalline) vivianite, Humna, New Zealand. AU: 2408.
I – Intensities for vivianite sample – column 5.

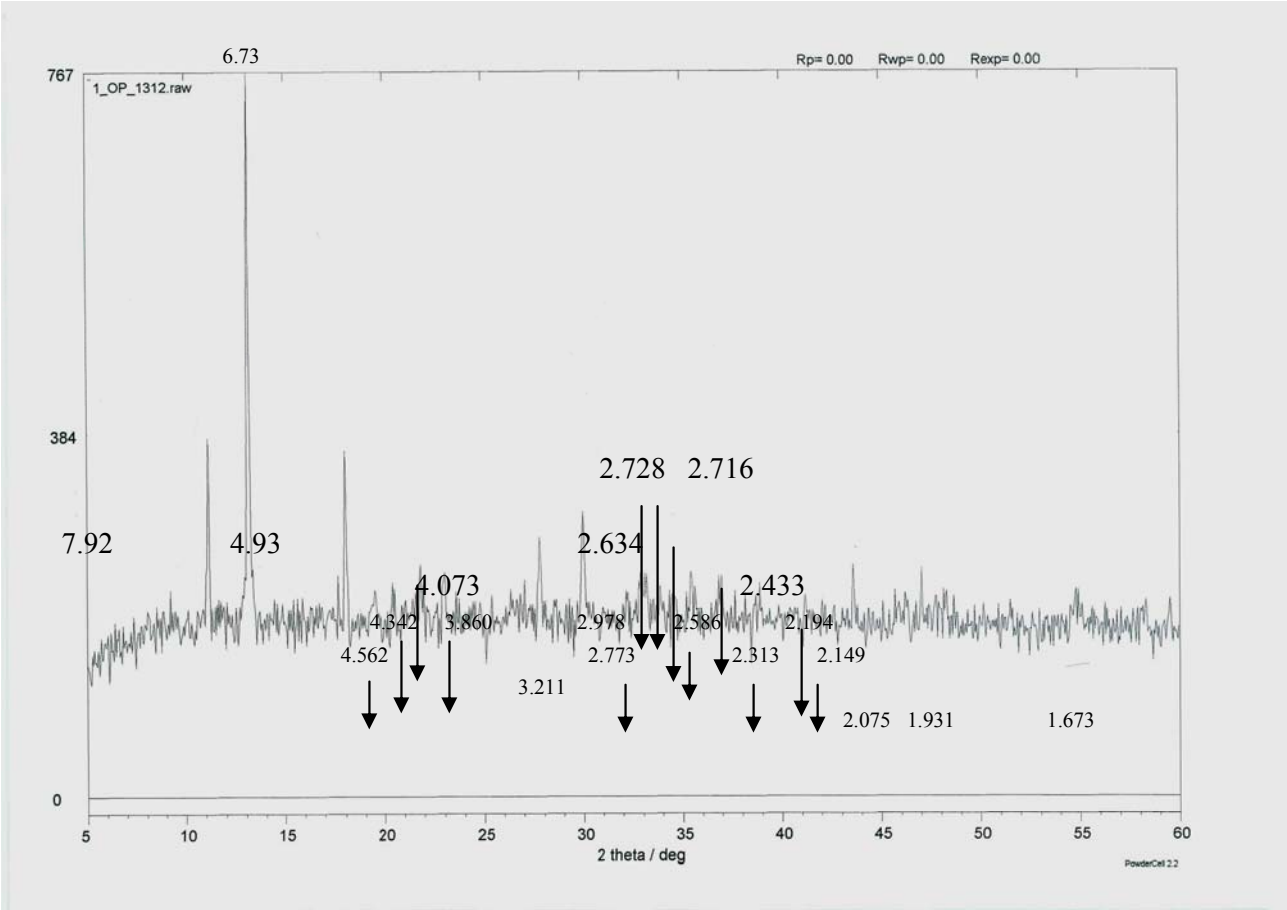


Fig. 3. X-ray powder diagram for vivianite from Suvodol village

DTA/TG-curve (Fig. 4) of the examined earthy-cryptocrystalline vivianite is very similar nearly identical with the same curves from literature date. The very big endo-peak at 160 °C is corresponding to the biggest water losses of cca 18% (visibly form the contributed TG-curve) while the other loss of weight of cca 6,3% is connected with OH^- groups.

