

Introduction of NANO-EPS

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Nano, a prefix for 10^{-9} , represents vast frontiers for both Earth and Planetary Solid Sciences. Conventional tools such as Electron Probe MicroAnalysis (EPMA) for ppm-level quantification at the micrometer scale and Power X-Ray Diffraction analysis (XRD) for the identification of submicron minerals are being transformed into the next generation instruments. In addition, it is possible to reveal the heterogeneity and oscillation of chemical and isotopic compositions at nano-spatial resolutions. It is becoming more aware that nano-sized solids with extremely large surface areas and distorted structures are ubiquitous in planetary materials and intimately relevant to many issues such as soil and groundwater contamination with metals and radionuclides, mineral resources exploitation, carbon sequestration and so on. In my presentation, nano-frontiers from various fields of Earth and Planetary Sciences and key technological advancements will be overviewed as the introduction of this session.

Keywords: nano

Properties and depositional process of sub-micron scale manganese oxide minerals in the aqueous surface environment

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A large variety of minerals form submicron compounds or minerals in the surface aqueous environments (sea waters, rivers, soils, underground waters, organisms etc.) Especially iron and manganese oxide are most mobile elements among others in such environments. The iron and manganese oxides often scavenge numbers of metallic elements and play significant role in material cycling and geochemical cycles. In this paper, we attempt to introduce several types of occurrences of manganese oxide in the diverse environments. For example a phyllo-manganate minerals, nano-scale aggregate are shown in the paper.

Keywords: manganese oxide mineral, manganese crust, manganese nodule, low-temperature hydrothermal activity, phyllo-manganate, redox condition

Development of PF-STXM and its application to environmental geochemistry

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Scanning transmission X-ray microscopy (STXM) has been applied to various fields in earth and environmental sciences such as aerosol chemistry, geomicrobiology, soil science, and nanomineral sciences. In particular, the technique has been used in the world because of its great importance in imaging distribution of carbon, or in particular carbon functional group, with about 50 nm spatial resolution. However, STXM that can be used to measure NEXAFS at carbon K-edge has not been in use in Japan. We have constructed STXM in Photon Factory (PF-STXM) from 2012 and started to use it for various topics in earth and environmental sciences.

In the PF-STXM, soft X-rays from the undulator are monochromatized by the grating and focused at the four-way aperture slit. The FZP with the outermost zone width of 30 nm is placed at 1 m distant from the aperture slit. First order diffraction selected through an order sorting aperture (OSA) is focused onto the sample with the focal distance of 0.7-5 mm, and then the transmitted X-rays are detected. The PF-STXM at present is mainly operated at BL-13A in Photon Factor, where the energy range available is from 250 eV to 1600 eV, which covers K-edges of carbon, nitrogen, oxygen, potassium, and aluminum. The beam size of the STXM was around 50 nm focused with Fresnel zone plates (FZP). The intensity of focused X-rays at the sample was expected to be up to 10^7 photons/s. Instead of a photomultiplier tube (PMT) which is commonly used in STXM, a silicon avalanche photodiode (APD) is utilized to detect the transmitted X-rays in PF-STXM. Compared with other STXM system in the world, our STXM is made so compact and light that it is easily connected to and removed from the multi-purpose beamlines. The experiments reported below are performed at BL-13A and BL-16A of Photon Factory.

The PF-STXM has been used for various applications. Among them, we would like to present recent results on (i) speciation of calcium in mineral dust with 50 nm spatial resolution, (ii) characterization of carbon adsorbed on particulate matter in river water, and (iii) spatial distribution of rare earth elements in bacterial cell.

Keywords: STXM, PF, Aerosol, Particulate matter, Bacteria

Nano-scale investigation of the microbe-mineral interaction by scanning transmission X-ray microscopy

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Microorganisms in the environment critically impact global geochemical cycles and redox reactions of various elements. Many geochemically important redox reactions (e.g., sulfate reduction, Fe(II) oxidation) are largely associated with microbial activity. In addition, microbes can mediate both mineral formation (biomineralization) and mineral dissolution (bioleaching). Recent studies suggest a significant relationship between Fe(II)-oxidizing bacteria and ancient Banded Iron Formation, one of the large geochemical events in Earth's history. The general ecological importance of environmental microbial reaction has been well recognized; however, the specific mechanisms of the reactions in the environments such as the reaction rate and spatial dynamics are poorly understood. In the environment such as sediments, microbial reactions and habitability vary locally and form complicated geochemical networks, which makes it difficult to characterize the specific biogenic reactions in detail.

