COFFINITIZATION OF URANINITE:
SEM/AEM INVESTIGATION AND GEOCHEMICAL MODELING

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ABSTRACT

Coffinite (USiO₄) has been found in numerous sedimentary and hydrothermal environments including those considered as natural analogues of nuclear waste repositories. Scanning electron microscopy (SEM) and analytical electron microscopy (AEM) studies have been conducted on a uraninite sample from a U-deposit in Canada. It is observed that the uraninite (UO₂⁺) is replaced by coffinite (USiO₄·nH₂O) and the replacing coffinite coexists with quartz. The TEM study shows α-recoil damage, lattice distortion, and low-angle boundaries among neighboring uraninite domains. Coffinitization seems more closely associated with α-recoil-damaged uraninite areas. Electron energy-loss spectroscopy (EELS) spectrum indicates that the ratio of U(+6)/U(+4) in the uraninite is about 2/3, while the coffinite is dominated by U(+4). A thermodynamic calculation indicates that coffinitization can take place most likely at temperatures below 130°C if dissolved silica concentrations are limited by amorphous silica mineral phase. In a sufficiently high silica concentration environment, coffinite can form under the oxygen fugacity of 10⁴⁵ - 10⁵₅ atm. The equilibrium model, however, is not able to explain the coexistence of coffinite with quartz. A kinetic model that takes account of Ostwald processes is thus proposed. The kinetic model indicates that the presence of U(+6) in uraninite and the enhanced uraninite dissolution rate may be an important factor controlling uraninite coffinitization.

INTRODUCTION

Understanding of spent fuel (UO₂) alteration in a subsurface environment is crucial for the long-term performance assessment of a high-level nuclear waste geologic repository, since the alteration processes and their products will directly control the radionuclide release from waste disposal rooms. Naturally-occurring uraninite (UO₂⁺) long has been used as a natural analogue for spent fuel, and it is believed that uraninite alteration in natural environments can provide useful information on the chemical behavior of spent fuel in geologic repositories (1). Uraninite Coffinitization — the replacement of uraninite by coffinite — has been observed in numerous sedimentary and hydrothermal environments including those considered as natural analogues of nuclear waste repositories (1.2). The coffinitization has therefore been proposed as a major process of spent fuel alteration in a silica-rich repository (1.3). In this paper, we summarize our scanning electron microscopy (SEM) and analytical electron microscopy (AEM) observations on a uraninite sample from a uranium deposit at Port Radium Mine of Northwest Territories, Canada. Based on the observations, we constraint the possible chemical conditions for uraninite coffinitization.

SEM AND AEM STUDIES

Scanning electron microscopy (SEM) and analytical electron microscopy (AEM) studies have been conducted on a uraninite sample from the Port Radium Mine U-deposit in Canada. The SEM observation shows that uraninite (UO₂⁺) is replaced by coffinite (USiO₄·nH₂O) and coffinite coexists with quartz (Fig. 1). TEM shows α-recoil damage, lattice distortion, and low-angle boundaries among neighboring uraninite domains (4). The α-recoil damaged area with low-grain boundaries in the uraninite may accelerate the diffusion of U within the uraninite crystal. The TEM observations also show that coffinitization is more closely associated with α-recoil-damaged uraninite areas.

Electron energy-loss spectroscopy (EELS) spectrum indicates that the ratio of U(+6)/U(+4) in the uraninite is about 2/3, while the coffinite is dominated by U(+4). EDS spectra indicate that the coffinite contains less Pb than the neighboring uraninite (4) implying that the coffinite was formed later than the uraninite and Pb, as alpha decay product of U, was leached out during the transformation of uraninite to coffinite (4.5). The chemical formula of the uraninite can be expressed as (U₂⁺ₐq,U⁺ₔₐₔₔ Pb₀.₈Pb₂⁺), and the observed coffinitization can be roughly described by

\[
(U^{4+}_{0.08},U^{6+}_{0.32},Pb^{2+}_{0.08})O_2^+ + 0.8SiO_2aq + 0.16H^+ \\
\rightarrow 0.8U^{4+}SiO_4^- + 0.08H_2O + 0.08Pb^{2+} + 0.16O_2^-.
\]

