

Slavikite—Revision of chemical composition and crystal structure

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ABSTRACT

Given its abundant occurrence at Wieściszowice, SW Poland, we have carried out a revision of the chemical composition and crystal structure of the sulfate mineral slavikite. Slavikite crystallizes in the trigonal space group $R\bar{3}$. The unit-cell parameters, determined using single-crystal X-ray diffraction ($R_1 = 0.0356$) at 100 K, are $a = 12.1347(6)$ Å, $c = 34.706(3)$ Å, and $V = 4425.9(5)$ Å³. The results of chemical analyses reported in the literature and made on material from Wieściszowice unequivocally show that Na is not an essential component of slavikite, at odds with the generally accepted Süsse formula and model of the crystal structure. Our chemical analyses and structure determination lead us to propose a new, more adequate, formula for slavikite: $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$. The crystal structure consists of infinite layers of Fe-hydroxy-sulfate linked with $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra, forming a honeycomb-like structure. These layers are perpendicular to the Z axis and are built up from two types of SO_4^{2-} tetrahedra and two types of Fe octahedra (Fe1 with O and OH, and Fe2 with O, OH, and H_2O ligands attached, respectively).

Compared to previous studies, the main skeleton of the slavikite structure, i.e., the layers of Fe^{3+} -hydroxy-sulfate, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra and disordered isolated sulfate ions, remains unchanged. However, on the basis of careful chemical analysis and single-crystal X-ray diffraction studies, we conclude that Na cations are absent from the structure of slavikite and their positions are occupied by disordered protonated water clusters balancing the excess of negative charge in the structure. These protonated water clusters are located at the inversion centers on the $\bar{3}$ axes of symmetry between two $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations also lying on such axes (but not at the inversion centers). This structure also contains another disordered moiety—an isolated sulfate anion located at the inversion center of the $\bar{3}$ axis. This SO_4^{2-} anion is disordered in such a way that each oxygen atom partially occupies 5 positions resulting from 5 different orientations of the anion. This complex anion is linked by hydrogen bonds with the O atoms of ordered water molecules. In consequence, the disordered sulfate anion is surrounded by 12 ordered water molecules, thus forming a spherical water environment around the sulfate.

Keywords: Slavikite, weathering sulfate, chemical composition, crystal structure