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Supplement of

Spatially resolved sorption of Cm(III) on crystalline rock: influence of surface roughness and mineralogy

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Spatially resolved sorption of Cm(III) on crystalline rock: influence of surface roughness and mineralogy

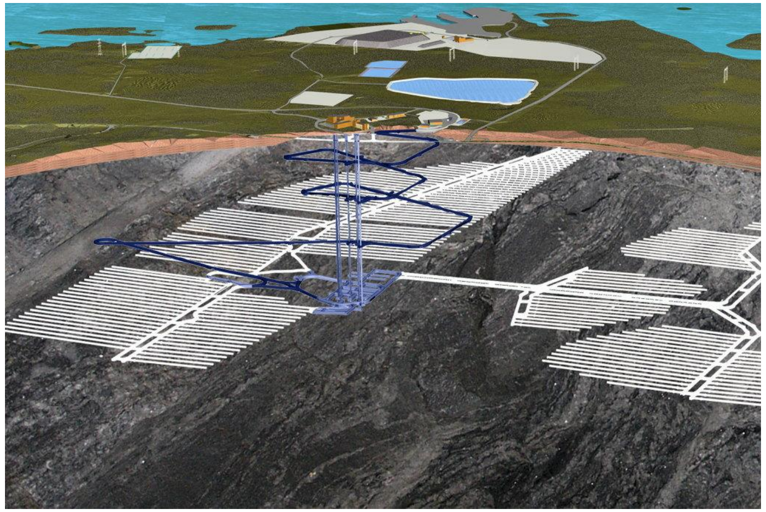
Session 2F: Chemistry and migration behaviour of radionuclides

SafeND Workshop 11.11.2021

Maximilian Demnitz, Konrad Molodtsov, Stefan Schymura, Ariette Schierz, Katharina Müller, Moritz Schmidt

Repositories for highly active nuclear waste

- Challenge for most countries worldwide:
  highly active nuclear waste
- **Safe deposition** of highly active nuclear waste for at least **100,000 to 1,000,000 years**
- Germany: 10,500 t or 27,000 m^3
- Considered host rocks: salt, clay or **crystalline rocks**



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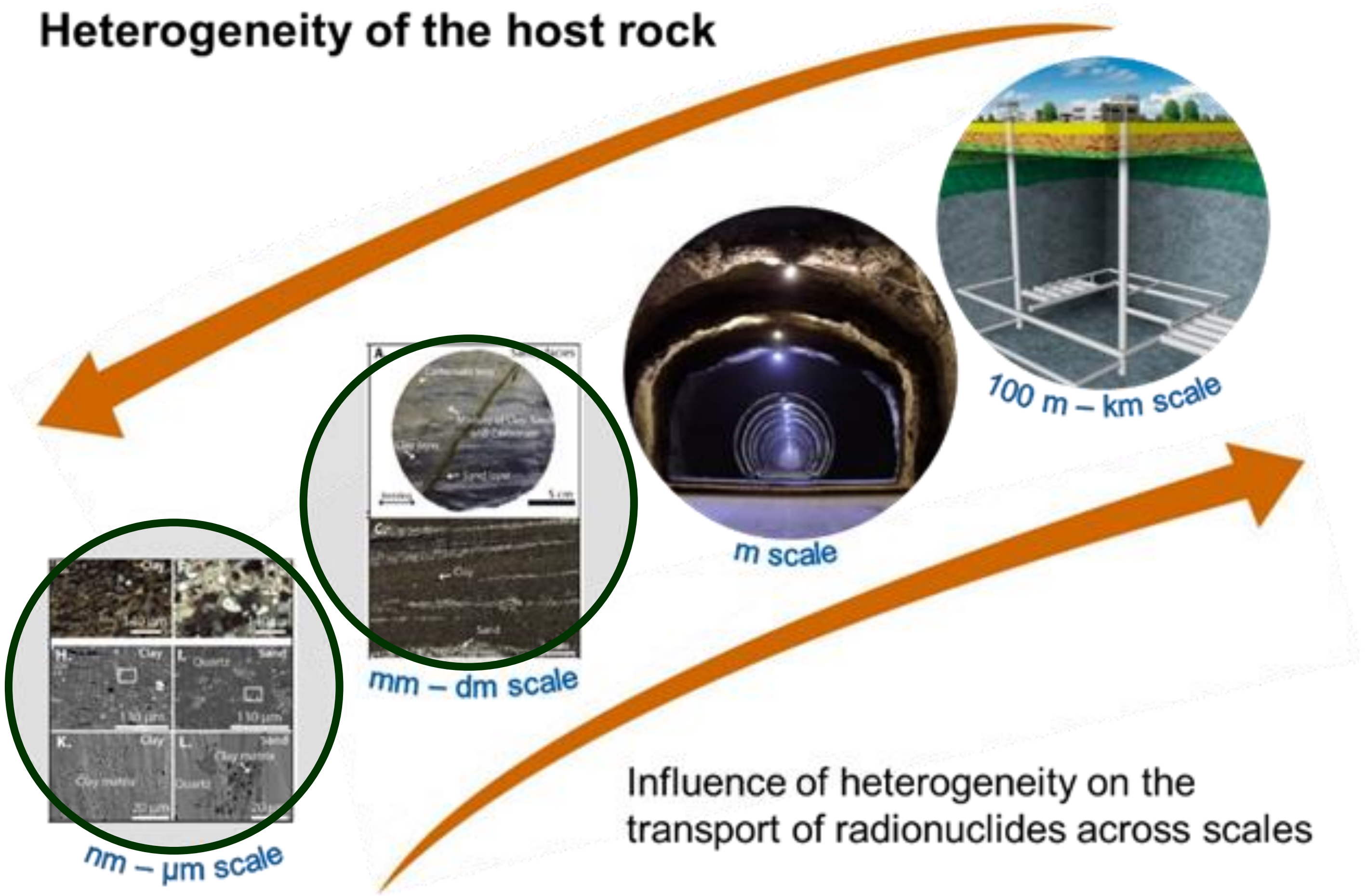
https://sanjindumisic.com/wp-content/uploads/2013/12/onkalo-spent-nuclear-fuel-repository.jpg Accessed: 18.06.2021
https://www.nsenergybusiness.com/wp-content/uploads/sites/3/2020/03/Image-3_Onkalo-Nuclear-Waste-Repository-Finland.jpg Accessed: 18.06.2021

Upscaling molecular scale findings

- Work is part of the iCross project
- **Radionuclide interaction and speciation** with rocks investigated on the **molecular scale** (homogeneous mineral powders)
- **Nuclear waste repository** will be built on the **km scale**
- Need for experimental findings on larger scales

Can we straightforwardly apply findings from the molecular scale to larger scales?

What other factors influence the transport of radionuclides on larger scales?