THERMODYNAMIC EQUILIBRIUM MODELING

Redox condition and silica concentration have been considered as two major factors controlling coffinite formation. Coffinitization of uraninite has been generally considered to take place in a relatively reducing and silica-rich environment (1,3). Figure 2A shows that coffinite is unstable with respect to quartz and uraninite (UO₂). The figure also indicates that coffinitization of uraninite can occur only at temperatures below ~ 130°C if the dissolved silica concentration is limited by amorphous silica phase. Beyond this temperature, coffinite seems difficult to form because of the depletion of SiO₂(aq) by amorphous silica precip-
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Fig. 1. SEM images showing the replacement of uraninite (U) by coffinite (C). The replacement starts in the micro-fractures of a uraninite crystal, and coffinite directly contacts with uraninite and quartz (Q). Coffinite coexists with quartz, and fine-grained (bright) PbS (Pb) crystals appear within the coffinite (left). Left image is an enlarged image of the boxed area of the right image.

utation. This thermodynamic prediction seems consistent with the observations that coffinite tends to form in low temperature environments and is often associated with poorly-crystallized metastable silica mineral phases.

In a crystalline-rock-based geologic repository, original mineral phases may not be able to bring dissolved silica concentration up to the level required for the coffinitization of spent fuel. Additional silica may be brought into the repository by using silicate-mineral-based backfills such as bentonite. However, an equilibrium calculation shows that the dissolution of bentonite is also not sufficient to bring silica concentration to the required level. High silica concentrations may be resulted from the thermal event caused by radionuclide decay. From this point of view, if it can occur, the coffinitization of spent fuel will take place most likely in the cooling-down time period after a thermal event when metastable silica phases are possible to precipitate.

To constrain redox conditions for coffinite formation, a reaction path calculation using EQ3/6 (6) is performed. In the calculation, a solution initially containing U(6+) is titrated with FeS (Fig. 2B). The calculation shows that as the system becomes reducing, haiweeite is gradually replaced by coffinite in the presence of sufficient high SiO$_2$(aq) concentration. The oxygen fugacity for coffinite formation is $10^{45}$ - $10^{55}$ atm. Note that the calculated mineral formation sequence is in a good agreement with the observed occurrence of coffinite with sulfide minerals and organic matters in the field (2,3).

The above calculation assumes that uraninite is dominated by U(4+). However, naturally-occurring uraninite contains a significant fraction of U(6+). The EELS spectra indicate that the ratio of U(6+)/U(4+) can be as high as 2/3. The coffinitization of uraninite (UO$_{2+x}$) is then described by reaction:

$$UO_{2+x} + SiO_2(aq) = USiO_4 + 0.5xO_2.$$  \hfill (2)

The required SiO$_2$(aq) concentration for coffinitization now becomes dependent of oxygen fugacity (Fig. 3). Figure 3 shows that the presence of U(6+) in uraninite can significantly change the stability field of the mineral and reduce the required silica concentration for coffinitization. From the figure, it may be concluded that coffinitization may occur even below the quartz saturation line in a low oxygen fugacity environment. However, caution must be taken in drawing this conclusion. Since coffinite is a metastable phase with respect to UO$_2$ and quartz, Fig. 3 is still unable to predict the replacement of uraninite by coffinite instead of by UO$_2$ and quartz. The occurrence of coffinite as a metastable phase indicates the control of reaction kinetics on the coffinitization of uraninite.
Fig. 2. (A) Equilibrium SiO$_2$(aq) concentration in UO$_2$ coffinitization calculated as a function of temperature. Note that the USiO$_2$-UO$_2$ line crossovers the solubility line of amorphous silica at 130°C. Thermodynamic data used in the calculation are taken from EQ3/6 database (6). (B) Moles of minerals precipitated as a function of the amount of FeS added to 1 kg of water initially containing 0.001 mole of U(6+). The solution is maintained in equilibrium with amorphous silica and calcite. All silica mineral phases except amorphous silica are suppressed in the calculation.
CHEMICAL KINETIC MODELING

The control of chemical kinetics on the formation of metastable mineral phases can be best demonstrated by silica precipitation. Various silica mineral phases such as amorphous silica, opal-CT, chalcedony, and quartz are routinely found in sedimentary and hydrothermal systems with quartz as the most stable phase. For simplicity, let's consider the precipitation of one silica metastable phase $\text{SiO}_2(m)$ and quartz from a silica-bearing solution. The reaction paths of silica precipitation is shown in Fig. 4A. Reaction path 3 is usually slow relative to the other two paths and can be ignored here. The relative rates of path 1 and path 2 thus directly determine which mineral phase to become a dominant phase in the precipitation. The rates of the two reactions can be expressed by:

$$R_1 = k_1\left(\left[\text{SiO}_2(aq)\right] - K_{\text{SiO}_2(m)}\right)$$

and

$$R_2 = k_2\left(\left[\text{SiO}_2(aq)\right] - K_{\text{quartz}}\right),$$

where $K_i$ is the dissociation constant of mineral $i$ with $K_{\text{SiO}_2(m)} > K_{\text{quartz}}$; $k_i$ is the reaction rate constant of reaction path $i$. According the Ostwald ripening rule (7), also as observed in the field, when a solution is highly supersaturated, a metastable phase tends to form more preferably than the stable phase probably due to the low energy barrier of metastable phase, it is therefore expected that $k_1 \gg k_2$.

