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Uranium-, vanadium- and chromium-bearing reduction spheroids in karst bauxite of the Unterlaussa mining district (Upper Austria)

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Reduction spheroids are millimeter- to centimeter-scale reduction features that are mainly known from siliciclastic red bed sediments. They are characterized by a core containing high amounts of redox-sensitive metals compared to their host rocks and by a Fe(III)-depleted halo. They are generally regarded as biosignatures in the geological record, but the processes leading to their formation remain largely enigmatic and studies on reduction spheroids from settings unrelated to siliciclastic red beds are highly underexplored. Here, we present geochemical and mineralogical results of U-bearing reduction spheroids in karst bauxite of the Unterlaussa mining district (Upper Austria) to better understand the formation of reduction spheroids and the accumulation of U in karst bauxite. For this purpose, we used laser ablation-inductively coupled plasma-mass spectrometry, scanning electron microscopy, micro-X-ray fluorescence and Raman spectroscopy.
The karst bauxite-hosted reduction spheroids of the Unterlaussa mining district are highly enriched in ΣREE (La-Lu) (up to ~2.6 wt.%), U (up to ~47 wt.%), V (up to ~7.6 wt.%), Cr (up to ~4.3 wt.%) and Ti as TiO_2 phases. The U-bearing mineral in the reduction spheroids was identified as carnotite and an unknown Cr-V-Al phase is responsible for the high Cr contents in the reduction spheroid cores. Anatase was found in Ti-rich reduction spheroid cores. The formation of the reduction spheroids started shortly after the burial of the karst bauxite. A clayey sediment was rapidly deposited on top of the karst bauxite and terminated its weathering-controlled formation. The immediate source of U, V and Cr in the reduction spheroids was either the uppermost part of the karst bauxite where U-, V- and Cr-bearing minerals and organic matter were incorporated during a redeposition event, or the clayey hanging wall of the karst bauxite where U and V were present in organic matter. In both cases, decaying organic matter and the consequent acidic conditions caused the mobilization of U, V and Cr. These solutes were reductively immobilized by organic remnants in the karst bauxite resulting in the enrichment of U, V and Cr, and the formation of the reduction spheroid core. The reduction of Fe(III) due to the reducing environment around the developing core led to the formation of the reduction spheroid halo. This mechanism is suggested to be of significance for the formation of U-rich karst bauxite.
Our study reveals that reduction spheroids can form by different mechanisms which makes their occurrence in the geological record unsuitable for a priori conclusions. Finally, the general concepts found for U accumulation in karst bauxite have potential implications for mining operations and environmental protection.

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