Eu(III) uptake in calcite: A model for actinide retardation by a secondary phase

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Safety assessment of radioactive waste repositories depends on models that include retardation data for all phases. When concrete structures break down, the high pH, Ca-rich environment favours calcite formation in fractures and pore spaces and although calcite is known to incorporate divalent cations within its atomic structure, thus immobilising them as long as the calcite remains stable, little was known about trivalent ion behaviour. We chose to study Eu(III), because it serves as a safe analogue for the trivalent actinides, especially curium and americium, its ionic radius is almost the same as calcite, and better understanding of its behaviour would also help to clarify relationships between the rare Earth Elements (REE's) that could be used to interpret rock genesis and geological processes.

This presentation summarises the reults of several investigations using different approaches. First, more than 100 calcite samples from various geological environments, analysed by inductively Coupled Plasma Mass Spectroscopy (ICP-MS), showed a variation in natural concentration with maximum values of several ppm. Then, precipitation experiments using the constant addition method proved that much more Eu(III) could be accomodated within the calcite structure than is found in natural samples and provided a Distribution coefficient for Eu-calcite solid solution of about 800. The results indicate that Eu(III), or elements with similar behaviour, are strongly sequestered to the solid phase and suggest that low Eu concentrations in natural samples result from low solution concentrations rather than the inability of the structure to accommodate it. The results also suggest that Eu is present in these natural samples as a solid solution with calcite, not as microscopic grains of a separate phase. Reaction stoichiometry suggests 3 Ca(II) ions are replaced by 2 Eu(III) and a cation vacancy. Other experiments used Atomic Force Microscopy (AFM) to observe surfaces exposed to various concentrations of dissolved Eu(III). They prove ready adsorption of Eu(III), even during calcite dissolution but surface behaviour is modified during exposure both to solution and to air. Surface mixing, in response to recrystallisation as a result of dynamic equilibrium, incorporates adsorbed material into the bulk but first results using X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) suggest the rate is low and solid state diffusion is orders of magnitude slower than for Cd(II) and Zn(II).

Monitoring partial melting processes in metabasites using trace elements

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It is difficult to investigate partial melting processes in metabasites using major elements in minerals because they re-equilibrate during the retrograde evolution, therefore destroying compositional evidence of the prograde melting reaction. In-situ trace element determination using laser-ablation ICP-MS of prograde, peak and retrograde minerals in migmatitic metabasites and extracted tonalitic melts has enabled us to monitor dehydration melting, melt segregation, and retrograde processes such as back-reaction between crystallising melt and restitic minerals.

This study uses metabasites from the Harts Range Meta-Igneous Complex at Mt Ruby in central Australia. Peak metamorphism (800ºC, 8-10 kbar) in these rocks occurred during the Ordovician (*c*. 470 Ma), and was associated with partial melting by the reaction:

$$\text{hbl} + \text{pl} + \text{qtz} \pm H_2O = \text{grt} \pm \text{cpx} + \text{melt} \qquad (1)$$

The earliest stage of melting is recorded in included phases in garnet. Hbl inclusions show heavy rare earth element (HREE) depletion and a strong negative Eu anomaly, indicating that the hbl was included while grt was forming, and before pl had been completely consumed into the melt. REE patterns of matrix minerals cpx, hbl and ttn indicate that they grew in equilibrium with melt. They have no Eu anomaly, suggesting that a large part of the pl component was contained in the melt. The first part of cooling in the presence of melt is recorded in the REE patterns of cpx, which show a small relative HREE enrichment due to initial grt resorption. Crystallisation of the melt produced pl-hbl assemblages and was associated with the partial resorption of grt. This process produced hbl that is characterised by HREE enrichment and a strong negative Eu anomaly.

The bulk rock trace element composition of all rock types suggest that a significant amount of melt was lost, and that the tonalites associated with the metabasites represent late stage, residual trace element depleted melts.

The fact that single minerals record different REE patterns, from prograde to peak to retrograde conditions, demonstrates that REE diffusion is not significant up to *c*. 800ºC. Therefore REE analysis in minerals can be a powerful tool to investigate high-grade metamorphic processes beyond the limits given by major elements.