

## **Oxidation of hydrothermal U deposits: influence of primary mineralization on type and appearance of secondary U minerals**

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In the Schwarzwald ore district in southwestern Germany, U deposits occur as hydrothermal barite-quartz-fluorite veins mainly hosted by granites containing pitchblende with Co-Bi-Ni-As ores or hematite and pyrite. In Wittichen in the central Schwarzwald and Menzenschwand in the southern Schwarzwald, hydrothermal veins were mined and in Menzenschwand 1000 t U were exploited until 1991. The supergene weathering of uranium deposits can lead to mobilization of high amounts of U, because oxidized  $U^{6+}$  is highly soluble compared to  $U^{4+}$ . In Wittichen and Menzenschwand oxidation lead to mobilization of U and abundant formation of secondary uranyl ( $[U^{6+}O_2]^{2+}$ ) minerals. These minerals comprise among many others uranophane (uranyl silicate) and various uranyl phosphates (in Menzenschwand) and arsenates (in Wittichen and subordinated in Menzenschwand).

To evaluate the processes that take place during supergene weathering, we analyzed primary hydrothermal pitchblende and secondary uranyl minerals with LA-ICP-MS for their rare earth element (REE) contents. Since the alteration products are assumed to have formed not too long ago, waters from the abandoned mines were sampled and also analyzed for their REE contents using ICP-MS.

The REE patterns of primary pitchblende can give information about the origin of the primary ore-forming fluid and suggest that at the Menzenschwand deposit, two fluids were involved, one influenced by the host granite and one from the adjacent gneisses. The REE patterns of the secondary minerals reveal different conditions of formation for the uranyl silicates and uranyl phosphates and arsenates. Negative Ce anomalies in the latter suggest a formation under more oxidized conditions and therefore at a more evolved stage of alteration. REE patterns of the uranyl minerals also suggest, that during uranophane formation no transport of U or REE over great distances took place. However, REE patterns of the uranyl arsenates and phosphates resemble those of the host rock-derived waters suggesting that host rock-derived fluids were involved in their formation. These observations are consistent with field observations, where uranyl arsenates and phosphates are often found on fissures in the host rock, whereas uranophane is found in the vicinity of pitchblende.

Since the Menzenschwand U deposit contains abundant pyrite, sulfide oxidation plays an important role during alteration. To show how this process can induce and influence secondary mineral formation, the computer program PHREEQC was used for thermodynamic modeling. The calculations show that water that has reacted with uraninite precipitates uranophane and that further reaction with sulfides can lead to uranyl phosphate precipitation. Both will be replaced by goethite if pH decreases during further sulfide oxidation. Since pseudomorphs of goethite after uranophane and torbernite are common, the modeled scenario is likely to play a role in the weathering of sulfide-bearing U deposits.