# Kinetic effects in the complexation of radionuclides with humic substances in the presence of Fe(III) and Al(III)

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Radiotoxic metals such as actinides are largely immobilized by adsorption onto mineral surfaces unless their positive ion charge is outweighed by negatively charged ligands. In geochemical systems, complexation with dissolved humic substances can render the metal species highly mobile [1]. To date, coupled speciation-transport codes for predicting humic-bound migration rely on equilibrium models for metal-humic interaction in multicomponent systems (e.g., NICA-Donnan model). Their applicability is, however, affected by specific kinetic effects, which are not yet understood.

The present kinetic study deals with metal-humate complexation under the competitive influence of Fe(III) and Al(III), the most abundant trivalent electrolyte constituents in terrestrial waters. $^{152}$Eu(III) and $^{160}$Tb(III) were employed as short-lived radioactive tracer analogues of trivalent actinides. Using ion exchange separation methods, their humic-bound fractions were determined for solutions of humic acid and Fe(III) or Al(III) which had been pre-equilibrated for different periods of time (up to 6 months).

Our results reveal that the competition effects of both Fe(III) and Al(III) significantly increase with contact time, over a period of 2 months for Fe(III) and of 2 days for Al(III), with their bound amounts remaining unchanged. On the basis of concomitant changes in pH, we found that the time dependence for Fe(III) can be explained by a slow degradation of bound Fe polycations (increasing the occupation of binding sites), whereas the effect for Al(III) must be due to changes concerning the binding sites themselves. Here, the time dependence corresponds to the kinetics of an increase in complex stability, which is observed in cation exchange experiments. This latter effect is often explained by an in-diffusion process within humic macromolecules. However, this reasoning cannot serve as an explanation for an increase in competition. We suggest structural rearrangements, induced by Al in its surroundings, as most probable cause, albeit time-dependent studies by laser fluorescence spectroscopy (steady-state and time-resolved) yielded no evidence of any massive changes.

[1] Choppin (1992) *Radiochim. Acta* **58/59**, 113-120.

# The response of sedimentary $^{231}$Pa/$^{230}$Th on particle flux–findings from the African margin

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In the Atlantic Ocean sedimentary $^{231}$Pa/$^{230}$Th ratios below the production rate are believed to mirror the advective export of $^{231}$Pa to the Southern Ocean correlated to the strength of the Meridional Overturning Circulation (AMOC). Times of increased $^{231}$Pa/$^{230}$Th related with prominent events of cooling support the conclusion that variations in the AMOC may incite climate changes [1]. However, the impact of particle flux and particle composition on the $^{231}$Pa/$^{230}$Th is still a great matter of discussion [2]. Further, the relevance of the upwelling regions off North- and Southwest Africa as an additional sink for $^{231}$Pa is yet not well understood. In response to a possibly weaker AMOC $^{231}$Pa would reside longer in the ocean basin and thus could be more efficiently trapped in the upwelling regions. In this case, the applicability of the sedimentary $^{231}$Pa/$^{230}$Th ratio as a proxy for advective transport would be strongly biased. Here we present three $^{231}$Pa/$^{230}$Th down core profiles from the African margin back to 30 kyr. Applying ICP-MS and first time low energy AMS [3], we obatined two $^{231}$Pa/$^{230}$Th records from the high-productivity region off Namibia (GeoB1711-4 and GeoB3722-2). During the Holocene both profiles display either the export of $^{231}$Pa with the active Holocene AMOC, or the influence of particle flux due to high productivity fully coresponding with a recently published holocene data set [4]. During glacial times the impact of productivity on the $^{231}$Pa/$^{230}$Th becomes intensified. Though, boundary scavenging of $^{231}$Pa was not vitally to an extend to bias the $^{231}$Pa budget of the ocean basin. The $^{231}$Pa/$^{230}$Th profile off West-Africa (GeoB9508-5) shows correlation to the particle input which is synchronized to Heinrich Events [5].

[1] McManus *et al.* (2004) *Nature* **428**, 834-837. [2] Keigwin and Boyle (2008) *Paleoceanography* **23**, PA1101. [3] Christl *et al.* (2007) *NIM-B* **262**, 379-384. [4] Scholten *et al.* (2008) *EPSL* **271**, 159-169. [5] Mulitza *et al*. (2008) *Paleoceanography* **23**, PA4206.