Going larger makes things more complex

Experiments

Mineralogy

Grain boundaries

Surface roughness

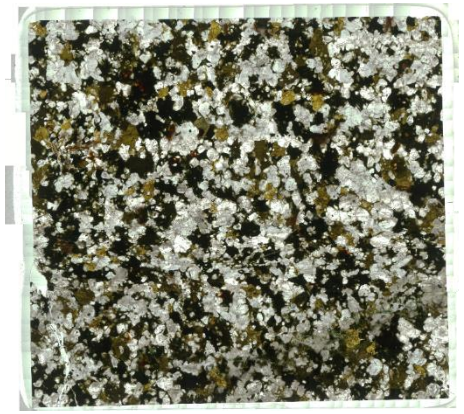
Heterogeneity

Competitive sorption

Reality & Complexity

Pure mineral powders

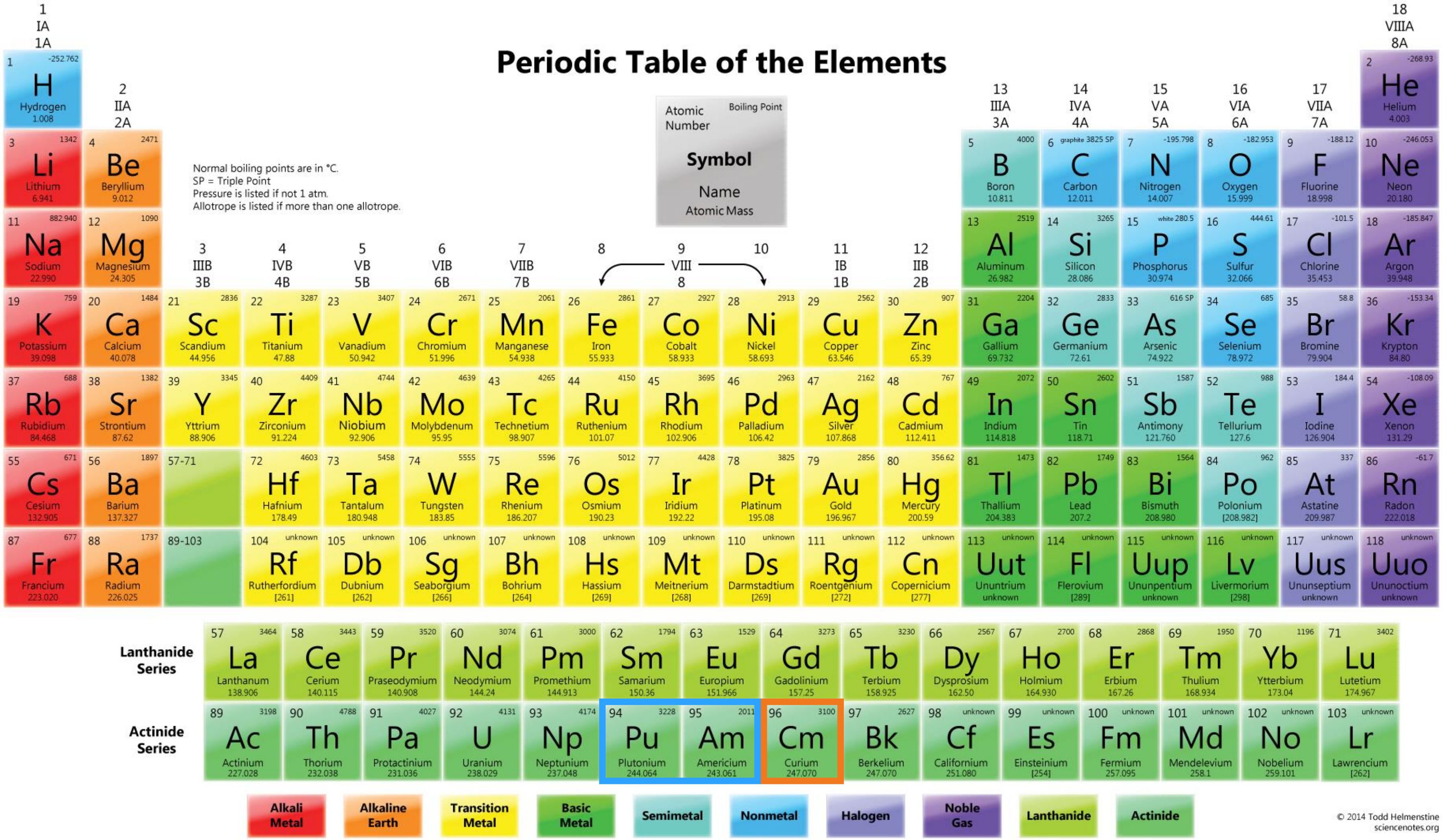
Single crystal



Heterogeneous crystalline rocks

Cm(III) as a luminescent probe

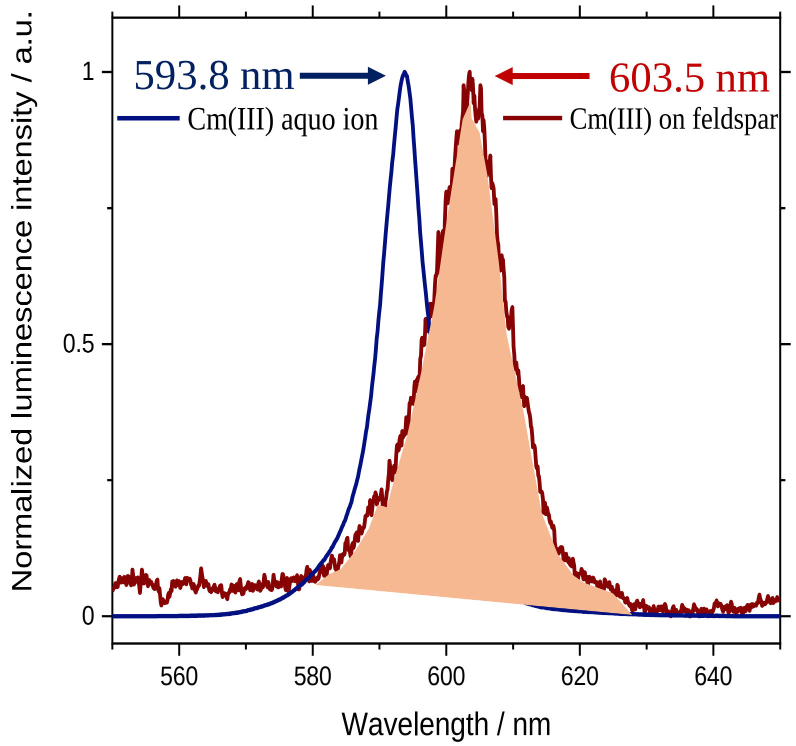
- Curium is an actinide, which primarily exist in its **trivalent state Cm(III)**
- Cm(III) is a **chemical analogue to Am(III) and Pu(III)**
- **Reducing conditions are expected** in a deep geological repository
- After short lived fission products have decayed, **majority of activity** stems from **transuranium elements**

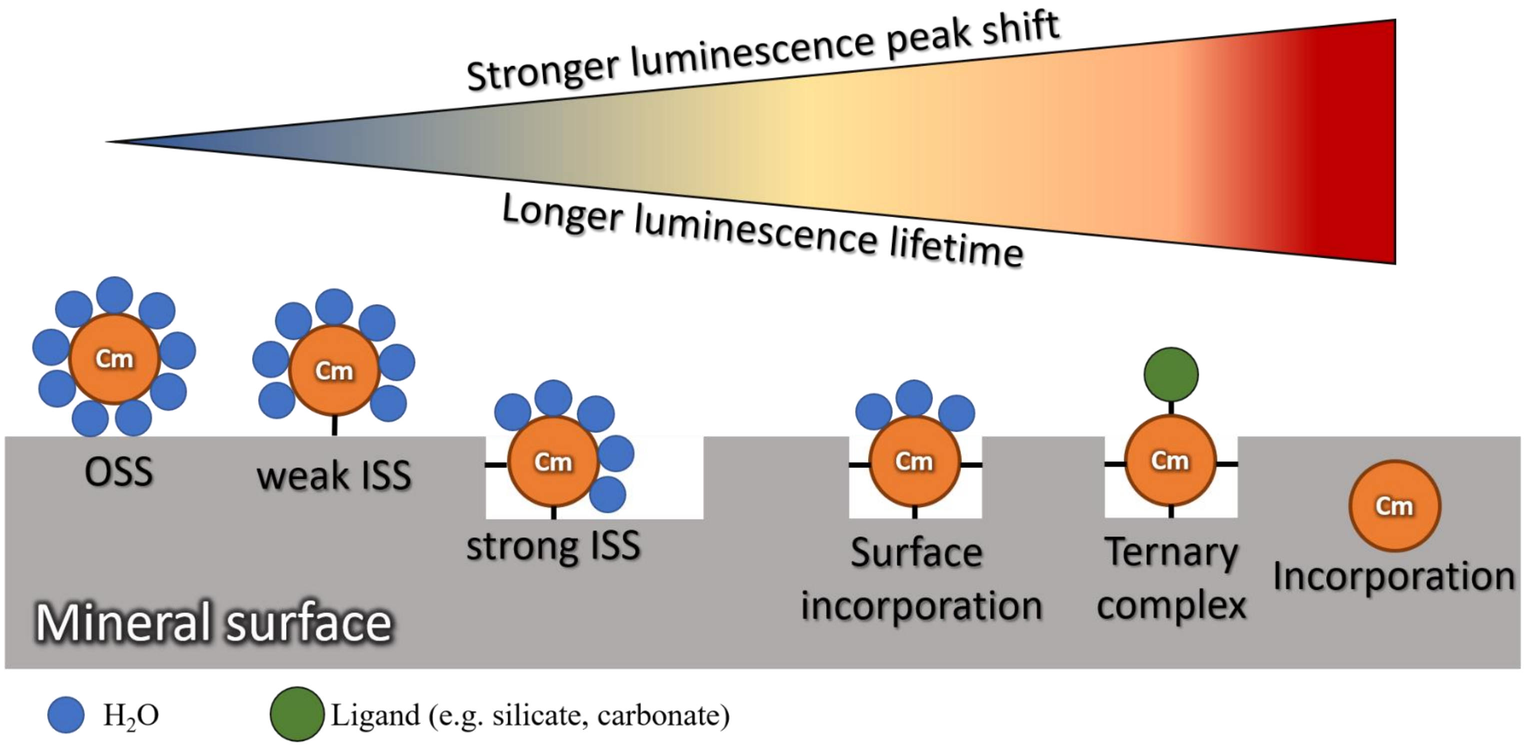


https://sciencenotes.org/wp-content/uploads/2014/11/PeriodicTableBoilingPoint.png Accessed: 14.06.2021

Cm(III) as a luminescent probe

- Cm(III) possesses excellent luminescence properties
- Cm(III) bound to the surface experiences a **luminescence peak shift**
- Cm(III) **peak position** is an indication of **sorption strength**





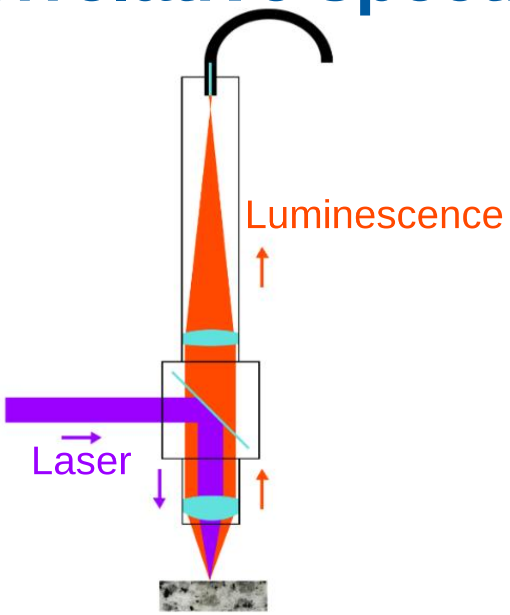
- Water is a luminescence quencher; **less water** means **longer lifetimes**
- From **lifetime** we can **calculate** the amount of **water bound to Cm(III)**
- Combination of **peak shift** and **lifetime** gives us information about **chemical speciation of Cm(III)** on a mineral surface

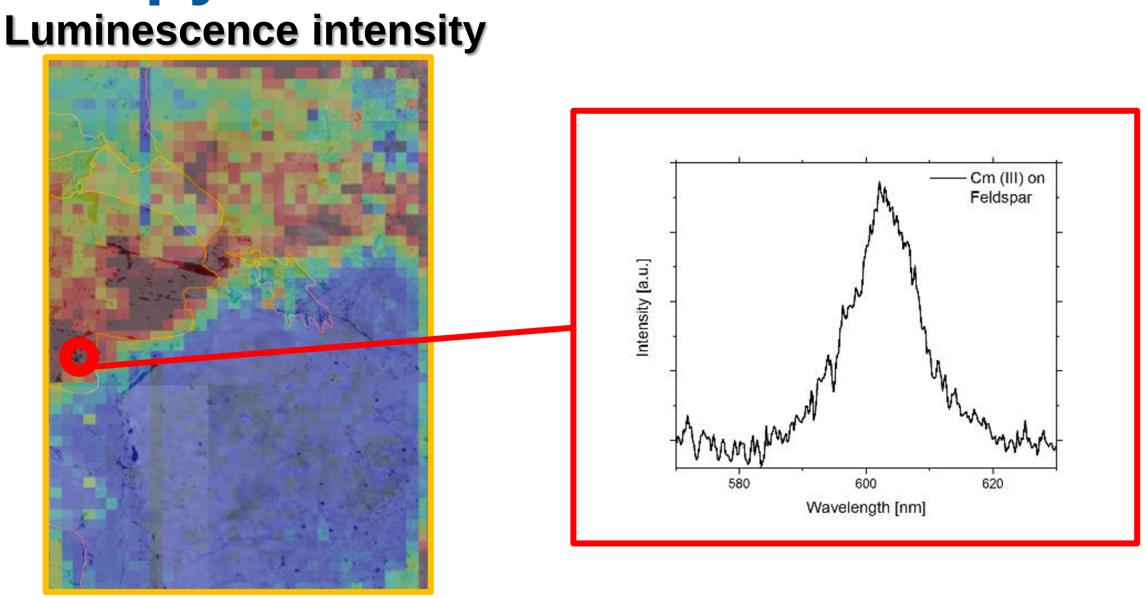
M. Demnitz et al.. Effects of surface roughness and mineralogy on the sorption of Cm(III) on crystalline rock, Journal of Hazardous Materials, 423 (2022) 127006.

Spatially-resolved correlative spectroscopy

µTRLFS

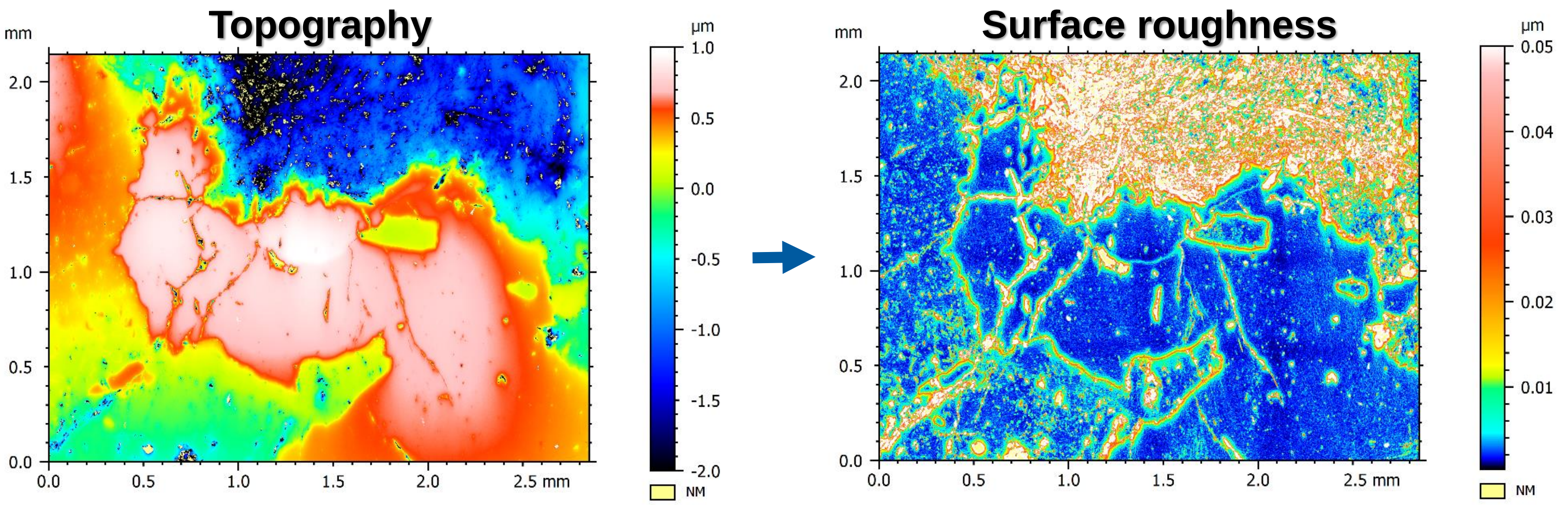
- Allows **spatially resolved** investigation of **luminescence** (Cm(III)/Eu(III))
- Scan surface pixel by pixel
- **Each pixel** represents **a luminescence spectrum**





