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MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF VIVIANITE OCCURRENCE IN SEDIMENTS OF THE PELAGONIA BASIN, REPUBLIC OF MACEDONIA

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Abstract: Crystalline vivianite occurrences in the Republic of Macedonia are very rare. It can be seen in the sediments of the Pelagonia basin, particularly in the tripolites of the Suvodol locality. For research on our sample were used the following four methods: infrared spectroscopy IR, scanning electron microscopy (SEM), inductively coupled plasma atomic emission spectrometry AES-ICP and X-ray diffraction. The crystals of the vivianite are prismatic and tabular with a different length of several cm across. The colour of studied vivianite is greenish blue. The streak is pale bluish, but the colour is soon changing dark blue due to oxidation. Lustre is pearly. Very often can be seen distinct cleavage planes parallel to {010}. The density determined by pycnometer is 2.62 g/cm^3 · Hardnes is 1.5–2. The concentration of the oxides is: FeO 42.89%, P_2O_5 28.67%, MnO 2.50%, MgO 0.34%. Also were detected the following trace elements: Cd, Cr, Ni, Ba, Sr, Bi, Zn, Pb, Cu Ag, Co, In, Tl, Ga and Li. The most intense registered maxima in the studied powder pattern [*d* values (in Å), *I*] are: 6.81 (100); 3.22 (6); 2.71 (6); 2.33 (5); 1.68 (12); 1.34 (5).The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: $a = 10.03$ Å, $b = 13.50$ Å, $c = 4.72$ Å, $\beta = 102.52°$, $V = 625.79$ Å^3. The results of all analyses showed that the studied sample is vivianite.

Key words: vivianite, IR; SEM-EDS; AES-ICP; XRD

INTRODUCTION

Vivianite, $Fe_3(PO_4)_28H_2O$, named after the English mineralogist John Henry Vivian (1785–1855), is a hydrous phosphate of ferrous Fe.

According to the earlier examinations, for the first time coarsely grained vivianite from Macedonia was discovered in the area of the city brickkiln, Bitola, by Marković-Marjanović (1956). Earthy cryptocrystalline vivianite from the trepel deposits near the Suvodol village, Bitola, was described by Jančev et al. (2011). Vivianite from Pelagon is also described by Jovanovski et al. (2012).

Vivianite is found in a number of geological environments. It is formed under reducing redox environments and alkaline conditions (Rosenquist, 1970). High ferrous ions and phosphate activities, as well as low sulphide activity, are required to stabilize vivianite in most chemical systems (Nriagu, 1972).

The presence of vivianite in deep sediment layers demonstrates that vivianite can persist for many thousands of years within the sediments (Rothe et al., 2016).

The formation of authigenic vivianite in lake sediments is not fully understood, but appears to be influenced by redox conditions, pH values, dissolved elements – primarily Fe and P, but often including impurities of Ca, Mn and Mg – organic matter contents, and sedimentation rate (Sapota et al., 2006). Vivianite is usually a stable mineral in environments over the pH range of 6 to 9 and low Eh values of less than 0.0 (Nriagu and Dell, 1974).

Vivianite is a mineral particularly susceptible to oxidation processes. In air vivianite readily oxidizes, turning from opaque or white to vivid blue in a short time, eventually altering to metavivianite-kerchenite (Rodgers, 1986) or santabarbaraite

(Pratesi et al., 2003), as the original Fe^{+2} becomes completely replaced by Fe^{+3}.

Phosphates due to their varying degrees of oxidation and dehydration can serve as indicators of degree of oxidation, acidic/alkaline and hydrated / dehydrated conditions of formation of mineral assemblages (Dyar et al., 2014).

ANALYTICAL METHODS

For our research were used the following four methods: infrared spectroscopy using diffuse reflectance method (FTIR/DRS), scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectrometer (EDS), AES-ICP and X-ray difraction (XRD).

The use of these four methods showed that they are very useful methods for rapid mineral analysis contributing important analytical information.

