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SREBRENICA OREFIELD, PODRINJE METALLOGENIC DISTRICT, REPUBLIC OF SRPSKA, B&H: HYDRATED Fe(Al)-PHOSPHATES AND THEIR PARAGENESES WITHIN THE Pb-Zn MINERALIZATION

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ABSTRACT

The Srebrenica orefield is mostly composed of Tertiary dacite-andesites, and quartz latites, pyroclastites, Paleozoic schists, and Quaternary sediments, but in a in a lesser extent. The latest research showed that in the Srebrenica orefield occur complex mineral parageneses and associations deposited in pneumatolytic-hydrothermal and hydrothermal (from high- to low-temperature) stage, accompanied with very rare minerals. Beside ore mineral parageneses and associations, specials emphasis was on rare hydrated phosphates: vivianite, ludlamite, and vauxite. It is important to say that vauxite from the Srebrenica orefield is fourth discovery in the world. The minerals above were studied using DTA-TGA, IR-spectroscopy, and XRPD.

Key words: *vivianite, ludlamite, vauxite, mineralogy, Srebrenica orefield, Republic of Srpska*

INTRODUCTION

According to the literature of the FeO-Fe_2O_3-P_2O_5-H_2O phase system, there are over 20 well-defined hydrated phosphates of iron. It has been synthesized several analogues of the above mentioned minerals, but also tithe of new synthetic products of various stoichiometry. Beside a few reviews [1,2] published years ago, there are no new mineralogical discusses of the FeO-Fe_2O_3-P_2O_5-H_2O phase system in the available literature. The reason for lack of generally accepted crystallochemical systematization of hydrated phosphates of iron is in its divalent cation character, causing polymorphism and autoxidation, which complicate dehydration processes.

These minerals, in terms of appearance, are considered as rare. From the aspect of their genesis, these are secondary minerals in supergene zones of sulfide ore deposits, complex granite pegmatites, organic matter replacement in fossil bones, lake sediments, moorland, and rarely in caves. All this further complicates an examination of these minerals. Accordingly, occurrence and determination of hydrated Fe-phosphates from different localities is precious for their further crystallochemical classification [3,4].

Beside studied hydrated phosphates of iron from the Srebrenica locality, in the territory of B&H occurrence of veszelyte - $(Cu,Zn)_2 \cdot Zn(PO_4)_2 \cdot 2H_2O$ was determined in the Zdravo Vrelo locality nearby Kreševo [5,6,7]. The results of differential thermal and thermo gravimetric analysis (DTA-TGA), infrared (IR) spectroscopy, and X-ray powder diffraction (XRPD) of vivianite, ludlamite, and vauxite are shown in this study.

GEOLOGY AND OCCURRENCE OF HYDRATED Fe(Al)-PHOSPHATES

Podrinje Metallogenic District (PMD) covers vast area from both sides of the River Drina, where the Srebrenica dacite-andesite (Republic of Srpska) complex dominates in the west, the Boranja granodiorite and the Cer Mt. granitoid massif (Serbia) in the east side. Within the multistage post-magmatic activity, a large number of sulfide deposits of Zn, Pb, Sb, and other metals were deposited. The Srebrenica orefield (SOF) is distinguished by its size and diversity of mineral parageneses and associations [8,9]. The main feature of the SOF is its complexity, in tecto-magmatic, as well as in metallogenic point of view. The geological structure of the SOF is composed of Paleozoic schist's, Tertiary magmatites, quartz-tourmaline-mica rocks (greisen), and Quaternary sediments. There are four ore systems within the SOF: North-East (the Sase mine, etc.), North (Vitlovac, Divljakuše, Kvarac etc.), North-West (Kazani, Čumavići etc.), and Central (Olovine, Vukosavljevići etc.) [10]. In the SOF, the mineralization is entirely in a form of vein ore bodies deposited in hydrothermally altered dacites, rarely andesites, Paleozoic sediments, and andesite tuffs and pyroclastites. The largest ore vein occurs in dislocation-breccia zones, where fragments of eruptive rocks and schists occur. Mineral associations are mainly composed of sphalerite-galena-marcasite-Mn-siderite and in a lesser extent polymetallic parageneses where various Sb with Pb, Cu, Ag, Sn, and Fe sulfosalts dominate [11].