Interferometry

- Method to determine topography (“height profile”) of a surface
- Nanometer lateral resolution; micrometer spatial resolution
- From topography surface roughness can be calculated

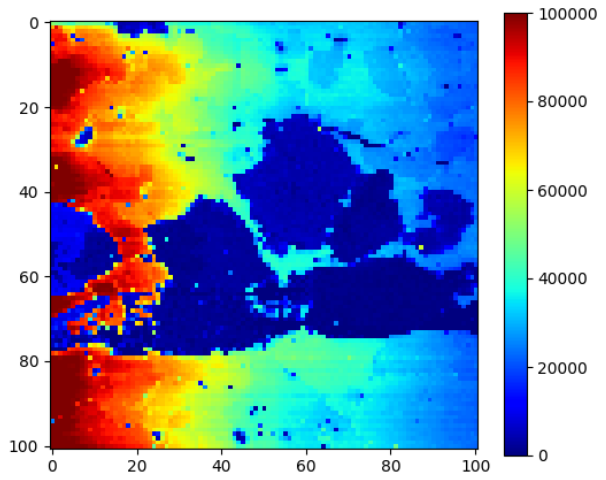


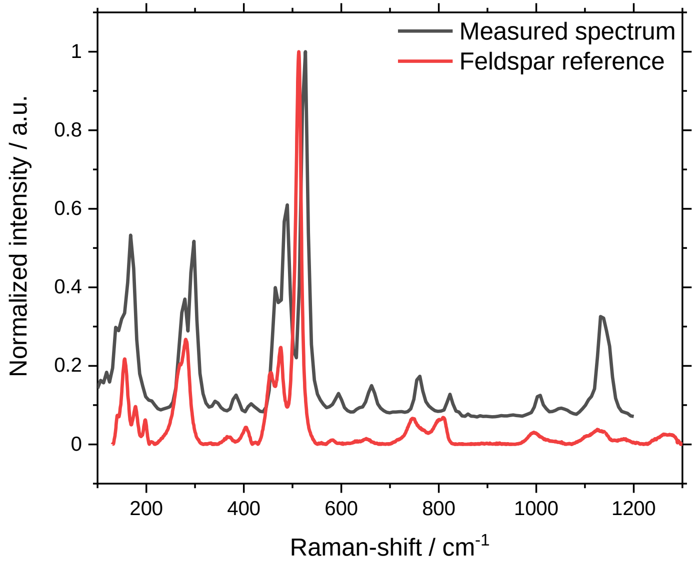
DRESDEN concept HZDR

Spatially-resolved correlative spectroscopy

Raman-microscopy

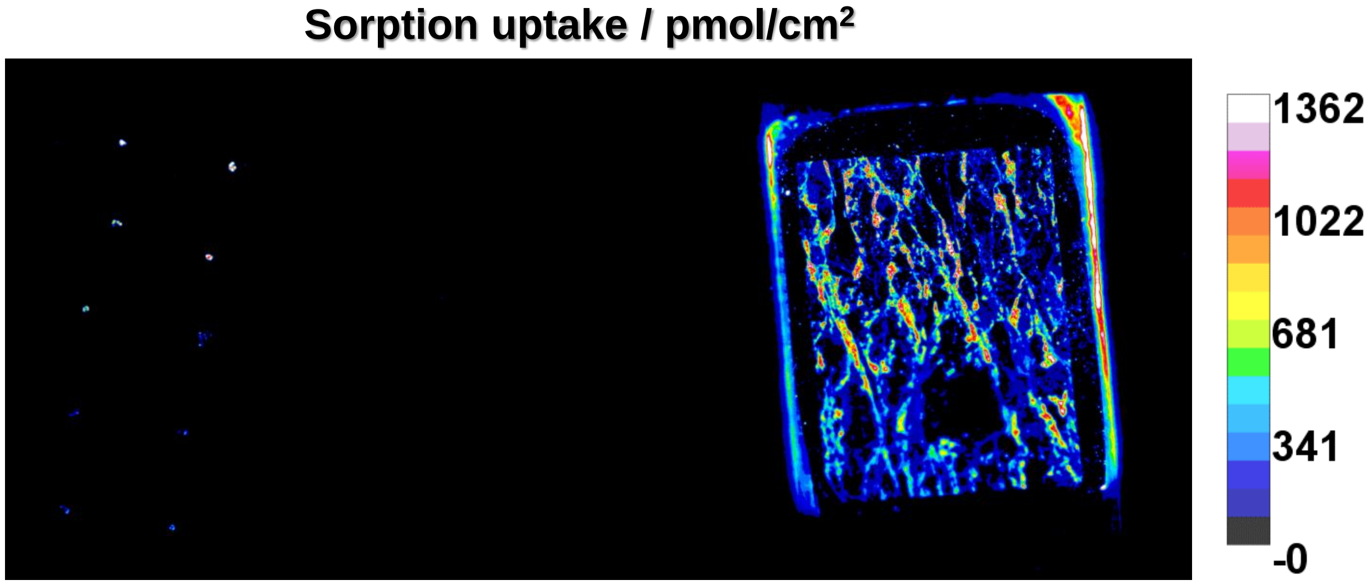
- Scanning of surface via Raman-microscope
- Comparison of spectra to RRUFF-database





Autoradiography

- Measurement of the activity (alpha, beta) on the sample
- Calibration of autoradiography allows numerical quantification of sorbed radionuclide



Cm(III) sorption on granite and gneiss

Effects of surface roughness and mineralogy on the sorption of Cm(III) on crystalline rock

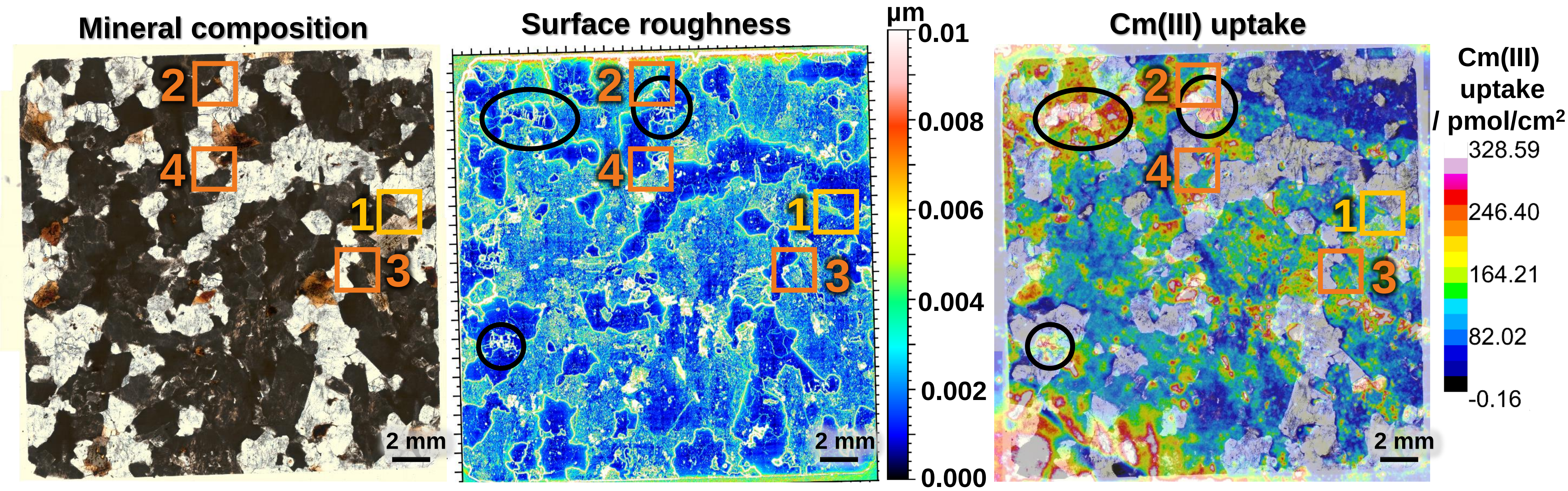
August 2021 Journal of Hazardous Materials 423(Pt A):127006

DOI: 10.1016/j.jhazmat.2021.127006

Cm(III) sorption on granite and gneiss

I = 0.1 M NaCl pH = 8.0
[Cm(III)] = 10^{-6} M t = 7 d

Granite – thin section



Sorption uptake:

Mica: $KAl_2(AlSi_3O_{10})(F,OH)_2$ / $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$
Feldspar: $KAlSi_3O_8$ / $NaAlSi_3O_8$ / $CaAl_2Si_2O_8$
Quartz: SiO_2

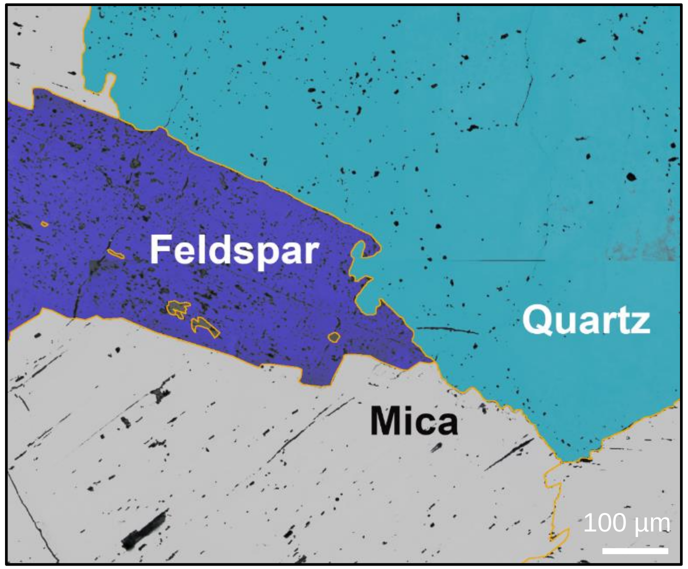
- Mica > Feldspar > Quartz
- **Surface roughness increases sorption uptake** by almost one order of magnitude