These methods have been used to identify sedimentary vivianite by several authors, such as: Fagel et al. (2005), Hsu et al. (2014) – used IR spectroscopy, Hearn et al. (1983), Stamatakis and Koukouzas (2001), Dodd et al. (2003) – used scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), and Postma (1981), Manning et al. (1991), Taylor et al. (2008), Heiberg et al. (2012), Cosmidis et al. (2014), Rothe et al. (2014) used X-ray powder diffraction (XRD).

Because vivianite is highly sensitive to oxidation, its identification by XRD has been reported to be difficult by some authors (Bricker and Troup, 1973; Olsson et al., 1997; März et al., 2008), suggesting that vivianite rapidly looses its characteristic crystal structure upon exposure to air. However, this assertion has been questioned by others (Rodgers, 1977; Suess, 1979; Manning et al., 1991; Frossard et al.,1997; Rothe et al., 2014).

Infrared spectroscopy. The analyses were accomplished by using an IR Prestige 21 spectrophotometer (Shimadzu, Japan). The spectra were recorded in spectral range 400–4000 cm^{-1} at a resolution of 2 cm^{-1} and 45 scans. For the spectra manipulation was used IRSolution 1.5 software (Shimadzu Corporation). Two methods were employed in these measurements:

a) *The KBr pellet method.* The pellets (4 mm dia) were prepared by mixing 0.5 – 1 mg of the sample powder and about 100 mg of the KBr.

b) *The diffuse reflectance spectroscopy (DRS).* The measurements were performed by use of DRS 8000 (Shimadzu, Japan) attachment. The powdered sample was diluted to about 5% by weight in KBr and placed into the sample holders (2 mm dia with 1mm deep). The infrared spectra were obtained by measuring the diffuse reflected light that was emerged from the sample surface after the first being absorbed inside the sample and reflected among the particles. The resultant spectra were converted to Kubelca-Munk function (Griffits, 2007) to make them more comparable to the absorption spectra.

Scanning electron microscopy. SEM is model VEGA3LMU, increasing 2 × 1000000, W-wire, voltage up 200 V to 20 kV, infrared camera, maximum sample size 81 mm height, 30 mm width. The standards used are as follows: O: SiO_2; Na: albite; Mg: MgO; Al: Al_2O_3; Si: SiO_2; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr. Results of SEM/EDS analyses of mineral phases demonstrated usefulness of this method for identification and characterization of mineral phases whose size is often below the resolution of an optical microscope.

ICP-AES. Chemical composition is also determinated with ICP-AES model Varian Liberty 110. This method provides a rapid and precise means of monitoring up to 50 elements simultaneously for minor- and trace-levels. The ICP-AES technique is widely regarded as the most versatile analytical technique in the chemistry laboratory. When the sample solution is introduced into the spectrometer, it becomes atomized into a mist-like cloud. This mist is carried into the argon plasma with a stream of argon gas. The plasma (ionized argon) produces temperatures close to 7.000°C, which thermally excites the outer-shell electrons of the elements in the sample.

XRD. Powder X-ray analysis was performed on a diffractometer (Shimadzu) XRD-6100, Cu (1.54060 Å) radiation operating at 40 kV and 30 mA. The powdered sample was scanned over the 5–80° range with step size of 0.02° and scanning speed of 1.2°/min. The analyzed material is finely ground, homogenized, and average bulk composition is determined. The most intense registered maxima in the studied powder diagrams were compared with the corresponding diagrams from PDF-2 software.

RESULTS AND DISCUSSION

Examined vivianite is found in the tripolites as prismatic to tabular crystals, often several centimeters in diameter (Figure 1). The mineral crystallizes in the monoclinic system, space group C2/m. The colour of viivianite is greenish blue. This colour change is attributed to the partial oxidation of the total iron within vivianite (Faye et al., 1968). Upon exposure to air, the crystals turn vivid blue due to partial oxidation of Fe^{2+} (Hush, 1967).

