

## Importance of nanominerals on the concentrations, isotopic abundances, and element cycles at earth's surfaces

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Nano-sized minerals (nanominerals) have substantial influences on the abundances of elements, isotopic ratios, and cycles of various elements at earth's surface. In this paper, I will give examples of essential roles played by nanominerals in various phases in environment.

In the atmosphere, aerosols are very important for the accurate prediction of global warming. Aerosols smaller than 1 micron are generated by physical and chemical processes in the atmosphere. Sulfate and oxalate aerosols are main species produced by such processes, which are considered to have a cooling effect of the earth due to their high hygroscopicity to assist cloud formation. If sulfate and oxalate form insoluble metal complexes, however, the species do not absorb water, which results in the mitigation of the cooling effect. We employed X-ray absorption fine structure spectroscopy (XAFS) to distinguish the sulfate and oxalate species. As a result, it was found that most of oxalate species was actually insoluble metal complexes, showing that cooling effect of the organic acids can be smaller than expected so far. For the analysis of sulfate in such fine particles, scanning transmission X-ray microscope (STXM), which is at present constructed in Photon Factory by our group, can give distribution of various chemical species with 50 nm spatial resolution.

In soil, various nanominerals are playing an important role to control the migration of various ions. Related to the Fukushima Daiichi Nuclear Power Plant accident, it has been indicated that 2:1 type clay minerals and micas strongly adsorb (radio)cesium within the soil. The affinity of Cs and availability of Cs to plants have been evaluated by Radiocesium Interception Potential (RIP) for various minerals and soils. On the other hand, we can determine the ratio of inner- and outer-sphere complexes of Cs adsorbed on the minerals and soils. We found that the amount of inner-sphere complex has a close linear-correlation to RIP value, showing that the mobility of Cs is decided by the amount of inner-sphere complex to the solid media.

In seawater, abundances and isotopic ratios of oxyanions such as chromate, molybdate, and tungstate are governed by the adsorption reactions on the nanominerals such as iron oxyhydroxides and manganese oxides. In particular, XAFS analysis and quantum chemical calculation (QC) revealed that chromate and molybdate form almost outer-sphere complexes, whereas tungstate inner-sphere complex on ferrihydrite. In particular, it was shown that inner-sphere complex is mainly a bidentate-binuclear complex. It has been indicated that affinity of the oxyanion to Fe (oxyhydr) oxides and the attachment mode (inner- or outer- sphere complex) is interpreted by linear free energy relationship (LFER) using pKa of conjugate acids. We here found that average pKa value, or  $(pK_{a1} + pK_{a2})/2$ , is better to explain the systematics, because contributions of two acid dissociation groups are important in terms of the structure of the surface complex.

Isotopic fractionation between hydrated molybdate and that adsorbed on manganese oxide was calculated from vibrational frequencies. The largest isotopic fractionation was observed when Mo formed inner-sphere complex with octahedral coordination. In our study, it was suggested that (i) taking account of the adsorbent in the calculation and (ii) calculation of hydration including actual water molecules are needed to quantify the large isotope fractionation by QC. Structural information at atomic level coupled with QC calculation is essential to study the interaction of various chemical species with nanominerals.

As seen in this paper, nanominerals have great impacts on the migration and cycle of any elements at earth's surface. Understanding of the interaction is essential to elucidate geochemical information from geological materials and to predict behaviors and cycles of any elements at earth's surfaces and their effects on the environment.