Wyartite: Crystallographic evidence for the first pentavalent-uranium mineral

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ABSTRACT

Determination of the structure of wyartite provides the first evidence for a pentavalent-U mineral. The structure of wyartite, CaU⁵⁺(UO₂)₂(CO₃)O₄(OH)(H₂O)₇, Z = 4, orthorhombic, a = 11.2706(8), b = 7.1055(5), c = 20.807(1) Å, V = 1666.3(3) Å³, space group P2₁2₁2₁, was solved by direct methods and refined to an agreement index (R) of 4.9% for 2309 unique reflections collected using MoKά X-radiation and a CCD-based detector. The structure contains three unique U positions; two contain U⁶⁺ and involve uranyl ions with typical pentagonal-bipyramidal coordination. Seven anions coordinate the other U position, but there is no uranyl ion present. The polyhedral geometry, the bond-valence sum incident at this U site, and electroneutrality requirements, all indicate that this site contains U⁵⁺. The Uφ₇ (φ: O, OH, H₂O) polyhedra share edges and corners to form a unique sheet in which a CO₃ group shares an edge with the U⁵⁺φ₇ polyhedron. The structure contains one Ca site coordinated by seven anions. The Ca atom and its associated H₂O groups occupy interlayer sites, along with two H₂O groups that are held in the structure by H bonds only. The Caφ₇ polyhedron is linked to one adjacent sheet by sharing an edge with the CO₃ group and an O atom with a U⁶⁺φ₇ polyhedron. Structural units are linked together through hydrogen bonds only.

INTRODUCTION

Interest in the paragenesis and structures of U minerals arises, in part, because of their role as alteration products of uraninite and other reduced U-ore minerals under oxidizing conditions (Frondel 1958; Finch and Ewing 1992). The U⁶⁺ phases are also important corrosion products of UO₂ in spent nuclear fuel (Forsyth and Werme 1992; Wronkiewicz et al. 1996), and they may control groundwater concentrations of U in U-contaminated soils (Buck et al. 1996; Morris et al. 1996). A clear understanding of the structural and thermodynamic stabilities of U carbonates is particularly germane to the environmental chemistry of U (Clark et al. 1995; Finch 1997) due to the potentially high mobility of U in carbonate-bearing groundwaters (Langmuir 1978; Grenthe et al. 1994). Most uranium minerals can be grouped into reduced species in which U occurs primarily as U⁴⁺, and oxidized species, in which U is fully oxidized to U⁶⁺. To date, no minerals have been described that contain essential U⁵⁺. Only two minerals have been described in which U occurs as both U⁴⁺ and U⁶⁺, ianthinite (Burns et al. 1997a) and wyartite (Guillemin and Protas 1959). Guillemin and Protas (1959) first described wyartite, reporting the formula 3CaO·UO₂₂(UO₂)₂CO₂·xH₂O where x = 12 to 14. In a crystallographic study of type material by X-ray precession photography, Clark (1960) showed that wyartite transforms in air to a phase that she called wyartite II (wyartite, sensu stricto, being designated wyartite I). Our interest in the crystal chemistry of U prompted the present structure determination of wyartite, and led to the surprising conclusion that the structure contains essential U⁵⁺.

EXPERIMENTAL METHODS

The specimen is from the Shinkolobwe mine, Shaba, Democratic Republic of Congo. We examined the crystal on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector (Burns 1998). Details pertaining to data collection are in Table 1. The unit-cell dimensions (Table 1) were determined and refined by least squares from 3929 reflections, and show that the crystal is wyartite sensu stricto (“wyartite I” of Clark 1960).

STRUCTURE SOLUTION AND REFINEMENT

Structure solution and refinement methods are as in Burns (1998). Systematic absences indicate space group P2₁2₁2₁, as noted by Clark (1960) and verified by successful solution and refinement of the structure by direct methods. The final refinement included positional parameters for all atoms, anisotropic-displacement parameters for U and Ca, isotropic-displacement parameters for C and O, and a weighting scheme of structure factors. Details of the structure