# INTERACTION OF METAMICT FERGUSONITE-(Y) WITH MINERALIZED HYDROTHERMAL FLUIDS

Radek Škoda

Department of Geological Sciences, Masaryk University, Brno, Czech Republic.
e-mail: rskoda@sci.muni.cz

## INTRODUCTION

The decay of radioactive elements in the minerals causes their structural damage, which has a strong influence on the physical and chemical properties. Two dependent processes are responsible for the structural damage: the emission of the α-particles caused displacement of hundred atoms at the end of their paths (10-15 μm), whereas the recoils of the radiogenic atoms produce several thousands displacements in the structure during relatively short path 10-20 nm, Ewing et al. (1987). The process of metamictization is characterized as transformation from crystalline to amorphous matter, and can be generalized in three steps: i) initial state - the isolated amorphous domains are surrounded within slightly disordered crystalline material. The amorphous domains start to form percolation clusters at ii) first percolation point, whereas at the iii) second percolation point, the crystalline domains cease to be interconnected (Geisler et al. 2003). Metamictization is traditionally accredited to recoil atoms, whereas recently Nasdala et al. (2005) published paper about long term stability damage due to α-particles. The degree of metamictization depends on several factors: i) absorbed radiation dose, ii) thermal history of the sample and iii) chemical composition and structural properties of the U, Th host mineral. Metamictization also leads to the important changes in physical and chemical properties. Increasing absorbed radiation dose causes: i) decrease of crystallinity (the X-ray diffraction maxima become smaller, broaden, asymmetric and shifted to the lower values of 2Θ), ii) the cell volume increase, and iii) the density decrease. Amorphization generally decreases the chemical durability of mineral; the dissolution rate of amorphous zircon is approximately two orders of magnitude greater than that of crystalline zircon. In fact, the diffusion coefficient in radiation-damaged zircon was determined to be 4–5 orders of magnitude greater than that of undamaged zircon (Cherniak & Watson, 2000). Amorphous domains are commonly highly hydrated.

Fergusonite group minerals used in experiments are tetragonal or monoclinic with general formula $ABO_4$, where A-site is occupied by Y,REE, U, Th, Ca, and B-site is occupied by Nb, Ta, Ti and W. Fergusonite commonly occurs in the metamict state.

## NATURAL OCCURRENCES

Zircon, allanite, gadolinite, Y,REE-Nb-Ta-Ti oxides, thorite, etc. are typical minerals incline to be metamict. Natural metamict zircons occasionally show anomalous composition. Entrance of non-formula elements Ca, Al, Bi, Nb, Ta, W, As, Y, Nb, P, Sc, and F as well as significant amount of water was reported by several authors (e.g. Breiter et al. 2006, Geisler et al. 2003). The incorporation of Ca and Al into metamict zircon describes Geisler et

al. (2003) also as a result of hydrothermal experiments at 200°C. Altered metamict Y,REE-Nb-Ta-Ti minerals commonly show enrichment of Si, Al, Ca. They are usually replaced by the pyrochlore group minerals (e.g. Ercit 2005). Increasing A-site vacancy in the pyrochlore group minerals during hydrothermal alteration describe Lumpkin and Ewing (1995).

## EXPERIMENTAL METHODS

Large grain of metamict fergusonite-(Y) from NYF pegmatite Landsverk 1, Evje, Norway was crushed and sieved to the fraction 64-512 μm. The crushed fergusonite (0.1 g) was loaded to the pressure vessel with PFTE liner and 5 ml of 1M mineralized multi-cationic-anionic solutions were added. In the first solution (ThUPb) were added $PbNO_3$, $Th(NO_3)_2$, and $(UO_2)(NO_3)_2$, the second solution (PAsF) was doped by KF, $Na_2HAsO_4$ and $NaPO_3$. The pressure vessels were consequently held at temperature 200°C for 60 days.

After the run the treated grain were mounted in to the epoxy resin, polished and carbon coated. Chemical composition of untreated and treated grain was determined by electron microprobe Cameca SX100. The accelerating voltage 15 kV, the beam current 20nA, and spot size 1 μm were applied. Well defined, homogeneous synthetic phases and natural minerals were used as standards.

Metamict state of fergusonite was confirmed by powder X-ray diffraction and by HRTEM (SAED). After heating on air at 650°C for 12 hours, the fergusonite structure appeared on the powder X-ray diffraction pattern.

The mineral formula calculation was based on the sum of cations occupy the B-site (Nb+Ta+Ti+W) = 1. The silicon was not included in the B-site due to its non-structurally bonded nature.

