

Structural incorporation of trivalent *f* elements into the trioctahedral clay mineral hectorite

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Clay minerals may play an important role in a high-level nuclear waste repository system. Clay-based materials have a high affinity for trivalent actinides, and several distinct molecular level mechanisms of actinide retention can operate: outer- and inner-sphere complexation, cation-exchange (interlayer), and structural incorporation.

Radionuclide immobilization by incorporation into the bulk structure of clay minerals may occur via coprecipitation. However, the size mismatch with the cations which typically occur in the octahedral sites of sheet silicates would result in large lattice strains [1]. Nevertheless, recent TRLFS data for Eu(III)/Cm(III) coprecipitated with hectorite at 90°C [2] suggest that such a substitution mechanism may operate [3,4].

Conventional EXAFS spectra collected on powders of Eu-containing hectorite suggested that Eu(III) was hexacoordinated with oxygens, as in a Mg structural site [5]. Neighbouring structural cations were not detected, maybe due to cancellation effects between EXAFS waves backscattered by (out-of-plane) Si and in-plane (Mg,Al) cations [6]. Polarized-EXAFS (P-EXAFS) experiments on self-supported films of these oriented clay minerals were thus carried out. Spectra were collected for varying europium contents to determine the influence of the degree of substitution on the local crystal structure.

References

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Potassium content in the Earth's core: A high-pressure and high temperature study of the Fe-K system

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The transition metal behavior of potassium at high pressure suggests that a significant amount of potassium could reside in the Earth's core. The radioactive isotope ⁴⁰K could indeed contribute to power the Earth's dynamo but a high concentration may prevent inner core formation. We report a diamond anvil cell study of the Fe-K system up to 42 GPa and 3000K. Using *in situ* X-ray diffraction carried out at the European Synchrotron Radiation Facility, we show that Fe and K can alloy in reducing conditions, provided the change in the chemical bonding character of K from alkaline- to transition-metal is complete (above 20-25 GPa). The incorporation of potassium causes iron lattice to expand with increasing potassium concentration. However, a precise determination of cell parameters of both Fe and K indicates that a maximum amount of 700±300 ppm in weight of K can be accommodated in the ε-Fe lattice. Such pure metal (K,Fe) experiments provide an upper limit to the potassium concentration in the Earth's core. Our estimate is lower than those proposed in previous studies and corresponds to a power limited to 4.3TW, may be more consistent with models of inner core growth and core-mantle boundary heat flow.