Cm(III) sorption on granite and gneiss

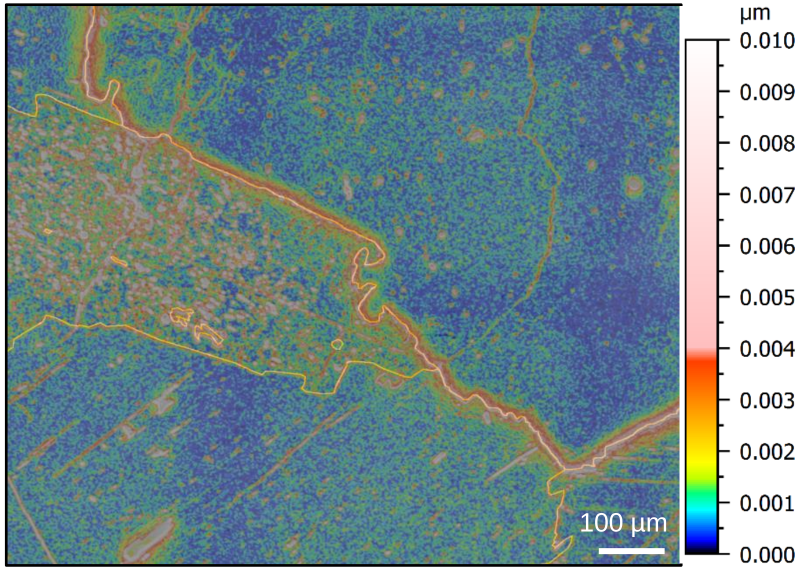
I = 0.1 M NaCl pH = 8.0
[Cm(III)] = 10^{-6} M t = 7 d

Granite – thin section ROI 1

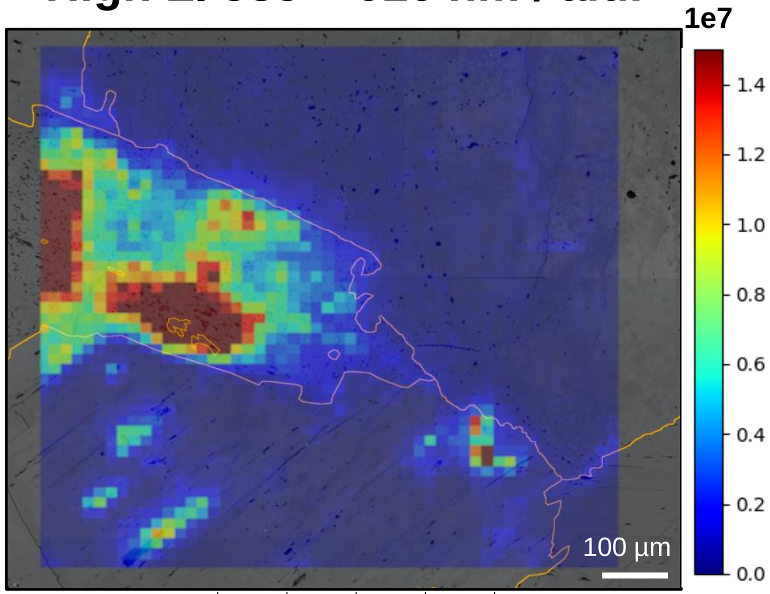
Mineral phases



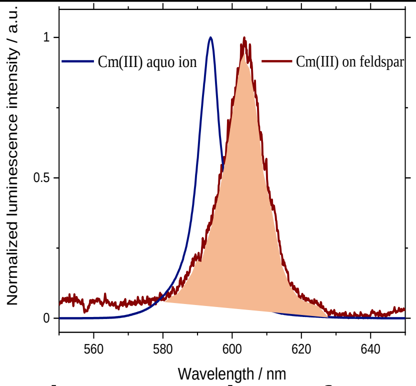
Surface roughness



High LI 585 – 616 nm / a.u.



Mica: $KAl_2(AlSi_3O_{10})(F,OH)_2$ / $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$
Feldspar: $KAlSi_3O_8$ / $NaAlSi_3O_8$ / $CaAl_2Si_2O_8$
Quartz: SiO_2



Luminescence intensity:

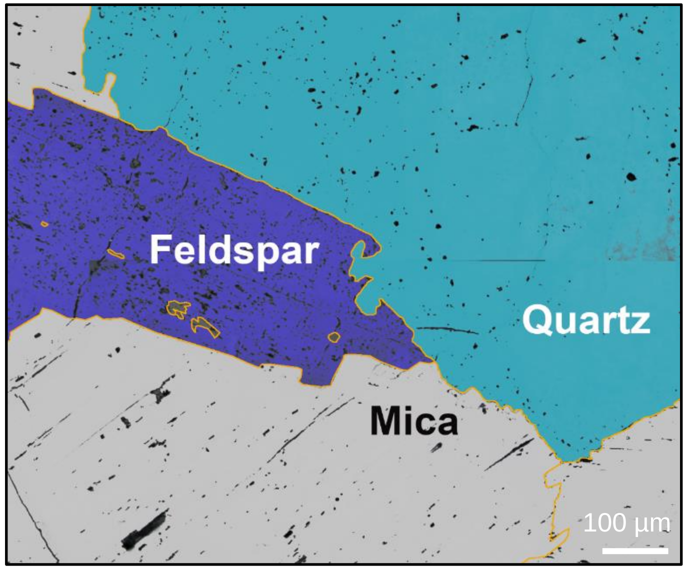
- Feldspar > Mica (quenching) > Quartz
- **Surface roughness increases sorption uptake** on feldspar and mica by around one order of magnitude

Cm(III) sorption on granite and gneiss

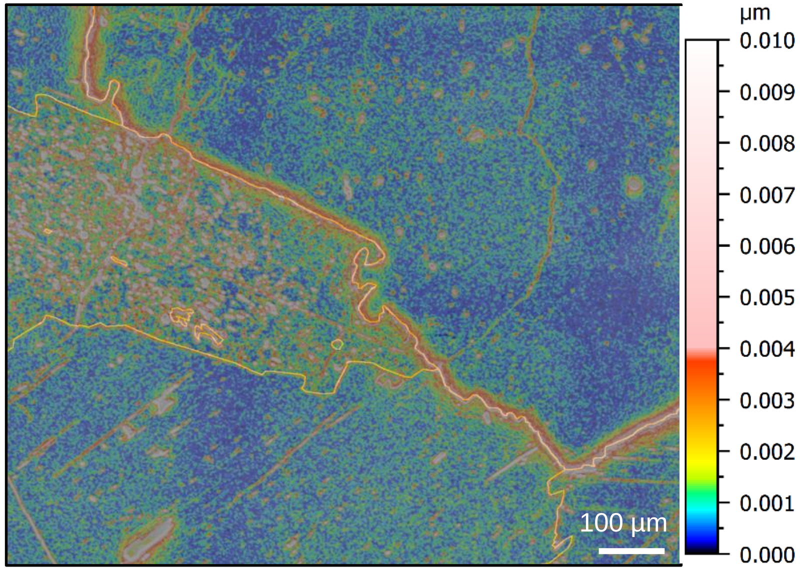
I = 0.1 M NaCl pH = 8.0
[Cm(III)] = 10^{-6} M t = 7 d

Granite – thin section ROI 1

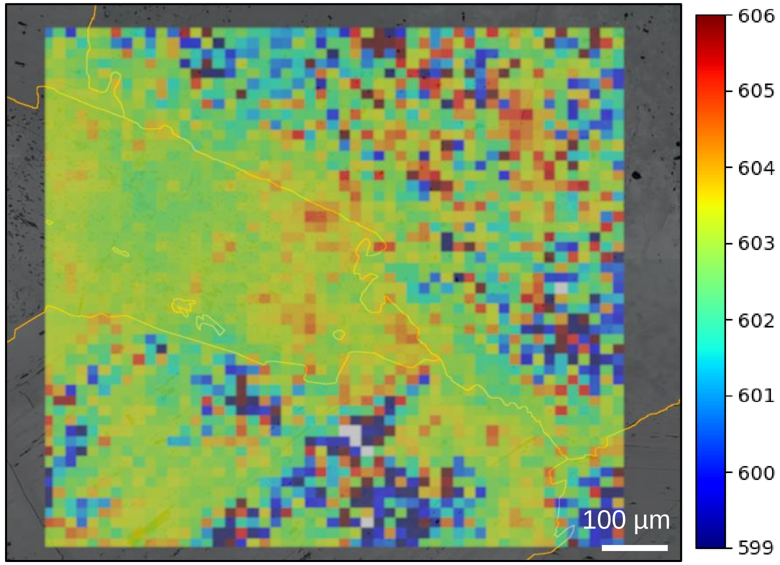
Mineral phases



Surface roughness



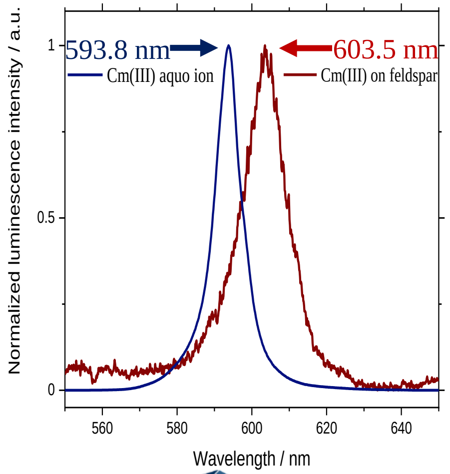
Peak position / nm



More **pronounced red-shifts** in regions **with higher surface roughness**

Feldspar: 602 – 605 nm Quartz: 602 – 605 nm Mica: 603 – 604 nm

Confirmation through lifetime: higher surface roughness leads to stronger complexation

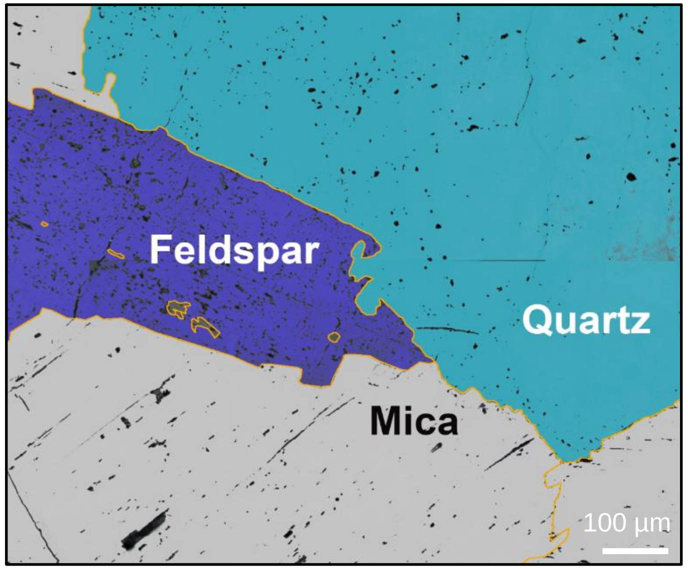


Cm(III) sorption on granite and gneiss

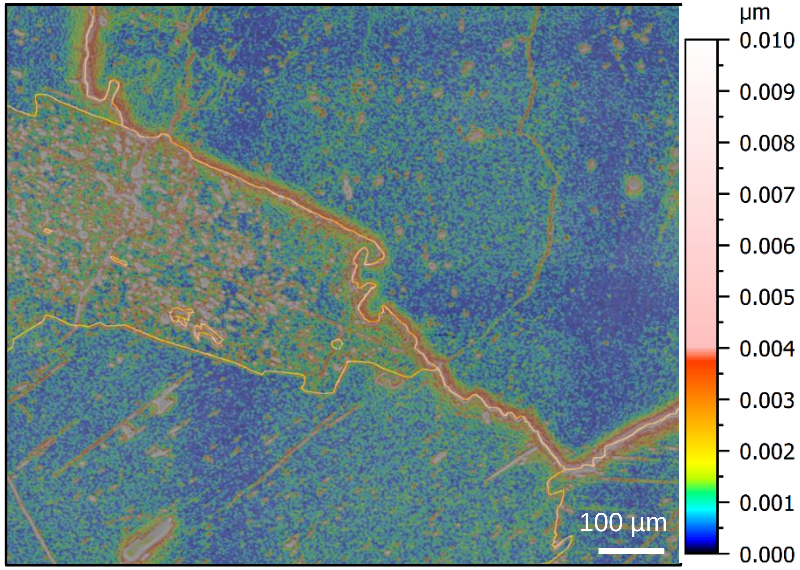
I = 0.1 M NaCl   pH = 8.0
$[Cm(III)] = 10^{-6}$ M   t = 7 d