The streak is pale bluish but the colour is soon changing dark blue due to oxidation. Lustre is pearly. Very often distinct cleavage planes parallel to {010} can be seen. The density determined by pycnometer is 2.62 g/cm^3. Hardnes is 1.5 – 2.

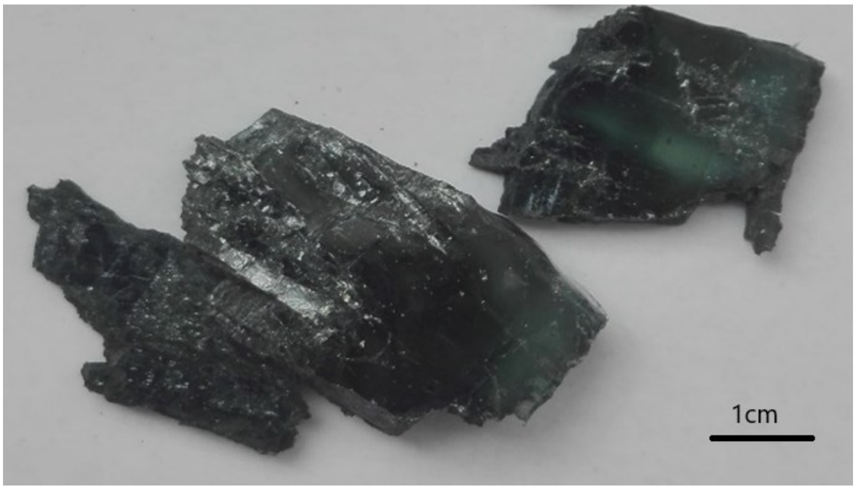

Fig 1. Vivianite from Suvodol, Republic of Macedonia

The infrared spectra of the vivianite, recorded by the use of KBr method and DRS, are presented in Figure 2, whereas Table 1 reports the band assignments from this study and corresponding literature data (Piriou and Poullen, 1987; Frost, 2002; Capitelli et al., 2012).

The vivianite (Figure 2) was characterized by the bands attributed to the PO_4 functional group: three well separated sharp bands at 1045, 975 and 940 cm^{-1} due to phosphate antisymmetric (v_3) and symmetric stretching modes (v_1) and intense bands at around 570 – 540 cm^{-1} ascribed to the out of plane bending modes (v_4). In comparison with the literature data (Table 1), the PO_4 modes values from this study best match those presented by Capitelli et al. (2012) for the vivianite specimen with calculated formula $Fe_{2.88}Mg_{0.12}(PO_4)_2\cdot 8H_2O$. It should be noted that a band due to PO_4 combination mode ($v_2 + v_3$) at 1439 cm^{-1} reported by Capitelli was not observed in our IR spectra.

In the spectral region attributed to the hydroxyl stretching modes two separated bands at 3483 and 3134 cm^{-1} can be seen in the presented spectra. These values are in good agreement with the literature data (Piriou and Poullen, 1987; Frost, 2002; Capitelli et al., 2012).

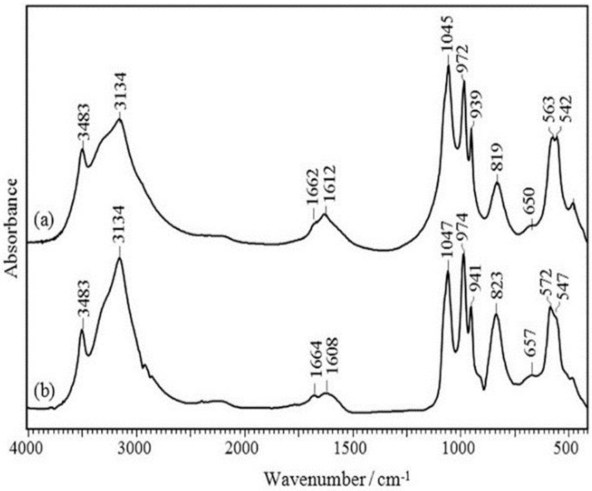

Fig. 2. IR spectra of vivianite: (a) absorption spectrum (KBr pellet) and (b) reflectance spectrum (DRS)

