

Cation sorption at the smectite edges: From transition metals to Y and Lu

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Introduction

Clay minerals can adsorb trace elements in soils and weathering formations, a sorption property which is also a key-point for the use of clay materials in nuclear waste repositories. Retention can occur either by adsorption on the clay basal plane or at the layer edges, depending on physico-chemical conditions. Building on previous identification of sorption sites of transition metals [1-3], this study shows how the geometry of Y and Lu surface complexes on layer edges of clay minerals can be identified.

Materials and methods

Suspensions of purified clay minerals (hectorite or Al-montmorillonite, 2 and 1 g/L, respectively) were reacted in 0.5 M NaCl at pH 6 (Al-montmorillonite) and 7 (hectorite) with sorbates at concentrations of 50 μ M (Y) and 100 μ M (Lu). Self-supporting films of reacted clay minerals were obtained by slowly filtering suspension aliquots on cellulose nitrate filters. Yttrium K-edge and Lu L3-edge polarized EXAFS (P-EXAFS) spectra of the self-supporting films were collected in fluorescence mode on the FAME beamline (ESRF, France). P-EXAFS data were reduced, and analyzed using standard procedures.

Results and interpretation

Small but significant angular dependences were observed for all P-EXAFS data, meaning that the Y and Lu binding environments are anisotropic. Coordination spheres of 7 O at 2.36 Å and 8 O at 2.27 Å, were observed for Y and Lu, respectively, comparable with d(Ln-O) distances measured by EXAFS spectroscopy [4]. Lutetium sorbed on Al-montmorillonite was surrounded by an Al-shell at 3.35 Å, consistent with Lu sharing edges with Al octahedra and partially incorporated in a gibbsite-like interlayer. Both Y and Lu sorbed on hectorite were surrounded by cationic shells. Modelling of these cationic contributions yielded one out-of-plane Si/Mg shell at 3.16 Å (Y) or 3.04 Å (Lu), and two in-plane (Mg/Si) shells at 3.50, and 3.97 Å for Y, or 3.33 and 3.91 Å for Lu. These distances and angular orientations collectively suggest that Y and Lu form inner-sphere surface complexes at the edges of hectorite platelets, but slightly above/below the hectorite octahedral plane, and tend to share edges with silicate groups of the clay tetrahedral sheet.

References

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Interaction between colloidal and organically complexed Iron (III) species in seawater by ultrafiltration

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Method and Theory

Ultrafiltration experiments (Viavflow 50 - 10kDa filter) were performed using ^{55}Fe in combination with artificial and natural organic ligands (in excess) in seawater. The activity of the ^{55}Fe in the permeate and retentate was measured using standard liquid scintillation methods. The permeation (P_c) and retention coefficient (R_c) were calculated as follows:

$$P_c = 1 - \left(\frac{\log c_p}{\log CF} \right) \quad R_c = 1 - \left(\frac{\log c_R}{\log CF} \right)$$

Where CF = concentration factor (CF). Some results are shown in the Table below:

Table 1: P_c and R_c values of the Fe (III) species

Ligand	P_c	R_c
None - UV irradiated Seawater	0.49	0.44
Natural - Antarctic Seawater	0.96	0.58
Natural - Coastal Seawater	0.93	0.63
2-(2-Thiazolylazo)- <i>p</i> -cresol (TAC)	0.99	0.75
Ethylenediaminetetraacetic acid (EDTA)	1.00	0.85
Desferrioxamine_B (DFO_B)	0.97	0.97
2-Keto-D-Gluconic Acid	0.88	0.59
Protoporphyrine IX	0.89	0.49
Phytic Acid	0.97	0.63

Discussion

These 2 parameters allow us to differentiate between very strong, strong and weak ligands based on their ultrafiltration properties. $P_c=R_c=1$ are significant for very strong ligands (e.g. DFO_B), where all added Fe is organically complexed. Strong ligands (e.g. TAC, EDTA) have additionally a colloidal fraction, but no interaction between both species ($P_c=1$, $R_c<1$). $P_c=R_c<1$ are observable for weaker ligands (e.g. Protoporphyrin IX) with an identifiable interaction between both species.

Conclusion

Using this approach helps us better understand the relationship between colloidal and dissolved Fe concentrations in natural seawater and how to quantify the interconnections between natural organic complexes and colloidal iron. The results strongly suggest that information on colloidal Fe concentrations is dependent on CF and this needs to be taken into account when reporting ultrafiltration data. This approach is particularly useful for assessing the bioavailability of iron in natural seawater as most colloidal iron is believed to be weakly bioavailable.