## RESULTS

### Untreated sample

Chemical composition of untreated fergusonite is only slightly heterogeneous. There are apparent parts with different degree of hydratation in the BSE image. The sum of oxides vary between 92.36-96.32 wt. %. In the A-site predominate Y (0.695-0.725 apfu) over REE. The highest concentration among REE shows Gd (0.055-0.059 apfu) and Dy (0.044-0.047 apfu). The Ca content ranges from 0.071 to 0.119 apfu. The uranium (0.031-0.043 apfu) prevails over the Th (0.010-0.020 apfu). In the B-site Nb (0.940-0.957 apfu) prevail over Ta (0.015-0.016 apfu) and Ti (0.024-0.036 apfu). The content of W does not exceed 0.011 apfu. The silicon is present in concentrations 0.005-0.109 apfu. Studied fergusonite shows elevated content of F (0.35 wt. % F). The sum of the ions in the A-site is 1.005-1.093.

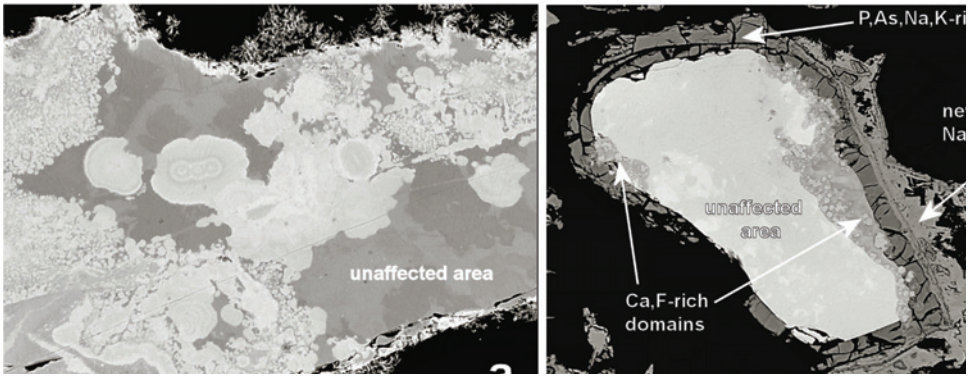


Figure 1- BSE images of treated fergusonite-(Y). Distinct shade of gray in unaffected areas stands for parts with different degree of hydratation, a) fergusonite-(Y) treated in the UThPb solution, bright areas are significantly enriched in U, Th and Pb. b) fergusonite-(Y) treated in the PAsF solution, two alteration processes are vissible: 1-Ca,F enriched domains and 2-P,As,Na,K,F enriched domains.

UThPb solution ($U^{6+}$, $Th^{4+}$, $Pb^{2+}$, $NO_3^-$)

In the BSE images the colomorph-like bright domains up to tens of micrometers occur in the majority of fergusonite grains. These parts show strong incorporation of U (≤ 29.31 wt. % $UO_2$), Th (≤48.35 wt. % $ThO_2$) and Pb (≤6.77 wt. % PbO) into their matter. During the incorporation the isolated Th-rich and U-rich domains were formed, whereas the Pb prefers the U-rich ones. In the Th-rich domains Y and REE are strongly depleted (≤2.05 wt. % $Y_2O_3$) and in the U-rich domains REE are completely removed and only traces of Y (0.31 wt. % $Y_2O_3$) remains. The A/B ratio is 0.45 and 0.96 for U-rich and Th-rich domains, respectively. The sum of oxides ranges from 93.32 to 95.73 wt. %. Secondary fibrous Nb-Th-U phase crystallized on the grain surface.

PAsF solution (K+, Na+, $AsO_4^{3-}$, $PO_4^{3-}$, $F^-$)

Two independent processes took a place in this treatment. I) Fluorine (≤6.41 wt. % F) and Ca (≤4.05 wt. % CaO) is incorporated in to the matter and Y,REE are slightly removed. Textures of these parts are similar to the U,Th,Pb-rich domains. II) The fergusonite-(Y) grains and/or F,Ca enriched domains are replaced by the welt which is strongly enriched in P (≤7.79 wt. % $P_2O_5$), As (<9.38 wt. % $As_2O_5$), Na (<7.36 wt. % $Na_2O$), K (<5.14 wt. % $K_2O$), and F (<2.43 wt. % F) and U, Th, Y,REE, Ca depleted. Secondary Na-Y-F phase precipitates on the grain surface.

