Studtite, [(UO$_2$)(O$_2$)(H$_2$O)$_2$](H$_2$O)$_2$: The first structure of a peroxide mineral

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ABSTRACT

Studtite, UO$_4$·4H$_2$O, and metastudtite, UO$_4$·2H$_2$O, are the only minerals thought to contain peroxide. Determination of the structure of studtite has shown it to contain peroxide, with the structural formula [(UO$_2$)(O$_2$)(H$_2$O)$_2$](H$_2$O)$_2$. The structure is monoclinic, space group C2/c, $a = 14.068(6)$ Å, $b = 6.72(1)$ Å, $c = 8.428(4)$ Å, $\beta = 123.356(6)^\circ$, $V = 665.6(3)$ Å$^3$, $Z = 4$. It was refined on the basis of $F^2$ for 1398 unique reflections collected using MoK$\alpha$ X-radiation and a CCD-based detector to $R_1 = 3.66\%$, calculated for the 716 unique observed reflections ($|F| \geq 4\sigma_F$). The structure of studtite contains one symmetrically distinct U$^{6+}$ cation and four O atoms, two of which occur as H$_2$O groups. The O-O bond-length in the peroxide group is 1.46(1) Å. The U$^{6+}$ cation occurs as part of a linear (UO$_2$)$_{2+}$ uranyl ion, and each U$^{6+}$ cation is bonded to six additional O atoms, two of which are H$_2$O groups, and four of which are O atoms of peroxide groups. The O-O bonds of two peroxide groups constitute two equatorial edges of each distorted uranyl hexagonal bipyramid. Uranyl polyhedra are polymerized into chains extending along [001] by sharing peroxide groups. Chains are linked by H bonds extending to and from an interstitial H$_2$O group. It is proposed that studtite forms by incorporating peroxide created by alpha-radiolysis of water, and that radiation is necessary for its formation in nature.

INTRODUCTION

Uranyl minerals display tremendous structural and chemical diversity (Burns 1999). They are important for understanding the genesis of U deposits (Frondel 1958), the mobility of actinides in the vadose zone (Buck et al. 1996; Roh et al. 2000), and alteration of nuclear waste in a geological repository such as Yucca Mountain, Nevada (Wronkiewicz et al. 1996; Finch et al. 1999). Despite their apparent chemical simplicity, the uranyl minerals studtite, UO$_4$·4H$_2$O, and metastudtite, UO$_4$·2H$_2$O, are fascinating because they are the only reported peroxide minerals. We have determined the crystal structure of studtite using single-crystal X-ray diffractometry and a CCD-based X-ray detector (Burns 1998), and report the details of the only peroxide mineral structure.

Studtite was originally described by Vaes (1947) as a uranyl carbonate from Shinkolobwe, Democratic Republic of Congo, and has since been reported from several localities (Cejka et al. 1996). Using material from Krunkelbach (Meszenschwand, Germany), Walenta (1974) established that studtite is a uranium peroxide hydrate with the formula UO$_4$·4H$_2$O. Cejka et al. (1996) provided X-ray powder diffraction data, thermal analysis, and an infrared spectrum for studtite from Krunkelbach.

Studtite and metastudtite may form from alteration of nuclear waste in a geological repository by incorporating peroxide formed by alpha-radiolysis of water (Sattonnay et al. 2001; Amme 2002; McNamara et al. 2002). Most studies of alteration of UO$_2$ or commercial spent nuclear fuel under simulated Yucca Mountain conditions have emphasized the importance of uranyl oxide hydrates and uranyl silicates (Wronkiewicz et al. 1996; Finch et al. 1999), and did not note the formation of uranyl peroxides. The design of some of these experiments may have precluded the formation of studtite or metastudtite. Specifically, the experiments of Wronkiewicz et al. (1996) used UO$_2$ containing depleted U that was not sufficiently radioactive to cause significant formation of H$_2$O$_2$ by alpha-radiolysis of water. Recently, McNamara et al. (2002) found extensive formation of studtite on the surface of spent nuclear fuel reacted at 25 °C with de-ionized water for 1.5 years in the atmosphere, and preliminary results indicate that the studtite incorporated significant $^{237}$Np. Sattonnay et al. (2001) observed formation of metastudtite on the surface of UO$_2$ under irradiation with a $^{4}$He$^{2+}$ (α-particle) beam, and concluded the peroxide was provided by alpha-radiolysis of water. Burakov et al. (1997) reported that studtite formed on nuclear material (“lava”) following the Chernobyl Nuclear Plant accident. Thus, there is considerable evidence that uranyl peroxides such as studtite and metastudtite will be important alteration phases of nuclear waste, and that these minerals may impact the long-term performance of a geologic repository such as Yucca Mountain.

EXPERIMENTAL METHODS

We have studied many specimens containing studtite over the past several years; most crystals either diffract very poorly or not at all. The crystal of studtite that provided the structure is from a specimen from Krunkelbach (Meszenschwand, Germany). Crystals were collected from the sample, labeled...