

Competitive effect of Al(III) on Eu(III) sorption to illite

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Clay rock formations present low permeability and strong sorption capabilities for cations, two properties that make them suitable as host rocks for nuclear waste disposal. Accurate description of radionuclide sorption onto clay rock based on geochemical sorption modelling is required to assess radionuclide migration properly. Examining published studies on trivalent actinide/lanthanide (An/Ln(III)) sorption to Illite batches (Illite du Puy) reveals data sets showing different metal ion sorption behavior [1-3] (and own experimental data). Surface complexation constants can differ by more than one order of magnitude ($\log^s K_1=1.9$ vs. 3.1).

Comparing Eu sorption data implies that in one case (stronger sorption) [3] the description of isotherms by the 2 SPNE SC/CE model requires the consideration of strong and weak sites, where binding to strong sites prevails at low $[Eu]_{tot}$ and sorption to weak sites at higher $[Eu]_{tot}$. In the other cases Eu(III) sorption appears to be linear over a wide range of $[Eu]_{tot}$, suggesting strong sites being absent or blocked. We explain this observation by slightly different Illite purification procedures notably by the effect of an acid washing step [1-3]. If Illite batches are washed at pH=3.5 with HCl during 1 week before Eu addition, we exclusively found weaker Eu sorption. A possible explanation for this observation is the incongruent Illite dissolution resulting in the release of Al(III), which in turn can compete with Eu(III) for sorption sites. In order to confirm this hypothesis we contacted Illite during 1 week with a solution containing 10^{-4} M of Al(III) (i.e. equal to [Al] due to illite dissolution at pH=3.5) at different pH. Again, we found Eu sorption behaviour similar to that of the acid treated clay. Taking the competing effect of Al(III) species into account can explain the different Eu(III) sorption data sets.

[1] Gorgeon (1994) Ph.D. thesis University Paris 6. [2] Bradbury & Baeyens (2009) *Geochim. Cosmochim. Acta* **73**, 990-1003. [3] Bradbury *et al.* (2005) *Geochim. Cosmochim. Acta* **69**, 5403-5412.

Deep ingression of meteoric water in late-metamorphic veins: a LA-ICPMS fluid inclusion study from the Rhenish Massif, Germany

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The fluid evolution of late-metamorphic quartz vein systems in the fold-and-thrust belt of the Rhenish Massif has been investigated by microthermometry and LA-ICPMS microanalysis. The quartz veins are hosted in very low-grade organic-matter-rich metapelites of the Hunsrückschiefer and record two major stages of textural evolution: (1) a massive vein filling assemblage with elongate-blocky quartz, chlorite, albite and apatite, and (2) an open space filling assemblage with euhedral crystals of quartz, ankerite/dolomite and minor calcite and sulfides. The euhedral quartz crystals host well preserved fluid inclusion assemblages and permitted to reconstruct the evolution of the fluid system with time. The fluid inclusions, all aqueous two-phase with low salinity, belong to three successive generations. They show a systematic decrease in salinity from 4.7-5.3 to 3.1-3.9 and 1.4-1.7 wt.% eqv. NaCl, and a decrease in homogenization temperatures from 210-225 °C to 148-164 °C and 124-139 °C. LA-ICPMS microanalysis of individual fluid inclusions yielded reproducible concentrations of Li, Na, K, Rb, Cs, Mg, Ca, Ba, Sr, B, Al, As, Sb, S, Cl and Br. Alkali metals and boron, arsenic and antimony are correlated with the fluid salinity. Element concentrations are highest in the early fluid generation and decrease systematically in the latter two generations. Changes in salinity, homogenization temperature and elemental concentrations are explained by fluid mixing between a hot metamorphic fluid (moderate salinity and elevated concentrations of B, As and Sb) and a cooler dilute meteoric fluid during late-metamorphic exhumation and uplift. Cl/Br ratios of the fluid inclusions extend from close to seawater to values that are substantially below seawater. Because evaporitic rocks are absent in the shallow-water marine sequence of the Rhenish Massif, the elevated Br concentrations and Cl/Br ratios below seawater are best explained by fluid-rock interaction and uptake of Br from the organic matter in the metasediments.