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Clinobisvanite and bismutoferrite from the village of Boyadzhik area, Yambol Region – new minerals for Bulgaria

Клинобисванит и бисмутоферит от района на с. Бояджик, област Ямбол – нови минерали за България

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Clinobisvanite, $Bi(VO_4)$, and bismutoferrite, $Fe^{3+}{}_2Bi(SiO_4)_2(OH)$, have never been described in Bulgaria. In fact the present report is the first description of a vanadate mineral from the country, although vanadinite from river sands was mentioned by Vitov and Sotirov (2014), but without providing any analytical data.

The examined samples were collected in 2018 during a field trip in the area of St. Iliya Heights, Yambol Province, SE Bulgaria, from a man-made pile of stones between the villages of Zlatari and Boyadzhik. According to Chatalov (1987), there is a small body of Srednogorie pluton with a predominant quartz diorite composition in the area. It is embedded in Triassic marble limestones and dolomites, and Paleozoic tufts. A zone of hornfelses and skarns of about 150 m width is formed in the western contact of the body with the host rocks. A small Fe-Cu occurrence has been discovered in the NE part of the area.

The collected skarn samples consist of andradite, diopside, calcite, and fluorapatite, as main minerals. Thin veins (about 2.5 cm wide) are observed within the metasomatic rock. They are filled by supergene minerals such as malachite and azurite with rims composed of quartz, and secondary iron oxides and hydroxides. These veins are subject of this research as they include three Bi-bearing minerals: clinobisvanite, bismutoferrite and bismutite $(BiO)_2CO_3$.

Chemical compositions of the studied minerals were obtained using scanning electron microscope Phenom XL (SEM-EDS) (Faculty of Earth Sciences, University of Silesia, Poland) and microprobe analyzer CAMECA SX100 (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, Poland). Electron probe microanalyses were performed at 15 keV, 20 nA and 1 µm beam diameter. The following lines and standards were used: Ca*Kα*, diopside; Cu*Kα*, cuprite; Bi*Mα*, Bi_2Te_3; V*Kα*, V_2O_5; Fe*Kα*, Fe_2O_3. The Raman spectra were recorded on a WITec confocal Raman microscope CRM alpha 300 in the 200–4000 cm^{-1} range at 10mW on the sample and 3 cm^{-1} spectral resolution (Institute of Physics, University of Silesia, Poland).

Clinobisvanite is a rare Bi vanadate, monoclinic polymorph of $BiVO_4$ (Bridge, Pryce, 1974). The other two polymorphs are pucherite (orthorhombic) and dreyerite (tetragonal). Due to the same chemical composition, a reliable recognition between these three minerals was done by using Raman spectroscopy. The Raman spectrum of the examined $Bi(VO_4)$ polymorph is characterized by one intense band at 825 cm^{-1} related to VO_4^{3-} group symmetric stretching vibrations and several low-intense bands below 500 cm^{-1} corresponding to VO_4^{3-} bending modes (Fig. 1C). Such bands arrangement corresponds to the clinobisvanite spectrum (Frost et al., 2006). The chemical composition of clinobisvanite from Boyadzhik (mean of 9) is: Bi_2O_3 68.41, V_2O_5 28.52, Fe_2O_3 0.46, CaO 0.43, CuO 0.66, total 98.48 wt%. The presence of Fe in the chemical composition can be related to the $Bi^{3+} \rightarrow Fe^{3+}$ substitution, while Ca and Cu can come from associated phases due to relatively small size of the analyzed

