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Selective detection of Fe and Mn species at mineral surfaces in weathered granite by conversion electron yield X-ray absorption fine structure

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Fe and Mn are critically important elements in environmental geochemistry because of their high abundances among transition metals and their various oxidation states such as Fe(II, III) and Mn(II, III, IV). Their chemical forms drastically change depending on the surrounding physico-chemical conditions. In particular, secondary minerals of Fe(III) and Mn(IV), which are readily produced due to their low solubilities are of importance since they control solid-water distributions of various trace elements. Therefore, development of a speciation method for Fe and Mn in environmental samples is particularly important.

Among the two elements, Fe is initially present as a constituent of minerals in igneous rocks such as biotite, pyroxene, hornblende, olivine, ilmenite, magnetite, and pyrite. Iron in these minerals alters its chemical form into oxides and hydroxides via weathering processes [4]. Although Mn is less abundant in crust relative to Fe, formation processes of secondary Mn oxides via weathering are similar to Fe. As a result, detrital phases containing Fe or Mn generally coexist with their secondary phases in soil and sediments. Hence, the investigations of speciation of Fe and Mn in solid materials can be difficult, particularly if selective detection of the minor phases in the samples is desired. However, it is considered that the behavior of transition metals is often controlled by the reactions with the secondary Fe and Mn (hydr)oxides formed at surfaces of primary minerals, even if their ratios to the total Fe and Mn abundances are small. Thus, surface sensitive method could play an important role to achieve the speciation of Fe and Mn for various solid samples formed at earth's surface.

In this study, a new method for the speciation of Fe and Mn at mineral surfaces is proposed using X-ray absorption fine structure in conversion electron yield mode (CEY-XAFS). This method generally reflects information of the species at sub-micrometer scale from particle surface due to the limited escape depth of the inelastic Auger electron. The surface sensitivity of this method was assessed by experimentations on two samples of granite having different degrees of weathering. The XANES spectra obtained at BL-12C at Photon Factory in KEK for Fe-K and Mn-K edge gave clearly different information between CEY and fluorescence (FL) modes. These XANES spectra of Fe and Mn show a good fit upon application of the least-squares fitting using ferrihydrite/δ-MnO_2 and biotite as the end members. The XANES spectra collected by CEY mode provided more selective information on the secondary phases which are probably present at mineral surfaces. CEY-XANES spectra of Mn (ML01-CEY in Fig. 1) indicated the presence of δ-MnO_2 in unweathered granite despite very small contribution of δ-MnO_2 by FL-XANES and selective extraction analyses. Such a small amount ofδ-MnO_2 cannot be found in micron scale searched by micron-scale XRF imaging measured at BL-4A in Photon Factory. This information is important, since δ-MnO_2 can play host to various trace elements. CEY-XAFS can prove to be a powerful tool as a highly sensitive surface speciation method. Combination of CEY and FL-XAFS will help identify minor phases that form at the mineral surfaces, but identification of Fe and Mn oxides at mineral surfaces is critical to understand the migration of trace element in water-rock interactions.

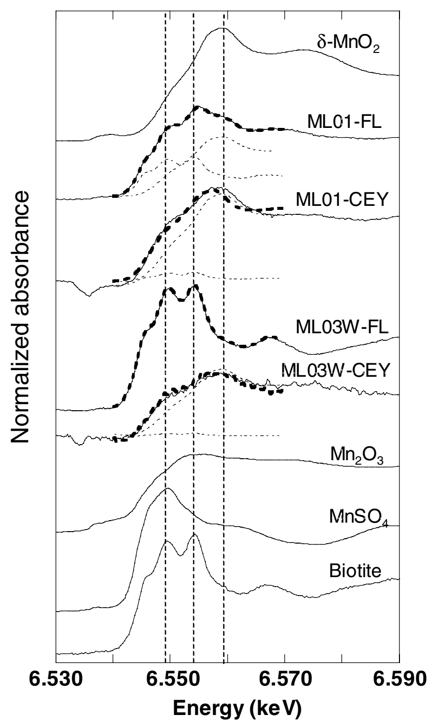

Fig. 1. Mn-K edge XANES spectra of granite sample smeasured by FL and CEY modes.

References

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