Figure 1 A vivianite crystal

Polymetallic ores characterizes very complex mineral composition. They are composed of carbonates, silicates and quartz with over 100 ore minerals, among which sulfides of Fe, Zn, and Pb prevail. Sn, Cu, and W minerals are less abundant, but in some parts of ore veins they occur as main minerals. The main characteristic throughout the SOF is occurrence of a significant number of hydrated phosphate minerals (vivianite, ludlamite, vauxite) [12].

Vivianite ($Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$), and ludlamite ($(Fe^{2+},Mg,Mn)_3 (PO_4)_2 \cdot 4H_2O$) studied in this paper, were found together in the mineral paragenesis with Mn-siderite as matrix. The samples, taken from the Sase mine (ore vein N^o-2A), filled cracks and fissures of dacite-andesite rocks (the North-East ore system). Both minerals were determined optically by Barić [13], as well as by Dimitrijević and Đorđević [12]. The vivianite crystal in analyzed druse reaches a size of up to 4 cm (Fig. 1), and sporadically there are small crystals up to 1 mm. The vivianite color is dark-blue with glassy luster. Ludlamite occurs in small poorly developed prismatic crystals up to 3 mm. They are translucent with glassy to pearly luster. Its color is characteristic pale-green. When grinding, both minerals show perfect cleavage. Color of powdered minerals is pale-blue (vivianite), and light-grey (ludlamite).

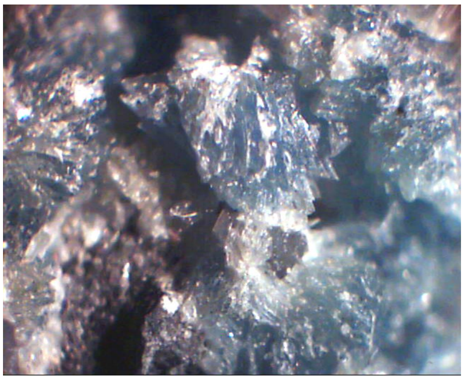

Figure 2 Crystal druse of vauxite

Vauxite ($Fe^{2+}Al_2(PO_4)_2(OH)_2 \cdot 6H_2O$) was first discovered in Vitlovac locality in the mineral paragenesis with quartz, sphalerite, and marcasite. It is important to emphasis that this is its fourth occurrence in the world [14]. The samples, taken from the gallery 24/3 (ore vein N^{o}-24), occur in a form of fine radial rosette as the youngest mineral (Fig. 2). Crystal size is up to a few mm. The vauxite color is sky-blue with high glassy luster. When grinding, it shows perfect cleavage. Color of powdered vauxite is pale-blue.

EXPERIMENTAL

All experimental investigations were done on samples which were carefully studied and singled out under the stereo microscope. After that, the minerals were powdered in agate mortar. The XRPD analyses confirmed high purity of monomineral concentrations of all three minerals. Thermal examinations (DTA and TGA) were obtained using Universal TA Instruments, model 2960 SDT V3.0F. Heating was at a rate of v = 10 ^{o}/min^{-1} in an inert atmosphere of nitrogen or in air.

The IR investigations were performed by Perkin-Elmer instrument; model 983G in the range from 4000-250 cm^{-1} wherein the KBr pellet technique was used.

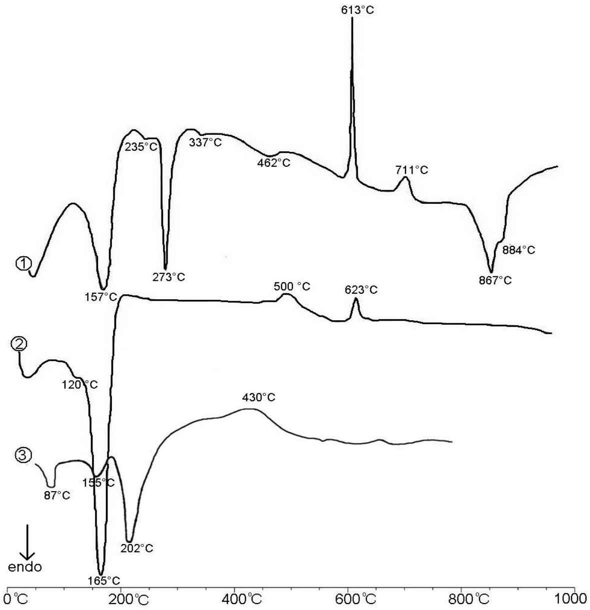

Figure 3 DTA diagrams: 1) vivianite; 2) ludlamite; 3) vauxite

The XRD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The divergence and receiving slits were fixed 1 and 0.1, respectively. All the XRD measurements were performed at room temperature in a stationary sample holder. The LSUCRIPC program was used for the refinement of the cell dimensions from the powder data [15].