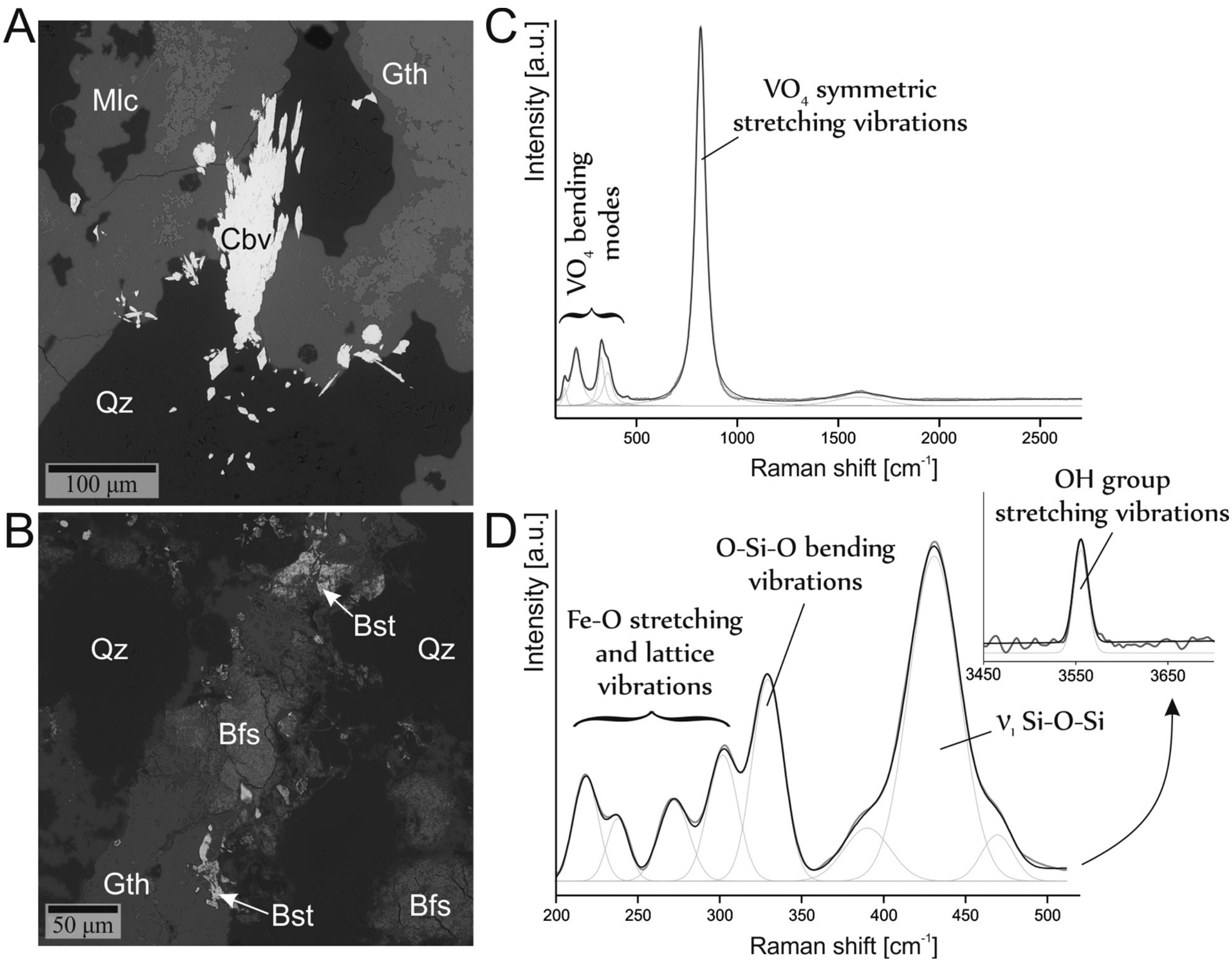

Fig. 1. *A*, BSE image of clinobisvanite in association with malachite, quartz and goethite; *B*, BSE image of bismutoferrite and bismutite in association with quartz and goethite; *C*, Raman spectrum of clinobisvanite; *D*, Raman spectrum of bismutoferrite (ranges 200–500 and 3450–3650 cm^{-1}). *Abbreviations*: *Bfs*, bismutoferrite; *Bst*, bismutite; *Cbv*, clinobisvanite; *Gth*, goethite; *Mlc*, malachite; *Qz*, quartz.

crystals. The clinobisvanite forms bright-yellow needle-like crystals, usually no more than 40 µm in length. An aggregate of clinobisvanite up to 200 µm in size formed at the border of the malachite-azurite vein is shown in Fig. 1A.

