

# Oxidation of iron in mica induced by weathering investigated by HERFD-XANES measurements and *ab initio* calculations

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Mica minerals, including biotite, are often weathered and transformed into clay minerals, which control the environmental behavior of various elements due to their high cation exchange capacities. In the weathering process, the oxidation reaction of iron (Fe) is important, but its details remain unclear.

X-ray absorption near edge structure (XANES) is a powerful tool for investigating the chemical states of Fe because it reflects the electronic states of the target element. However, its purely theoretical interpretation is difficult at present. Thus, an XANES spectrum is usually analyzed by linear combination fitting (LCF) with some spectra of standard samples. There are some problems in the LCA-XANES analysis. One is the difficulty obtaining appropriate XANES spectra for the target sample. Another is that some XANES spectra of standard samples, such as Fe in ferrihydrite and goethite, show similar spectra.

In recent years, the high-energy resolution fluorescence detection (HERFD)-XANES method has been applied to Fe in some minerals [1], showing that HERFD-XANES can detect minor differences that cannot be found in normal XANES. In addition, advances in software for *ab initio* calculation have made it possible to simulate XANES more accurately. The combination of the HERFD-XANES measurement and the XANES simulation can provide more accurate fitting and more information of Fe speciation than before.

This study focused on the weathering reaction of biotite. Weathered biotite samples with several degrees of weathering were artificially produced. Their XANES and HERFD-XANES spectra at Fe K-edge showed that the spectra were systematically changed. The HERFD-XANES spectra had sharper peaks, although HERFD-XANES spectra can be affected by oxidation reactions by incident X-ray. In addition, the XANES spectrum of pure biotite was simulated by using the Vienna *Ab initio* Simulation Package (VASP) and WIEN2k. The characteristics of the simulated spectra were consistent with the XANES and HERFD-XANES results, which can bring us clues to understanding the effect of weathering on Fe in biotite. The clear identification of Fe(II)- and Fe(III)-bearing phyllosilicates based on XANES and *ab initio* calculations is highly important to understand redox reactions in soil and sediment samples.

[1] S. Natori et al., *Minerals* **12**, (2022).