This chemical kinetics imposes a constraint on the occurrence of silica mineral phase that coexists with coffinite. If coffinitization were mainly controlled by silica concentration, since the required silica concentration is so high as indicated in Fig. 2A, coffinite would tend to coexist with a metastable silica phase such as opal-CT, and the coexistence with quartz would seem unlikely. This is obviously contradictory to observations (Figs. 1 and 2).

The above kinetic framework can be used to explain coffinite formation. The reaction paths for coffinitization is shown in Fig. 4B. Assume that the direct transformation from coffinite $\text{USiO}_4$ to $\text{UO}_2$ and quartz (path 8) is slow. The relative rates of path 6 and path 7 thus direct which uranium mineral, either $\text{UO}_2$ or $\text{USiO}_4$, to become a dominant phase. The reaction rate of path 6 can be expressed by:

$$R_6 = k_6\left(\left[\text{SiO}_2(aq)\right] \left[U(\text{OH})_4(aq)\right] - K_{\text{coffinite}}\right)$$

where $K_{\text{coffinite}}$ is the dissociation constant of coffinite, and $k_6$ is the reaction rate constant of reaction path 6, which is postulated to be higher than that for reaction path 7. When the coffinitization rate depends on both silica and $U(\text{OH})_4(aq)$ concentrations, as long as $U(\text{OH})_4(aq)$ concentration is high enough, coffinite can form even when silica concentration is low. This is why coffinite can coexist with quartz as observed. Therefore, the kinetic model can give a consistent explanation for the coffinitization and the coexisting silica mineral phases.

From Fig. 4B, a high concentration of $U(\text{OH})_4(aq)$ can be achieved by fast dissolution of less unstable uraninite ($\text{UO}_2$) phase. As shown in Fig. 3, uraninite becomes less stable with the increase of $U(6+)$ in the mineral. Also, experiments have indicated that uraninite dissolution rate increases as $U(6+)$ content in the mineral increases. All these pieces of information lead us to postulate that the chemical behavior changes of uraninite due to partial oxidation of $U(4+)$ may be another important factor controlling coffinitization. This consistent with our TEM observations that coffinitization tends to be more closely associated with $\alpha$-recoil-damaged uraninite areas, since radiation damage usually causes partial oxidation of $\text{UO}_2$.

CONCLUSIONS

Scanning electron microscopy (SEM) and analytical electron microscopy (AEM) studies have been conducted on a uraninite sample from a U-deposit in Canada. Uraninite ($\text{UO}_2$) in the sample is replaced by coffinite ($\text{USiO}_4\cdot n\text{H}_2\text{O}$) and the coffinite coexists with quartz. The TEM study shows $\alpha$-recoil damage, lattice distortion, and low-angle boundaries among neighboring uraninite domains. Coffinitization seems more closely associated
with α-recoil-damaged uraninite areas. The ratio of U(+6)/U(+4) in the uraninite is about 2/3, while the coffinite is dominated by U(+4).

Thermodynamic calculations indicate that coffinitization take place most likely at temperatures below 130°C if dissolved silica concentrations are limited by amorphous silica mineral phase. In the presence of sufficiently high dissolved silica, coffinite can form under the oxygen fugacity of 10^{48} - 10^{49} atm. A kinetic model that takes account of Ostwald processes is proposed to explain the coexistence of coffinite with quartz. The kinetic model indicates that the presence of U(+6) in uraninite and the enhanced uraninite dissolution rate may be an another important factor controlling uraninite coffinitization.

From our observations and modeling work, the coffinitization of spent fuel in a repository may not be as common as it has been proposed. If it can occur, it will take place most likely in the cooling-down period after a thermal event when metastable silica phases are possible to precipitate. The post-closure radiation damage and its induced partial oxidation can increase the possibility of the coffinitization of spent fuel in the repository.

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REFERENCES