The water bending vibrations result as a broad band with two maximums: 1662 and 1612 cm^{-1} in the absorption spectrum (Figure 2a) and 1664 and 1608 cm^{-1} in the DRS spectrum (Figure 2b). According to the literature (Frost, 2002; Capitelli et al., 2012), the HOH bending mode observed at the higher wave number (around 1660 cm^{-1}) suggests chemically bonded water and the band at around

1610 cm^{-1} is indicative for the presence of strong hydrogen bonding network. The intense absorption observed at about 820 cm^{-1} is comparable with the band at 813 cm^{-1} reported by Frost (Frost, 2002) suggesting this band is due to water librational mode.

The results for the chemistry of the vivianite obtained by SEM-EDS are given in Figures 3 – 6 and Table 2. From the data on the chemistry given in Table 2 can be concluded that the examined sample is vivianite.

Table 1

IR data from this study in comparison with literature data

This study		Capitelli (2012)	Frost (2002)	Piriou (1987)	Assignments
Vivianite (Ab)	Vivianite (DRS)				
3483	3483	3433	3460	3400	Hydroxyl stretching
			3281		
3134	3134	3172	3104		
1662	1664	1624	1666	1635	Water HOH (bending)
1612	1608		1615		
			1586		
		1439			PO (stretching)
1045	1047	1043	1079	1040	
972	974	972	1027	990	
939	941		950		
			923		
819	823	876	813	890	Water librational
		814	783	872	
563	572	542	634	600	Outplane bends
542	547	472	561	575	
				560	
				492	

Ab – absorption spectra, DRS – reflectance spectra

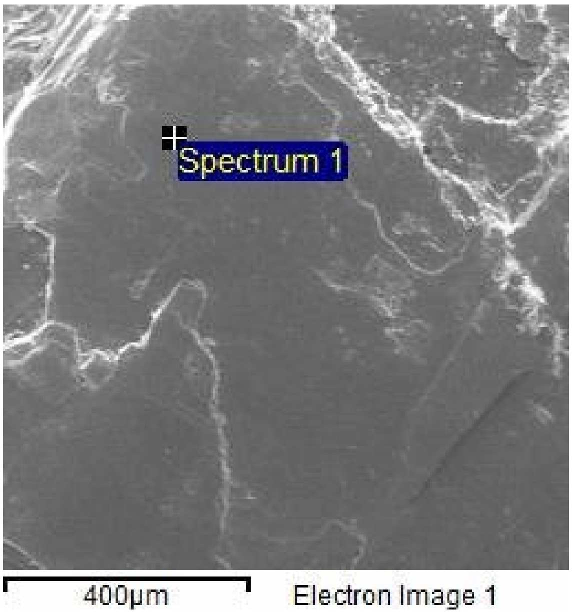

Fig. 3. SEM image of vivianite (spectrum 1)

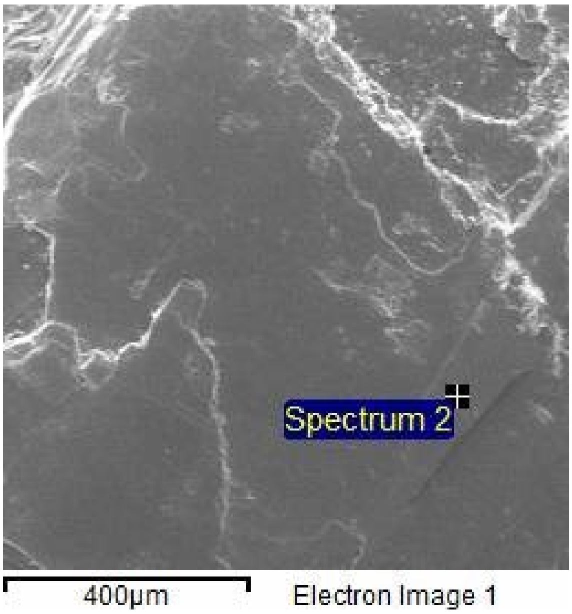

Fig. 4. SEM image of vivianite (spectrum 2)

