

Crystal Structure of Ajoite, $(\text{Na}+\text{K})_3\text{Cu}_{20}\text{Al}_3\text{Si}_{29}\text{O}_{76}(\text{OH})_{16}\sim 8\text{H}_2\text{O}$, from the Arizona Porphyry Copper/Hydrothermal Deposits

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Introduction

Ajoite occurs rarely in the oxidized zone of porphyry copper deposits in Arizona [1]. It was first described by Schaller and Vlisidis [2] and again by Chao [3], but the crystal structure was never determined.

Methods and Materials

A $60 \times 15 \times 5\text{-}\mu\text{m}^3$ green crystal from the type locality Ajo, AZ, yielded just enough intensity from streaked diffractions by using beamline 13-BM-D at GSECARS to solve the structure with 2-sigma accuracy of $\sim 0.01 \text{ \AA}$ for Si-O.

Results

Data were collected by using bending magnet x-ray radiation, monochromatized [Si(311) crystal] to a wavelength of 0.82657 \AA and focused by using horizontal and vertical Rh-coated float glass Kirpatrick-Baez mirrors to produce a $50 \times 50\text{-}\mu\text{m}^2$ beam. Data were collected by using a Bruker 2K SMART charge-coupled device (CCD) detector mounted at a fixed angle of $42^\circ 2\theta$ and scanning ϕ in 0.5° steps with 15-s counting per frame. The goniometer was a single-axis Klinger rotation stage, with the axis of rotation perpendicular to the plane of the synchrotron orbit. A total of 366 frames were collected. Unit-cell dimensions of $a = 13.638(2)$, $b = 13.691(2)$, $c = 14.518(2)$, $\alpha = 110.765(4)$, $\beta = 106.825(3)$, and $\gamma = 105.828(5)$ were refined by least squares by using 813 reflections. A total of 8938 reflections were obtained from 3° to $84^\circ 2\theta$. Of the 8934 unique reflections, 3298 were classed as observed ($|F_o| \geq 4\sigma_F$). The structure refined to a final R of 0.145.

Discussion

Figure 1 is a projection of ajoite down the a axis showing oxygen and hydroxyl atoms at the vertices of octahedra and tetrahedra. A sheet of edge-shared octahedrally coordinated Cu atoms (green) lies at a c of ~ 0.5 . Above and below the Cu layer is a layer of Si,Al tetrahedra (yellow) with most of the vertices shared with those of the Cu-O octahedra and some shared with the adjacent tetrahedral layer to generate an octahedral-tetrahedral 3-D framework (Fig. 1). Each tetrahedral layer is based topologically on a nonplanar twisted 2-D net with T atoms in 5-, 6-, and 7-rings (Fig. 2). Each T atom is at the center of a tetrahedron. The 3-D net contains a 2-D

channel system defined by elliptical 12-rings along a and circular 8-rings along b . Figure 2 isolates a tetrahedral layer with a c of ~ 0.3 . Four tetrahedra, lying near the origin of the unit cell, form zig-zag strings and share vertices with an identical string and layer related by a center of symmetry. The tetrahedra that link with the Cu octahedra form zig-zag bands of 6-rings parallel to a . The 5- and 7-rings result from the linkage between the strings and bands. As is typical of Cu(II)-O linkages, each Cu atom has four short distances to adjacent oxygen atoms in a square, and two longer distances to generate opposing vertices of a distorted octahedron. Eight tetrahedra are larger than the other 24 tetrahedra, consistent with half occupancy by Si and Al. Valence bond estimates indicate

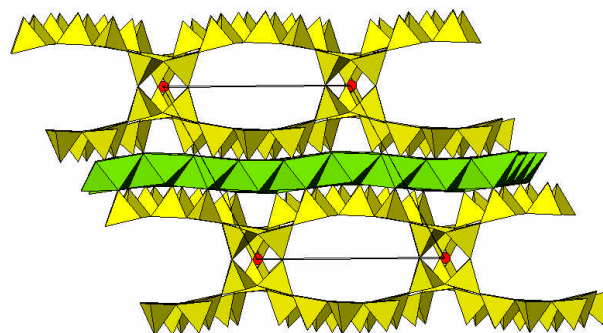


FIG. 1. Ajoite structure viewed down a , b across, and c up. CuO_6 octahedra are green, $(\text{Si,Al})\text{O}_4$ tetrahedra are yellow, and the (K,Na) site is red.

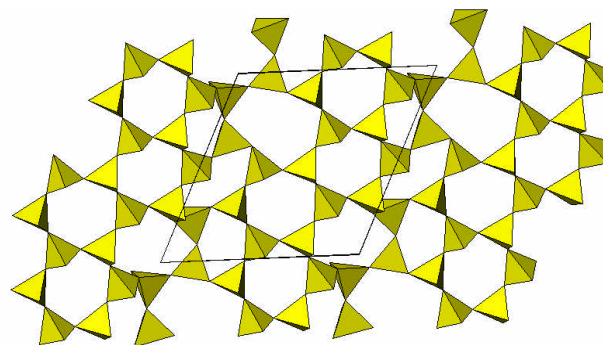


FIG. 2. Ajoite $(\text{Si,Al})\text{O}_4$ tetrahedral layer viewed down c , a down, b across.

that 16 of 92 oxygen atoms are hydroxyl. Ajoite contains a total of three (K,Na), of which ~25% is Na from the electron probe analysis. Figure 1 shows that a (K,Na) position (red ball) in distorted octahedral coordination accounts for one of the cations. The remaining two (K,Na) and nonhydroxyl water from the chemical analysis presumably reside in the channels as disordered molecules, as in zeolites, and are not detected.

The crystal structure of ajoite opens up a further window into zeolite (microporous) materials. It contains an edge-sharing Cu-O octahedral layer sandwiched between two zeolitelike slabs. Ion exchange experiments are needed to determine the selectivities and possible industrial use. Removal of the zeolitic water molecules may permit molecular sorption or catalysis. A theoretical study of polygonal linkages may allow the invention of new octahedral-tetrahedral frameworks, and a family of copper silicate zeolitic materials may ensue.

Acknowledgments

This work was performed at GSECARS sector 13 at the APS. GSECARS is supported by the National Science Foundation (Earth Sciences), U.S. Department of Energy (Geosciences), W. M. Keck Foundation, and the U.S. Department of Agriculture. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

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