

## Actinide uptake by Powellite

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Powellite (CaMoO<sub>4</sub>) forms as a secondary alteration product during the corrosion of high-level nuclear waste borosilicate glass. It has a scheelite (CaWO<sub>4</sub>) like structure and forms a complete solid solution series with scheelite. The scheelite-like structure can accommodate a range of substitutions involving monovalent and trivalent elements, including lanthanides and actinides (Pu, Am, Cm). Trivalent f-elements can occupy a Ca lattice site via a coupled substitution forming a complete mixing series Na<sub>0.5</sub>Ln/An<sub>0.5</sub>MoO<sub>4</sub>-CaMoO<sub>4</sub>. Depending on the geochemical conditions, these mixed compounds may control the solubility of these elements during the evolution of a waste repository system [1, 2]. Here, we have characterised synthetic La/Eu/Yb-containing powellite compounds which were prepared at 1000°C from MoO<sub>3</sub>, CaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>/Eu<sub>2</sub>O<sub>3</sub>/Yb<sub>2</sub>O<sub>3</sub> powders. A complete mixing series occurs with a significant negative excess volume of mixing for La-containing powellite compounds as indicated by powder XRD, TRLFS and Raman spectroscopy. Low-T EXAFS measurements confirmed the difference of local ordering phenomena between different lanthanides. Complementary co-precipitation experiments with Cm(III) and Eu(III) (1.2E-6 – 1.2E-10 mol/L) at 50°C (pH = 6.2) in a mixed-flow reactor under steady state conditions, a solid solution formed with a Eu content of up to  $X_{\text{NaEuPw}}=0.004$  at precipitation rates down to 2.1E-9 mol/(m<sup>2</sup>s). Consistently with the experiment our Monte Carlo simulations suggest that the Ca<sub>2</sub>Mo<sub>2</sub>O<sub>8</sub> – NaEuMo<sub>2</sub>O<sub>8</sub> solid solution is very limited in this temperature range due to the effects of cation ordering.

[1] Bosbach *et al.* (2004) *Radiochim. Acta* **92**, 639-643.

[2] Grambow *et al.* (1991) *Radiochim. Acta* **52**, 501-506.

## Accessory minerals as petrogenetic tracers: Insights from *in situ* analyses

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Accessory minerals such as zircon, apatite, rutile or titanite are widely used as powerful thermochronological tools in order to constrain the timing and/or thermal evolution (cooling) of magmatic and/or metamorphic events. In this study, we use these minerals not only as radiochronometers but also as petrogenetic tracers of processes and sources for various petrographic rocks outcropping in a fossil arc crustal section in Pakistan. To reach such a goal, we used a variety of different geochemical tracers (titanium thermometry, trace elements, Sr-Nd-Pb isotopes...) on accessory minerals from which we obtained geochronological constraints. A previous geochemical conventional study (major and trace elements combined with isotopes) allowed us to propose a multi-stage complex evolution for the intra-oceanic Kohistan arc [1]. Datings of accessory minerals extracted from different lithologies from the crustal section of the arc allow putting precise temporal constraints for the geodynamical evolution of this section, i.e. both for the volcanic arc *s.s.* building (from ~110Ma to ~98My) and for major underplating events occurring during the section evolution at ~98My, ~91My and ~85My. Major and trace elements have been measured « *in situ* » by EPMA or LA-ICPMS on these accessory minerals either in thick sections or included in epoxy mounts. Isotopes have been measured « *in situ* » by LA-ICPMS method or by the microdrill technique followed by chemical separation of isotopes and MC-ICPMS analyses. In order to assess the geochemical responses of accessory minerals investigated, we discuss and compare our results to those obtained on whole-rocks and pyroxenes separated from different lithologies (gabbros, diorites, granites...) and analyzed for the same elements.

[1] Dhuime *et al.* *Journal of Petrology* (submitted).