

## Interaction between Uranium and Biotite

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### 1. Introduction

Over the past 50 years there has been an intense effort to characterize the interaction of U(VI) with geological materials. The motivation has stemmed from dual desires to find and exploit uranium ore deposits and to isolate long-lived radionuclide wastes. The primary goal of this contribution is to determine whether Fe-bearing mica can effectively sorb radionuclides. Phyllosilicates are known sorbents for aqueous U(VI), and some of the rock-forming species are ubiquitous reservoirs of Fe(II), a possible reducing agent for U(VI). The interaction of uranyl with micas is an important determinant of the mobility of U in granitic terrains, which have been proposed as radionuclide waste disposal sites. Fe(II) in aqueous solutions and in minerals is one of the more ubiquitous potential reducing agents for uranium in natural systems. Homogeneous reduction of uranium by Fe(II)<sub>aq</sub> has been well documented. However, as discussed by White and Yee (1985), Fe(II) in silicates can be a particularly important reducing agent in poorly-poised aqueous systems, and it can be a more powerful reductant than Fe(II)<sub>aq</sub> at lower pH. Biotite is of interest because it is an ubiquitous Fe(II)-silicate with a structure similar to many clay minerals.

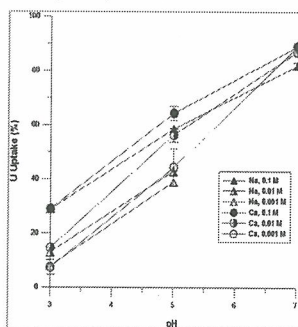


Fig. 1. Uptake of uranyl ions by biotite at different NaCl and CaCl<sub>2</sub> concentrations.

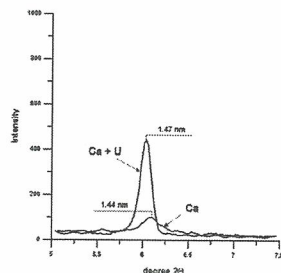


Fig. 2. XRD patterns after reaction with uranyl ions in 0.1 M CaCl<sub>2</sub> at pH 3.

### 2. U(VI) Adsorption and X-ray diffraction (XRD)

U(VI) adsorption increased to a maximum at near-neutral pH (Fig. 1). Generally, at low pH uranyl ions exist as mononuclear species, and outer-sphere complexation is the principal adsorption mechanism. Cation exchange at negatively charged surface sites has been shown to be an important mechanism of U adsorption at low pH. Increasing Na<sup>+</sup> or Ca<sup>2+</sup> concentrations also increased the adsorbed amount of U (Fig. 1). At low pH, the

amount of U(VI) adsorbed depended considerably on the concentrations of the background electrolyte. This shows that U(VI)-exchange was promoted by higher molar concentrations of  $\text{Na}^+$  or  $\text{Ca}^{2+}$  ions at lower pH. When  $\text{UO}_2^{2+}$  ions were exchanged together with  $\text{Ca}^{2+}$  ions, the intensity of the basal reflection increased and the basal spacing was 1.47 nm (Fig. 2). This indicates that  $\text{UO}_2^{2+}$  ions diffused into the interlayer space expanded by  $\text{Ca}^{2+}$  ions. The broadly distributed U within the biotite particles and the observed strong XRD reflection at ~1.4 nm verify the progressive U diffusion into the interlayer space.

### 3. Conclusions

Biotite adsorbed uranyl ions from aqueous solution in the presence of  $\text{CaCl}_2$  and  $\text{NaCl}$ . As the exchange of interlayer  $\text{K}^+$  ions by  $\text{Ca}^{2+}$  ions was favored as compared with  $\text{Na}^+$ , larger amounts of uranyl ions were adsorbed in  $\text{CaCl}_2$  solutions. Interlayer expansion by background cations enhanced U adsorption in the interlayer region and might probably promote the reduction of U(VI) via the electron transfer from the structural ferrous iron. Thus, concentrated major cations such as  $\text{Ca}^{2+}$  in natural groundwater that comes into contact with micaceous soils and rocks might play an important role in the U migration via U interlayer adsorption, suppressing the rapid remobilization of U.

### References

- [1] A.F. White, A. Yee, "Aqueous oxidation-reduction kinetics associated with coupled electron-cation transfer from iron-containing silicates at 25°C," *Geochim. Cosmochim. Acta* 49, p. 1263-1275, 2008.