

Recent trend of reactive transport modeling of rock weathering

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The weathering of rock proceeds by the dissolution of primary minerals, the precipitation of secondary products, and the transport of materials in the pores of the rock. To quantitatively understand these processes, the analysis using the reactive transport equation is performed (reactive transport modeling). The following equation is an example of the one-dimensional reaction-transport equation:

$$p(dc/dt) = D(d^2c/dx^2) - vp(dc/dx) + Ar_0f(c)$$

where c is the solute concentration, t is the time, x is the distance, p is the porosity, D is the effective diffusion coefficient, v is the flow rate in pores, A is the surface area per unit volume of rock, r_0 is the rate constant, and $f(c)$ is the function that expresses the concentration dependence of the dissolution rate. By solving the reaction-transport equation, we can know the distributions of the solute concentration and dissolution rate in the rock, and their time variations. As the method to determine the parameters used in the calculation, for example, D can be determined by direct experimental measurement (Yokoyama and Nakashima, 2005) or by empirical equation (Archie's law). As for the reaction term, several rate laws, such as linear TST law (Aagaard and Helgeson, 1982; Lasaga, 1984), Al inhibition model (Oelkers et al., 1994), and parallel rate law (Hellmann and Tisserand, 2006), have been proposed. In the case of the reaction of quartz, $f(c)$ is equal to $1 - c/c_{eq}$, where c_{eq} is the equilibrium concentration (Lasaga, 1998). By comparing the result of calculation with the actual weathering profile, we can discuss various topics including the mechanism of weathering and the reason of the discrepancy between the dissolution rates obtained in the field and in the laboratory (White and Brantley, 2003).

As some of the recent studies on reactive transport modeling, Maher et al. (2009) showed that the weathering profiles observed in soils can be reproduced by using the rate constants (based on the Al inhibition model and parallel rate law) similar to those estimated from the results of laboratory dissolution experiments, and also suggested that the precipitation of secondary products plays an important role in controlling the amount of dissolution of primary minerals. Maher (2010) proposed that weathering rate is strongly dependent on fluid residence time and flow rate. Navarre-Sitchler et al. (2011) showed that the rate of formation of the weathering rind and the distribution of the primary and secondary minerals in basalt can be explained by incorporating the time variations of p , D , and A into the modeling. Moore et al. (2012) indicated that the average flow rate and the reactive surface area that are smaller than measured values need to be used to reproduce the weathering profile of granite by the modeling.

At present, the concentration dependences of the dissolution rates obtained at temperature higher than ambient temperature (e.g., 150 degree C) are usually directly used to analyze the reaction at ambient temperature, but its relevance is uncertain. In addition, although the precipitation rate of secondary product largely affects the result of modeling, information of the precipitation rate law of a secondary product of interest (e.g., poorly crystalline aluminosilicate) is often insufficient. Furthermore, the pores in the rock near the ground surface often become unsaturated, but little is known about the extent to which reactive surface area differs under unsaturated and saturated conditions. To resolve these problems would be important to improve the accuracy of the reactive transport modeling.

Keywords: Weathering, Reactive transport modeling

Adsorption of sulfate to ferrihydrite: surface complexation modeling and in-situ infrared spectroscopy

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Sulfate, a major anion in nature, can affect the mobility of coexisting dissolved toxic trace elements by influencing the adsorption properties of the species on mineral surfaces. Ferrihydrite is an important scavenger for trace elements in natural water because of its adsorption capacity and its ubiquitous formation in surface conditions. To elucidate the adsorption behavior of the trace elements in natural water, it is important to construct a predictive model of sulfate adsorption on ferrihydrite that can predict the adsorption behavior of sulfate quantitatively under widely various environmental conditions based on the spectroscopic information of sulfate adsorption.

In-situ infrared spectra for sulfate adsorption on ferrihydrite as a function of pH (3-7), ionic strength ($I = 0.01$ and 0.1) and sulfate loading ($[\text{SO}_4^{2-}] = 0.1$ and 0.2 mM) were obtained to constrain the surface speciation of sulfate on ferrihydrite. The shape of the spectra was pH-dependent. The degree of ν_3 band splitting decreases with pH. Little difference of the spectra was found between different ionic strengths and sulfate loadings for the same pH. The little influence of ionic strength on the IR spectra indicates that the inner sphere and outer sphere species most likely do not exist simultaneously at the same pH condition. Based on the IR spectra obtained from lower pH showing the splitting of ν_3 band to two peaks with activation of ν_1 band, the surface species is identified to be single inner sphere monodentate sulfate. The changes of spectra with pH are most likely attributable to the changes of the electric field strength posed to the sulfate on ferrihydrite surface, which is strongly pH-dependent.

The predictive model for sulfate adsorption was constructed using an extended triple layer model (ETLM). The pH adsorption edges and proton surface charges in the presence of sulfate as a function of ionic strength and sulfate concentration were obtained, respectively, from batch adsorption and acid-base titration experiments. The sulfate adsorption on ferrihydrite increases continuously with decreasing pH and ionic strength. These macroscopic adsorption data were analyzed using ETLM to retrieve the sulfate adsorption reaction and the equilibrium constant. Results of ETLM analyses showed that adsorption of sulfate on ferrihydrite is a single monodentate inner sphere process that is consistent with in-situ infrared spectroscopic observation.

