Fe(II)/Fe_{tot} and U(IV)/U_{tot} in pegmatite minerals from southern Finland

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ABSTRACT

Oxidation states for Fe and U were determined in three allanites, fergusonite, gadolinite and monazite of Proterozoic pegmatites from southern Finland. Fe(II)/Fe_{tot} range 0.70–0.82 and U(IV)/U_{tot} 0.33–0.43 in allanites of different locations. In fergusonite Fe is in partly oxidized form (0.4) and U is totally oxidized (0.06). Fe in monazite is partly oxidized (0.3) but U is strongly reduced (0.93). Gadolinite has Fe in reduced form (0.95) and U in weakly reduced form (0.52). Small inclusions and heterogeneity in minerals may complicate results; homogeneity of minerals must be carefully checked.

***Keywords**: Iron, uranium, oxidation state, pegmatite, Finland.*

INTRODUCTION

Radioactive pegmatite minerals are always interesting. The oxidation state of iron and uranium in minerals is mainly due to oxygen fugacity, pressure, temperature and chemical composition of the crystallizing magma or result of later redox potential changes. They may tell about magmatic processes. The available sites for ions and their charge balance in mineral also determine the original oxidation state distributions of elements.

According to Deer et al. (1986), FeO>Fe_2O_3 is often reported in allanite. Fergusonite and monazite may comprise small amounts of iron (Chang et al., 1996, Anthony et al., 1997). Gadolinite contains Fe^{2+} or Fe^{3+} (Ito & Hafner, 1974), but in gadolinite-Y and gadolinite-Ce iron seems to be in reduced form (Lokka, 1950, Segalstad & Larsen, 1978).

Uranium occurs in minerals in oxidation states of +IV and +VI. The U(IV)/U_{tot} in allanite, fergusonite and monazite from Finnish pegmatites varies in the 0.06–0.93 range (Ervanne, 2004). Comparative behaviour of the oxidation states of Fe and U in a single mineral sample is not well known. The subject is here studied with data of 6 pegmatite mineral grains.

SAMPLES

The studied minerals are from known rare-element pegmatites in southern Finland. One allanite-Ce (1) is from pegmatite dyke at Åva, Brandö, in the archipelago of southwest Finland. Second allanite-Ce (2) and a fergusonite are from the Pyörönmaa pegmatite in parish of Kangasala, southern Finland. Third allanite-Ce (3) is from the Varala pegmatite, also in Kangasala. Gadolinite-Y is from the Lövböle pegmatite, Kemiö, southwest Finland. Monazite-Ce is from a dyke at Kännätsalo, parish of Luumäki, southeast Finland. The pegmatites represent late Svecofennian magmatism (~1.80–1.81 Ga) except that in Luumäki, which is associated with anorogenic ~1.6 Ga Rapakivi granites. The dykes belong to the rare-earth type of the rare-element class using pegmatite classification of Černý (1991). For detailed descriptions of the above pegmatites and their geological environment, see Lokka (1950), Vorma et al. (1966), Siivola (1975), Vaasjoki (1977), Lahti & Kinnunen (1993), Lindroos et al., (1996), and Hytönen (1999).

Homogeneity of samples was checked by microprobe. Allanites were relative homogeneous. Monazite was zoned having a rim depleted in U and Th, but elevated in P, Ce and La. Fergusonite was heterogeneous, and sum of its chemical element concentrations was only ~86 wt% indicating hydration. Ervanne (2004) has reported microprobe analyses of these minerals.

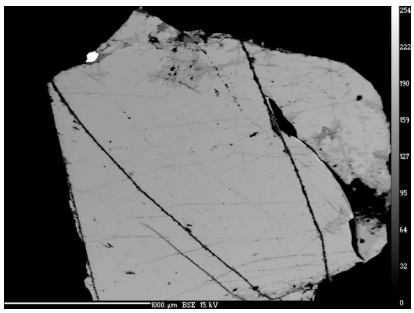

FIGURE 1. Backscatter electron image of the rather homogeneous Lövböle gadolinite-Y (diameter ~2.5 mm), which contains a small inclusion of Th-Pb-U mineral seen as light spot in upper left corner.

Gadolinite was rather homogeneous, but compared Th-Pb-U inclusion rich in uranium (~76 wt% $UO_{2\ tot}$) (Fig. 1). Its chemical composition determined by microprobe is (in wt%): 22.4 SiO_2, 13.0 FeO_{tot}, 0.1 MnO, 0.5 CaO, 0.1 ZrO_2, 33.8 Y_2O_3, 3.7 Dy_2O_3, 2.6 Gd_2O_3, 0.5 SmO, 0.5 PbO, 1.1 Ce_2O_3, 0.1 La_2O_3, 1.1 NdO, 0.4 ThO_2, 0.2 Pr_2O_3, 0.1 Ta_2O_5. However, sum of chemical element concentrations is low, ~80 wt%, because Be, Er and Ho were not analyzed. Gadolinite of the Lövböle pegmatite contains ~10 wt% of BeO (Lokka, 1950).