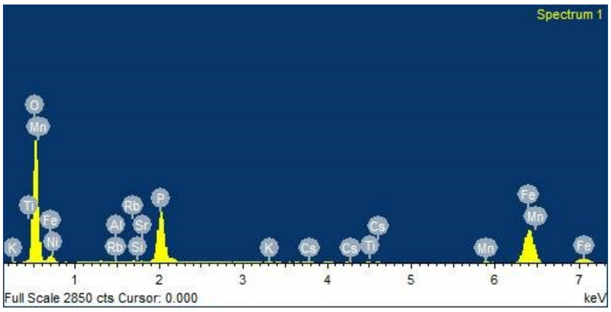

Fig. 5. EDX spectrum 1 of vivianite

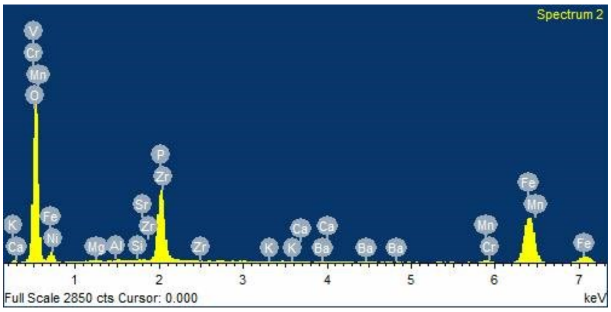

Fig. 6. EDX spectrum 2 of vivianite

Table 2

Chemistry of vivianite by SEM-EDX

Spectrum 1		Spectrum 2	
Element	Weight %	Element	Weight %
O	57.62	O	56.19
Al	0.15	Al	0.13
Si	0.07	Si	0.18
P	11.79	Mg	0.25
K	0.08	K	0.03
Ti	0.13	P	12.10
Mn	0.89	Mn	1.03
Fe	26.23	Fe	27.33
Ni	0.08	Ni	0.26
Rb	0.92	Ca	0.11
Sr	1.52	Sr	1.02
Cs	0.51	Cr	0.04
		V	0.03
		Zr	0.96
		Ba	0.34

The results for the chemistry of the examined vivianite obtained by ICP-AES and comparison with literature data by Capitelli et al. (2012) and Jovanovski et al. (2012) are given in Table 3.

From the data given in Table 3 can be concluded that the examined sample has higher content of Mn than the samples given by Capiteli et al. (2012). Also, the following trace elements were detected: Cd, Cr, Ni, Ba, Sr, Bi, Zn, Pb, Cu, Ag, Co, In, Tl, Ga and Li. (Table 4).

According to a classical geochemical procedure the formula of the examined vivianite sample was calculated as follows: $Fe_{2.93}$, $Mn_{0.14}$ $Mg_{0.001}$, $Ca_{0.001,}$ $Na_{0.001})_{3.07}$ $(PO_4)_{1.98}$ $8H_2O$.

In Figure 7 XRD patterns of the investigated vivianite are given.

The most intense registered maxima in the studied powder pattern (Table 4) were compared with the corresponding maxima of vivianite sample from PDF-2 softwer. ICDD card: 01 079 1928.

The comparison has shown that the X-ray powder pattern of the natural vivianite taken from the ICDD card are practically identical with the studied powder pattern. No impurity phases were detected.