Batch adsorption data from earlier studies of sulfates on ferrihydrite were reasonably reproduced using ETLM with the same adsorption reaction and equilibrium constant.

Keywords: ferrihydrite, sulfate, surface complexation modeling, in-situ infrared spectroscopy

Formation, dissolution, migration and Pu-sorption of ferrihydrite nanoparticles

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This paper describes the behavior of Pu and ferrihydrite nanoparticles in the Lake Karachai area. The Pu in the Lake Karachai area is sorbed to colloidal ferrihydrite and moves with the ferrihydrite in the groundwater. The Pu is incorporated in the inner part of ferrihydrite because the partition coefficients of Pu between solution and ferrihydrite have a wide variation. The ferrihydrite is formed from Fe(III), which is supplied through the dissolution of Fe(II) from metallic iron in Lake Karachai and iron-bearing minerals in rock and the oxidation of the Fe(II) by oxygen or nitrate. The formation of hematite or goethite, which is more stable than ferrihydrite, decrease the concentration of ferrihydrite. When the supply of Fe(III) exceeds the formation of hematite or goethite, the concentration increases, and when the supply of Fe(III) is less than the formation of hematite or goethite, the concentration decreases. The formation rate of hematite or goethite is proportional to the concentration of ferrihydrite nanoparticles, the formation rate decreases by more than one order of magnitude in groundwater because of the present of trace amount of dissolved silica. The migration of ferrihydrite nano-particles depends on the concentration and the size of nanoparticles, and the pH of the groundwater. When the concentration of nano-particles exceeds the critical aggregation concentration (around 10^{-3} mol Fe /L), the nano-particles aggregate and precipitate. Large nano-particles are trapped in the dimples of fractures or filtrated in constrictions. When the size of ferrihydrite nano-particles is 70 nm, which is the same as that in the Lake Karachai area, the 99 % of the particles are trapped in a dimple of 3 mm. The gravity also significantly affects the downward movement of nano-particles. The ferrihydrite nano-particles with the diameter of 70 nm move downward with the velocity of 0.12 m/year, which is significant because the assessment period of radioactive nuclear wastes is more than 10,000 years.

Keywords: sorption, ferrihydrite, nanoparticles, formation, dissolution, migration

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.

Significance of nano minerals in the planetary materials science

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Introduction: Nowadays we can investigate diverse planetary materials in laboratories: meteorites, interplanetary dust particles, micrometeorites, returned samples from the Moon, the Wild 2 comet, and the asteroid Itokawa, and so on. These planetary materials often contain submicron minerals (hereafter nano minerals).

Nano minerals in planetary materials: Why nano minerals are common among planetary materials? Their small sizes are probably related to their formation conditions and/or mechanisms. Now we look out several examples of nano minerals in planetary materials.

Nano minerals in hydrated chondritic meteorites: CIs, CMs, CVoxBs, CRs, CHs, CBs, and some UOCs contain various amounts of hydrated minerals [e. g. 1]. Phyllosilicates in them are saponite and/or serpentine. Their crystallinity is poor and only a few to at best a few tens repetitions of (001) lattice fringes can be seen in TEM images. When they coexist, they often form mixed layers. After accretion of anhydrous materials, water ice and organics, water ice was melted probably by ²⁶Al decay heat and water was reacted with anhydrous materials within their parent bodies to form hydrated minerals and the other minerals such as carbonates. The alteration temperatures and water/rock ratios are estimated to have been different between CIs and CMs: >100 °C and ~1 and <20 °C and 0.3-0.6, respectively [e. g. 1]. Low water rock ratios and possibly stagnant fluids might be related to their poor crystallinity. Because no remarkable elemental fractionation by aqueous alteration is not observed in these meteorites, fluid may have been lost by freeze-dry on their parent bodies.

Aqueous alteration products in Martian meteorites: Nakhilites are a kind of Martian meteorites formed in lava flows or shallow intrusions [e. g. 2]. The meteorites are unique because they contain aqueous alteration products formed on Mars, which typically appear as reddish brown veinlets in olivine phenocrysts. The alteration product of Lafayette meteorite is composed of siderite, poorly crystalline saponite and serpentine, and silicate gel. The hydrothermal assemblage suggest that a CO₂-rich hydrothermal fluid reacted at 150-200 °C, pH 6-8 with a water/rock ratio of <300 [3]. Because elemental fractionation is remarkable in the alteration product, the fluid obviously moved along clacks. Another intriguing example is ALH84001 orthopyroxenite containing bacteria-like objects [4]. Although it contains truncated nanomagnetite, debates on its origin have not finished even today [5].

Nano minerals in chondritic porous interplanetary dust particles: Chondritic porous interplanetary dust particles (CP IDPs) are typically ~10 micron-sized planetary materials, which have been regarded as cometary dust and the most primitive planetary materials that can be investigated in laboratories even after the Stardust mission [6]. They are loose aggregates of nano minerals with some isolated minerals larger than 1 micron. Because CP IDPs experienced almost no modification on their parent bodies, each constituent has its own history. The most curious object in CP IDPs are GEMS (glass with embedded metal and sulfide), which is <500 nm spheroidal amorphous silicate containing nanocrystals of Fe-Ni metal and Fe sulfide [7]. Its origin is still in dispute [8].

Summary: As described above, nano minerals in planetary materials hold the key to understand their formation conditions and origins although some are still in debate.

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