Observations of Chemical Evolution in Environmental Systems

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Much effort has been made to understand the mechanisms and kinetics of various environmental interfacial reactions. Probing natural chemical complexity at a high spatiotemporal resolution and tracking down more accurate non-equilibrium properties are crucial for predicting and controlling the fate and transport of environmental toxins. However, only limited studies have been trying to address these aspects due to technical difficulties of a high spatiotemporal resolution as well as lack of proper *in situ* observation techniques. In this talk, three examples will be introduced for further discussion.

(1) Early nucleation and growth of iron oxide nanoparticles and their growth kinetics in the environment. Surface-mediated nucleation and growth of iron and manganese oxide nanoparticles and nanofilms on environmental interfaces can significantly influence the fate and transport of toxic metal contaminant. Therefore, more accurate quantitative and qualitative information about the mechanisms and kinetics of nanoparticle development at surfaces is required. However, direct *in situ* observations of nanoscale surface particle development have been challenging because of lack of proper tools. Using a time-resolved simultaneous small angle x-ray scattering (SAXS)/grazing incidence (GISAXS) setup as well as atomic force microscopy (AFM), we investigated real-time the nanoparticle formation at mineral interfaces and the uptake of heavy metals by newly formed nanoparticles (1). The size, shape, and distribution of iron oxide nanoparticles on quartz surfaces as well as in solutions and their growth modes were monitored as a function of exposure time, ionic strength, and the presence of aqueous arsenate. Advantages to use this setup is that the formation of hydrous mineral phases in bulk solution can be monitored *in situ* and quantities of nanoparticles in bulk water and at mineral surface can be identified. Therefore, this approach can provide more accurate depiction of evolving nanoparticle distributions and topology at an active interface without dehydration.

(2) Electron transfer-induced structure changes and dissolution of minerals: Recent advance in electron transfer in natural minerals has been vigorously made. Using AFM, Yania and Rosso found that in the presence of Fe^{2+}, electron transfer occurs through bulk hematite crystal and promotes the dissolutions of hematite at (*hk0*) vicinal sides, while ferric ions are reprecipitated at (001) surfaces (2). Developing a technique which can directly monitor the electron transfer real-time is a crucial step to further advance the understanding of complex chemical reactions in the environment. Most recent work by Katz et al., reported transient iron (II) formation in dye-sensitized maghemite (γ-Fe_2O_3) nanoparticles by time-resolved x-ray spectroscopy (3). This study utilized a combination of a laser pulse pump and a probe pulse (x-ray beam). Using x-ray near-edge absorption spectroscopy (XANES), they recorded the evolution (specific structural and electronic changes) of the system, which is induced by the pump laser. By a laser pulse, Fe^{3+} in maghemite was reduced to Fe^{2+} and this was monitored by the ferrous signal loss with time ranges of several ns. This study was able to observe the speciation of Fe atoms in maghemite with ~ 100 ps resolution. As this study indicated, obtaining the proper temporal resolution is a key improvement for monitoring electron transfer in environmental systems.

(3) Understanding chemical reactions under extreme conditions of geological CO_2 sequestration sites. Understanding the shape, size, location, and phase of secondary minerals during the early period of CO_2 injection in geological CO_2 sequestration (GCS) is crucial, because they could affect how the permeability and wettability of rocks will change. In this study, we investigated the mechanisms and kinetics of reactions at supercritical CO_2–water(brine)-clay mineral interfaces at molecular scale. Clay minerals (Mg and Fe-containing mica) are present in both formation rocks and caprocks in potential CO_2 sequestration sites (4-5). By incorporating aqueous chemistry with synchrotron-based *in situ* x-ray scattering and high resolution x-ray diffraction, atomic force microscopy, and scanning electron microscopy with energy dispersive X-ray spectroscopy, we monitored *in situ* and *ex situ* nanoscale morphological evolutions resulting from dissolution of pre-existing clay minerals and precipitation of new mineral phases. Challenges in the studies about the chemical reactions at geological CO_2 sequestration are to observe the non-equilibrium intermediate phase formation *in situ*; to monitor the real-time morphological conditions; and to visualize the location of newly formed mineral phases, which can be related to porosity and permeability evolution. Under these extreme conditions, there are concentration and pH gradients close to mineral surfaces. In addition, aqueous metal ion concentrations in bulk solution could also be fluctuated owing to simultaneous dissolution and precipitation.

Main questions remain to be addressed:

- Can we determine the structures of the precursors of amorphous (intermediate) phase formation using ultrafast synchrotron x-ray techniques?
- Can we successfully observe the real-time evolution of nanoparticle distributions and topology at an active interface without dehydration?
- Can we initiate the reaction with sufficient temporal resolution and efficiency to permit the observations of electron transfer and structural changes?
- Can we track down simultaneous dissolution and precipitation reactions of minerals in water? While metal concentration's and pH's gradients from the mineral surfaces keep generating complexity in experimental environments, can we elucidate these complexity and their effects on chemical reactions?
- Under extreme environments such as high pressures and temperatures, how can we measure non-equilibrium intermediate mineral phases and visualize their morphological changes?

References:

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