

ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Remobilization of U and REE and the formation of secondary minerals in oxidized U deposits†

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ABSTRACT

The hydrothermal uranium vein-type deposits of Menzenschwand and Wittichen in the Schwarzwald in southwestern Germany have been investigated with regards to their primary and secondary mineralization. Primary magmatic uraninite I from the host granite of Menzenschwand, primary hydrothermal uraninite II and secondary (supergene) uranyl silicates (uranophane and cuprosklodowskite), uranyl phosphates (torbernite and uranocircite), and uranyl arsenates (zeunerite, heinrichite, nováčekite, walpurgite, and uranospinite) were analyzed for their REE contents by LA-ICP-MS together with uraninite II samples from other known Schwarzwald uraninite II occurrences for comparison. Water samples were taken from drillings and abandoned mines and were analyzed for their major and trace element composition including U and REE.

The REE patterns of uraninite show significant Eu anomaly variations: negative Eu anomalies are related to granitic host rocks, whereas positive Eu anomalies imply a gneissic REE source. This is in agreement with the observation of Eu anomalies in granite and gneiss derived waters, which display negative and positive Eu anomalies, respectively.

Rare earth element distributions in the secondary uranyl minerals provide information about the sequence of mineral precipitation and the degree of remobilization of U. Cerium anomalies (or their absence) imply that uranyl silicates formed during an earlier stage of weathering under more reduced conditions than the uranyl arsenates and phosphates. The REE patterns of the uranyl silicates in Wittichen are similar to those of uraninite II, suggesting a very local redistribution on the millimeter- to centimeter-scale. In contrast, the REE patterns of uranyl arsenates and phosphates are different from uraninite II patterns and resemble those of the waters. This shows that the uranyl phosphates and arsenates are formed not only by redistribution of U in the hydrothermal veins but are influenced by waters from the host rock implying that U was probably transported over a greater distance. These conclusions are supported by field observations, where uranyl silicates are often found in the vicinity of uraninite II, whereas uranyl phosphates and arsenates are commonly found on fissures in the host rock.

To explain specific features in the sulfide-rich (pyrite, chalcopyrite) Menzenschwand deposit, we conducted thermodynamic reaction modeling using the PHREEQC computer code. Sulfide oxidation was modeled by reaction of a U-rich water in equilibrium with atmospheric oxygen with FeS₂ and CuFeS₂. A water that initially precipitates uranophane gradually evolves to more acidic pH values, thereby reaching torbernite saturation. This is in agreement with observed paragenetic sequences. Ongoing reaction results in a further decrease of pH and in the destabilization of uranophane and torbernite. Since goethite precipitates even at low-pH values, these calculations can explain observed pseudomorphs of goethite after both uranophane and torbernite, which are frequently observed at Menzenschwand. If the reaction proceeds and *f*_{O₂} in the system is buffered by the surrounding minerals, U⁶⁺ can be reduced to U⁴⁺ and uraninite can form and replace pyrite and earlier formed secondary uranium minerals such as ianthinite. Also these textures have been observed. We show that the combination of REE geochemistry, careful paragenetic observations and thermodynamic modeling allows to reconstruct the formation and weathering of uranium deposits in great detail.

Keywords: Uranium, rare earth elements, supergene alteration, thermodynamic stability