

Influence of Iron Oxide Minerals on the Uranium Migration in Granitic Rock

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1. Introduction

During rock weathering in the natural environment, physical and mineralogical changes occur in the host rock material, and many studies of more weathered rock show a tendency for trace elements, including uranium (U), to be associated with iron oxides [1,2]. Mineralogical changes, such as alteration of biotite and the new formation of iron oxides, provide different phases for various species to react with. An understanding of the interaction between U and iron oxides is very important for assessing the retardation capacity of geological systems into which U may be disposed. Along with U, some rare earth elements (REEs) are usually considered to be good chemical analogues of certain radiotoxic nuclides [3]. Our work is focused on studying the behavior of U in granitic rock and its interaction with primary and secondary oxide minerals.

2. Materials and Methods

The granite was investigated by collecting samples from the KAERI Underground Research Tunnel (KURT) site. The collected fresh and weathered rock samples were examined by mineralogical methods. Polished thin sections of the samples were examined by optical microscopy, and the elemental distribution in minerals was examined by EPMA. SEM has been used to investigate rock-forming minerals and their secondary products, such as iron oxides.

In laboratory experiment, some fresh biotite crushed to less than 3 mm was reacted with aqueous U (0.2 mM) in the pH range of 3.0-9.0 condition. A range of experimental reactions were conducted at a solid to solution ration of 1:100 in 40 mL centrifuge tubes. The U sorption experiment was performed for 1 week, and aqueous U concentration was analyzed with ICP-MS.

3. Results

3.1 Granite Weathering and U Enrichment

As granitic rock weathers, some Fe^{2+} in fresh biotite is slowly released and partly oxidized in situ, progressively becoming a vermiculitic phase [4]. The released Fe^{2+} often passes along mineral boundaries and into surrounding micro-cracks, and precipitates as secondary or surface-coating materials during its movement. In microscopic observation, the iron precipitates have irregular and vague textures, and are

often intermixed with clay minerals. The amorphous oxide was identified as ferrihydrite which does not have distinctive crystallized forms and an outstanding sorption for U as well. In the electron image, U is not enriched in the ferrihydrite and is evenly distributed over the secondary phases with low concentration.

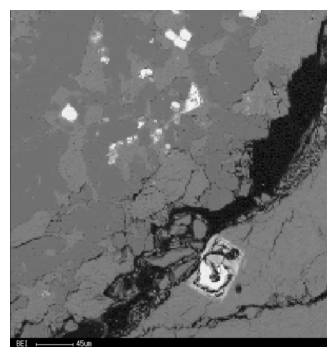


Figure 1. A backscattered electron image of a highly weathered granite sample showing crystalline iron oxides such as goethite and hematite (white region), in which accumulated U spots are detected.

During granitic rock weathering, Fe accumulation increases and some crystallized iron oxides (goethite or hematite) are often made by the transformation of Fe precipitates, appearing as small grains with $\sim\mu\text{m}$ sizes (Figure 1). Most of them are surrounded by kaolinite [$Al_2Si_2O_5(OH)_4$], a weathering product of the host rock. Zones rich in iron oxides, occurring as crystallized form, contain significant detectable concentrations of U. In our samples, the U-enriched spots observed by EPMA are not very distinctive and are difficult to be detected due to their inherently low concentrations in the granitic rock. However, the detected U distribution shows that crystallized iron oxides are highly preferred by U, whereas the kaolinite and amorphous oxides are relatively excluded in the U sorption reaction.

3.2 U Sorption Experiment

The distribution coefficients (K_d) of U for the biotite has been measured, and they are shown to be dependent on the mineral oxidation states and the solution pH conditions (Figure 2). Much more U was sorbed on the oxidized biotite rather than the fresh one, which are affected by specific surface areas.

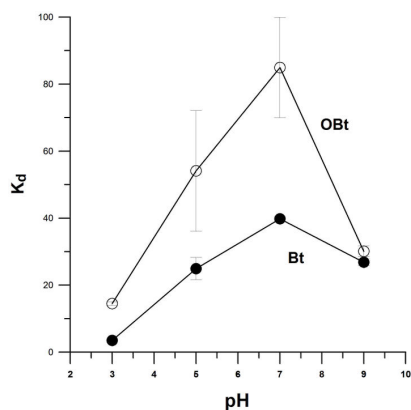


Figure 2. The various U sorption coefficient (K_d) values for the fresh biotite (Bt) and oxidized biotite (OBt) by the pH change.

Under pH 7 condition, U has been distributed along the iron phase which was secondarily developed at the edges of the fresh biotite during the experiment. The newly formed iron oxide, confirmed as goethite, strongly attracts the U^{VI} from solution.

4. Conclusion

In subsurface environment, underground rock-forming minerals are altered during the geologic time scale. The Fe-bearing minerals such as biotite are also dissolved and transformed by the influence of groundwater. When such a mineral is dissolved, the Fe^{II} component in its structure is released, and then oxidized in solution. Some Fe^{II} in the mineral structure can be in situ oxidized in order to reduce U^{VI} into U^{IV} on the surface. On the other hand, during the biotite alteration process, crystalline iron oxides (e.g., goethite) are locally formed preferably at the edges of the mineral, and they effectively sorb U as compared with the amorphous iron phases.

REFERENCES

- [1] J. A. Coston, C. C. Fuller, and J. A. Davis, Pb^{2+} and Zn^{2+} adsorption by a natural aluminum- and iron-bearing surface coating on an aquifer sand, *Geochimica et Cosmochimica Acta*, Vol.59, p.3535, 1995.
- [2] J. R. Bargar, R. Reitmeyer, J. J. Lenhart, and J. A. Davis, Characterization of U(VI)-carbonato ternary complexes on hematite: EXAFS and electrophoretic mobility measurements, *Geochimica et Cosmochimica Acta*, Vol.64, p.2737, 2000.
- [3] K. B. Krauskopf, Thorium and rare earth metals as analogs for actinide elements, *Chemical Geology*, Vol.55, p.323, 1986.
- [4] G. Y. Jeong and H. B. Kim, Mineralogy, chemistry, and formation of oxidized biotite in the weathering profile of granitic rocks, Vol.88, p.352, 2003.