Reduction of U(VI) to U(IV) by Fe(II)-bearing smectite

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Environmental behavior of uranium (U) is highly important in geochemistry and environmental chemistry from various aspects such as paleoredox change in the earth history, microbial effect on its behavior, and radioactive waste management. On the other hand, many studies have been conducted recently on the reduction of various metal ions in the presence of smectite that retains ferrous iron within the layer structure, possibly due to the reduction effect by the oxidation of ferrous ion into the ferric ion.

In this study, we studied reduction of U(VI) to U(IV) by Fe(II)-bearing smectite. Smectite (Kunipia) originally containing mainly Fe(III) was treated by dithionate under reducing condition in a glove box with O_2 conc. less than 10 ppm. Iron K-edge XANES spectra proved that iron in the smectite was reduced nearly completely to Fe(II). Moreover, Fe K-edge EXAFS showed that 1st coordination sphere of Fe(II) in the layer structure is similar to that of Fe(III) in the structure before reduction. This may suggest that Fe(III) in the layer structure was reduced to Fe(II) with keeping its site within the structure.

Uranyl solution was prepared from uranyl nitrate. The synthetic Fe(II)-bearing smectite washed with Milli-Q water was added into the uranyl solution at pH 8, and the mixture was stirred in the glove box for various elapsed times from 1 to 24 hours. The smectite recovered by filtration was immediately washed by Milli-Q water and packed into a polyethylene bag, which was sent to SPring-8 for the measurement of XAFS at U LIII-edge at BL01B1. Based on the linear combination fitting of U LIII-edge XANES spectra of the samples using U(IV)O2 and U(VI)O2 solution as endmembers, we found that U(VI) was reduced to U(IV) and distributed to the solid phase even after 1 hour. On the other hand, U species in the solid phase prepared by mixing of uranyl solution and original Kunipia without reduction was not reduced to U(IV). These results revealed that Fe(II)-bearing smectite can be a strong reductant agent which can reduce U(VI) to U(IV).

Similar reduction can be expected to saponite (Fe(II)-bearing trioctahedral smectite), which is abundant in aqua planet. Based on this study, it is strongly expected that the reduction reaction caused by the Fe(II)-bearing smectite plays an important role on the various chemical reactions in water.

Keywords: smectite, reduction, uranium