Granite – thin section ROI 1

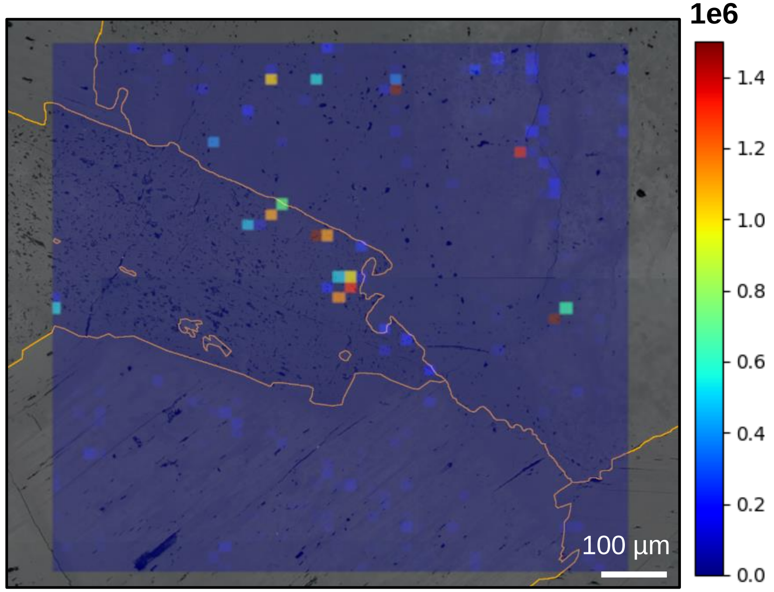
Mineral phases



Surface roughness



LI 614 – 640 nm / a.u.

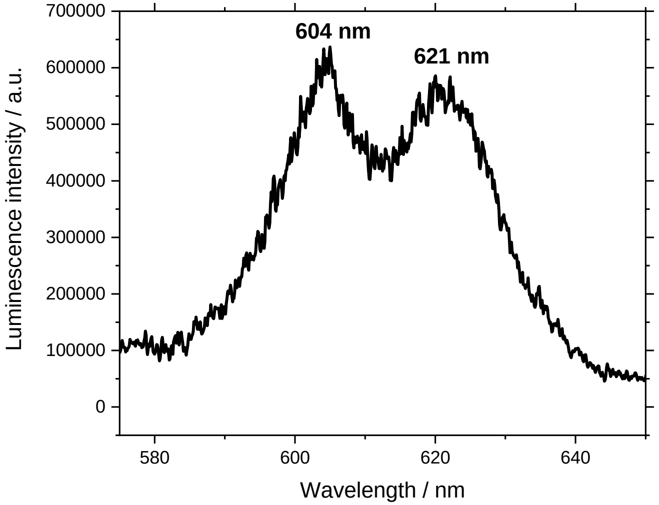


Regions with **high surface roughness** occasionally show **2^{nd} Cm(III) peak**

On feldspar, quartz and their grain boundary with each other

Feldspar: 621 – 625 nm   Quartz: 625 – 630 nm

High peak shift suggest incorporation, which is unlikely



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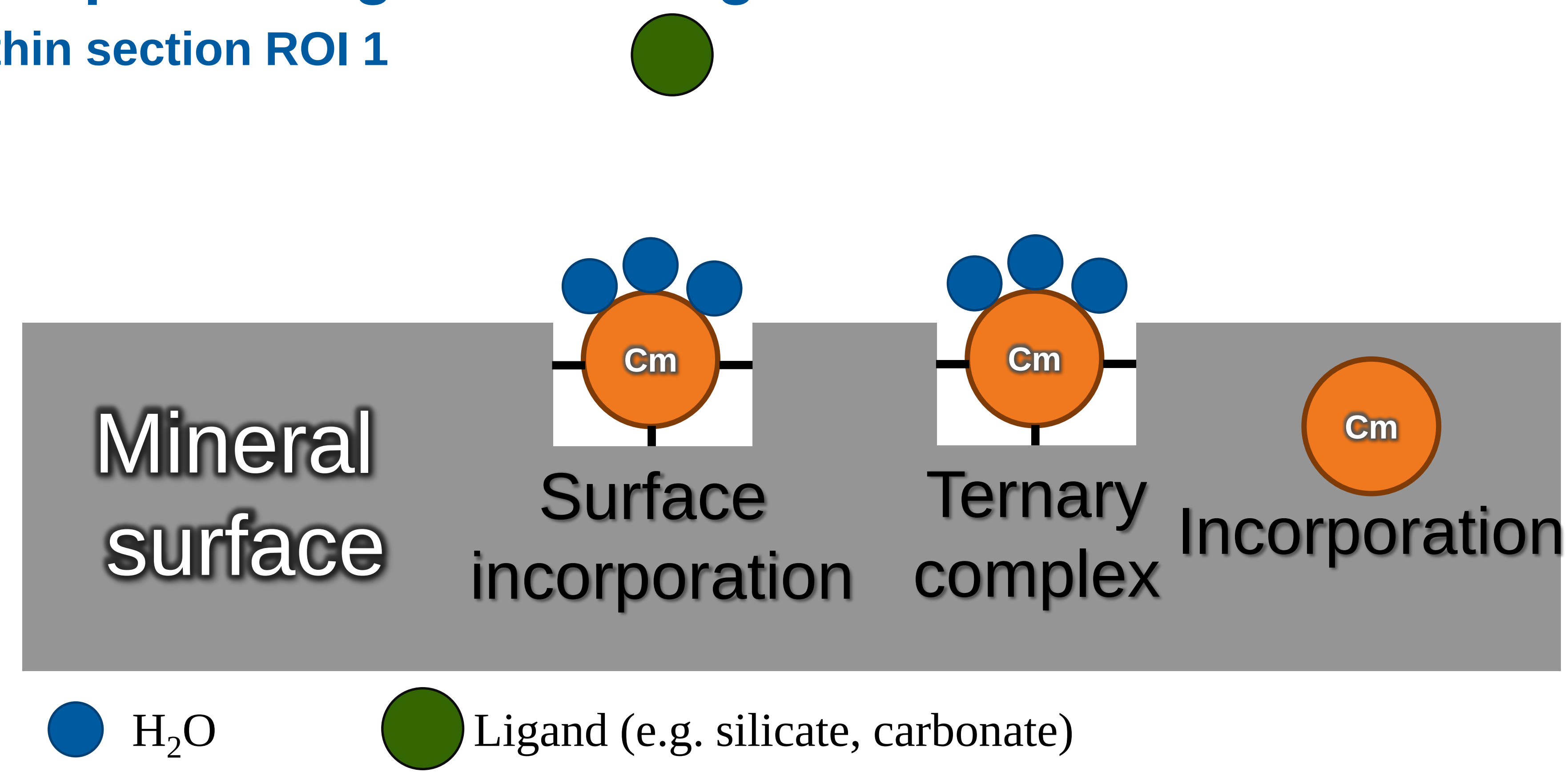
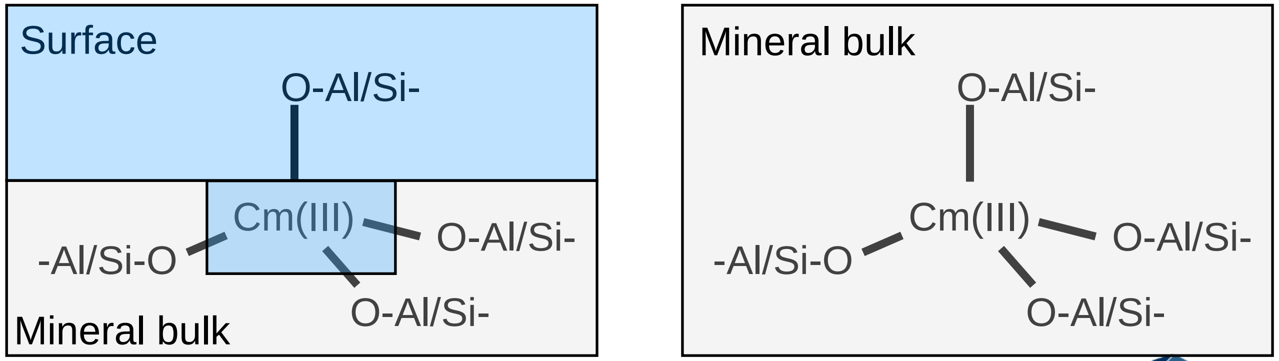
Cm(III) sorption on granite and gneiss

Granite – thin section ROI 1



Chemical environment of Cm(III) ternary complex and bulk incorporated Cm(III) might be similar

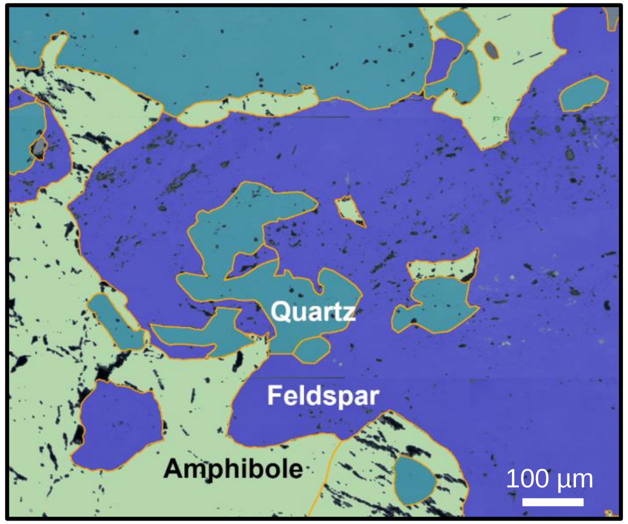


Cm(III) sorption on granite and gneiss

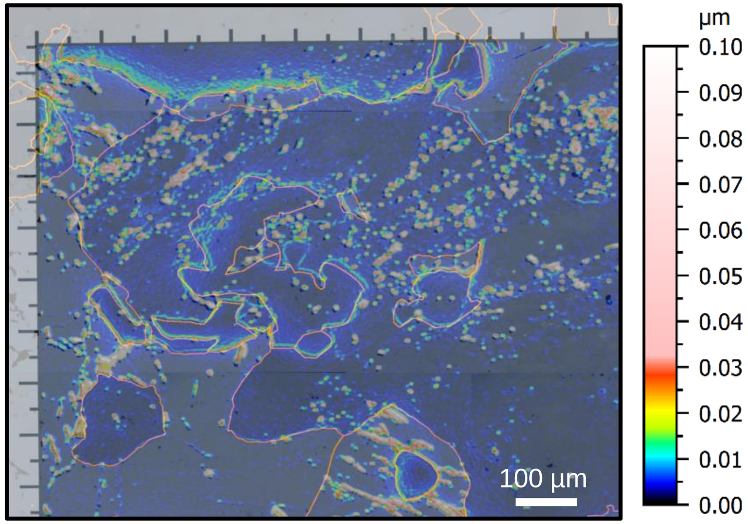
I = 0.1 M NaCl pH = 8.0
[Cm(III)] = 10^{-6} M t = 7 d