Table 3

Comparison on chemistry of the studied vivianite obtained by ICP-AES with literature data by Capitelli et al., 2012, and Jovanovski et al., 2012

Oxides %	Examined sample	Capitelli et al.,2012			Jovanovski et al., 2012		
		Commentry, France	Settefrati-Frosinone, Italy	Ibex Mine, Colorado, USA			
	1	2.1	2.2	2.3	3.1	3.2	3.3
FeO	42.89	50.27	50.77	45.30	43.44	43.37	45.46
P_2O_5	28.67	33.74	33.22	33.58	28.84	28.08	26.48
MnO	2.50	0.19	0.60	1.07	1.77	2.64	2.24
CaO	0.01	0.01	0.04	0.05			
Al_2O_3	0.01	0.01	0.23	0.01			
MgO	0.34	0.62	0.08	0.19			
Na_2O	0.04	0.03	0.02	0.19			
K_2O	<0.10	0.03	0.04	0.02			
TiO_2	<0.02	–	–	–			

Table 4

Trace elements in examined vivianite

Elements	ppm	Elements	ppm
Cd	0.002	Ba	<0.001
Cr	0.003	Sr	<0.001
Ni	0.002	Bi	<0.023
Ag	<0.002	Zn	0.006
Co	0.010	Pb	0.003
In	<0.001	Cu	<0.001
Tl	<0.040	Li	0.019
Ga	0.023		

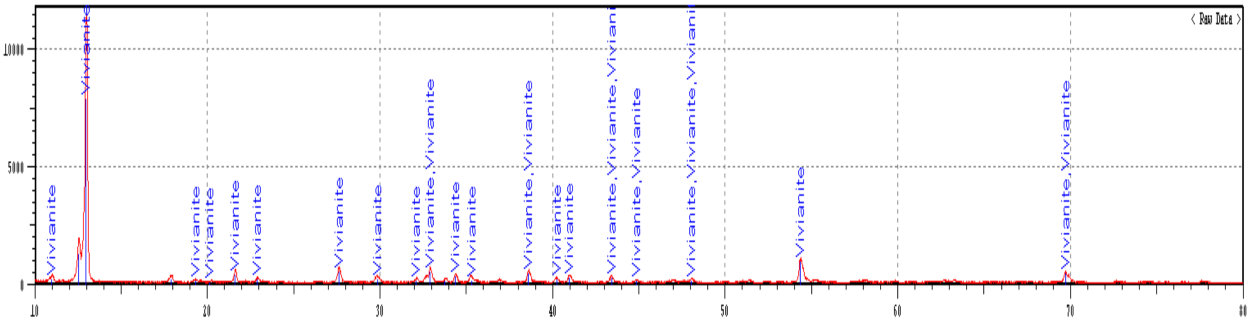

Fig. 7. XRD patterns of the investigated vivianite

Table 5

X-ray powder pattern for vivianite from Suvodol, Republic of Macedonia

2θ (obs)	2θ (calc)	d (obs)/Å	d (calc)/Å	I	hkl
10.98	11.14	8.05	7.93	2	110
12.98	13.09	6.81	6.75	100	020
19.32	19.38	4.59	4.57	1	–101
20.14	20.31	4.40	4.36	1	011
21.61	21.70	4.10	4.09	4	130
22.88	22.98	3.88	3.86	2	101
27.61	27.65	3.22	3.22	6	031
29.84	29.86	2.99	2.98	2	–301
32.10	32.17	2.78	2.78	1	240
32.90	32.73	2.71	2.73	6	–321
34.37	34.41	2.60	2.60	3	150
35.34	35.26	2.53	2.54	2	141
38.60	38.63	2.33	2.32	5	–112
40.24	40.26	2.23	2.23	2	–341
40.97	40.97	2.20	2.20	3	–251
43.42	43.42	2.08	2.08	3	350
44.88	44.88	2.01	2.02	1	251
54.35	54.35	1.68	1.68	12	080
69.70	69.70	1.34	1.34	5	143

Table 6

Comparison of unit cell data on the examined vivianite with data reported by Francesco Capitelli et al., 2012; Jovanovski et al., 2012

