The crystal structure of Ca[Zn$_8$(SO$_4$)$_2$(OH)$_{12}$Cl$_2$](H$_2$O)$_9$, a new phase from slag dumps at Val Varenna, Italy

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Abstract: The new phase Ca[Zn$_8$(SO$_4$)$_2$(OH)$_{12}$Cl$_2$](H$_2$O)$_9$ has been discovered on a specimen from slag dumps at Val Varenna, Italy. The crystal structure, rhombohedral, $a = 8.3797(4)$, $c = 68.123(5)$ Å, $V = 4142.7(9)$ Å$^3$, space group $R_3c$, $Z = 6$, has been determined and refined to an agreement index ($R$) of 4.9% and a goodness-of-fit ($S$) of 1.11 for 713 unique observed [HFl $24oF$] reflections collected using graphite-monochromated MoKα X-radiation and a CCD area detector. The structure contains two unique Zn positions; one is octahedrally coordinated by five OH$^-$ groups and one O$_2^-$ anion, and the other is tetrahedrally coordinated by three OH$^-$ groups and one Cl$^-$ anion. The Zn$_1$<1>6 (<I>: unspecified ligand) octahedra share edges to form brucite-type sheets with one-seventh of the octahedral sites vacant. The Zn$_2$<1>4 tetrahedra are attached to the sheet of octahedra above and below the vacant site by sharing three anions with the Zn$_1$<1>6 octahedra. The single unique S position is tetrahedrally coordinated by four O$_2^-$ anions, and is linked to the tetrahedral-octahedral sheet by a single shared ligand. The structure contains one unique Ca position that is coordinated by nine H$_2$O groups; it is located in an interlayer position. A network of H bonds provide additional connectivity within the tetrahedral-octahedral sheet, as well as the only linkages between the tetrahedral-octahedral sheets and the interlayer Ca<9> polyhedron. The structure is closely related to that of gordaite, NaZn$_4$(SO$_4$)(OH)$_6$·6H$_2$O.

Key-words: Ca[Zn$_8$(SO$_4$)$_2$(OH)$_{12}$Cl$_2$](H$_2$O)$_9$, new phase, crystal structure, Val Varenna, Italy.

Introduction

A mineralogically diverse assemblage of halides, oxides, carbonates, sulphates and arsenates was recently discovered at Val Varenna, Italy (Palenzona et al., 1996). Major flooding in late 1993 exposed slag dumps from Etruscan-aged smelting operations; the manufacture of copper pottery and bronze/brass fittings for boats were primary industries within this valley during ancient times.

Over the past few years, several Italian mineral species collectors, notably Marco Ciriotti and Roberto Allori, have sent one of us (A.J.N.) numerous micromounts of the various minerals found at this locality. SEM EDS examination of one such micromount led to the discovery of a Zn-S-O-Cl-Ca phase that appeared to be new to science; subsequent X-ray powder-diffraction, precession single-crystal and crystal structure studies have confirmed this hypothesis. Here we report the crystal structure of this phase which has the ideal formula Ca[Zn$_8$(SO$_4$)$_2$(OH)$_{12}$Cl$_2$](H$_2$O)$_9$.

Under other circumstances, the mineralogical data (including a synopsis of the structure) would have been submitted to the New Minerals and Mineral Names Commission, I.M.A. for a formal vote. Unfortunately, because of its dubious “parentage” i.e. formation on a man-produced slag, the phase falls under the category of “geologically modified anthropogenic substances” (Nickel, 1995) and, as such, cannot hold mineral species status. We have, however, decided to publish the structural details, and note that the compound may yet be found in a more favourable geological environment.