Scanning transmission X-ray microscopy (STXM), which uses near-edge X-ray absorption spectroscopy (NEXAFS) is a powerful new tool that can be applied to hydrated biological materials with high spatial resolution. The STXM provides spatial resolution of better than 50 nm, which is suitable for imaging bacteria and bacterial biofilms.

In the present study, we applied the STXM into the bioleaching of sulfide mineral (pyrite) to determine carbon, oxygen, and iron species in nano-scale. Both metal and biogenic organic materials in pyrite-microbe interface were investigated in the single cell level. Our study shows that the STXM could be a potential technique to provide direct information on specific biogenic reaction microorganism.

Keywords: STXM, pyrite, bioleaching

In-situ trace element quantification of geological samples using LA-ICPM

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Laser-Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) is a type of mass spectrometry which is capable of in-situ trace element quantification of a solid sample. We introduce an typical application to characterize sub-micron scale particles based on the variation of their geochemical compositions.

Keywords: LA-ICPMS, femtosecond laser, in-situ analyses, trace-element quantification

Formation rate of iron colloids at pH 2-3

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Various types of iron colloids are widely distributed in the earth's surface conditions, and their formation process, adsorption characteristic, and the material transport mediated by iron colloids are receiving attention. Iron colloids are often formed through several reactions including the dissolution of Fe^{2+} and Fe^{3+} from minerals, oxidation from Fe^{2+} to Fe^{3+} , hydrolysis, and crystallization. In the present study, the reaction rate was evaluated focusing on the process in which iron colloids are formed from dissolved Fe^{3+} .

A solution of Fe^{3+} 100 ppm was prepared by dissolving FeCl_3 into pure water. This solution was reacted at 15, 25, 35, 45, and 55 °C. At 25 °C, pH of the solution was ~ 2.7 at the start of the reaction and decreased to ~ 2.2 as reaction time passed. Such change in pH is known to occur as a result of the following reactions: hydration of Fe^{3+} (release of H^+) \rightarrow formation of dissolved $\text{Fe}(\text{OH})_3 \rightarrow$ formation of solid $\text{Fe}(\text{OH})_3$ (Grundl and Delwiche, 1993). Therefore, information of the formation rate of iron colloids can be obtained by monitoring the pH of the solution. After the initial period of the reaction in which the rate of the decrease of dissolved $\text{Fe}(\text{OH})_3$ concentration was slow presumably due to nucleation, the concentration of dissolved $\text{Fe}(\text{OH})_3$ decreased in a manner like first-order reaction, and the reaction behavior deviated from the first-order reaction at the later stage. By assuming first-order reaction, rate constants of $3.3\text{E-}5 - 1.1\text{E-}2 \text{ s}^{-1}$ were obtained at 15-55 °C, and good linearity was confirmed in an Arrhenius plot of these rate constants.

In addition to the above experiments in which time variation of the total amount of solid is considered, the time variation of the grain size of iron colloids was evaluated. A solution of Fe^{3+} 100 ppm was prepared and the change of grain size at 25 °C was continuously measured using a dynamic light scattering apparatus (Zetasizer μV , Malvern). As a result, enough scattering intensity began to be detected after the mean diameter of iron colloids grew to 10 nm, then the grain size increased. The increase of the grain size almost stopped after 8 hours, and mean diameter at this stage was approximately 30 – 40 nm. By evaluating the number of grains from the total amount of solid and mean grain size, the grain number was estimated to decrease with time.

Surface complexation modeling for lead adsorption on nano-sized aluminum silicate

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There are many abandoned lead-produced mines in Japan. The water pollutions by lead due to the weathering of the mine wastes are environmental concern. The concentrations of lead released from the mine wastes is usually low. Therefore, the adsorption process is expected to dominate the mobility of lead in the affected area. It is well recognized that the materials widely occurred in earth surface conditions are comprised with low-crystalline and/or nano-sized minerals. There are some reports for lead adsorption behavior on crystalline phases such as clay minerals and low-crystalline iron oxides. On the other hand, there are very little reports on nano-sized aluminum silicates which must be dominant phases in surface condition. The quantitative understandings of lead adsorption on nano-sized aluminum silicate is essential for the prediction of lead migration in earth surface conditions. The purpose of the study is to clarify the lead adsorption behavior on nano-sized aluminum silicate under wide range of solution conditions and model the adsorption behavior by means of surface complexation modeling.

