Sorption of Cm(III) on crystalline rock

Upscaling approach for heterogeneous samples
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Upscaling from the nm to the mm scale
Multi-techniques approach using spatially-resolved methods

How do we perform upscaling without loss of molecular information?

➢ Investigation of heterogeneous material using multi-technique approach
Upscaling from the nm to the mm scale
Multi-techniques approach using spatially-resolved methods

How do we perform **upscaling without loss of molecular information**?

- Investigation of heterogeneous material using **multi-technique approach**

**Techniques**:
- Raman-microscopy
- Interferometry
- Autoradiography
- \(\mu\)TRLFS

Influence of heterogeneity on the transport of radionuclides across scales
Sorption of Cm(III) on Bukov migmatised gneiss
Multi-techniques approach using spatially-resolved methods

Thin section was immersed upside down in the sorption solution for 7 days

\[ [\text{Cm}] = 10^{-6} \text{ M (trivalent actinide; highly luminescent)} \]

\[ I = 0.1 \text{ M NaCl} \]

\[ \text{pH} = 8 \]

Four different regions of interest (ROIs) were investigated (1x1mm)
Sorption of Cm(III) on Bukov migmatised gneiss
Mineralogy in correlation to surface roughness

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Sorption of Cm(III) on Bukov migmatised gneiss

Cm(III) luminescence intensity correlated to mineralogy

µTRLFS

High LI [a.u.]

Low LI [a.u.]

Mineral phases

Each pixel corresponds to one Cm(III)-spectrum

Cm(III) luminescence intensity:

Feldspar > Quartz > Amphibole
Sorption of Cm(III) on Bukov migmatised gneiss
Cm(III) luminescence intensity correlated to surface roughness

Highest sorption uptake on **feldspar** areas with a **rough** surface
Almost no sorption on **smooth** **feldspar** planes
Sorption of Cm(III) on Bukov migmatised gneiss

Cm(III) peak position in correlation to surface roughness

Gaussian fitting of peaks:

**Peak position [nm]**

- **Rough** surface: red shifted peaks (603 – 605 nm)
  - stronger sorption
- **Plain** surfaces: blue-shifted peaks (602 – 603 nm)
  - weaker sorption
Sorption of Cm(III) on Bukov migmatised gneiss
Cm(III) luminescence lifetime correlated to mineralogy

μTRLFS

$$n(H_2O) = \frac{0.65 \ (ms)}{\tau} - 0.88$$

Fully hydrated Cm(III) in solution: 9 H$_2$O
Sorption of Cm(III) on Bukov migmatised gneiss
Cm(III) luminescence lifetime correlated to mineralogy

μTRLFS

Determination of number of species

\[ n(H_2O) = \frac{0.65 \ (ms)}{\tau} - 0.88 \]

Fully hydrated Cm(III) in solution: 9 H_2O

Quartz:
- strong sorption 2 – 4 H_2O; Inner-sphere sorption complex (ISS)

Feldspar:
- multiple species
- 2 – 5 H_2O; strong ISS complex
- 6 – 8 H_2O; weak ISS complex
Sorption of Cm(III) on Bukov migmatised gneiss
Cm(III) luminescence lifetime correlated to surface roughness

**Feldspar:**
- On smooth surfaces weaker ISS complexes are formed
- On rough surfaces stronger ISS complexes are formed

<table>
<thead>
<tr>
<th>Peak position [nm]</th>
<th>Mineral phases</th>
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<tr>
<td>Smooth</td>
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<table>
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<tr>
<th>Rough</th>
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</table>
Sorption of Cm(III) on Bukov migmatised gneiss
Complex Cm(III) speciation on quartz

Secondary Cm(III) peak:

Three peaks identified:

- 604 nm: ISS peak of Cm(III) on quartz (2 – 4 H₂O)
- 612 nm: ⁷F₂ peak of natural Eu(III)
- 622 – 626 nm: secondary Cm(III) peak (0 H₂O)
Sorption of Cm(III) on Bukov migmatised gneiss

Cm(III) speciation on quartz

Probably no incorporation in quartz

Sorption of Cm(III) on kink/defect sites in the nanometer scale and formation of ternary complexes

No water coordination of Cm(III)
Summary

Upscaling approach successful

- Sorption uptake was quantified: amphibole/mica > feldspar > quartz
- Strong correlation between surface roughness and sorption uptake/speciation
- Qualitative speciation was determined on feldspar and quartz
  - **Feldspar**: weakly bound ISS species on smooth surfaces; strongly bound species on rough surfaces
  - **Quartz**: ISS species on smooth surface; ternary complex close to feldspar/quartz mineral grain boundaries

Thin section was analysed in the cm region with more detailed analysis in mm region

Upscaling possible: molecular information retained on the mm scale
Thank you for your attention!
Powder studies – Bukov Gneiss

I: pH < 3, no sorption, Eu(III)/Cm(III) in solution

II: pH > 3, likely outer-sphere sorption on mica and amphibole

III: pH > 5.2, inner-sphere sorption on feldspar and quartz

IV: pH > 7.5, almost complete sorption

Powder grain size: < 63 µm

I = 0.1 M NaCl

5E-7 M Cm-Eibenstock
5E-7 M Eu-Rez
Mineralogy – Bukov Gneiss

Feldspar = NaAlSi$_3$O$_8$

*Plagioclase – Albite*

= (Na,Ca)Al(Si,Al)$_3$O$_8$

*Plagioclase – Andesine*

Amphibole = Ca$_2$[Mg$_4$(Al,Fe$^{3+}$)](Si$_7$Al)O$_{22}$(OH,F)$_2$

*Magnessio-hornblende*

= NaCa$_2$(Mg$_3$Ti$^{4+}$Al)(Si$_6$Al$_2$)O$_{22}$(OH)$_2$

Kaersutite

Mica = KAl$_2$(AlSi$_3$O$_{10}$)(F,OH)$_2$

*Muscovite*

= K(Mg,Fe)$_3$AlSi$_3$O$_{10}$(F,OH)$_2$

Biotite

Chlorite = (Mg,Fe)$_3$(Si,Al)$_4$O$_{10}$(OH)$_2$.·(Mg,Fe)$_3$(OH)$_6$

Titanite = CaTiSiO$_5$

Pyrite = FeS$_2$

Quartz = SiO$_2$
Single Spectra of Cm(III) on feldspar

Cm(III) peak shows a slight shoulder around 611 – 612 nm corresponding to naturally incorporated Eu(III) $^7F_2$ luminescence band.
Peak position in correlation to surface roughness

Difference of around 1 nm between Cm(III) on smooth and rough feldspar surfaces

Stronger sorption on rough surfaces, probably due to more kink and defect sites
Comparison to TRLFS powder sorption studies

Complexation on quartz and feldspar on thin section:
- Measured pH post-sorption was 7.80 (first hydrolyzed inner-sphere sorption complex)
- Peak maxima (602 – 605 nm) suggest generally ISS (non-hydrolzed, mono- and bihydrolyzed)
- Mainly first ISS complex is formed

Identification of species by peak deconvolution
- 1 – Cm aquo ion
- 2 – Inner sphere (IS) complex
- 3 – 1st IS hydrolysis species
- 4 – 2nd IS hydrolysis species
Speciation of Cm(III) on quartz

Study on Cm(III) incorporation in CSH (calcium silicate hydrate) phases

Incorporation of Cm(III) into CSH phases during long contact times

Identification of two species at 618.9 nm and 620.9 nm