ANALYTICAL PROCEDURES

The Fe and U oxidation state analyses for a particular mineral were made from same crystal sample having weight of a few grams. The least altered part of larger crystal was chosen for the determinations. The concentration of ferrous iron was titrimetrically determined and Fe_{tot} was analyzed by ICP-AES method in the Chemical laboratory of Geological Survey of Finland. For monazite and fergusonite the results are semiquantitative. The uranium oxidation states were determined by a method based on ion exchange in the Laboratory of Radiochemistry of University of Helsinki (Ervanne, 2004). U_{tot} was determined by alpha spectrometry. The U(IV)/U_{tot} data for allanite,

fergusonite and monazite is from Ervanne (2004), but for gadolinite it is unpublished (Table 1).

TABLE 1. Amount of reduced form oxidation states and total contents (wt%) of Fe and U in the minerals. Analyses made by microprobe (Cameca SX100) are referred as m.probe.

Mineral	Fe(II)/ Fe_{tot}	U(IV)/ U_{tot}	FeO_{tot}	FeO_{tot} m.probe	UO_{2tot}	UO_{2tot} m.probe
Allanite (1)	0.70	0.33*	14.8	15.3*	0.06	nd.*
Allanite (2)	0.70	0.35*	13.5	14.1*	0.02	nd.*
Allanite (3)	0.82	0.43*	13.6	13.9*	0.14	nd.*
Fergusonite	0.4	0.06*	~0.05	nd.*	1.81	2.1*
Gadolinite	0.95	0.52	13.5	13.0	0.25	nd.
Monazite	0.3	0.93*	~0.05	nd.*	0.34	0.5–nd*

* from Ervanne (2004), nd. = not detected (detection limits for microprobe were 0.1 wt% FeO_{tot} and 0.2 wt% UO_{2tot}). Microprobe voltage was 15 kV, beam current was 20 nA and beam diameter 5 µm.

RESULTS AND DISCUSSION

Within the allanite grains, there seems to be a correlation between $Fe(II)/Fe_{tot}$ and $U(IV)/U_{tot}$ (Table 1), but this needs to be confirmed by further studies. Anyway, the situation is complicated, Fe being in reduced form but U in more oxidized form. Uranium requires more reducing conditions than iron to be in reduced form. Allanite poses a challenge with these mixed oxidation states. Interesting is also that Fe has two different vacancies to be filled. Therefore there are more possibilities for variation of the oxidation state distributions. The allanite (3) may comprise small U-rich inclusions, because its UO_{2tot} is relative high, 0.14 wt% (Table 1).

The altered fergusonite of Pyörönmaa has Fe in partly oxidized form and U is strongly oxidized. Thus the oxidation states differ compared to those in allanite (1) from the same Pyörönmaa dyke. Fergusonite obviously has a "weaker structure" for radiation damage than other mentioned minerals. This agrees with the fact that fergusonite is often metamictic. A correlation may occur between the alteration of the mineral and the oxidation states of its iron and uranium.

Iron in the Lövböle gadolinite is in reduced state, but uranium is partly oxidized. The mineral is reported to occur in close contact with pyrite, and comprises $FeO>Fe_2O_3$ (Lokka, 1950). The UO_{2tot} obtained from dissolved gadolinite by alpha spectrometry is higher compared to the microprobe data. The former must be a "combination" of two uranium phases shown in Figure 1. Unfortunately the $U(IV)/U_{tot}$ in the inclusion is not known. Careful checking of the homogeneity of samples is necessary for good analytical results.

In the monazite of Luumäki Fe is partly oxidized but U is in reduced form; this is reverse for oxidation in the earlier allanite grains. Monazite structure probable prefers Fe in oxidized state, since alteration is weak. Moreover, reduced U may substitute Th in the structure. The UO_{2tot} results differ because the mineral was zoned.

CONCLUSIONS

The oxidation state of Fe and U in the allanite grains are rather constant – perhaps because of the relative coeval age and similar type of host pegmatite. They vary between mineral species, however. Low oxidation state in fergusonite may be due to hydration or metamictization. Alteration in mineral may also oxidize uranium resulting in a change of uranium solubility. Minor inclusions and heterogeneity in samples have crucial role in the Fe_{tot} and U_{tot} determinations from pulverized samples. Comparative behaviour of oxidation state (ie. obtained analytical data) in minerals seems to have many contexts. Oxidation state of U may explain the discrepancies in radiometric dating results.

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