Revised crystal structure and chemical formula of weeksite, \(K_2(UO_2)_3(Si_5O_{13}) \cdot 4H_2O\)

KARLA FEJFAROVÁ,1 JAKUB PLÁŠIL,2,* HXIONG YANG,3 JIŘÍ ČEJKA,4 MICHAL DUŠEK,1 ROBERT T. DOWNS,3 MADISON C. BARKLEY,5 AND RADEK ŠKODA2

1Institute of Physics ASCR, v.v.i., Na Slovance 2, 18221, Praha, Czech Republic
2Institute of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37, Brno, Czech Republic
3Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.
4Arizona Historical Society, 1502 W Washington Street, Phoenix, Arizona 85007, U.S.A.

ABSTRACT

The previously published structure determination of weeksite from the Anderson mine, Arizona, U.S.A., suggested that it is orthorhombic, \(\text{Cmnb}\), with \(a = 14.209(2)\,\text{Å}\), \(b = 14.248(2)\,\text{Å}\), and \(c = 35.869(4)\,\text{Å}\), and \(V = 7262(2)\,\text{Å}^3\), and an ideal chemical formula \((K,\text{Ba})_3(UO_2)_3(SiO_3)_5H_2O\). Using single-crystal X-ray diffraction, electron microprobe analysis, and thermal analysis, we reexamined weeksite from the same locality. Our results demonstrate that weeksite is monoclinic, with the space group \(\text{C2/m}\) and unit-cell parameters \(a = 14.1957(4)\,\text{Å}\), \(b = 14.2291(5)\,\text{Å}\), \(c = 9.6305(3)\,\text{Å}\), \(\beta = 111.578(3)^\circ\), \(V = 1808.96(10)\,\text{Å}^3\), and an ideal formula \(K_2(UO_2)_3(SiO_3)_5\cdot 4H_2O\). The previously reported orthorhombic unit cell is known to result from twinning of the monoclinic cell. The structure refinement yielded \(R = 2.84\%\) for 1632 observed reflections \(|I_a > 3σ(I)|\) and 5.42\% for all 2379 reflections. The total \(H_2O\) content derived from the structure refinement agrees well with that from the thermal analysis. Although the general topology of our structure resembles that reported previously, all Si sites in our structure are fully occupied, in contrast to the previous structure determination, which includes four partially occupied \(\text{SiO}_4\) tetrahedra. From our structure data on weeksite, it appears evident that the orthorhombic cell of the newly discovered weeksite-type mineral coutinhoite, \(\text{Th}_2\text{Ba}_{3}(\text{UO}_2)_3\text{Si}_3\text{O}_{13}\cdot 3\text{H}_2\text{O}\), needs to be reevaluated.

Keywords: Weeksite, uranyl silicate, crystal structure, X-ray diffraction, open framework

INTRODUCTION

Weeksite is one of 19 known uranyl silicates that occurs in nature as a secondary alteration product typically found in the oxidized zones of uranium deposits. Uranyl silicate minerals have been the subject of extensive investigations in the past two decades (e.g., Burns 1999, 2005), not only because of their bearing on the genesis and weathering processes of uranium deposits, but also because of their formation as a result of the alteration of spent nuclear fuel under conditions similar to those that were expected at the proposed repository at Yucca Mountains, Nevada (Finn et al. 1996; Wronkiewicz et al. 1996; Finch et al. 1999). For example, weeksite was identified as an alteration product in batch tests using modified groundwater from Yucca Mts. and actinide-bearing borosilicate waste glass (Buck and Fornter 1997), as well as an interaction product between simulated nuclear wastes and crystalline silicate rocks (Oji et al. 2006). Detailed knowledge of the crystal chemistry of uranyl silicates, therefore, is critical to understanding the long-term performance of a geological repository for nuclear waste and the incorporation of other actinide elements, present in spent nuclear fuel, into their structures (Burns et al. 1997, 2000; Burns 1999; Chen et al. 1999, 2000; Friese et al. 2004; Klingensmith et al. 2007).

Weeksite from the Thomas Range, Juab County, Utah, was first described by Outerbridge et al. (1960) as orthorhombic, with space group \(\text{Pnmb}\), unit-cell parameters \(a = 14.26(2)\,\text{Å}\), \(b = 35.88(10)\,\text{Å}\), and \(c = 14.20(2)\,\text{Å}\), and an ideal chemical formula \((K,\text{Ba})_3(UO_2)_3(SiO_3)_5\cdot 4H_2O\). Using single-crystal X-ray diffraction, electron microprobe analysis, and thermal analysis, we reexamined weeksite from the same locality. Our results demonstrate that weeksite is monoclinic, with the space group \(\text{C2/m}\) and unit-cell parameters \(a = 14.1957(4)\,\text{Å}\), \(b = 14.2291(5)\,\text{Å}\), \(c = 9.6305(3)\,\text{Å}\), \(\beta = 111.578(3)^\circ\), \(V = 1808.96(10)\,\text{Å}^3\), and an ideal formula \(K_2(UO_2)_3(SiO_3)_5\cdot 4H_2O\). The previously reported orthorhombic unit cell is known to result from twinning of the monoclinic cell. The structure refinement yielded \(R = 2.84\%\) for 1632 observed reflections \(|I_a > 3σ(I)|\) and 5.42\% for all 2379 reflections. The total \(H_2O\) content derived from the structure refinement agrees well with that from the thermal analysis. Although the general topology of our structure resembles that reported previously, all Si sites in our structure are fully occupied, in contrast to the previous structure determination, which includes four partially occupied \(\text{SiO}_4\) tetrahedra. From our structure data on weeksite, it appears evident that the orthorhombic cell of the newly discovered weeksite-type mineral coutinhoite, \(\text{Th}_2\text{Ba}_{3}(\text{UO}_2)_3\text{Si}_3\text{O}_{13}\cdot 3\text{H}_2\text{O}\), needs to be reevaluated.

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* E-mail: jakub.horrak@gmail.com