The structures of becquerelite and Sr-exchanged becquerelite

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ABSTRACT

The crystal structures of becquerelite, Ca[(UO₂)₆O₄(OH)₆](H₂O)₈, and Sr-exchanged becquerelite obtained by ion exchange, Sr₁₋ₓ[(UO₂)₆O₄(OH)₆](H₂O)₈, have been refined using diffraction data collected with MoKα X-rays and a CCD-based detector. The structure of becquerelite, orthorhombic, space group Pn2₁a, a = 13.8527(5), b = 12.3929(4), c = 14.9297(5) Å, V = 2563.2(1) Å³, has been refined on the basis of F² for 4875 unique reflections to R₁ = 3.39%, calculated using 4581 unique observed reflections (I/F ≥ 4σ(F)), and a goodness-of-fit (S) of 1.04. Sr-exchanged becquerelite was obtained by placing single crystals of synthetic becquerelite in 2.5 M SrCl₂ solution for 60 h at 160 °C. The structure of Sr-exchanged becquerelite is trigonal, space group P3, a = 7.020(4), c = 6.992(6) Å, V = 298.4(3) Å³, and has been refined on the basis of F² for 683 unique reflections to R₁ = 4.26%, calculated using the 564 unique observed reflections (I/F ≥ 4σ(F)), and an S of 1.01. The results for becquerelite confirm the cation polyhedra and structural connectivity reported previously, but collection of data for a high-quality crystal using a CCD-based detector has substantially improved the precision of the atom positions. The structure contains α-UO₂₆-type sheets of uranyl pentagonal bipyramids, with a single symmetrically distinct Ca cation and eight symmetrically distinct H₂O groups located in the interlayer. The structure of Sr-exchanged becquerelite also contains α-UO₂₆-type sheets of uranyl pentagonal bipyramids, although the amount of H in the sheets is lower than for becquerelite. The interlayer contains two symmetrically distinct Sr cations and a single H₂O group. Ion exchange of Sr into the interlayer of becquerelite without destruction of the crystals has potential important implications for the mobility of ⁹⁰Sr in contaminated areas, and for the geologic disposal of nuclear waste.

INTRODUCTION

Uranyl oxide hydrates are common constituents of the oxidized portions of U deposits, and are typically the first U⁶⁺ phases to form at the onset of alteration of uraninite (Frondel 1958). They are important for understanding water-rock interactions in U deposits, form as products of the oxidation of U mine and mill tailings, and are prominent alteration phases in laboratory experiments involving UO₂ and spent nuclear fuel in a moist, oxidizing environment similar to the proposed repository at Yucca Mountain (Wronkiewicz et al. 1996; Finn et al. 1996; Finch et al. 1999). Many of the radionuclides released from spent nuclear fuel during alteration in a geological repository may be incorporated into uranyl oxide hydrates (Burns et al. 1997a; Chen et al. 1999, 2000).

The known structures of uranyl oxide hydrate minerals are each based upon sheets of edge- and corner-sharing uranyl polyhedra, with low-valence cations and H₂O groups located in interlayer positions (Burns 1999b). Analogous to clays, in some cases the interlayer cations are exchangeable. Burns (1999b) demonstrated ion exchange of Cs for K and Na in the interlayers of single crystals of boltwoodite, as shown by crystal structure analyses before and after cation exchange. The single crystals of boltwoodite remained intact with optically smooth faces and sharp edges following exchange, ruling out a solution-reprecipitation mechanism. The capacity of uranyl phases to exchange interlayer cations, particularly radionuclides such as ⁹⁰Sr, ¹³⁵Cs, and ¹³⁷Cs, may have important implications for the geological disposal of nuclear waste.

Becquerelite, Ca[(UO₂)₆O₄(OH)₆](H₂O)₈, is a common uranyl oxide hydrate in natural systems. The crystal structure of becquerelite was determined by Piret-Meunier and Piret (1982) using single-crystal X-ray data and was refined to an agreement index (R) of 7.0% on the basis of 1983 unique observed reflections. Pagoaga et al. (1987) also published the structure of becquerelite, and reported an R of 8.3% for 2853 unique observed reflections. In the latter case, problems with the refinement were attributed to disorder in the crystals, as reflected by moderate to intense streaking in the diffraction patterns, a feature that presumably contributed to reported uncertainties in the U-O bond lengths that ranged from 0.04 to 0.09 Å.

Here we present a modern refinement of the structure of a natural crystal of becquerelite, and report the ion exchange of Sr for Ca in the interlayer of single crystals of synthetic becquerelite, as demonstrated by a single-crystal structure determination for Sr-exchanged becquerelite.

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