

Distribution, Fluxes in the water column and early diagenesis in the bottom sediments of ^{210}Po and ^{210}Pb in the sea

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The ^{210}Po activity, granddaughter of ^{210}Pb activity, has been widely studied to elucidate various oceanic processes, such as quantifying the scavenging and removal of particle-reactive species including organic matter. The deficit and excess of ^{210}Po with respect to its grandparent ^{210}Pb in dissolved and particulate phases in the surface ocean is well documented through the ocean. However, in deep waters below 1000 m, secular equilibrium between ^{210}Po and ^{210}Pb was observed in some areas, but a large deficiency of ^{210}Po with respect to ^{210}Pb in dissolved phase was also observed in several places in the world ocean. Recent efforts were made extensively by GEOTRACES [1, 2] to resolve the unresolved issues in determination of ^{210}Po and ^{210}Pb remaining from the earlier GEOSECS studies in late 1970s. Here we report new measurements of dissolved, particulate, and sediment porewater ^{210}Po and ^{210}Pb in a deep marginal sea in the Northwest Pacific (East Sea/Japan Sea) using the state-of-the-art measurement methods considering all relevant correction factors in the calculation of the final *in situ* their activities provided by GEOTRACES $^{210}\text{Po}/^{210}\text{Pb}$ group. The earlier discrepancy may be resolved as we can generalize the vertical distribution of dissolved ^{210}Po with respect to dissolved ^{210}Pb in the sea as the surface deficit, subsurface excess and secular equilibrium below the 500 m or 1000 m depth based on our measurements with great variation of total activities due to their variation in the sources as well as the amount of suspended particulate matter in the water column. An order of magnitude greater concentration of dissolved ^{210}Po and ^{210}Pb concentration activities were present in the interstitial waters of the bottom sediment with ^{210}Po deficit or excess with respect to ^{210}Pb in the East Sea. Detailed quantitative analysis on the distribution, chemistry, flux, and early diagenesis is presented at the meeting.

[1] Church *et al* (2012). *Limnol. Oceanog.: Methods* **10**, 776-789. [2] Baskaran *et al* (2013). in press.

Redox behavior of uranium incorporated into hematite

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The development of long-term geological waste repositories is an important response to ever increasing amounts of spent nuclear fuel. One of the principle considerations at any potential storage site is the possibility for radionuclides to leach from waste forms and undergo subsurface transport. The solubility of radionuclides in the repository environment, their redox behavior, and possible incorporation into proximal mineral phases are inter-related mechanisms that synergistically affect the subsequent hydrological transport of the nuclides.

It has been shown that U(VI) can be incorporated into bulk hematite with a similar coordination environment as Fe(III) [1,2]. In this study, we analyze the incorporation of U(VI) into hematite as a possible mechanism of limiting the aqueous uranyl concentration in contaminated areas. Atomistic simulations were conducted to evaluate the incorporation mechanism (*i.e.*, substitution reaction energies and substitution geometries). The redox behavior of uranyl incorporated into bulk hematite was investigated using cyclic voltametry with a powder microelectrode. In addition, the redox behavior of uranyl incorporated into hematite is compared with that of uranyl at the hematite surface to evaluate the role of hematite as a uranyl host and as a substrate for uranyl sorption, reduction and precipitation.

The sample was preconditioned for thirty minutes at -0.25V and scanned between $\pm 0.7\text{ V}$ at a rate of 50 mV/s . Under these conditions, uranyl was observed to undergo an irreversible oxidation from U(IV) to U(VI) on the first positive voltage scan. Subsequent cycles indicate reduction and re-oxidation between U(VI) and U(V). Similar experiments examined uranyl in solution with hematite and measured comparable uranyl redox behavior. Due to the strong relation between uranium solubility and oxidation state, these initial results are significant with regards to potential aqueous uranyl immobilization.

[1] Duff (2002) *Geochimica Acta* **20**, 3533-3547 [2] Ilton (2012) *Environmental Science and Technology* **46**, 9428-9436