A new type of cubic-stacked layer structure in anthoinite, AlWO$_3$(OH)$_3$

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ABSTRACT

Anthoinite, AlWO$_3$(OH)$_3$, from the Mt. Misobo Mine, Democratic Republic of the Congo, has triclinic symmetry with cell parameters $a = 8.196(1)$ Å, $b = 9.187(1)$ Å, $c = 11.316(1)$ Å, $\alpha = 92.82(1)^\circ$, $\beta = 94.08(1)^\circ$, $\gamma = 90.23(1)^\circ$, space group $\overline{I}1\overline{1}$, $Z = 8$. The structure was solved by applying ab initio structure solution methods (Reverse Monte Carlo/Simulated Annealing) to both X-ray and neutron powder diffraction data and was refined using the Rietveld method. The structure is built up of two types of M$_4$(O,OH)$_n$ planar tetrameric clusters of edge-sharing octahedra, one containing predominantly Al and the other predominantly W. The Al-rich and W-rich clusters interconnect via corner sharing to form stepped layers parallel to (001). The layers are held together by strong hydrogen bonding. The structure can be described as a rocksalt derivative structure, with the close-packed anion layers parallel to (012), and with Al and W atoms ordered into one third of the octahedral sites within the cubic close-packed anion lattice. The structure is complicated by partial disorder between Al and W in the tetrameric clusters and associated disorder in the H atom sites. Infrared and $^{27}$Al MAS NMR results are also presented for anthoinite.

Keywords: Structure of anthoinite, ab initio structure determination, new layer structure in AlWO$_3$(OH)$_3$, layer structure of anthoinite

INTRODUCTION

Varlamoff (1947) first described anthoinite from the Mt. Misobo tungsten mine, Democratic Republic of the Congo, where it forms microcrystalline masses, often pseudomorphed after scheelite. His chemical analyses conformed to the composition Al$_2$O$_2$WO$_3$·3H$_2$O. The first crystallographic studies on anthoinite were made by Niggli and Jager (1957). They reported the powder X-ray diffraction (XRD) pattern, and gave electron microscopy results, which showed that the crystals are generally submicrometer in size and have a platy habit. They determined the basal plane cell parameters from electron diffraction patterns of the oriented platelets ($a = 9.33$ Å, $b = 8.17$ Å) and proposed that the symmetry was monoclinic or triclinic. Sahama et al. (1970) studied samples of anthoinite from Uganda and Rwanda and confirmed the electron diffraction results of Niggli and Jager (1957). They used the preferred-orientation enhancement of basal plane reflections to determine the third crystal axis and indexed the powder pattern with a triclinic cell. From thermogravimetric analysis, they determined that the water was lost in the relatively high temperature range 400 to 545 °C, leading them to give the formula for anthoinite as AlWO$_3$(OH)$_3$. Sahama et al. (1970) commented that the pronounced cleavage exhibited by the mineral suggested a sheet structure. Sahama (1981) subsequently re-indexed the powder pattern and he gave the unit-cell dimensions of the new triclinic cell as $a = 9.21$ Å, $b = 11.36$ Å, $c = 8.26$ Å, $\alpha = 94.75^\circ$, $\beta = 90.0^\circ$, and $\gamma = 92.58^\circ$.

The first occurrence of anthoinite outside Africa was reported by Matsubara et al. (1984). They identified anthoinite pseudomorphed after scheelite in the Kara tin/tungsten mine in northwest Tasmania. The anthoinite was intimately associated with mporoito, AlWO$_3$(OH)$_3$·nH$_2$O, $n = 1–2$ (Von Knorring et al. 1972). Mporoito has a powder pattern that is closely related to that for anthoinite, and it is considered to be a hydrated form of anthoinite.

It was not until 34 years after the discovery of anthoinite that consistent indexing of the powder pattern was obtained, and a further 28 years have lapsed without further reported advances on the crystal chemistry of the mineral. The low symmetry, relatively large cell volume, lack of single crystals, and combination of light (H, O) and heavy (W) atoms, all conspire to make the structure analysis difficult. In this study, we have used powder diffraction ab initio structure solution methods, applied to both X-ray and neutron diffraction data for anthoinite, to solve the structure. We report here the results of the structure analysis, together with thermal analyses, $^{27}$Al MAS NMR, and infrared spectroscopy data for the mineral.

EXPERIMENTAL METHODS

A white, microcrystalline sample of anthoinite from the Mt. Misobo Mine, Kalima mining district, Maniema Province, Democratic Republic of the Congo, was used for the study. Chemical analyses of this material were reported by Varlamoff (1947). Thermogravimetric analyses (TGA) were conducted in the temperature range 24–1000 °C using a Setaram Simultaneous TGA/DTA instrument model 92. The evolved gases were analyzed using a Balzers Thermostar QS422 mass spectrometer (MS). The sample mass of ~50 mg was contained in a platinum crucible.