The atomic structure of deuterated boyleite ZnSO$_4$.4D$_2$O, ilesite MnSO$_4$.4D$_2$O, and bianchite ZnSO$_4$.6D$_2$O

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Abstract

Deuterated boyleite ZnSO$_4$.4D$_2$O, was synthesized and the atomic structure, including D positions, was successfully refined in a combined histogram neutron diffraction refinement. The cell dimensions for boyleite are $a = 5.9144(2)$, $b = 13.5665(4)$, $c = 7.8924(2)$ Å, and $\beta = 90.668(2)^\circ$ with space group $P2_1/n$ and $Z = 4$. The atomic structure including D positions of the isostructural mineral ilesite, MnSO$_4$.4D$_2$O, was refined and the cell dimensions are $a = 5.9753(1)$, $b = 13.8186(3)$, $c = 8.0461(1)$ Å, and $\beta = 90.826(2)^\circ$. Deuterated ilesite MnSO$_4$.6D$_2$O was synthesized and the atomic structure, including D positions, was successfully refined with a unit cell of $a = 9.969(1)$, $b = 7.2441(7)$, $c = 24.249(3)$ Å, and $\beta = 98.488(5)^\circ$ in space group $C2/c$ and $Z = 8$. A comparison of the hydrogen bonding in MnSO$_4$.4D$_2$O with that in MnSO$_4$.6D$_2$O shows that bifurcated hydrogen bonds are common in the tetrahedryl sulfates but nonexistent in the hexahydrate structures. This is a result of the packing constraints of the rings of the sulfate and metal-containing octahedra in the tetrahydrates. In the hexahydrate sulfates there is no direct linkage between the sulfate and metal-containing octahedra and hydrogen bonds are optimized without packing constraints, and no bifurcated hydrogen bonds are observed.

Keywords: Bianchite, boyleite, ilesite, hexahydrate, moorhouseite, Ni-hexahydrate, rozenite, crystal-structure refinement, neutron diffraction, hydrogen bonding

Introduction

The minerals boyleite, ZnSO$_4$.4H$_2$O, and ilesite, MnSO$_4$.4H$_2$O, are members of the rozenite group (M$^{2+}$SO$_4$.4H$_2$O; M$^{2+}$ = Fe, Mg, Mn, Co, Zn) $P2_1/n$ (Table 1) (Gaines et al. 1997). All rozenite group minerals structures are composed of isolated [M$^{2+}$(SO$_4$)$_4$]$^{2-}$/8H$_2$O ring-shaped structural units (Fig. 1), linked to each other by a three-dimensional network of H-bonds.

Boyleite was first described by Walenta (1978) as a product of sphalerite decomposition in the presence of gypsum. The type specimen of boyleite has a chemical composition of (Zn$_{6.34}$Mg$_{0.16}$)SO$_4$.4H$_2$O and was found as white, earthy, reniform masses at the Kropback quarry, southern Black Forest, Germany (Walenta 1978). More recently described occurrences of boyleite include the Kropback quarry, southern Black Forest, Germany (Walenta 1999), and Valais, Switzerland (Perroud et al. 2000). The presence of boyleite is dependent on the dehydration rate; therefore, boyleite may be present in many localities where goslarite ZnSO$_4$.7H$_2$O, bianchite ZnSO$_4$.6H$_2$O, and gunningite ZnSO$_4$.H$_2$O are found. Notable hydrous Zn-sulfate mineral localities include the type locality of gunningite, Keno Hill-Galen Hill area, Yukon, (Jambor and Boyle 1962) and the Geul Valley goslarite locality near Moresnet, Belgium (Schuiling 1992). Ilesite was first described in 1881 by Iles as an alteration product of sulfide veins at the head of the Hall Valley, Park County, Colorado. The optical properties of synthetic material were described by Larsen and Glenn (1920).

The atomic structure of boyleite was determined by X-ray diffraction analysis of a single crystal produced as an unexpected by-product of another experiment (Blake et al. 2001, annotated by Baur 2002). The use of X-rays to determine H-positions, whose bond lengths were then restrained, and the hydration/dehydration of the sample during data collection, which was partially corrected with a linear isotropic crystal decay correction factor, contributed to the compromised quality of the boyleite data set (Blake et al. 2001). Baur (2002) predicted that the structure of ilesite is very similar to that of rozenite and the atomic structure and approximate hydrogen positions of ilesite were confirmed by Held and Bohaty (2002) through the least-squares refinement of single-crystal X-ray diffraction data.

Bianchite is a member of the hexahydrate group group (M$^{2+}$SO$_4$.4H$_2$O; M$^{2+}$ = Fe, Mg, Mn, Co, Zn, Ni) $C2/c$ (Table 1) (Gaines et al. 1997). All hexahydrate group minerals structures are composed of isolated [M$^{2+}$(H$_2$O)$_6$] octahedra and sulfate tetrahedra held together only by hydrogen bonding. Minerals of the hexahydrate group are commonly associated with metal sulfide minerals that have been exposed to hydration and oxidation processes. Natural occurrences of the hexahydrate group of minerals indicate that these minerals are often intermixed with...