Coffinite in the KURT Environments and in Natural Analogue Sites

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1. Introduction

Coffinite, $USiO_4$, is the second most abundant uranium(IV) mineral [1] and one of the major uranium(IV) sources in reduced uranium ore deposits. Thus, from the perspective of radioactive wastes disposal, coffinite is considered as an important secondary phases that could be formed during radioactive wastes leaching and/or after the long-term contact of groundwater to dissolve the UO_2 matrix. Under preferable geological conditions, coffinite is expected to precipitate and then to impact the uranium release based on the relative stability of coffinite and uraninite.

KAERI has been investigating the long-term behaviors of uranium under the Korean granite environments. Thus, the understanding and analysis of the coffinite existence under the KURT (KAERI Underground Research Tunnel) environments provides insights into the long-term uranium behaviors under the Korean granite environments. Here, we analyze and compare the coffinite in the KURT environments and the natural analogue sites. Based on the favorable environments and thermochemical perspectives, we conclude that the coffinite will be one of the major U(IV) mineral to control the U concentration with time after the disposal of radioactive wastes.

2. Coffinite

With its importance in geology and radioactive waste disposal among uranium minerals, coffinite belongs to the nesosilicate group with crystal structure of tetragonal ($I4_1$/amd) and is isostructural to orthosilicates zircon ($ZrSiO_4$) and thorite ($ThSiO_4$). We note that the area of the metamictization in $ZrSiO_4$ contains the activity of coffinite ($USiO_4$), thorite ($ThSiO_4$), and/or uranothorite ($(U,Th)SiO_4$, a solid-solution of coffinite and thorite).

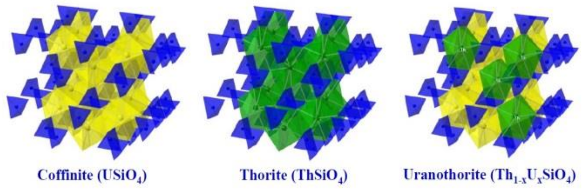

Fig. 1. The structure of (a) coffinite, (b) thorite and (c) uranothorite. Yellow, green, and blue polyhedra represent U, Th, and Si sites, respectively.

3. Occurrence of coffinite in KURT environments and natural analogue sites

We analyzed the KURT rock samples and observed an occurrence of uranothorite phase [2]. It is found that the uranium coexists mostly with thorium under the KURT environments. This accords with thermodynamics perspectives since the pure coffinite phase cannot be synthesized directly from uraninite and quartz whereas the thorite can from thorite and quartz. Also, the uranothorite are more abundantly found than the pure coffinite.

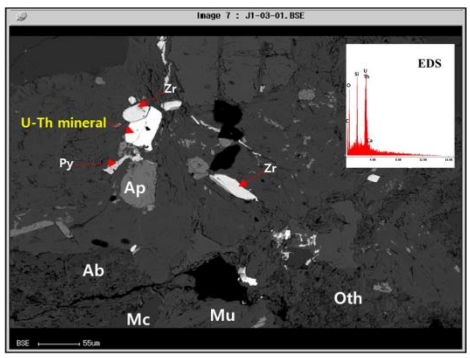

Fig. 2. Electronmicroprobe results obtained from a representative KURT rock sample. Inset shows spectrums from energy dispersive X-ray spectroscopy (EDS).

In several natural analogues study sites, such as Cigar Lake, Oklo, and Palmottu, the coffinitization of UO_2 were observed. The existence of the coffinite phase from the uranium mineralization at Cigar Lake underwent quite a substantial characterization by the use of XRD, SEM, and XPS, followed by EMPA and BSE imaging. The samples from borehole 615, 620 both indicate the presence of coffinite in cavities of the hosting uraninite, which implies its secondary formation. The results from microprobe analysis of the samples from Oklo RZ 10 indicate significant alteration of uraninite through partial dissolution along grain coundaries, volume diffusion and finallyreplacement by coffinite. Results from Palmottu samples also indicate the coffinite was formed soon after uraninite precictation and it would have involved uranium remobilization because it is found in association with fracture infillings.

We analyzed and compared the groundwater characteristics associated with the rock/borehole samples (Table 1). We note that the major elements in groundwater that most likely impacted the occurrence of coffinite under given environments are Na, Ca, and Si, along with U and Th.

Table 1. Comparison between groundwater compositions of KURT and Cigar lake

	Cigar Lake [2]			KURT
	Clay zone	Basement	Ore zone	
Na mg/l	3.40 – 18.00	55.00 – 59.00	**19.20 – 31.20**	**17.01 – 23.42**
K	1.24 – 2.10	5.50 – 5.60	5.64 – 8.81	0.39 – 2.80
Ca	3.00 – 6.80	5.40 – 6.76	**10.90 – 14.80**	**11.98 – 16.36**
Mg	1.37 – 1.89	2.75 – 3.09	3.40 – 5.30	1.34 – 2.44
Fe	0.81 – 3.40	< 0.01 – 0.49	< 0.01 – 5.50	0.00 – 0.01
Si	6.32 – 9.80	4.29 – 4.30	4.30 – 6.10	8.46 – 9.80
U ug/l	1.05 – 54.74	5.44 – 12.39	**5.81 – 25.50**	**5.17 – 14.66**
Th	< 0.02 – 0.11	0.09 – 0.17	< 0.02 – 0.23	< 1

4. Conclusion

The existence of coffinite phase under the KURT environments and under the natural analogue sites (including Olko, Palmottu, Cigar lake, etc.) was compared and analyzed. The major elements in groundwater that likely impact the coffinite existence under the given environments include Na, Ca, Si, U and Th. We note that the coffinitization can be realized under the KURT environments when groundwater dissolve UO_2 and transport U(VI) ion to the more reducing environments with silica-rich conditions.

Acknowledgements

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