Gneiss – thin section ROI 1

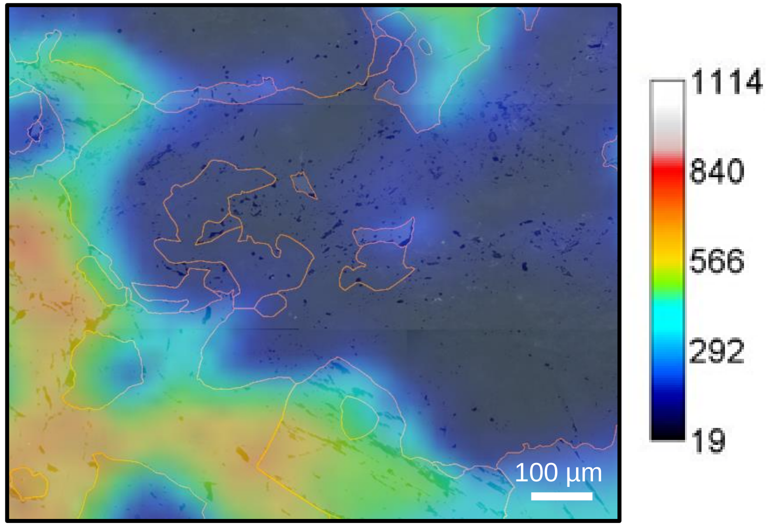
Mineral phases



Surface roughness



Cm(III) uptake / pmol/cm²



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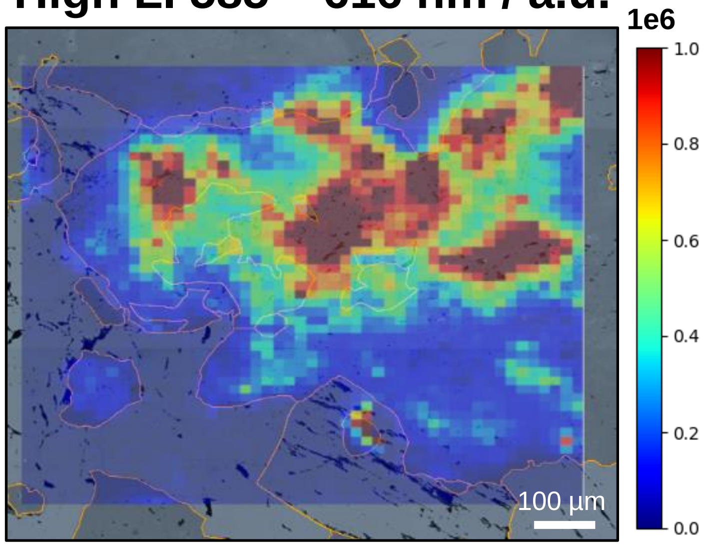


- ➢ Sorption on gneiss almost exclusively occurs on amphibole
- ➢ Sorption on feldspar and quartz mineral phases is far lower than on granite sample
- ➢ Sorption on feldspar and quartz occurs **only** in regions with a high surface roughness
- ➢ Surface roughness becomes driving parameter for sorption on low uptake mineral phases

Amphibole: $(K,Na)_{0-1}(Ca,Na,Fe,Mg)_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$
Feldspar: $KAlSi_3O_8$ / $NaAlSi_3O_8$ / $CaAl_2Si_2O_8$
Quartz: SiO_2

Conclusions and implications

Cm(III) sorption on crystalline rock surfaces:

- Mineralogy is the most important parameter; closely followed by surface roughness
- Higher surface roughness leads to higher sorption uptake and stronger surface complexes
- Surface roughness becomes driving parameter on minerals in a competitive sorption environment
- pH dependent sorption behavior leads to strong preferential sorption at lower pH
- Observation of Cm(III) ternary complex formation/incorporation

During an upscaling process new parameters need to be considered

Parameters determined at smaller scales will not necessarily behave linearly or additively at larger scales

Thank you for your attention ☺

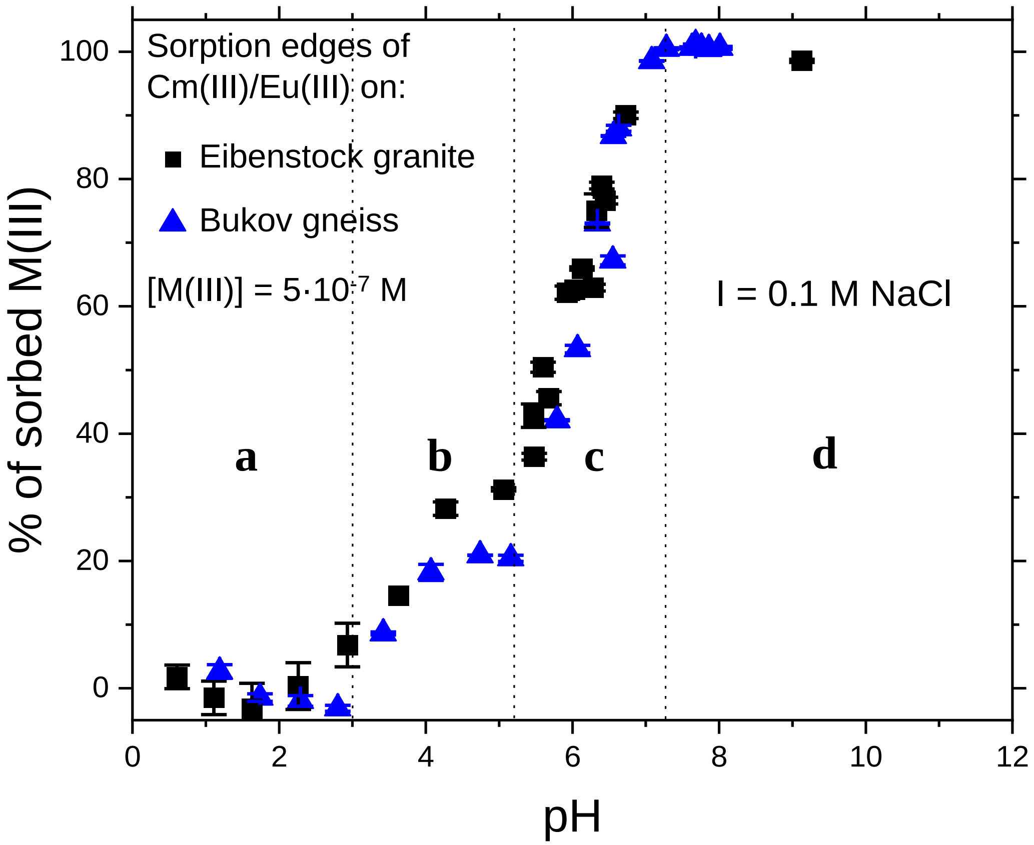
Sample locations

- Crystalline rock samples from different locations in Europe
- **Eibenstock:** granite, former uranium mine in Erzgebirge, Germany
- **Bukov:** migmatized gneiss, underground research lab in Czech Republic
- **Onkalo:** granitic pegmatite, underground research lab in Finland
- **Grimsel:** likely granodiorite/mylonite/fault gouge, Grimsel test site in Switzerland

Cm(III) sorption on granite and gneiss

Granite/Gneiss – powder

I = 0.1 M NaCl pH = 8.0
[Cm(III)] = 10^{-6} M t = 7 d



a) No significant sorption

b) Slight increase to 20/30% sorption

c) Accelerated sorption up to 100% sorption

d) Complete sorption

Chosen pH for thin section experiments: pH 8.0

Appendix

Mineral Granite	Percentage [%]
Quartz	45.0
Feldspar	42.5
Mica	11.5
Minor	0.9

Mineral Gneiss	Percentage [%]
Feldspar	44.8
Amphibole	33.3
Quartz	13.5
Mica	9.2
Chlorite	1.5
Alkali-feldspar	0.7

Mineral Granitic pegmatite	Percentage [%]
Albite	35.0
Illite	18
Quartz	16.0
Microcline	16.0
Babingtonite?	9.0
Minor	5.7

Mineral Grimsel	Percentage [%]
Orthopyroxene	27.0
Quartz	24.9
Albite	16.4
Microcline	9.8
Aragonite	9.4
Polylithionite	5.7
Orthoclase	2.5
Phlogopite	2.5
Titanite	1.8

Lifetime analysis

Granite minerals	$n(H_2O)$	Species
Feldspar (smooth)	7.4 ± 0.5	Weak ISS (23%)
	5.7 ± 0.5	Strong ISS (47%)
	3.3 ± 0.7	SF incorporation (30%)
Feldspar (rough)	9.0 ± 0.5	OSS (5%)
	7.5 ± 0.5	Weak ISS (6%)
	5.1 ± 0.3	Strong ISS (26%)
	3.4 ± 0.8	SF incorporation (63%)
	0.0 ± 0.5	Ternary complex/ Bulk incorporation
Quartz (smooth)	5.5 ± 0.5	Strong ISS
	3.0 ± 1.0	SF incorporation
Quartz (rough)	5.7 ± 0.5	Strong ISS
	0.0 ± 0.5	Ternary complex/ Bulk incorporation
Topaz (smooth)	4.0 ± 0.5	SF incorporation
Topaz (rough)	6.0 ± 0.5	Strong ISS
	2.8 ± 1.6	SF incorporation
Mica (smooth)*	9.0 ± 0.5	OSS
	7.0 ± 0.5	Weak ISS
	6.0 ± 0.5	Strong ISS
	3.0 ± 1.0	SF incorporation
Mica (rough)*	7.5 ± 0.5	Weak ISS
	5.0 ± 0.5	Strong ISS
	3.0 ± 1.0	SF incorporation

Gneiss minerals	$n(H_2O)$	Species
Feldspar (smooth)	9.0 ± 0.5	OSS (14%)
	7.2 ± 0.4	Weak ISS (24%)
	5.7 ± 0.5	Strong ISS (33%)
	3.5 ± 0.8	SF incorporation (29%)
Feldspar (rough)	7.3 ± 0.5	Weak ISS (23%)
	5.3 ± 0.4	Strong ISS (31%)
	2.5 ± 1.3	SF incorporation (46%)
Quartz (smooth)	7.5 ± 0.5	Weak ISS
	6.0 ± 0.5	Strong ISS
	3.0 ± 0.5	SF incorporation
Quartz (rough)	3.0 ± 1	SF incorporation
	0.0 ± 0.5	Ternary complex/ Bulk incorporation
Amphibole*	7.7 ± 0.5	Weak ISS
	6.0 ± 0.5	Strong ISS

