

Competition between lanthanides and Al for humic acid binding

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Lanthanides or rare earth elements (REE) are commonly studied as analogues of actinides. This group of 14 elements present a unique feature related to their similar and coherent chemical properties. In natural waters, REE aqueous concentrations and transport is strongly affected by dissolved organic matter such as humic acids (HA). However, in organic-rich waters, different REE concentration patterns are observed. A first explanation is the heterogeneity of HA binding sites: REE-HA pattern is the fingerprint of the dominant REE binding HA sites. Previous study showed that light REE (LREE) are more bound to HA carboxylic sites whereas heavy REE (HREE) are more bound to HA phenolic sites. Secondly, in natural waters, various cations are also bound to HA and might therefore affect REE-HA binding and subsequent pattern. Al is one of the major competitor cation for REE regards to its high affinity for HA and its strong concentration in natural waters.

Al-REE competition experiments for HA binding were performed between pH 3 and 6. Results were modelled with Model VI, a specific humic-ion binding model. It appeared that Al^{3+} and $\text{Al}(\text{OH})_2^+$ present the same affinity for HA sites as already assumed in Model VI. However, Al^{3+} and $\text{Al}(\text{OH})_2^+$ are stronger competitors for HREE than LREE, which is not expected in the model and was attributed to Al strong affinity for HA phenolic groups. From pH 5 to 6, Al competitive effect decreases because of $\text{Al}(\text{OH})_3$ precipitation. However, Al becomes more competitive for LREE than HREE regards to the $\text{Al}(\text{OH})_2^+$ binding to HA carboxylic groups. Model VI parameters were re-evaluated and, for the first time, $\text{Al}(\text{OH})_2^+$ was also considered to bind to HA. The new set of Al parameters improved model accuracy for both our REE-Al competitive experiments and Al-HA data from literature.

REE-Al competitive study for HA shows a new Al-HA binding mechanisms which was not observed before. These results highlight the strong impact of competitor cations on the REE-HA binding behaviour in natural organic-rich waters. This study provides a more accurate description of Al-HA binding and, therefore, will indirectly improve REE and actinides speciation modelling in environmental systems.

Recycling agents in subduction zones: Fluids, melts and solids!

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Sediment melts and hydrous fluids loaded with solutes generated in the subducting slab at elevated *P-T* conditions are thought to transport differing amounts of trace elements and variable isotopic signatures from the subducting slab into the overlying mantle, where they ultimately contribute to the source region of magmas produced at convergent plate margins. Conventional geochemical models of subduction zones consider trace elements to be derived from two distinct sources: hydrous fluids derived from altered oceanic crust during subduction and partial melts derived from the thin sedimentary veneer. However, the physical processes of transport and mixing of these contributors within the subduction factory are largely enigmatic.

Studies on exhumed subduction mélanges suggest that hybrid rocks with newly grown minerals concentrate, sequester and redistribute water and key trace elements [1, 2]. The strong petrologic and chemical contrast at the slab-mantle interface, produces these hybrid rock compositions by metasomatic reactions, diffusion and mechanical mixing: the Al-, Si- and alkali-rich slab that carries crustal isotopic signatures and trace-element abundances is juxtaposed with the Mg-rich ultramafic rocks of the harzburgitic mantle. Mechanical mixing of crustal and mantle rocks will propagate the formation of hybrid rocks, and fluxing by hydrous fluids derived from the dehydrating slab will enhance reactivity and lead to fluid saturation of the newly formed rocks.

The identification of cold plumes in high-resolution numerical experiments [3] provides a mechanism to transport buoyant hybrid rocks from the slab-mantle interface towards the source region of arc magmas. Mélangé rocks travelling into the mantle wedge in 'wet' diapirs would be subjected to *P-T* conditions dramatically different from those at the slab surface. Partial melting of hybrid rocks may produce the large range of major and trace-element compositions found in modern island arc volcanic rocks.

[1] Bebout & Barton (2002) *Chem. Geol.* **187**, 79–106.

[2] Miller *et al.* (2009) *Lithos* **107**, 53–67. [3] Zhu *et al.* (2009) *G-cubed* **10**, Q11006.