The others thermal effects – egzo-peaks at 600 °C and 710 °C are probably connected with the oxidation changes of Fe^{2+} to Fe^{3+}.

The total weight loss of the examined vivianite amounts 24,3%.

The chemical analysis performed on a relatively pure monomineral (?) fraction by the classical wet chemical procedure shows results as follows:

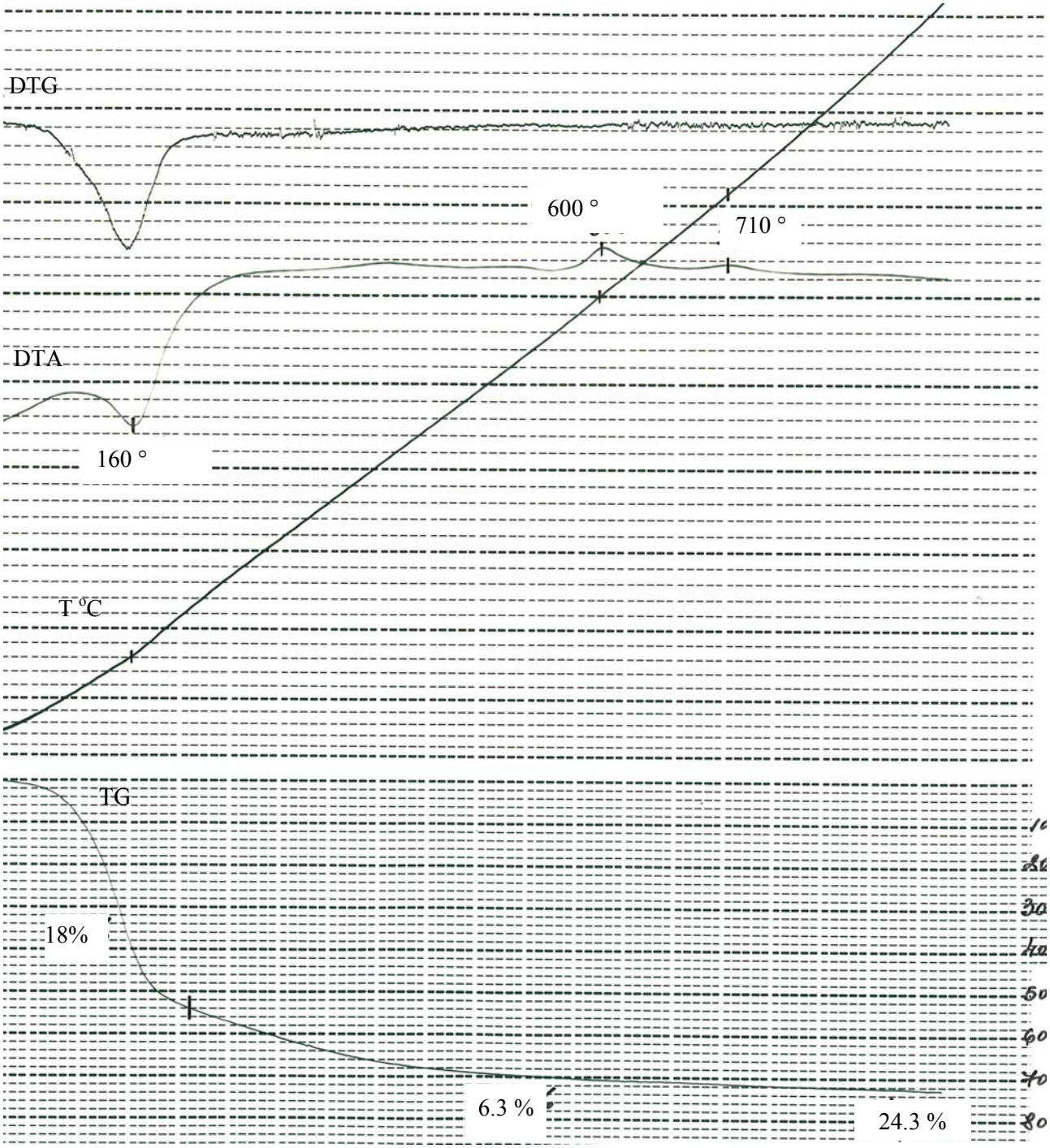
Table 2

Chemical analysis of vivianite (%)