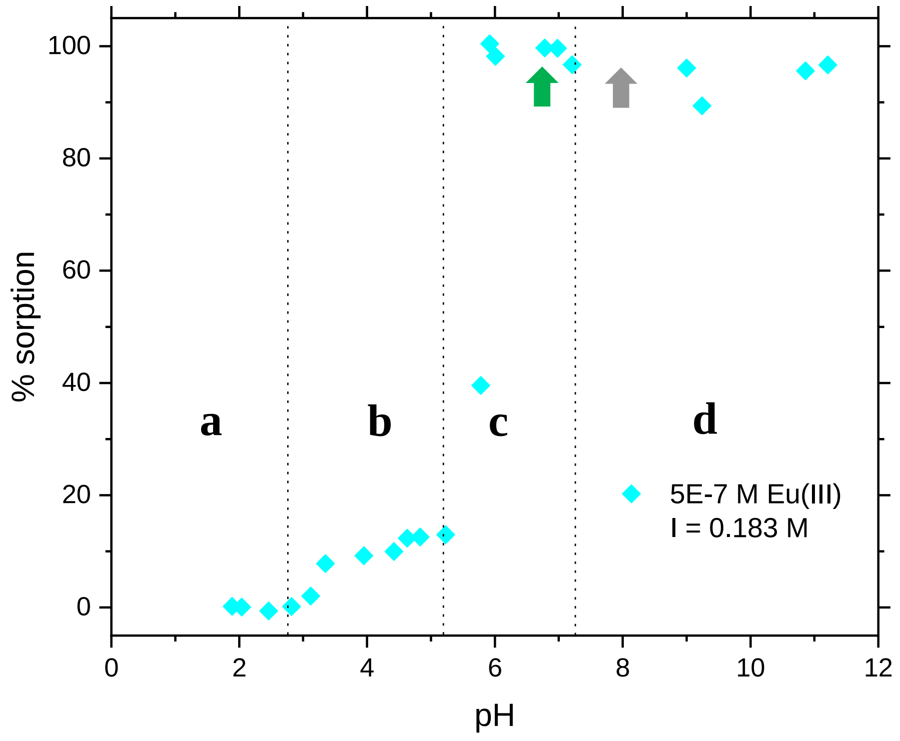
Cm(III) sorption on granitic pegmatite

Cm(III) sorption on granitic pegmatite

I = 0.183 M NaCl pH = 6.83
[Cm(III)] = 10^{-5} M t = 7 d

Granitic pegmatite – powder

Sample from Onkalo, Finland



a) No significant sorption

b) Slight increase to 15% sorption

c) Abrupt sorption step to 100% sorption

d) Complete sorption

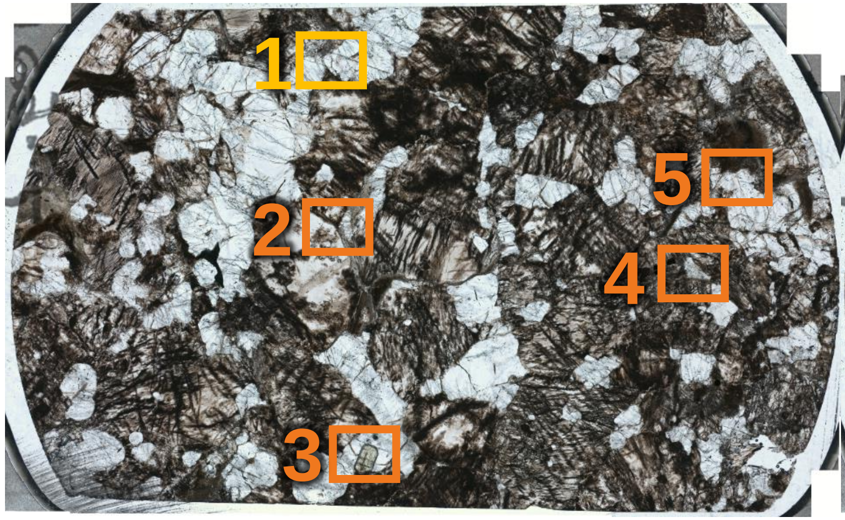
Chosen pH for thin section experiments: **pH 6.83**
(compared to **pH 8.0** in previous experiments)

Cm(III) sorption on granitic pegmatite

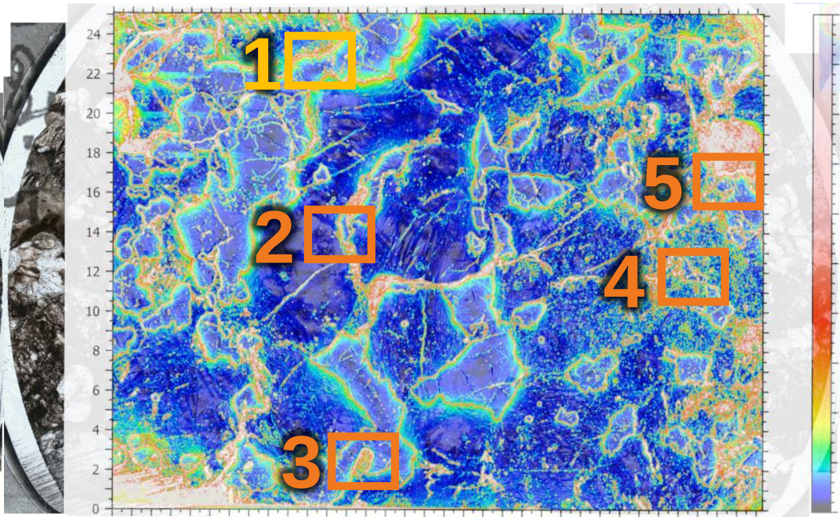
I = 0.183 M NaCl pH = 6.83
[Cm(III)] = 10^{-5} M t = 7 d

Granitic pegmatite – thin section

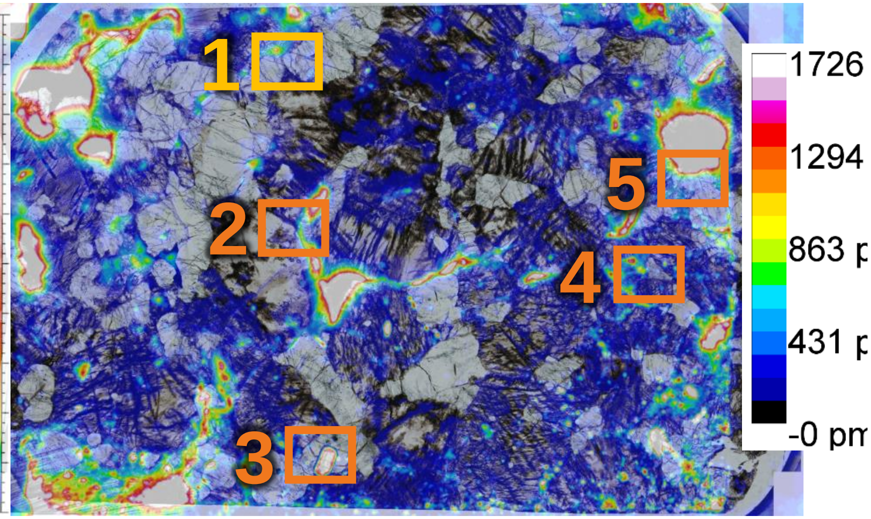
Mineral composition



Surface roughness



Cm(III) uptake / pmol/cm²



- Sorption occurs in primarily **“hot spots”** (identified as mica/apatite)
- Hot spot regions also exhibit a high surface roughness

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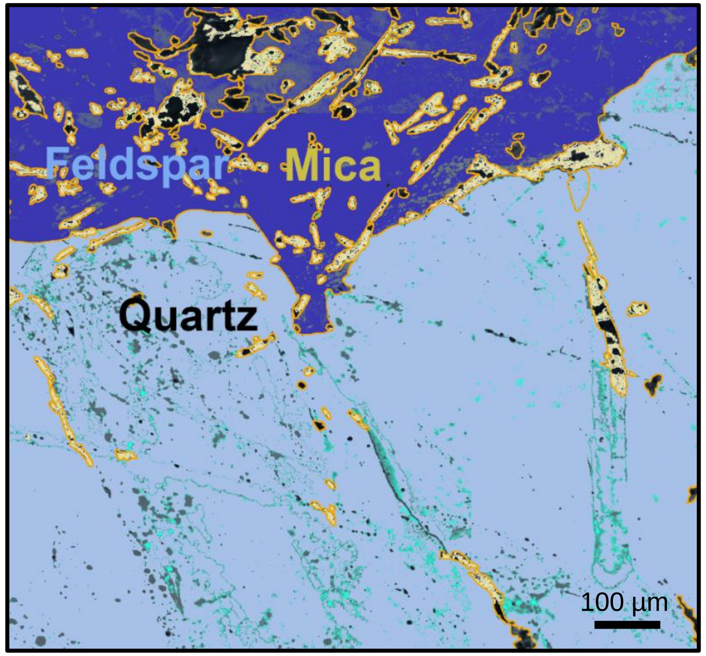
Cm(III) sorption on granitic pegmatite

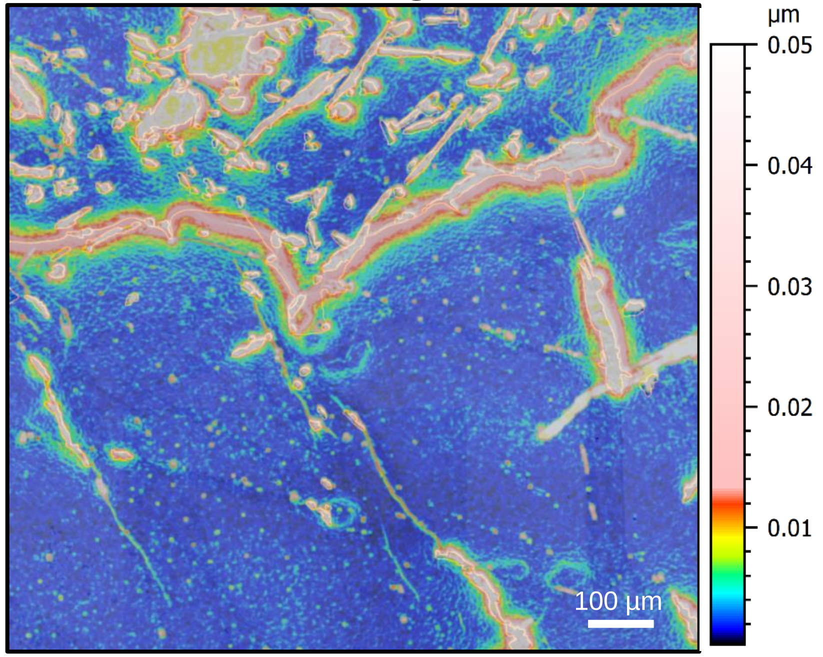
I = 0.183 M NaCl pH = 6.83
[Cm(III)] = 10^{-5} M t = 7 d

Granitic pegmatite – thin section ROI 1

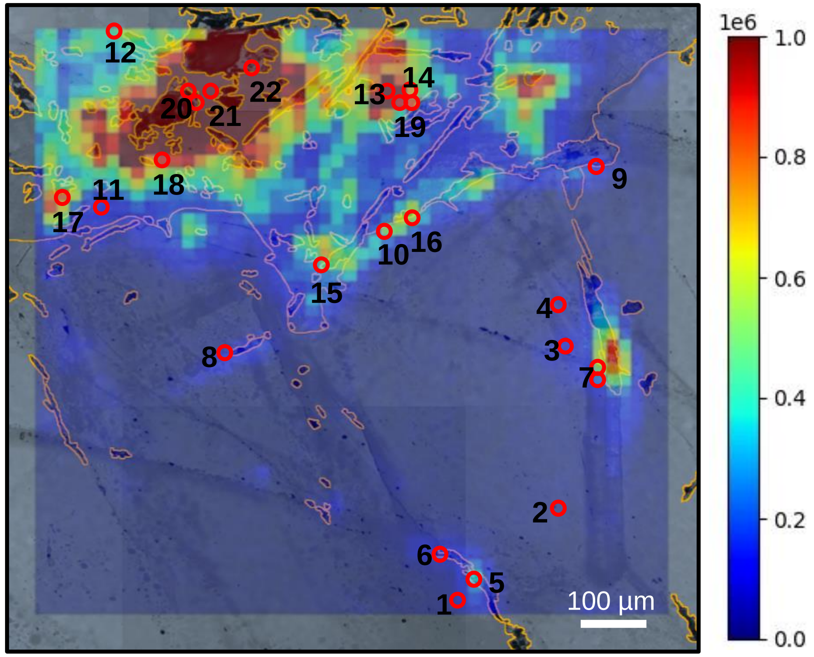
Mineral composition



Surface roughness



LI 580 – 630 nm / a.u.



