Crystal chemistry and polytypism of tyrolite

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ABSTRACT

The crystal structures of the 1M and 2M polytypes of tyrolite have been solved from single-crystal X-ray diffraction data. The structure of tyrolite-1M [monoclinic, P2/c, a = 27.562(3), b = 5.5682(7), c = 10.466(15) Å, β = 98.074(11)°, V = 1590.3(3) Å³] has been refined to R₁ = 0.086 on the basis of 2522 unique observed reflections collected using synchrotron radiation at the Swiss-Norwegian beamline BM01 of the European Synchrotron Research Facility (SNBL at the ESRF). The structure of tyrolite-2M [monoclinic, C2/c, a = 54.520(6), b = 5.5638(6), c = 10.4647(10) Å, β = 96.432(9)°, V = 3154.4(6) Å³] has been refined to R₁ = 0.144 on the basis of 2666 unique observed reflections obtained from a non-merohedrally twinned crystal using in-house X-ray radiation and a STOE IPDS II image-plate diffractometer. The structures are based upon complex nanolayers consisting of Cu, As, and Ca coordination polyhedra. The core of the nanolayer is a copper arsenate substructure consisting of A and B sublayers. The B sublayer consists of chains of edge-sharing Cu octahedra running along the b axis. The A sublayer contains trimeric units of Cu octahedra sharing corners with AsO₄ tetrahedra. Two adjacent A sublayers are linked by the octahedral chains of the B sublayer resulting in formation of the 18 Å thick ABA slab. The ABA slab is sandwiched between sublayers of Ca²⁺ cations and H₂O molecules. Adjacent nanolayers are connected by hydrogen bonds to the interlayer species (carbonate anions and H₂O molecules). The structures of tyrolite-1M and tyrolite-2M differ by the stacking sequence of the nanolayers only. The adjacent nanolayers in tyrolite-2M are shifted by h/b = 2.8 Å in comparison to the relative position of the nanolayers in tyrolite-1M. The structural formula of tyrolite can be written as [Ca₉Ca₂(AsO₄)₄(OH)₄(CO₃)(OH)₁₀]·10H₂O, where x = 0–1.

Keywords: Tyrolite, “clinotyrolite,” crystal structure, copper arsenate, nanolayers, polytypes

INTRODUCTION

Copper arsenates are common minerals in oxidation zones of sulphide ore deposits. There are more than 70 different copper arsenate mineral species reported so far (see, e.g., recent papers: Pushcharovskii et al. 2000; Zubkova et al. 2003; Locock and Burns 2003). The restricted stability of As-bearing minerals such as the copper arsenates may play a significant role in the mobility of arsenic in the near-surface environment. Structural investigations of secondary As-bearing phases may lead to a better understanding of the geochemical behavior of As and thereby help to elucidate mechanisms of transportation and accumulation of As under natural conditions.

Tyrolite, a complex copper arsenate carbonate hydrate, was first described by A.G. Werner in 1817 (published in Haidinger 1845; cf. Blackburn and Dennen 1997) from Schavz-Brixlegg, Tyrol, Austria. The mineral is widely distributed (Anthony et al. 2000) and has been reported at more than 128 localities worldwide.

On the basis of wet chemical analysis of material from Falkenstein, Austria, Church (1895) assigned the formula Ca₉Cu₅(AsO₄)₄(CO₃)(OH)₁₀·6H₂O to tyrolite. Berry (1948) reported tyrolite as orthorhombic, probable space group Pmma, a = 10.50, b = 54.71, c = 5.59 Å, V = 3211 Å³, with Z = 4 and formula Cu₅Ca₉(AsO₄)₄(OH)₁₀·6H₂O (notably lacking any carbonate). Palache et al. (1951) considered the formula of tyrolite to be uncertain, particularly with respect to the presence or absence of carbonate and/or sulfate, and reported both previously cited formulae along with supporting chemical data. Guillemin (1956) assigned the formula Ca₉Cu₅(AsO₄)₄(CO₃)(OH)₁₀·6H₂O to tyrolite and considered the mineral as orthorhombic, space group Pmma, a = 10.212, b = 55.510, c = 5.602 Å, V = 3175.6 Å³. Li et al. (2004) reported 0.73 wt% SO₃ in tyrolite from China. Castillo and Mallego (1972) provided chemical analysis of tyrolite with 7.17 wt% Fe₂O₃ and 0.73 wt% SO₃ in tyrolite from China. Castillo and Mallego (1972) provided chemical analysis of tyrolite with 7.17 wt% Fe₂O₃ and 0.73 wt% SO₃ in tyrolite from China.