Neptunium incorporation in sodium-substituted metaschoepite

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ABSTRACT

Uranyl oxide hydrate minerals are common in the altered zones of U deposits and are expected to form where spent nuclear fuel is altered in an oxidizing environment. Consistent with all known uranyl oxide hydrate minerals, metaschoepite [(UO₂)₄O(OH)₅](H₂O)₅, contains sheets of uranyl polyhedra with H₂O groups located in the interlayer. Several crystals along the series from metaschoepite to Na-substituted metaschoepite (Na-MS), approximate formula Na[(UO₂)₄O(OH)₅](H₂O)₅, have been synthesized and their structures have been determined. Each contains sheets of uranyl pentagonal bipyramids that are topologically identical to those in metaschoepite, schoepite and fourmarierite. The sheets are electroneutral in metaschoepite, but substitution of O for OH located at the equatorial vertices of the uranyl polyhedra gives a charged sheet that is balanced by incorporation of Na in the interlayer. Synthesis of crystals of Na-MS from a solution containing ~500 ppm Np⁵⁺, followed by analysis of the crystals using laser-ablation inductively coupled-plasma mass-spectroscopy, demonstrated that the crystals incorporate Np. This is in contrast to earlier studies that showed no incorporation of Np⁵⁺ in synthetic metaschoepite (which has electroneutral sheets), and supports the hypothesis that Np⁵⁺ incorporation is more likely in uranyl oxide hydrates with charged species in the interlayer.

Keywords: Metaschoepite, uranyl, uranium, nuclear waste, geologic repository, crystal structure, neptunium

INTRODUCTION

Hexavalent U (uranyl) minerals occur in the oxidized zones of U deposits, where it is common for several uranyl mineral species to coexist, often in intimate intergrowths (Frondel 1958; Finch and Ewing 1992). Uranyl oxide hydrate minerals are typically the first to form during the onset of alteration of uraninite (Finch and Ewing 1992). Uranyl oxide hydrates have been the focus of considerable research recently, including analysis of their crystal structures (Burns 2005), the relationships between their structures and crystal morphology (Schindler et al. 2004a, 2004b, 2004c), and their thermodynamic properties (Kubatko et al. 2006). About 20 species have been described, and the structures are known for 16 of these (Burns 2005). In all cases the structures consist of sheets of uranyl polyhedra. The interlayer regions always contain H₂O in these minerals, and in all but schoepite and metaschoepite the interlayers also contain lower-valence cations (Burns 2005).

The crystal structures of schoepite, [(UO₂)₈O₂(OH)₁₂](H₂O)₁₆ (Finch et al. 1996), metaschoepite, [(UO₂)₈O(OH)₁₆](H₂O)₁₆ (Weller et al. 2000) and fourmarierite, Pb[(UO₂)₄O₂(OH)₆](H₂O)₆ (Piret 1985) contain topologically identical sheets formed by the sharing of edges and vertices between uranyl pentagonal bipyramids. In each structure, the uranyl ions are oriented roughly perpendicular to the plane of the sheet, and linkages between the polyhedra are through equatorial edges and vertices only. In the case of fourmarierite, the sheet of uranyl polyhedra has a net negative charge and Pb²⁺ cations are located in the interlayer. The structures of metaschoepite and schoepite contain chemically identical sheets that are electroneutral, and the sheets are linked through H bonds extending to and from H₂O groups located in the interlayers of the structures.

Alteration of spent nuclear fuel in a geological repository contained within the unsaturated zone, such as the proposed geological repository at Yucca Mountain, Nevada, is likely to result in a suite of uranyl phases that will include uranyl oxide hydrates. Wronkiewicz et al. (1992, 1996) examined the alteration of unirradiated UO₂ in slowly dripping water at 90 °C over ten years. The water used was from well J-13 at the Yucca Mountain site, and was reacted with crushed Tonopah Springs tuff at 90 °C for 80 days. The resulting water, designated EJ-13, contains more Na and Si than J-13 water, with Na and Si concentrations of 46.5 and 34.4 μg/mL, respectively (Wronkiewicz et al. 1992). Alteration of the UO₂ in these studies was rapid, and resulted in a suite of uranyl oxide hydrate and uranyl silicate minerals, with the uranyl oxide hydrates being the first to form at the onset of alteration. Metaschoepite was observed to form early following the onset of alteration (Wronkiewicz et al. 1996). In similar studies using commercial spent nuclear fuel and EJ-13 water, Finch et al. (1999) also reported the formation of metaschoepite when water was dripped onto the spent fuel, and also when the spent fuel altered in the absence of dripping water, but in an atmosphere with 100% relative humidity.

Burns et al. (1997a) proposed that uranyl minerals that form...