Bismutoferrite was described for the first time by Frenzel (1871) under the name "hypochlorite" because of its yellow-green color. It is a common component of the so-called bismuth ochres. Bismutoferrite from the Boyadzhik area forms irregular aggregates up to 200 µm in diameter, composed of very small (up to 2–3 µm in size) solitary grains (Fig. 1B). Good quality microprobe analysis was not possible due to the very small size of individual grains. Bismutoferrite was identified by SEM-EDS analyses and Raman spectroscopy (Fig. 1C). The main bands in the Raman spectrum of bismutoferrite are in the 200–500 cm^{-1} range and correspond to Si-O-Si, O-Si-O and Fe-O vibrations (Fig. 1D). A single band at 3557 cm^{-1} corresponds to stretching vibrations of OH group. The obtained Raman spectra of bismutoferrite are in good agreement with the literature data (Frost et al., 2009).

A third Bi-bearing mineral – bismutite occurs together with clinobisvanite and bismutoferrite. Kirjazova (1961) described this mineral from several placers in SW Bulgaria. In our samples it occurs as aggregates similar to those of bismutoferrite (Fig. 1B) and small inclusions (2–3 µm) in clinobisvanite crystals. The bismutite was confirmed by Raman spectroscopy. Its main band in the Raman spectrum is related to symmetric stretching vibrations of CO_3 group.

We consider that bismutoferrite and bismutite from the village of Boyadzhik area have been formed as secondary minerals during the weathering of primary bismuth minerals, most likely bismuthinite. Orthorhombic pucherite changes into the monoclinic clinobisvanite at temperatures higher than 500 °C (Frost et al., 2006). The latter has been described in association with pucherite formed during the final hydrothermal stages of pegmatites (Sustavov, Fedorov, 2015). Collier and Plimer (2002) published data about supergene clinobisvanite from Lively's gold mine, South Australia. Clinobisvanite from the village of Boyadzhik area associates with copper and Bi secondary minerals hosted in skarns. We believe that our clinobisvanite find is also supergene in origin.

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References

Bridge, P. J., M. W. Pryce. 1974. Clinobisvanite, monoclinic $BiVO_4$, a new mineral from Yinnietharra, Western Australia. – *Mineral. Mag.*, *39*, 847–849.

Chatalov, G. 1987. *Geological Map of the St. Iliya Heights in Scale 1:25000, Prochorovo Deposit.* – In: *Report on the Results of Geological Surveys of Copper Deposit Prochorovo for the Period 1959–1989 with a Calculation of Reserves as on 15.01.1988*). Sofia, National Geological Found, Ministry of Energetic (in Bulgarian).

Collier, I. R., J. B, Plimer. 2002. Supergene clinobisvanite pseudomorphs after supergene dreyerite from Lively's Mine, Arkaroola, South Australia. – *N. Jahrb. Mineral., Monat.*, 9, 401–410.

Frenzel, A. 1871. Mineralogisches. 3. Hypochlorit. – *J. für praktische Chemie*, *4*, 355–361 (in German).

Frost, R. L., D. A Henry, M. L. Weier, Matt, W. Martens. 2006. Raman spectroscopy of three polymorphs of $BiVO_4$: clinobisvanite, dreyerite and pucherite, with comparisons to $(VO_4)_3$-bearing minerals: namibite, pottsite and schumacherite. – *J. Raman Spectroscopy*, *37*, 722–732.

Frost, R. L., S. Bahfenne, J. Čejka, J. Sejkora, J. Plášil, S. J. Palmer. 2009. Raman and infrared study of phyllosilicates containing heavy metals (Sb, Bi): bismutoferrite and chapmanite. – *J. Raman Spectroscopy*, *41*, 814–819.

Kirjazova, L. 1961. Bismutite from some localities in Bulgaria. – *Rev. Bulg. Geol. Soc.*, *22*, 3, 292–295 (in Bulgarian with German abstract).

Sustavov, S. G., S. A. Fedorov. 2015. Bismuth vanadates from rare metal pegmatites from Svetlinskoe locality, South Ural. – *Metallogeny of Ancient and Modern Oceans*, *21*. Institute of Mineralogy, RAS. Miass*, Russia*, 211–214 (in Russian).

Vitov, O., A. Sotirov. 2014. Mineral content of the river sands in Kyustendil region with ecological risks for the quality of soils, water and building materials. – *Ecological Engineering and Environment Protection*, *3–4*, 86–93 (in Bulgarian with English abstract).