



On the comparison of uranium isotopes behavior in polycrase and betafite as natural analogues of actinides

Hosseinpour Khanmiri M.^{1,2*}, Samadfam M.¹, Outokesh M.¹

¹ Department of Energy Engineering, Sharif University of Technology, 11365-11155, Tehran, Iran

² Radiochemistry Department, Saint-Petersburg State University, 199034, Saint-Petersburg, Russia

* Email: hosseinpourkhanmiri@energy.sharif.edu

Abstract

Knowing the behavior of uranium isotopes in metamict minerals carries predictive information about the state of solidified forms of HLW and the behavior of radionuclides under conditions of geological disposal. This work deals with the behavior of uranium isotopes in polycrase. Radiochemical and alpha-spectrometric analyzes show that the ²³⁸U in the metamict structure of polycrase preserves stronger binding with the mineral than its daughter product (²³⁴U) does, and unlike betafite, 32 percent of uranium atoms preserve the initial valence state, U(IV) in polycrase. It is the authors' opinion that the results of our research demonstrate the need for more extensive studies of solidified waste forms based on polycrase for immobilization of actinides.

Keywords: immobilization of actinides, metamict minerals, disequilibrium in the ²³⁸U series

Introduction

Metamict minerals are useful natural analogues for high level radioactive waste forms that will be stored in underground repositories for a long time [1-4]. For this reason, such minerals are objects of intensive research by radiochemists who deal with challenges associated with the back-end of the nuclear fuel cycle. In some cases, however, it is difficult to attribute metamict minerals to a specific group of minerals or to identify a metamict mineral as part of a particular group. The reasons for this are clear: two key parameters that are essential for conclusive identification are missing, namely the crystalline structure of the mineral and its original chemical composition. These difficulties are particularly characteristic for the titano-tantalo-niobates, which make up several groups of minerals and isomorphous series. The original crystalline structure of a metamict mineral can be reproduced in some cases and to some degree of accuracy by carefully annealing a specimen [4]. On the other hand, the mass loss of the mineral due to the leaching effect of natural waters remains unknown. It should be noted that the choice of betafite as an object of investigation cannot be considered accidental: Ti-Ta-Nb-oxides of pyrochlore supergroup, in particular, betafite, are considered as natural analogs of matrices for the immobilization of actinides [5-7]. Therefore, the question of their hydrochemical stability in nature is very relevant.

It is possible to obtain some useful information from data about the state of the secular equilibrium between the longest-lived radionuclides in the uranium-238 series, i.e. the ²³⁰Th, ²³⁴U, ²³⁸U found in any given mineral. According to [8], all of the U(IV) in the betafite is oxidized into higher oxidation states of U(V) and U(VI) forms. In this mineral, the activity ratios $AR(^{234}\text{U}/^{238}\text{U}) = 1$, whereas $AR(^{230}\text{Th}/^{238}\text{U}) > 1$. This

means that the bonding of radiogenic uranium (²³⁴U) with the host material is as weak as the bonding of its parent nuclide (²³⁸U). It is also important that, calculation of the original betafite formula based on the kinetics of uranium leaching showed that betafite can lose 80% of the uranium in weathering processes.

It is interesting to study the behavior of uranium isotopes in another Ti-Ta-Nb-oxide and compare their ability as natural analogues of matrices for actinides immobilization. The test object in this study was a metamict Ti-Ta-Nb-oxide that was classified as polycrase.

Experimental

Sample description

The investigation object in this study was polycrase (a metamict mineral) based on uranium-containing Ti-Ta-niobates from granite pegmatites found on the Nuolayniemi Peninsula, in Priladozhye (the Ladoga area), Karelia. These pegmatites were formed 1,780-1,800 million years ago. The corresponding sample is taken from the Radiochemistry Department, St. Petersburg State University (Russia). Coarse pieces of the rock were crushed in a metal mortar and fractionated with a set of sieves. For all analysis, a < 0.12 mm fraction was used.

Radiochemical analysis

The separation of tetravalent and hexavalent forms of uranium was performed by the method used in [9] and based on the incongruent dissolution of the sample in concentrated hydrofluoric acid. The chemical yield of isotope ²³⁰Th was determined by the method proposed in [10].



Table 1. Isotope Characteristics in polycrase

N	AR(²³⁴ U/ ²³⁸ U)			Content, %		AR(²³⁰ Th/ ²³⁴ U)
	U(IV)	U(VI)	U(Σ)	U(IV)	U(VI)	
1	1.001 ± 0.020	0.945 ± 0.009	0.963 ± 0.011	32.1	67.9	1.140 ± 0.020
2	1.004 ± 0.009	0.943 ± 0.009	0.964 ± 0.007	32.8	67.2	
3	1.004 ± 0.020	0.945 ± 0.007	0.963 ± 0.007	30.5	69.5	
mean value	1.003 ± 0.010	0.944 ± 0.005	0.963 ± 0.005	31.8	68.2	

Alpha-spectrometric analysis

The activity ratios for the isotopes ²³⁴U/²³⁸U and ²³⁰Th/²³⁴U were determined by alpha spectrometry. Uranium and thorium were separated by anion exchange chromatography and Alpha-sources of uranium and thorium were prepared by molecular electrodeposition as described in [11, 12]. The alpha spectra were analyzed using the computer code given in [13].

