THE CRYSTAL STRUCTURE OF A NEW SECONDARY ZINC MINERAL FROM LAVRION, GREECE: $Zn_9(SO_4)_2(OH)_{12}Cl_2 \cdot 6H_2O$

Kolitsch, U.[1,2] & Giester, G.[2]

[1]Mineralogisch-Petrographische Abt., Naturhistorisches Museum, Burgring 7, A-1010 Wien, Austria
[2]Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstraße 14, A-1090 Wien, Austria
e-mail: uwe.kolitsch@nhm-wien.ac.at

During a long-term study of new finds, mineral species and slag phases from the famous Pb-Zn-Ag-Fe mining district of Lavrion, Greece (KOLITSCH et al., to be submitted), a new secondary Zn mineral was encountered on material collected underground in the Hilarion mine. The mineral forms tiny, thin hexagonal platelets with a white colour and a slightly pearly lustre. These platy crystals show subparallel intergrowth and form thin crusts associated with a presently unidentified Zn-sulphate hydrate.

The crystal structure was solved from single-crystal X-ray intensity data (CCD area detector; T = 293 K) and refined in space group $R\bar{3}$ [a = 8.275(1), c = 32.000(6) Å, V = 1897.7(5) Å^3, Z = 3] to $R1(F)$ = 3.87 % and $wR2_{all}$ = 9.31 % for 1694 'observed' reflections with $F_o > 4\ \sigma(F_o)$; number of parameters: 77. The derived formula is $Zn_9(SO_4)_2(OH)_{12}Cl_2 \cdot 6H_2O$. The presence of Zn, S, Cl and O was confirmed by semiquantitative SEM-EDS analyses (JEOL JSM-6610LV).

The asymmetric unit contains three unique Zn positions. The first one is (5+1)-coordinated by OH^- anions [Zn1-O distances range from 2.025(2) to 2.347(2) Å]. The second one, Zn2, is octahedrally coordinated by H_2O molecules [6x 2.130(3) Å]. The third one, Zn3, is tetrahedrally (3+1) coordinated by three OH^- groups and one Cl^- anion. The $Zn1(OH)_6$ polyhedra share edges to form a brucite-like sheet, with 1/7 of the octahedral sites vacant. The $Zn3(OH)_3Cl$ tetrahedra are attached to the brucite-like sheet above and below the vacant site. The SO_4 tetrahedron is linked to the tetrahedral-octahedral sheet by a shared ligand. The $Zn2(H_2O)_6$ octahedra are located in the interlayer space. Thus, the structural formula may be written as $^{[6]}Zn2(H_2O)_6{}^{[5+1]}Zn1_6(OH)_6[^{[3+1]}Zn3(OH)_3Cl]_2(SO_4)_2$.

If the simplified formula of the new mineral is halved, giving $Zn_{4.5}(SO_4)(OH)_6Cl \cdot 3H_2O$, the close relation with gordaite, $NaZn_4(SO_4)(OH)_6Cl \cdot 6H_2O$ (ADIWIDJAJA et al., 1997; ZHU et al., 1997), and the secondary slag phase $Ca_{0.5}Zn_4(SO_4)(OH)_6Cl \cdot 4.5H_2O$ (BURNS et al., 1998) becomes obvious. In fact, all three compounds share the same brucite-like octahedral sheet with attached $Zn(OH)_3Cl$ tetrahedra, only the interlayer cation is different (Zn^{2+} vs. Na^+ and Ca^{2+}, respectively). Furthermore, the new mineral contains less interlayer H_2O than the two related compounds.

ADIWIDJAJA, G., FRIESE, K., KLASKA, K.-H., SCHLÜTER, J. (1997): Z. Kristallogr., 212, 704-707.
BURNS, P.C., ROBERTS, A.C., NIKISCHER, A.J. (1998): Eur. J. Mineral., 10, 923-930.
ZHU, L., SEFF, K., WITZKE, T., NASDALA, L. (1997): J. Chem. Crystallogr., 27, 325-329.