The crystal chemical role of Zn in alunite-type minerals: Structure refinements for kintoreite and zincian kintoreite

IAN E. GREY,1,* W. GUS MUMME,1 STUART J. MILLS,2 WILLIAM D. BIRCH,3 AND NICHOLAS C. WILSON3

1CSIRO Minerals, Box 312, Clayton South, Victoria 3169, Australia
2University of British Columbia, Department of Earth and Ocean Sciences, Vancouver, British Columbia V6T 1Z4, Canada
3Geosciences, Museum Victoria, GPO Box 666, Melbourne, Victoria 3001, Australia

ABSTRACT

Kintoreite, PbFe3H6[3(PO4)3]3(AsO4)3(OH)6, and zincian kintoreite, PbZn3Fe3H6[3(PO4)3]4(SO4)3(OH)6, have rhombohedral symmetry, space group $R\bar{3}m$, with hexagonal cell parameters $a = 7.2963(5)$ Å, $c = 16.8491(5)$ Å, and $a = 7.3789(3)$ Å, $c = 16.8552(7)$ Å, respectively. The structures have been refined using single-crystal X-ray data to $R_1 = 0.030$ for 374 observed reflections and $R_1 = 0.035$ for 399 observed reflections, respectively. The structures of both minerals comprise rhombohedral stacking of (001) composite layers of corner-shared octahedra and tetrahedra with Pb atoms occupying icosahedral sites between the layers, as in the alunite-type structure. The corner-connected octahedra form three-membered and six-membered rings as in hexagonal tungsten bronzes. The structure of zincian kintoreite differs from other alunite-type structures in having partial occupation, by Zn, of new sites within the six-membered rings in the octahedral layers. The Zn is displaced to an off-center position in the hexagonal ring, where it assumes fivefold trigonal-bipyramidal coordination, to three of the hydroxyl anions forming the ring, and to the apical O anions of the XO4 tetrahedra on opposite sides of the ring. The different structural modes of Zn incorporation into SO4-dominant and (P,As)O4-dominant members of $A^3B^6_2(XO_4)_2(OH)_6$, alunite-type minerals are discussed in terms of the different charge-compensation mechanisms involved.

Keywords: Zincian kintoreite, crystal structure, alunite-type structure, single-crystal study

INTRODUCTION

Minerals of the alunite supergroup, with general composition $AB_4(XO_4)_2(OH)_6$, are remarkable for the diversity of elements that can be incorporated into the three types of cation sites: A, B, and X. The icosahedral A sites incorporate a range of large cations including monovalent Na+, K+, Rb+, NH4+, H3O+, divalent Ca2+, Sr2+, Ba2+, Pb2+, and trivalent Bi3+, Ln3+ (Ln = lanthanide) elements. The B sites are octahedrally coordinated and are usually occupied by trivalent cations, Fe3+, Al3+, Cr3+, V3+, and Ga3+, but are known to also incorporate divalent Cu2+ and Zn2+, as well as pentavalent SbV+. The X sites are tetrahedral, most commonly occupied by S4-, P3-, and As5- but can also contain C3-, C4-, and Si4- (Scott 1987; Kolitsch and Pring 2001). Extensive solid solutions involving mixed substitution at one or more of the three sites are common. The composition often requires modification to accommodate different combinations of cations. Such modifications include hydroxyl substitution for oxygen in the XO4 tetrahedra, substitution of H2O or oxygen for OH, and partial occupancy of the A and/or B sites (Jambor 1999).

The majority of alunite-type minerals have rhombohedral symmetry, space group $R\bar{3}m$, with hexagonal cell parameters $a \sim 7$ Å, $c \sim 17$ Å (Jambor 1999). The structure is made up of (001) sheets of corner-shared octahedra and tetrahedra, which are stacked along c according to the rhombohedral symmetry. The A atoms occupy icosahedral sites between the layers. The stacking of two composite octahedral/tetrahedral layers, with interlayer A atoms, is shown in Figure 1. The octahedra share corners via hydroxyl anions, labeled O3 in Figure 1, to form a planar network of triangular clusters, encompassing hexagonal voids. Such a motif is common to many structures including those of zirconolite polytypes, pyrochlore, and hexagonal tungsten bronze (HTB) phases, and is often described as a HTB layer (e.g., Grey et al. 2006). The apical oxygen anions (O2 in Fig. 1) of the triangular groupings of octahedra are shared with the XO4 tetrahedra. The corner-shared octahedra in the HTB layer have considerable flexibility to tilt about the corner-linkages to accommodate different sized XO4 tetrahedra. This is a major contributing factor to the compositional diversity of the alunite-type minerals.

The three different cation sites in the alunite-type minerals have quite different sizes and valency requirements, and so generally there is no ambiguity in assigning cations to the A, B, or X sites. Possible exceptions include Cr, that can occupy the B site as Cr3+ and the X site as Cr4+, and elements such as Ge4+, that readily adopt both tetrahedral and octahedral coordination (Mills et al. 2006).