	Examined vivianite	F. Capitelli et al.			Jovanovski et al.
Crystal system, space group	Sample 1 Monoclinic C2/m	Sample 2.1 Monoclinic C2/m	Sample 2.2 Monoclinic C2/m	Sample 2.3 Monoclinic C2/m	Sample 3 Monoclinic C2/m
Unit cell dimension	a = 10.03 Å b = 13.50 Å c = 4.72 Å β = 102.52°	a = 10.10 Å b = 13.49 Å c = 4.71 Å β = 104.24°	a = 10.12 Å b = 13.47Å c = 4.71 Å β = 104.33°	a = 10.08 Å b = 13.46Å c = 4.72 Å β = 104.47°	a = 10.14 Å b = 13.38 Å c = 4.65 Å β = 104.52°
Volume	625.7 Å^3	622.1 Å^3	621.5 Å^3	620.3 Å^3	610.6 Å^3

CONCLUSION

Summarizing available data from this study, we concluded that the investigated sample is vivianite. Vivianite appears in the sediments of the Pelagonia basin, particularly in the tripolites of the Suvodol locality. The specimens have prismatic and tabular shape and different size on several cm across. Very often distinct cleavage planes parallel to {010} can be seen. The colour of studied vivianite is greenish blue. The streak is pale bluish but the colour is soon changing dark blue due to oxidation. The concentration of the oxides is: FeO 42.89%, P_2O_5 28.67%, MnO 2.50%, MgO 0.34%.

The most intense registered maxima in the studied powder pattern [*d* values (in Å), *I*] are: 6.81 (100); 3.22 (6); 2.71 (6); 2.33 (5); 1.68 (12); 1.34 (5). The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: a = 10.03 Å; b = 13.50 Å[c = 4.72 Å; β = 102.52°; V = 625.79 Å^3.

Investigated vivianite is diagenetic in origin. Sedimentation rates and pore-water chemistry are major factors controlling the formation of vivianites as long as P and Fe are supplied in sufficient amount. This vivianite is Mn-rich. Mn enrichment probably reflects diagenetic redistribution from precursor Fe and Mn hydroxides.

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Резиме

МИНЕРАЛОШКИ КАРАКТЕРИСТИКИ НА ВИВИЈАНИТ КОЈ СЕ ЈАВУВА ВО СЕДИМЕНТИТЕ НА ПЕЛАГОНИСКИОТ БАСЕН, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: вивијанит; инфрацрвена спектроскопија; скенирачки електронски микроскоп; атомско-емисиона спектроскопија – индуктивно спрегната плазма; рендгенска дифракција

Во овој труд се презентирани резултати за минералошка карактеризација на вивијанит кој се јавува во седиментите на Пелагонискиот Басен во Република Македонија. Испитувањата се вршени со следниве четири методи: IR – инфрацрвена спектроскопија, SEM/EDS – скенирачка електронска микроскопија, AES-ICP – атомско-емисиона спектроскопија–индуктивно спрегната плазма, XRD – рендгенска дифракција.

Вивијанитот се наоѓа во седиментите на Пелагонискиот Басен, особено во триполитите на локалитетот Суводол. Се појавува во призматични и сплеснати кристали со големина од неколку сантиметри. Јасно е видлива цепливост по {010}. Бојата е зеленикаво сина. Огребот е бледосин, но бојата бргу се менува во темносина поради оксидацијата. Концентрацијата на оксидите е: FeO 42.89%, P_2O_5 28,67%, MnO 2,50%, MgO 0,34%.

Со рендгенските испитувања се добиени следниве податоци: 6.81 (100); 3.22 (6); 2.71 (6); 2.33 (5); 1.68 (12); 1.34 (5). Пресметаните димензии на елеметарната ќелија се: a = 10.03 Å, b = 13.50 Å, c = 4.72 Å, β = 102.52°, V = 625.79 $Å^3$.

Резултатите добиени со сите четири методи дадоа јасна идентификација и потврдија дека испитуваниот примерок е вивијанит. Испитаниот вивијанит има дијагенетско потекло. Степенот на седиментација и хемизамот на порната вода се главни фактори кои го контролираат формирањето на вивијанит, сè додека P и Fe се обезбедуваат во доволна количина. Овој вивијанит е богат со Mn. Збогатувањето со Mn веројатно ја рефлектира дијагенетската редистрибуција на претходните Fe и Mn хидроксиди.