

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 $V = 3600.65(14)$ Å³ 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 α -U₃O₈ type (protasite topology) and an interstitial complex comprising Pb²⁺, Fe²⁺, Mg²⁺ cations and molecular H₂O. 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 U⁵⁺. The U17 Φ_7 (Φ : 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 U⁵⁺ in the structure. The current results show that α -U₃O₈ type of sheet can incorporate U⁵⁺. Richetite is the third mineral containing pentavalent uranium that occurs in nature.

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