

The immobilisation of Eu(III) and Cm(III) by calcium silicate hydrates

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The uptake of radionuclides by calcium silicate hydrates (CSH phases) could play an important role in retarding the migration of radionuclides in the near field and the altered far field of a cementitious radioactive waste repository. In the near field, CSH phases are a major component of the cement used to condition the radioactive waste and as backfill and construction material. In the altered far field, the interaction of hyperalkaline fluids from the cementitious repository (pH plume) with a sedimentary rock may produce a range of CSH-type secondary minerals with high sorption capacities. The actinides are an important class of elements present in almost all radioactive waste streams. Their long-term retention behaviour in the near field and the far-field of a nuclear waste repository is a very important factor in assessing the safety of future repositories.

In the present study, the Eu(III) and Cm(III) retention by CSH phases is investigated using a macroscopic (batch sorption experiments) and spectroscopic (Time-Resolved Laser Fluorescence Spectroscopy (TRLFS)) approach. Eu(III) and Cm(III) are two analogs for Am(III), an important trivalent actinide. CSH phases with different compositions were synthesised in the presence of varying Eu(III) and Cm(III) concentrations. Parallel sorption studies with both elements were performed on well-characterised CSH phases. The distribution of both elements between solid and liquid phase was determined by radiochemical analysis. Desorption studies were performed to evaluate the reversibility of the uptake. The coordination of Cm(III) in the solids was probed using TRLFS. This technique delivers information about the number of H₂O molecules in the first coordination sphere of the Cm(III) in the CSH phase.

The radiochemical data and the TRLFS data show that in both the sorption and co-precipitation experiments, practically all the Eu(III) and Cm(III) is taken up by the CSH-phases, independent of the CSH composition. This results in very high distribution ratios (R_d) of the order of $(6\pm 3)\cdot 10^5$ L kg⁻¹. The higher R_d values found in the desorption experiments suggest that the uptake of these elements is at least partially irreversible. TRLFS revealed that in both the co-precipitation and sorption experiments the same Cm(III) species are associated with the solid. Two different incorporated Cm(III) species could be detected: one species replacing Ca(II) in the interlayer space of the CSH phases, and the other replacing Ca(II) in the octahedron layer of the CSH phases.

Isotopic study of two co-existing magmas in the Western Carpathians

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In the Nizke Tatry Mountains which belong to the Western Carpathians (Slovakia) granitic rocks with dioritic enclaves are exposed near Liptovska Luzna. In order to find out the relationship between these two magmas we did a TIMS isotope study using Pb, Sr and Nd on whole rock samples.

The investigated area is the so-called Rastocna valley, where a common granodiorite of the so-called "Prasiva type" bears oval dioritic enclaves from 5 to 60 cm in diameter. For our study we sampled the country rock and drilled several cores out of a large enclave. The resulting samples covered 100% dioritic material as well as several mixtures up to one with only 20% dioritic phase.

The alumina saturation index of the granodioritic dominated samples vary between 1.15 and 1.09, whereas the more mafic samples range from 1.08 to 1.05. The dioritic endmember has an ASI of 0.89.

The differences in geochemistry are also visible in the isotopic characteristics. Whereas the ²⁰⁶Pb/²⁰⁴Pb of the diorites are above 18.722 and the ²⁰⁷Pb/²⁰⁴Pb are higher than 15.698, the corresponding values for the more granodioritic samples are scattering between 18.609 to 18.720 and 15.688 to 15.668 respectively. The differences in the Pb composition are not very large, nevertheless they document a mixture of crustal and mantle material.

The Nd isotopes reflect the different sources of the granodiorite and the enclaves even better. The Prasiva granodiorite has an ϵ Nd(0) of -5.3, the dioritic enclave has an ϵ Nd(0) of -1.4. A similar distribution can be seen in the Sr isotopic values.

Using the Pb, Sr and Nd isotope data we calculated a three component mixture for the Rastocna samples involving the upper crust, the lower crust and the upper mantle as mixing members.

The calculations gave that the dioritic enclaves consist of roughly 65% mantle and 35% upper crustal component. A contribution from the lower crust is obviously negligible for the diorites. The Prasiva granodiorite can be modeled out of a mixture with 70% mantle, 20% upper crustal and 10% lower crustal component.

These calculations document that two different sources were responsible for the diorites and the Prasiva granodiorite and therefore they reflect the mixing processes which happened during the Variscan orogeny in the Western Carpathians rather well. The incorporation of the lower crust possibly reflects the reworking of older material and might be important for further geodynamic models during Variscan time for this region.