THERMAL STUDIES OF HYDRATED PHOSPHATES

The DTA curve of vivianite in temperature range up to 500 ^{o}C characterizes several endothermic peaks (strong at 157 and 273, and weak at 235, 337, and 462 ^{o}C, Fig. 3-1). The overall loss of weight in the temperature range up to 500 ^{o}C amounts to 16.3 %, and corresponds to the dehydration of vivianite [16, 17, 18]. Further increase of temperature up to 1000 ^{o}C characterizes a strong exothermic peak at 613, and weak at 623 ^{o}C, and two strong endothermic peaks followed by additional loss of weight of 4.6 %. According to the literature data, after the dehydration of vivianite at around 300 ^{o}C the crystal structure collapses, and after recrystallization of amorphous matter at 613 ^{o}C into orthophosphate of iron (nitrogen atmosphere).

DTA curve of ludlamite characterizes a weak endothermic peak at 120 and a strong peak at 165 ^{o}C, corresponding to the dehydration process (Fig. 3, 2). The overall loss of weight up to 200 ^{o}C amounts to 16,5 %, which is in a good agreement literature data [16,17]. Further increase of temperature up to 1000 ^{o}C characterizes weak peaks at 500 and 623 ^{o}C and additional loss of weight of 8.3 %. According to the literature data, after dehydration of ludlamite at 250 ^{o}C the crystal structure collapses and after that recrystallization into orthophosphate (nitrogen atmosphere). Processes of structure transformation in examined temperature range are very complex [19].

DTA curve of vauxite characterizes weak endothermic peaks at 87 and 155 °C; and a strong peak at 202 °C, corresponding to the dehydration process (Fig. 3-3). The overall loss of weight up to 250 °C amounts to 29.05 %, which is in a good agreement literature data [17]. Further increase of temperature up to 800 °C characterizes the oxidation of Fe^{2+}, when the sample becomes red (air atmosphere).

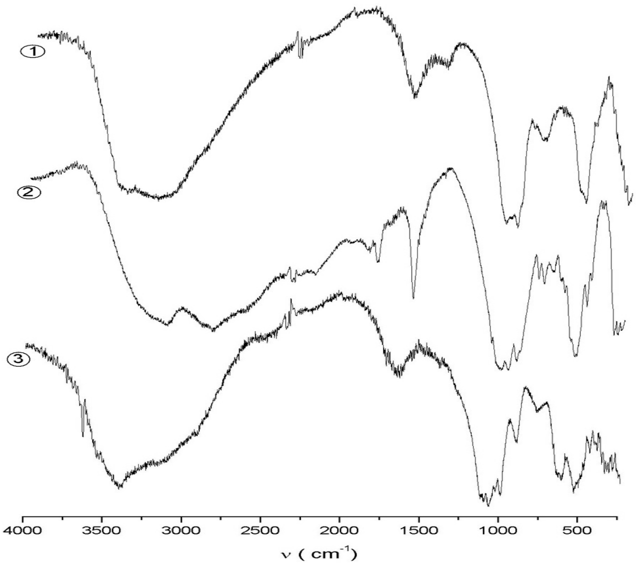

Figure 4 IR spectra: 1) vivianite; 2) ludlamite; 3) vauxite

IR SPECTROMETRY OF HYDRATED PHOSPHATES

The IR spectra of vivianite, ludlamite, vauxite are shown in Fig. 4. The vivianite spectrum vibration bands are as follows: 3241, 1627, 1411, 1046, 873, 784, and 542 cm^{-1}. The ludlamite spectrum vibration bands are as follows: 3136, 2841, 2334, 1860, 1814, 1587, 1033, 988, 936, 794, 760, 702, 565, and 490 cm^{-1}. 3136, 2841, 2334, 1860, 1814, 1587, 1033, 988, 936, 794, 760, 702, 565, and 490 cm^{-1}. The vauxite spectrum, obtained under the same experimental conditions, vibration bands are as follows: 3400, 1630, 1130, 1110, 1080, 1030, 1010, 770, 650, 620, 540, 515, 480, and 440 cm^{-1}. Comparison of these spectra with literature data showed excellent agreement [17].

