Sorption of uranium(VI) and radium(II) at trace level onto kaolinite and montmorillonite

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Clays are one of the main components of soils and sediments, and are known to have the distinctive property of retaining ions, generally with a high affinity for cationic species. Since retention processes confer a retardation effect on the migration rate of contaminants, the clay content and the intrinsic properties of clays will determine the prevailing process during the transport of contaminants through subsurface environments.

Uranium and the long-lived decay product radium-226 are abundantly present in the vast mine waste produced during uranium extraction activities. However, in the case of release to the surrounding environment, these radionuclides would be found at trace level compared to major cations present in interstitial waters; and hence, the extent of radionuclide sorption will be conditioned by the predominant occupancy of surface sites by the latter solutes. Therefore, the aim of this work was to study the sorption of trace level uranium(VI) and radium(II) on two common phyllosilicate minerals, kaolinite and montmorillonite, alongside with the sorption of sodium, potassium, calcium and magnesium at higher concentration.

Batch type experiments using chemical and radiochemical analytical techniques were carried out to obtain the intrinsic ion-exchange properties of both clay minerals and the ion-exchange equilibria occurring at the mineral-solution interface with the associated selectivity coefficients for Na/H, K/H, Cs/H, Ca/H and Mg/H ion couples. Sodium, K, Cs, Ca and Mg were introduced in sufficiently high amount in separated batches containing the respective homo-ionic clay forms and the adsorbed cation concentration was measured as a function of pH. The results enabled to determine the clay surface sites characteristics (i.e. the number and concentration of sorption site types) and to confirm the multi-site ion-exchanger properties of these clay minerals, as previously observed for montmorillonite [1]. The sorption of U(VI) and Ra(II) at trace level was determined through distribution coefficient (K_d) measurements at different pHs.

Finally, the sorption data for both clays was processed according to a general multi-site sorbent / multi-species sorbate model which has already been applied to successfully describe the sorption reactions on mineral surfaces [2, 3]. The modeling results will provide with fundamental sorption equilibria stoichiometries and constants crucially needed for the calculation of the interfacial chemistry to be coupled to transport in predictions of radionuclide migration rates.

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Reevaluating osmium isotopes as tracers of glacial-interglacial cycling

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Over the past 15 years, several studies [1-5] have demonstrated correlations between the Os isotopic compositions of hydrogenous marine sediments and glacial-interglacial variations. These are often attributed to decreased continental erosion during glacial episodes. However, the short Os marine residence time (< 5ka) inferred from these rapid variations is inconsistent with that derived from mass balance considerations (~25 to 40 ka, [6-8]). This observation has prompted the proposal that rapid weathering during deglaciations produces transient spikes in the concentration and/or isotopic composition of Os delivered to the ocean, thus arguing that the riverine flux and the oceans are far from steady state equilibrium [9].

Nevertheless, these interpretations rest on the assumption that the available Os isotopic records faithfully reflect the past Os compositions of global seawater. However, many records may be biased by basin isolation, detrital input, and low sedimentation rate. To obtain a reliable, high resolution record of Quaternary marine Os isotopic variations, we are analyzing sediments from ODP Leg 175, Site 1084, drilled beneath the Benguela Upwelling System (BUS) off Namibia. As an open ocean site with rapidly deposited (~ 18 cm/kyr) organic rich sediments, it should be unaffected by the problems noted above. Results from 24 samples analyzed to date, spanning the past ~130 ka, show much less variability ($^{187}Os/^{188}Os = 1.037 \pm .026$; 2σ) than that found in previous studies (~10%), and no correlation with glacial-interglacial variations. Instead, the uniformity of the BUS Os record ressembles that of an early Pleistocene record from the equatorial Pacific Ocean [9]. One explanation for the discrepancy between the BUS results and other late Quarternary records may be that the latter reflect local, rather than global, processes. However, while this explanation seems logical for sediments deposited in semi-isolated near-shore basins [2-4], local effects are unlikely to modify the Os compositions of open ocean sites [1,5]. Instead, we consider the fact that dissolved Os may be present in several oxidation states, and experimental studies suggest that it is difficult to pass from one to another [11]. Os incorporated into metalliferous sediments [1] or planktic foraminifera [5] under oxidizing conditions may not be in the same form as that incorporated under the reducing conditions prevailing in the BUS. Thus it may be too simplistic to consider that all of the Os present in the oceans is contained within a single uniform reservoir with a well-defined residence time.

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