

## REE systematics of fluorites in (per-)alkaline systems

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The mid-Proterozoic Gardar Province (South Greenland) is a failed rift province hosting 12 major (per-)alkaline intrusions [1]. High fluorine contents occur in a great variety of magmatic rocks all over the Gardar Province. Rare earth element (REE) patterns of fluorite and associated minerals like cryolite ( $\text{Na}_3\text{AlF}_6$ ), calcite and siderite provide information about the magma source, crystallisation history, fluid-melt interaction and late-magmatic processes.

We focused on fluorites from three intrusions representing the whole compositional range of the Gardar Province: the Ilímaussaq intrusion which is mainly composed of silica-undersaturated apatitic nepheline syenites; the Motzfeldt intrusion with its mostly miaskitic nepheline syenites; and the Ivigtut intrusion famous for its now mined-out cryolite deposit hosted by an A-type granite [1].

All chondrite-normalized REE patterns of fluorite show a negative Eu anomaly which is attributed to feldspar fractionation. The REE patterns of the Motzfeldt and Ilímaussaq intrusions in the eastern part of the Gardar province show a positive Y anomaly if Y is plotted between Dy and Ho according to [2]. In contrast, the patterns of the Ivigtut intrusion (in the western part of the province) exhibit a negative Y anomaly. This regional difference might be ascribed to heterogeneities in the magma source as XRF data of basaltic to rhyolitic dykes in the Ilímaussaq and Motzfeldt region are characterized by higher Y contents than dykes from the Ivigtut region.

Primary magmatic fluorite of the Motzfeldt and Ilímaussaq intrusions show almost identical patterns with an enrichment in light REE suggesting an early crystallisation [3]. Later crystallised fluorites of veins are less concentrated in REE and exhibit flatter patterns or enrichment of the middle/heavy REE typical of the late-magmatic to hydrothermal crystallisation stage. The REE patterns of minerals from Ivigtut are slightly enriched in heavy REE and indicate a strong interaction with a fluid phase as evidenced by the very pronounced tetrad effect.

Our preliminary results show that REE in fluorite reflect the source but can also act as tracers for the transition from early magmatic to hydrothermal conditions during the crystallisation of (per-)alkaline intrusions. The tetrad effect reflects strong water-rock interaction and the fluid's influence on the fluorite genesis.

### References

- [1] Upton *et al.* (2003), *Lithos* **68** 43-65.
- [2] Bau and Dulski (1995), *Contr. Min. Petr.* **119** 213-223.
- [3] Möller *et al.* (1976), *Mineral. Dep.* **11** 111-116.

## Structural Chemistry of Cation-doped Bacteriogenic $\text{UO}_2$

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The chemical stability of bacteriogenic uraninite, " $\text{UO}_2$ ", is one of the seminal issues governing its success as an *in situ* immobilization strategy in remediated subsurface locations. Little detail is known about the structure and reactivity of this material, but based on comparison to its closest abiotic analog,  $\text{UO}_{2+x}$  ( $0 < x < 0.25$ ), we expect that it is complex and disordered, likely to exhibit non-stoichiometry, and capable of structurally incorporating common ground water cations and U(VI). These subtle changes in mineralogy are expected to substantially impact its stability in ground water.

In this study, the product of microbial U(VI) reduction under varying conditions of pH, carbonate and divalent cation concentration ( $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ca}^{2+}$ ) was investigated. To facilitate x-ray scattering measurements, a gentle aqueous cleaning method was developed to separate the biooxide and organic components without altering the biooxides. The local and long-range atomic structures and nano-scale structures of the wet oxides have been measured using EXAFS, WAXS, SAXS and TEM. The material exhibits a range of particle sizes with a mean around 4 nm. The first oxygen shell is distorted, consistent with a nonstoichiometric composition.  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  were found to attenuate the particle size of bacteriogenic  $\text{UO}_{2+x}$  and to be structurally incorporated. These findings suggest that ground water composition can have a pronounced impact on the structure and properties of bacteriogenic uraninite.