

ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

## Crystal structure of richetite revisited: Crystallographic evidence for the presence of pentavalent uranium

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### ABSTRACT

Revision of crystal structure of the rare U-oxide mineral richetite provided crystallographic evidence for the presence of pentavalent U. The structure of richetite, space group  $P\bar{1}$ ,  $a = 12.0919(2)$ ,  $b = 16.3364(4)$ ,  $c = 20.2881(4)$  Å,  $\alpha = 68.800(2)$ ,  $\beta = 78.679(2)$ ,  $\gamma = 76.118(2)^\circ$ , with  $V = 3600.65(14)$  Å<sup>3</sup> and  $Z = 1$ , was solved by charge-flipping algorithm and refined to an agreement index ( $R$ ) of 5.6% for 9955 unique reflections collected using microfocus X-ray source. The refined structure, in line with the previous structure determination, contains U-O-OH sheets of the  $\alpha$ -U<sub>3</sub>O<sub>8</sub> type (protasite topology) and an interstitial complex comprising Pb<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup> cations and molecular H<sub>2</sub>O. However, the polyhedral geometry, the bond-valence sum incident at one U site within the sheet (U17) together with charge-balance requirements, indicate that U17 site is occupied by U<sup>5+</sup>. The U17 $\Phi_7$  ( $\Phi$ : O, OH) polyhedra is distorted, with two shorter U–O bond-lengths (~2.01 Å), four longer U–O bond-lengths (~2.2 Å) and one, very long U–O bond (2.9 Å). The color of richetite also supports the presence of U<sup>5+</sup> in the structure. The current results show that  $\alpha$ -U<sub>3</sub>O<sub>8</sub> type of sheet can incorporate U<sup>5+</sup>. Richetite is the third mineral containing pentavalent uranium that occurs in nature.

**Keywords:** Richetite, uranyl oxide hydroxy-hydrate, crystal structure, pentavalent uranium, weathering