Keywords: nano-sized aluminum silicate, lead, adsorption, surface complexation modeling

Mineralogical study of serpentinite from Akamatsu, Yatsushiro, Kumamoto prefecture.

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Serpentine group minerals are one of the 1:1 layer type sheet silicates and the main component of serpentinite. They are classified into three mineral species chrysotile, lizardite and antigorite. The ideal formula of chrysotile and lizardite is $Mg_3Si_2O_5(OH)_4$ and that of antigorite is $Mg_{48}Si_{34}O_{85}(OH)_{62}$.

In our previous study, we researched serpentinite from a large area in Kyushu Kurosegawa belt (Tanaka et al., 2012), but there are only few reports for each area. So, the purpose of this study is to identify the composition minerals of serpentinite in Akamatsutaro Pass and Tanoura, located in west of Kyushu Kurosegawa belt, and to conduct a detailed study of serpentine.

Mineral species was identified by XRD pattern and serpentinite was classified into three type: antigorite main serpentine (Type AA, 16 specimens), antigorite rich serpentine (Type A, 10 specimens) and antigorite poor serpentine (Type LC, 8 specimens). Antigorite was most abundant. Magnetite, chromite, clinocllore, brucite and hydrotalcite group minerals were identified in specimens from both areas. Only the specimen from Akamatsutaro Pass had andradite, calcite, heazlewoodite (Ni_3S_2) and millerite (NiS), while forsterite, hydromagnesite, pyroaurite and awaruite (Ni_3Fe) were seen only in Tanoura. The supply of H_2S in Akamatsutaro Pass can be estimated from the presence of heazlewoodite and millerite. Relict forsterite was observed in serpentinites from Tanoura, indicating the smaller degree of serpentinization compared to Akamatsutaro Pass.

Serpentine contained in massive serpentinite had variable textures such as vein texture, reed shape texture and mesh texture with core and rim, which was formed after serpentinization of olivine. In the specimens of Type LC, mesh texture was often observed, and there were cores with no rim in samples without mesh textures. Also some core texture was replaced by reed shape texture. Chemical compositions obtained by SEM-EDS show some trends for serpentines in each texture. Reed shape texture contains 0.041 (apfu) Al which replaces Mg, while core texture contain 0.07 Al and rim texture contains 0.006 Al, so reed shape texture is rich Al than mesh texture. Reed shape texture contain larger amount of SiO_2 weight percent compared with the ideal formula of chrysotile and lizardite, and resemble that of antigorite.

Reference

K.Tanaka, T. Inoo and S. Uehara (2012): Microtexture and chemical composition of serpentine minerals from Kurosegawa belt, Kyushu, Japan. The 2nd Asian Clay Conference, Abstract Book.

Keywords: serpentine, antigorite, reed shape texture, mesh texture, Kyushu Kurosegawa belt, Yatsushiro

The lithium existence form in a lithium ore deposit

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In the ore deposit containing lithium, Spodumene, Petalite, Lepidolite, etc. are known as a lithium mineral, but these minerals are not contained in the lithium ore deposit examined this time. So, in this research, the result analyzed using XRD and SEM+EDS is released.

In the ore deposit containing lithium in this time, it roughly divides of a white portion and a portion of ashes green. From the result of XRD, it mainly becomes a white portion from Searlesite($\text{NaBSiO}_5(\text{OH})_2$), Calcite(CaCO_3), and Orthoclase(KAlSi_3O_8), and the mineral containing lithium is not shown. On the other hand into the portion of ashes green, Calcite(CaCO_3), Orthoclase(KAlSi_3O_8), Illite($\text{K}(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}$), Rozenite($\text{FeSO}_4\cdot 4\text{H}_2\text{O}$), and Cryolite($\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$) are contained was obtained. Since the peak of various minerals had appeared, it could not declare that Cryolite existed clearly, but it was suggested that Cryolite may exist as a lithium content mineral.

Next, from the results of SEM+EDS analysis, in the white part, Calcite and Orthoclase were contained at about 10-100 micrometers, and Searlesite existed in it at those circumferences. And in the green gray part, Orthoclase, Calcite, Illite, Rozenite were contained at about 10-30 micrometers, and the particle with a size of 1 micrometer or less existed in those circumferences. Although measurement of Li was not completed in analysis of EDS, it was checked that F is contained in the analysis of these microscopic particles.

From the above result, it was surmised that the lithium content mineral examined this time was Cryolite.

Keywords: lithium, ore deposit, mineral