The crystal structure of philolithite, a trellis-like open framework based on cubic closest-packing of anions

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ABSTRACT

The crystal structure of philolithite, Pb12O6Mn(Mg,Mn)2(Mn,Mg)4(SO4)(CO3)4Cl4(OH)12, P42/nmm, a = 12.627(9), c = 12.595(9) Å, V = 2008(2) Å3, Z = 2 has been solved by Patterson difference-Fourier syntheses and refined to R = 0.053 for 814 F > 4σF, using MoKα X-ray data. In the structure, MnO6 octahedra form straight chains parallel to [110] and [110] by sharing opposite octahedral edges. Octahedra within the chains are further linked by sharing free corners with MnO4 tetrahedra and CO3 triangles. The MnO4 and SO4 tetrahedra also form bridging struts between octahedral chains, connecting them in the [001] direction into an open framework. The Pb, Cl, and non-framework O atoms occupy the open spaces within the framework. The 10- and 12-fold coordinations of the Pb atoms exhibit the lone-pair effect. Pb atoms link via short bonds to non-framework O atoms to form chains parallel to [110] and [110]. When viewed down [111], [111], [111], or [111], the framework (less the CO3 groups) is seen to be based upon cubic closest-packing of anions. This open framework of composition [Mn4.24(Mg,4.24)(04)6–(SO4)2–(CO3)4–(OH)12]12–, referred to as a closest-packed trellis, is the fundamental unit for the structure.

INTRODUCTION

The new mineral philolithite from the Långban mines, Filipstad district, Värmland, Sweden (see Holtstam and Langhof 1999), was described by Kampf et al. (1998). The initial powder and single-crystal X-ray diffraction and EDS chemical analysis of philolithite, which confirmed it to be a new species, were conducted on crystals on a specimen obtained from the Swedish Museum of Natural History in 1965-66 by one of the authors (P.B.M.). This specimen, now designated as one of theotypes, is in the collection of the Los Angeles County Museum of Natural History (LACMNH no. 41794). The crystal upon which an initial structure determination was attempted came from a second co-type specimen, provided by William W. Pinch, and now in the collection of the Canadian Museum of Nature (CMNH no. 58623). The low quality of this crystal coupled with absorption effects only allowed an approximate solution of the structure. Subsequently, the new species was identified on other specimens in the collection of the Swedish Museum of Natural History. A crystal from one of these specimens (SMNH no. 37389), also designated as a type, allowed the complete solution and refinement of the crystal structure reported herein.

STRUCTURE DETERMINATION

Single-crystal X-ray precession and four-circle diffractometer studies showed philolithite to be tetragonal, space group P42/nmm, a = 12.627(9), c = 12.595(9) Å, V = 2008(2) Å3, Z = 2. The cell parameters were obtained by least-squares refinement from the setting angles of 25 reflections between 2θ = 18° and 28°, automatically centered by the diffractometer.

X-ray intensity data were collected on a Huber four-circle diffractometer using a crystal of philolithite ground to a spheroid of dimensions 75 × 70 × 55 μm3. The operating conditions were: room temperature, 45 kV, 25 mA, graphite-monochromatized MoKα radiation (λ = 0.71069 Å), scan mode 0–2θ, scan width 3°(2θ), scan speed 2°/min, 2θmax = 60°, three standard reflections measured every one hundred reflections. The 6139 measured intensities (0 ≤ h ≤ 17, −17 ≤ k ≤ 17, 0 ≤ l ≤ 17) were corrected for Lorentz and polarization effects and an absorption correction by the ψ-scan method was applied. The final data set reduced to 1568 unique reflections.

The metal atoms (Pb, Mn, Mg) were readily located by Patterson synthesis and the positions of the other atoms were obtained from subsequent difference-Fourier syntheses. Lead was assigned to two sites, Pb1 and Pb2. The other three metal sites, M1, M2, and M3 were assumed to contain only Mn for the initial refinements. In later refinements the allotments of Mn and Mg to the M1, M2, and M3 sites were refined. Based upon the results, the M1 (fourfold-coordinated) site was assigned full occupancy by Mn alone, the M2 site assigned full occupancy by 54% Mg and 46% Mn, and the M3 site was assigned full occupancy by 68% Mn and 32% Mg. Over the three sites this yields (Mn4.24,Mg2.42)(SO4)6–[CO3]4–[OH]12. Electron microprobe analyses reported in Kampf et al. (1998) for crystals from the same specimen (SMNH no. 37389) provide (Mn4.25,Mg3.75)37.6. The structure was refined in space group P42/nmm (second setting with origin on 2/m) with the SHELXL-93 program (Sheldrick 1993). In the final cycles anisotropic displacement parameters for Pb, Mn, Mg, S, and Cl and isotropic displacement parameters for C and O atoms were refined. The final...