

Evidence and Implications of U(VI) Uptake into Natural Rhabdophane

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Uranium (U) is a toxic and radiogenic contaminant that is perceived to be more mobile in its hexavalent form (U[VI]) than its tetravalent form (U[IV]) in natural fluids, while rhabdophane ($REEPO_4 \cdot xH_2O$, $REE = La - Lu$, $x = 0 - 1$) is a mineral that often mediates the mobility of uranium in soils, nuclear repositories and critical metal deposits [1, 2]. Studies that delineate the oxidation state of uranium in natural minerals like rhabdophane can subsequently inform environmental remediation efforts. This work combines synchrotron X-ray adsorption near edge structure analysis with nanoscale secondary ion mass spectroscopy (Fig. 1) and quantum-mechanical modelling to understand the oxidation state of U in natural rhabdophane. Contrary to current understanding, it finds that U-rich rhabdophane from the Kapunda Cu mine, South Australia, hosts *hexavalent* uranium. The U(VI) was observed to be particularly enriched in Ce-depleted zones, suggesting that the unavailability of major cations (i.e., Ce (III), following its oxidation to Ce (IV) and lesser uptake into rhabdophane) facilitates significant U(VI) immobilisation in the rhabdophane structure. Quantum-mechanical modelling indicates that the uranyl ion can be incorporated into rhabdophane without reduction, before subsequent U(VI)-Ce(III) interactions result in a U(V)-like electronic state. Results provide a novel and direct link between the mobilisation and (re)-accumulation of U(VI) in critical REE deposits, nuclear waste repositories and contaminated P-rich surface environments by presenting a mechanism of ‘mobile’ U(VI) uptake into authigenic REE-phosphate minerals. Since these minerals were previously thought to rely on the reduction of U(VI) to U(IV) in order to sequester U from geological fluids, such results also advocate for case-by-case analyses to understand the local geochemical schematics of U mobilisation and accumulation across unique hydrothermal systems.

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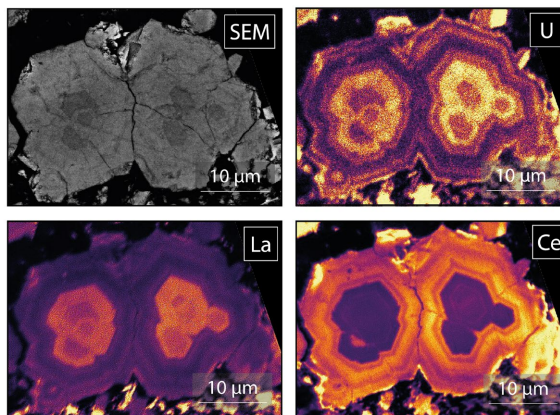


Fig. 1 Nanoscale secondary ion mass spectroscopy (NanoSIMS) element maps of rhabdophane grains from the Kapunda Cu mine, South Australia. The depletion of Ce in the cores of the grains (especially relative to La and the other REEs) likely resulted from Ce (III) oxidation and allowed for more significant U(VI) sequestration into the rhabdophane structure when compared to the rims.