Table 1. Representative chemical composition of the studied phases. Chemical formula was calculated on the basis of (Nb+Ta+Ti+W)=1

| | Untr. | UThPb | UThPb | PAsF(1) | PAsF(2) | | Untr. | UThPb | UThPb | PAsF(1) | PAsF(2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $WO_3$ | 0.20 | 0.20 | 0.25 | 0.58 | 0.00 | $W^{6+}$ | 0.003 | 0.003 | 0.003 | 0.009 | 0.000 |
| $As_2O_5$ | 0.00 | 0.00 | 0.00 | 0.00 | 9.38 | $As^{5+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.187 |
| $Ta_2O_5$ | 1.17 | 1.10 | 1.24 | 1.20 | 1.44 | $Ta^{5+}$ | 0.015 | 0.018 | 0.015 | 0.018 | 0.015 |
| $Nb_2O_5$ | 44.84 | 34.06 | 46.59 | 37.73 | 55.12 | $Nb^{5+}$ | 0.955 | 0.936 | 0.952 | 0.944 | 0.949 |
| $P_2O_5$ | 0.00 | 0.11 | 0.00 | 0.00 | 7.79 | $P^{5+}$ | 0.000 | 0.006 | 0.000 | 0.000 | 0.251 |
| $SiO_2$ | 0.10 | 0.28 | 0.37 | 4.70 | 0.05 | $Si^{4+}$ | 0.005 | 0.017 | 0.017 | 0.260 | 0.002 |
| $TiO_2$ | 0.80 | 0.94 | 0.87 | 0.71 | 1.26 | $Ti^{4+}$ | 0.029 | 0.043 | 0.030 | 0.030 | 0.036 |
| $UO_2$ | 3.01 | 4.08 | 28.52 | 4.07 | 1.52 | $U^{4+}$ | 0.032 | 0.055 | 0.287 | 0.050 | 0.013 |
| $ThO_2$ | 1.05 | 48.35 | 9.26 | 1.36 | 0.00 | $Th^{4+}$ | 0.011 | 0.669 | 0.096 | 0.017 | 0.000 |
| $Y_2O_3$ | 28.94 | 2.05 | 0.25 | 21.65 | 0.00 | $Y^{3+}$ | 0.725 | 0.067 | 0.006 | 0.638 | 0.000 |
| $Pr_2O_3$ | 0.16 | 0.00 | 0.00 | 0.15 | 0.00 | $Pr^{3+}$ | 0.003 | 0.000 | 0.000 | 0.003 | 0.000 |
| $Nd_2O_3$ | 1.56 | 0.00 | 0.00 | 1.04 | 0.73 | $Nd^{3+}$ | 0.026 | 0.000 | 0.000 | 0.021 | 0.010 |
| $Sm_2O_3$ | 1.63 | 0.13 | 0.00 | 1.33 | 0.37 | $Sm^{3+}$ | 0.027 | 0.003 | 0.000 | 0.026 | 0.005 |
| $Gd_2O_3$ | 3.75 | 0.38 | 0.00 | 2.99 | 0.33 | $Gd^{3+}$ | 0.059 | 0.008 | 0.000 | 0.055 | 0.004 |
| $Dy_2O_3$ | 2.94 | 0.25 | 0.00 | 2.59 | 0.26 | $Dy^{3+}$ | 0.045 | 0.005 | 0.000 | 0.046 | 0.003 |
| $Er_2O_3$ | 1.44 | 0.18 | 0.00 | 1.23 | 0.00 | $Er^{3+}$ | 0.022 | 0.004 | 0.000 | 0.022 | 0.000 |
| $Yb_2O_3$ | 1.70 | 0.13 | 0.00 | 1.42 | 0.10 | $Yb^{3+}$ | 0.025 | 0.003 | 0.000 | 0.024 | 0.001 |
| CaO | 0.43 | 0.02 | 0.00 | 4.05 | 0.61 | $Ca^{2+}$ | 0.022 | 0.002 | 0.000 | 0.240 | 0.025 |
| MnO | 0.05 | 0.00 | 0.00 | 0.07 | 0.07 | $Mn^{2+}$ | 0.002 | 0.000 | 0.000 | 0.004 | 0.003 |
| FeO | 0.00 | 0.53 | 0.00 | 0.29 | 0.28 | $Fe^{2+}$ | 0.000 | 0.027 | 0.000 | 0.014 | 0.009 |
| PbO | 0.79 | 1.29 | 5.92 | 0.44 | 0.50 | $Pb^{2+}$ | 0.010 | 0.021 | 0.072 | 0.007 | 0.005 |
| $Na_2O$ | 0.00 | 0.00 | 0.00 | 2.06 | 7.36 | $Na^{+}$ | 0.000 | 0.000 | 0.000 | 0.221 | 0.544 |
| $K_2O$ | 0.00 | 0.00 | 0.04 | 0.73 | 5.14 | $K^{+}$ | 0.000 | 0.000 | 0.003 | 0.052 | 0.250 |
| $Cs_2O$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | $Cs^{+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| F | 0.35 | 0.18 | 0.09 | 6.41 | 2.43 | $F^{-}$ | 0.052 | 0.035 | 0.013 | 1.122 | 0.293 |
| | | | | | | $O^{2-}$ | 3.984 | 4.346 | 3.361 | 4.233 | 3.936 |
| O=F | -0.15 | -0.08 | -0.04 | -2.70 | -1.02 | □ cat. | 2.011 | 1.953 | 1.480 | 2.697 | 2.312 |
| TOTAL | 94.76 | 95.73 | 93.36 | 94.10 | 93.79 | □ an. | 4.036 | 4.380 | 3.373 | 5.355 | 4.228 |