XRPD OF HYDRATED PHOSPHATES

The unit-cell parameters of all three minerals were obtained by LSUCRIPC software using least square method [15]. This way all diffraction maximums of vivianite, ludlamite, and vauxite were indexed. The calculated unit-cell parameters along with literature data are presented in the Table 1. Vivianite and ludlamite were calculated in monoclinic system (space group $I2/m$ (12) for vivianite, and $P2_1/a$ (14) for ludlamite) [17], while vauxite was calculated in triclinic system (space group $P\bar{1}$(2)) (Table 1) [17,20,21].

Table 1 The calculated unit-cell parameters of vivianite, ludlamite and vauxite.

mineral	*a (Å)*	*b (Å)*	*c (Å)*	$\alpha^{(o)}$	$\beta^{(o)}$	$\gamma^{(o)}$	Literature
vivianite	10.016(5)	13.433(4)	4.704(2)	-	102.69°(4)	-	This study
	10.034- 10.086	13.434- 10.441	4.687- 4.714	-	102.65- 104.27°	-	[17]
ludlamite	10.545(3)	4.642(1)	9.308(2)	-	102.69°(3)	-	This study
	10.541(5)	4.646(4)	9.324(5)	-	100.25°(1)	-	[17]
vauxite	9.141(4)	11.578(2)	6.143(2)	98.22°(2)	92.01°(2)	108.19°(2)	This study
	9.142(3)	11.599(3)	6.158(2)	98.29°(2)	91.93°(3)	108.27°(3)	[17]

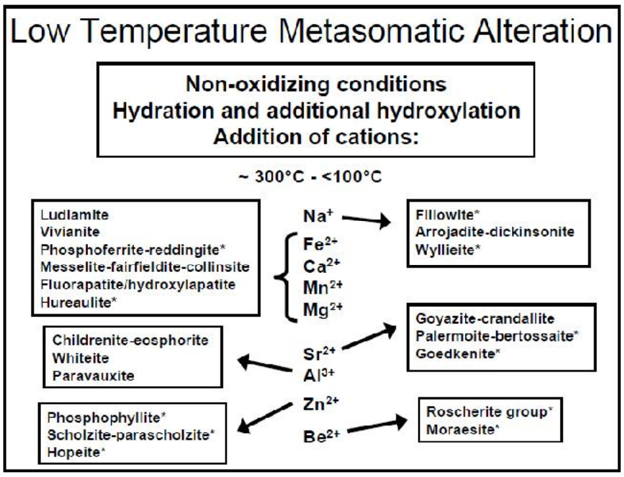

Figure 5 Scheme of the low-temperature phosphate formation in reducing conditions [22].

DISCUSSION

Some 200 mineral species of secondary phosphates, that crystallizes in metasomatic transformation processes of primary phosphates from different magmatic rocks (pegmatites, greisens, etc.) by ascendant and descendant hydrothermal solutions. This alternating process happens in the temperature range from 500 to ~ <100 °C under different oxidation and reduction conditions [22]. Moore [4] divided this metasomatic process into two phases: high-temperature (~ 500-300 ºC), and low-temperature metasomatic changes (~ 300-100 ºC). The 300 ºC boundary is proximally to the approximate temperature of ~250 ºC, when crystal structure can adopt linked water molecules in a stable structured packing [4]. Fransolet et al. [23] suggested that secondary phosphates can crystallize in room temperature conditions in internal/surface environments, and that phenomenon should not be ignored.

The schematic metasomatic alteration of pegmatite, which can be applied in the conditions of secondary alterations of mineralized dacite-andesite rocks from the SOF, is shown in Fig. 5. This may explain the origin of PO_4 anions, most probably formed in alterations of magmatic rocks and greisens (silification, kaolinization, etc.), containing primary phosphates (apatite, monazite-(Ce), xenotime, etc.). Post-ore hydrothermal solutions reacted with already formed ore parageneses, mainly with Mn-siderite. As a result vivianite-ludlamite druses crystallized in reduction conditions along cracks or caverns of degraded carbonates. In a similar manner may be explained the crystallization of vauxite from solutions containing Al^{3+} cations.

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