FeO	23,17
Fe_2O_3	22,91
P_2O_5	29,22
CaO	0,37
MgO	0,12
Loss of igm.	24,10
Total	99,89

According to a classical geochemical procedure was calculated the formula of the examined vivianite sample as follows:

$$(Fe^{2+}_{1,6}\ Fe^{3+}_{1,4})_{3,0}\ (PO_4)_2\ (OH)_{1,4}\ 5H_2O$$



CONCLUSION

According to the geological prospecting activities, inside the area of the trepel sedimentary rock of biogenetic origin (of Pliocene age) at the Suvodol village, Bitola city, Macedonia, there was discovered earthy-cryptocrystalline vivianite with dark bluish color.

The mineral was examined by means of the complex mineralogical methods – X-ray powder diffraction, SEM, chemical, DTA/TG, infra-red analyses.

The examined earthy-cryptocrystalline vivianite sample – $(Fe^{2+}_{1,6}Fe^{3+}_{1,4})_{3,0}(PO_4)_2(OH)_{1,4}5H_2O$, reveals a structure type in which there is a progressive oxidation relation between Fe^{2+} to Fe^{3+} with consequently FeO/Fe_2O_3 contents nearly 1:1.

Infra-red analysis confirms that in the examined vivianite sample there are HOH molecules.

According to earlier examinations (by R. L Frost, W. Martens, P. A. Williams and J. T. Kloprogge) for vivianite was reported that the hydroxyl stretching vibrations are identified at 3460, 3281, 3104, 3012 cm^{-1}, while HOH bending was reported around 1660 cm^{-1}. Our IR-examinations are compatible with the mentioned literature data.

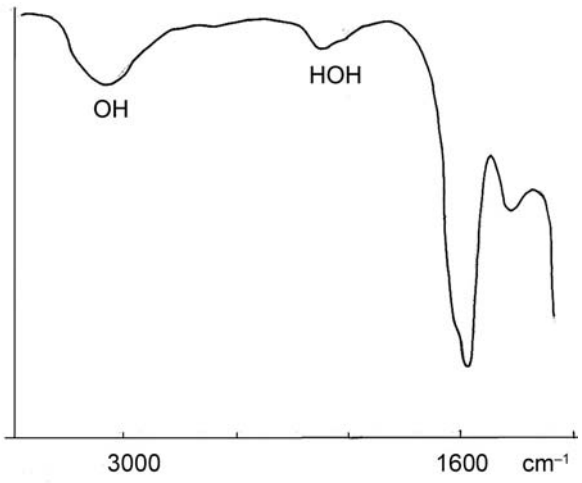


Fig. 5. Infra-red curve of vivianite

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Р е з и м е

ЗЕМЈАНО-КРИПТОКРИСТАЛЕН ВИВИЈАНИТ ОД НАОЃАЛИШТАТА НА ТРЕПЕЛ БЛИЗУ СЕЛОТО СУВОДОЛ, БИТОЛА, МАКЕДОНИЈА

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Клучни зборови: земјано-криптокристален вивијанит

Во трепелот од наоѓалиштето кај селото Суводол, Битола, беа откриени (Љ. Петрески) појави на земјано-криптокристален вивијанит (сл. 1). Испитуваниот вивијанит ($Fe^{2+}_{1,6}$ $Fe^{3+}_{1,4})_{3,0}$ $(PO_4)_2$ $(OH)_{1,4}$ $5H_2O$ беше детерминиран со комплексни физичко-хемиски анализи (рендгенско-прашкаста, хемиска, SEM, DTA/TG, инфра-црвена). Овој земјано-криптокристален вивијанит се карактеризира со напреднат степен на оксидација на Fe^{2+} во Fe^{3+}, при што квантитативниот однос помеѓу FeO/Fe_2O_3 е приближно 1:1. Податоците од рендгенско-прашкастите (d-Å-вредности и DTA/TG анализи на испитуваниот вивијанит се многу добро компатибилни со податоците добиени за разни земјано-криптокристални вивијанити од други микролокалитети во светот.