## DISCUSSION

The laboratory experiments caused considerable changes in chemical compositions of metamict fergusonite-(Y). If we take into account a long geological time, these processes can run at lower temperatures and much less mineralized solutions.

During dramatic changes of the chemical composition of the treated fergusonite-(Y), the molar proportions of the B-site cations (Nb, Ta, Ti) shows minimal deviation from the untreated fergusonite-(Y). The Ta/(Nb+Ta) ratio in the untreated fergusonite-(Y) is 0.020. The Ta/(Nb+Ta) of fergusonite-(Y) form the UThPb solution is 0.014-0.019, form the PAsF solution is 0.016-0.019 and from the MCl solution is 0.017-0.019. Weak decrease of the Ta/(Nb+Ta) ratio indicate slightly higher mobility (diffusion?) of Ta

compared to Nb under above described conditions. The (Nb+Ta)/(Nb+Ta+Ti) ratio of treated and untreated fergusonite-(Y) shows also minimal variation.

Phosphorus enriched rims are morphologically and chemically similar to those observed on the samarskite group minerals from the Kracovice pegmatite, Czech Rep. (Škoda et al. 2006). Enrichment of As was reported on altered rims of *„písekite"* (samarskite group) from the granitic pegmatite near Písek, Czech Rep. (M. Novák, personal communication). These experiments confirmed the possibility of post crystallization, external origin of P and As.

The texture of the U,Th,Pb-rich domains originate during the experiments are similar to the replacement textures of Y,REE-Nb-Ta-Ti oxides commonly found in nature. Using discrimination plots of Ercit (2005), the U,Th,Pb-rich domains falls in to the pychochlore field. It is questionable if this texture is product of dissolution/reprecipitation process or diffusion of cations into and out of the metamict matter. Further HRTEM investigation of affected domains is necessary.

Acknowledgments: This work was supported by the research project GAAV KJB301630801.

## REFERENCES

Breiter, K., Förster, H.-J., Škoda R. 2006. Extreme P-, Bi-, Nb-, Sc-, U- and F-rich zircon from fractionated perphosphorous granites: The peraluminous Podlesí granite system, Czech Republic. *Lithos*, 88: 15-34

Cherniak, D., J., Watson, E., B. 2001. Pb diffusion in zircon. *Chemical Geology*, 172: 5-24

Ercit, T., S. 2005: Identification and alteration trendsof granitic-pegmatite hosted (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals: a statistical approach. *Canadian Mineralogist*, 43: 1291-1303.

Ewing R., C., Chakoumakos, B., C, Lumpkin, G., R., Murakami, T. 1987. The metamict state. *Materials Research Society Bulletin*, 12: 58-66.

Geisler, T., Pidgeon, R., T., Kurtz, R., van Bronswijk, W., Schleicher H. 2003. Experimental hydrothermal alteration of partially metamict zircon. *American Mineralogist,* 88: 1496-1518.

Lumpkin, G., R., Ewing, R., C. 1995. Geochemical alteration of pyrochlore group minerals: Pyrochlore subgroup. *American Mineralogist*, 80: 732-743.

Nasdala, L., Hanchar, J., M., Kronz, A., Whitehouse, M., J. 2005. Long-term stability of alpha particle damage in natural zircon. *Chemical Geology*, 220: 83-103.

Škoda, R., Novák, M., Houzar, S. 2006. Granitic NYF pegmatites of the Třebíč Pluton (Czech Republic). *Acta Musei Moraviae*, 91: 129-176. (In Czech with English summary)