Results and discussion

Results of the isotope analysis in polycrase are given in Table 1. As seen from Table 1, the AR (Σ) value, equal to 0.963, shows that the initial sample is characterized by a deficiency of the radiogenic uranium isotope (²³⁴U). In addition, unlike betafite [8], 32 percent of uranium atoms preserve the initial valence state, U(IV) in the metamict structure of polycrase. Preservation of U(IV) in polycrase is manifested in a smaller isotopic ratio of AR(²³⁰Th/²³⁴U) in polycrase compared with that of betafite (1.140 < 1.300). It should also be noted that in the U(IV) fraction, the secular equilibrium was established and has been maintained. The results of determining the leaching rate constants of uranium in polycrase showed that the half-leaching time for ²³⁸U atoms is 2 times longer than that in betafite. Moreover, in contrast to betafite, in polycrase the ²³⁸U atoms are more resistant to the action of the liquid phase than ²³⁴U as demonstrated by an isotopic ratio smaller than unity.

Conclusions

The results obtained in this research work give the relative and primary superiority of polycrase over betafite as natural analogues of matrices for actinides immobilization. However, the authors believe that more extensive studies of solidified waste forms based on euxenite group minerals are still necessary for the immobilization of Np, Pu, and other actinides in natural minerals.

Acknowledgments

The authors wish to thank the International Affairs & Technological Exchange Center, Vice- Presidency for Science and Technology of the Islamic Republic of Iran.

References

[1] R. V. Bogdanov, et al. *The Thermochemistry of*

Uranium and Cerium in Native Britholite, J. Nucl. Mater. 440, pp. 440-444. (2013)

- [2] R. Gieré, et al. *Metamict fergusonite-(Y) in a spessartine-bearing granitic pegmatite from Adamello*, Italy. Chemical Geology. 261, pp. 333-345. (2009)
- [3] G. R. Lumpkin, *Alpha-Decay Damage and Aqueous Durability of Actinide Host Phases in Natural Systems*, J. Nucl. Mater. 289, pp. 136-166. (2001)
- [4] Q. Cao, et al. *Natural metamict Minerals as Analogues of aged radioactive Waste Forms*, J. Radioanal. Nucl. Chem. 304, pp. 251-255. (2015)
- [5] S. A. McMaster, et al. *Synthesis and characterisation of the uranium pyrochlore betafite (Ca,U)2(Ti,Nb,Ta)2O7*, J. Hazard. Mater. 280, pp. 478-486. (2014)
- [6] S. A. McMaster, et al. *Characterisation and leaching studies on the uranium mineral betafite [(U,Ca)2(Nb,Ti,Ta)2O7]*, Miner. Eng. 81, pp. 58-70. (2015)
- [7] A. P. Deditius, et al. *Role of vein-phases in nanoscale sequestration of U, Nb, Ti, and Pb during the alteration of pyrochlore*, Geochim. 150, pp. 226-252. (2015)
- [8] M. Hosseinpour Khanmiri, et al. *Uranium as a possible criterion for the hydro-chemical alteration of betafite*. Phys. Chem. Miner. 45, pp. 549-562. (2018)
- [9] M. Hosseinpour Khanmiri, R. V. Bogdanov, *Nuclear chemical effects in the paragenetic mineral association based on polycrase*. Radiochemistry. 60, pp. 74-85. (2018)
- [10] M. Hosseinpour Khanmiri, R. V. Bogdanov, *On the feasibility of determining the 230Th activity in minerals without the addition of a Th radiotracer*. Appl. Radiat. Isot. 133, pp. 57-60. (2018)
- [11] R. V. Bogdanov, et al. *Radiogenic uranium in paragenetic mineral associations*, Radiochemistry. 53, pp. 651-661. (2011)
- [12] M. Weber, N. Trautmann, H. Menke, *Herstellung dünner Präparate durch Molecularplating*. Institut fuer Kernchemie der Universität Mainz, Mainz, pp 118-121 (Jahresbericht 1974.) (1975)
- [13] R. V. Bogdanov, Yu. V. Khrisanfov, "Program for calculating the content of alpha-active nuclides using radioactive tracers" CERTIFICATE of the state registration of the computer program №. 2017611127 of 19.01.2017. (2017)