Uraninite from the Olympic Dam IOCG-U-Ag deposit: Linking textural and compositional variation to temporal evolution

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ABSTRACT

The Olympic Dam IOCG-U-Ag deposit, South Australia, the world's largest known uranium (U) resource, contains three main U-minerals: uraninite, coffinite, and brannerite. Four main classes of uraninite have been identified. Uraninite occurring as single grains is characterized by high-Pb and ΣREE+Y (ΣREY) but based on textures can be classified into three of these classes, typically present in the same sample. Primary uraninite (Class 1) is smallest (10–50 μm), displays a cubic-euhedral habit, and both oscillatory and sectorial zoning. "Zoned" uraninite (Class 2) is coarser, sub-euhedral, and combines different styles of zonation in the same grain. "Cobweb" uraninite (Class 3) is coarser still, up to several hundred micrometers, has variable hexagonal-octagonal morphologies, varying degrees of rounding, and features rhythmic intergrowths with sulfide minerals. In contrast, the highest-grade U in the deposit is found as micrometer-sized grains to aphanitic varieties of uraninite that form larger aggregates (up to millimeter) and vein-fillings (massive, Class 4) and have lower Pb and ΣREY, but higher Ca.

Nanoscale characterization of primary and cobweb uraninite shows these have defect-free fluorite structure. Both contain lattice-bound Pb+ΣREY, which for primary uraninite is concentrated within zones, and for cobweb uraninite is within high-Pb+ΣREY domains. Micro-fractured low-Pb+ΣREY domains, sometimes with different crystal orientation to the high-Pb+ΣREY domains in the same cobweb grain, contain nanoscale inclusions of galena, Cu-Fe-sulfides, and REY-minerals. The observed Pb zonation and presence of inclusions indicates solid-state trace-element mobility during the healing of radiogenic damage, and subsequent inclusion-nucleation + recrystallization during f_{S_2}-driven percolation of Cu-bearing fluid.

Tetravalent, lattice-bound radiogenic Pb is proposed based on analogous evidence for U-bearing zircon. Calculating the crystal chemical formula to UO_2 stoichiometry, the sum of cations (M*) is ~1 for most classes, but the presence of mono-, di-, and trivalent elements (ΣREY, Ca, etc.) drive stoichiometry toward hypostoichiometric M^*O_{2-x}. In the absence of measured O and constraints of hypostoichiometric fluorite-structure, charge-balance calculations showing O deficit in the range 0.15–0.36 apfu is compensated by assumption of mixed U oxidation states. Crystal structural formulas show up to 0.20 apfu Pb and 0.25 apfu ΣREY in Classes 1–3, while for Class 4, these are an order of magnitude less. Low-Pb and ΣREY subcategories of Classes 2 and 3 are similar to massive uraninite with ~0.2 apfu Ca. Other elements (Si, Na, Mn, As, Nb, etc.), show two distinct geochemical trends: (1) across Classes 1–3; and (2) Class 4, whereby low-Pb+ΣREY sub-populations of Classes 2 and 3 are part of trend 2 for certain elements. Plots of alteration factor $(CaO+SiO_2+Fe_2O_3)$ vs. Pb/U suggest two uraninite generations: early (high-Pb+ΣREY, Classes 1–3); and late (massive, Class 4). There is evidence of Pb loss from diffusion, leaching and/or recrystallization for Classes 2–3 (low-Pb+ΣREY domains).

Micro-analytical data and petrographic observations reported here, including nanoscale characterization of individual uraninite grains, support the hypothesis for at least two main uraninite mineralizing events at Olympic Dam and multiple stages of U dissolution and reprecipitation. Early crystalline uraninite is only sparsely preserved, with the majority of uraninite represented by the massive-aphanitic products of post-1590 Ma dissolution, reprecipitation, and possibly addition of uranium into the system. Coupled dissolution-reprecipitation reactions are suggested for early uraninite evolution across Classes 1 to 3. The calculated oxidation state $[U^{6+}/(U^{4+}+U^{6+})]$ of the "early" and "late" populations point to different conditions at the time of formation (charge compensation for ΣREY-rich early fluids) rather than auto-oxidation of uraninite. Late uraninites may have formed hydrothermally at lower temperatures ($T < 250$ °C).

Keywords: Uranium, uraninite, Olympic Dam, IOCG deposits