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Feldspar: $KAlSi_3O_8$ / $NaAlSi_3O_8$ / $CaAl_2Si_2O_8$
Quartz: SiO_2

- Luminescence intensity: Mica > Feldspar > Quartz
- Luminescence on mica measurable

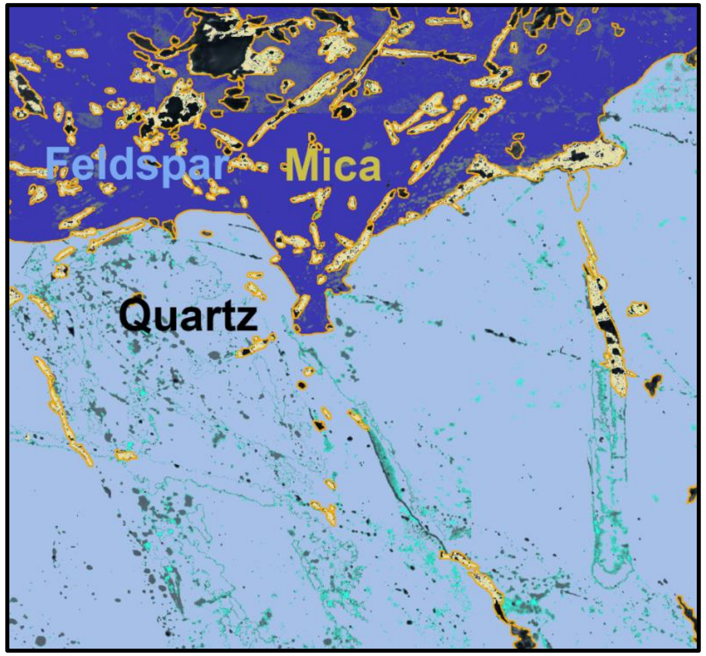
DRESDEN concept HZDR

Cm(III) sorption on granitic pegmatite

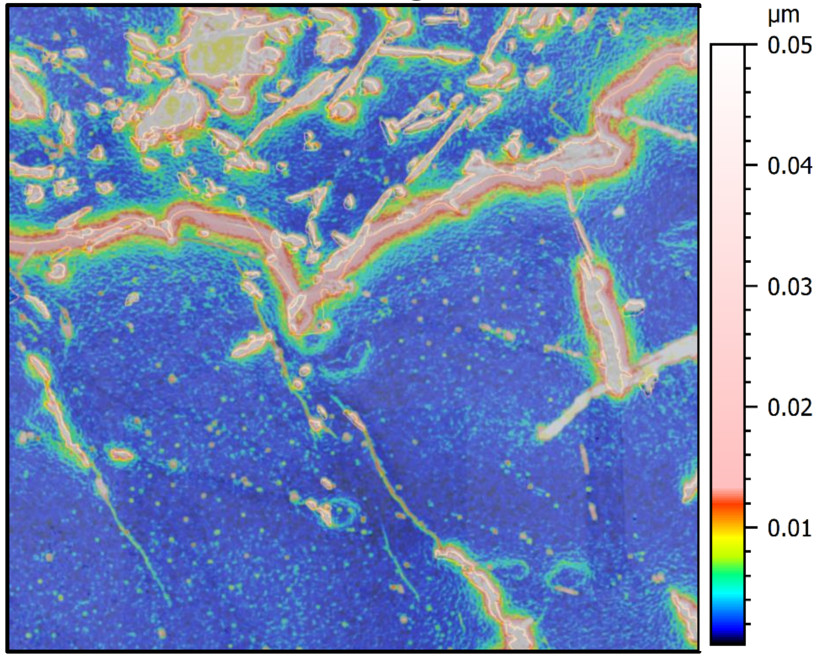
I = 0.183 M NaCl pH = 6.83
[Cm(III)] = 10^{-5} M t = 7 d

Granitic pegmatite – thin section ROI 1

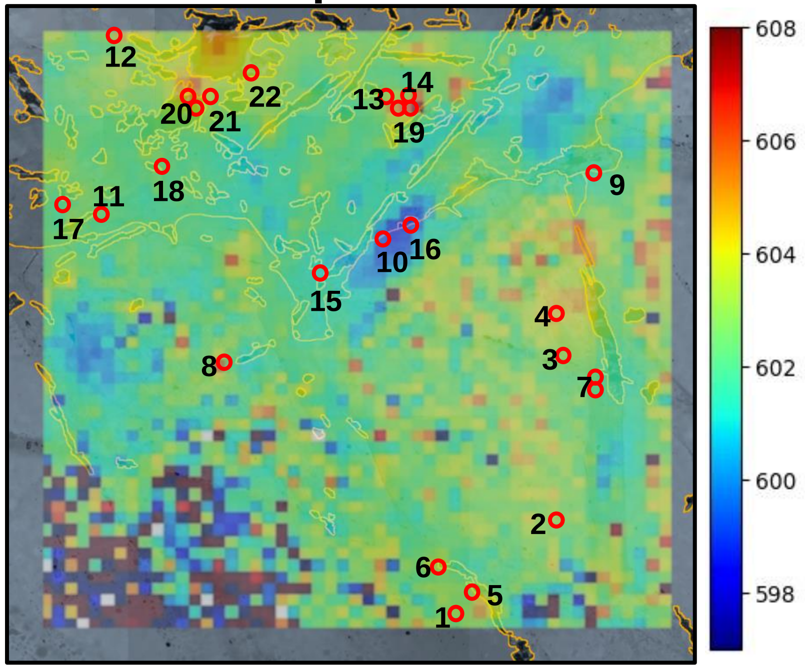
Mineral composition



Surface roughness



Peak position / nm



Mica: $KAl_2(AlSi_3O_{10})(F,OH)_2$ / $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$
Feldspar: $KAlSi_3O_8$ / $NaAlSi_3O_8$ / $CaAl_2Si_2O_8$
Quartz: SiO_2

Quartz: individual bond strengths per pixel

Feldspar: homogeneous sorption strength

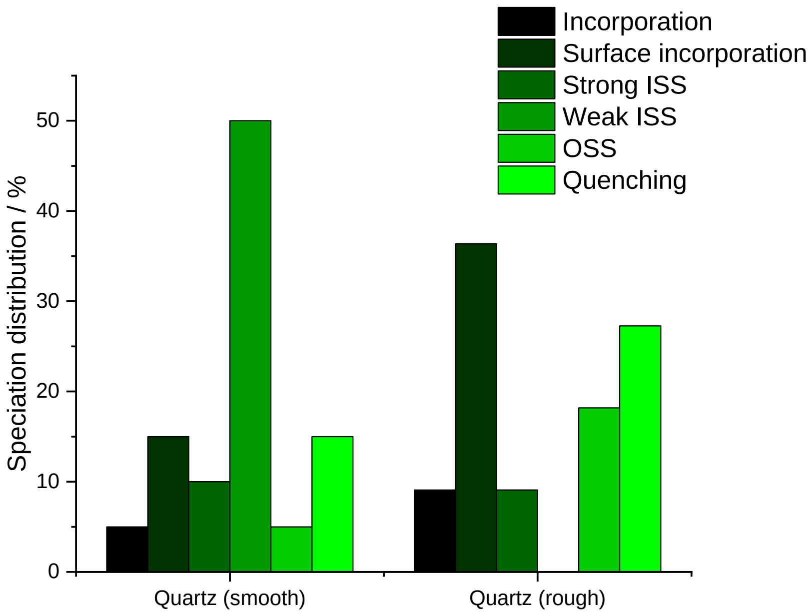
Mica: clusters of high/low strength

DRESDEN concept HZDR

Cm(III) sorption on granitic pegmatite

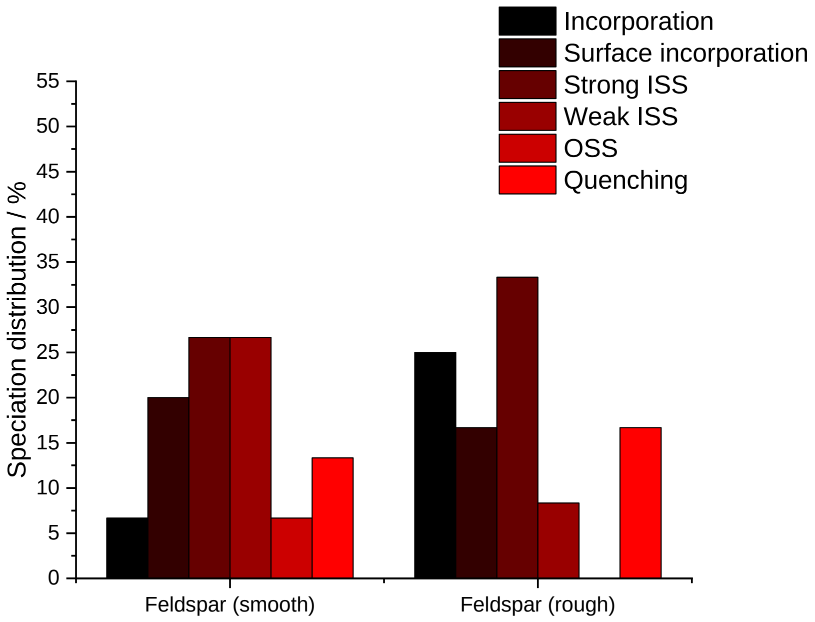
I = 0.183 M NaCl pH = 6.83
[Cm(III)] = 10^{-5} M t = 7 d

Granitic pegmatite – thin section lifetimes



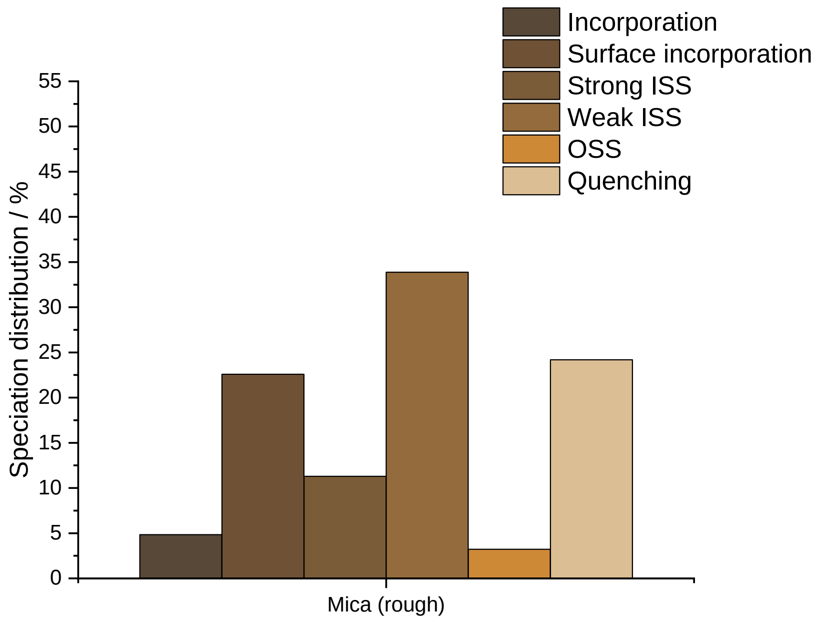
Quartz

Speciation largely depended on surface roughness



Feldspar

Trend towards stronger complexation
(not as prominent)



Mica

Speciation depended on how many sorption sites are taken

Presumably: strong sites are occupied first, then weak sites

pH dependent sorption on different crystalline rocks

	Granitic pegmatite pH 6.83	Granite pH 8	Gneiss pH 8
Quartz:	**598 – 605 nm** (598 – 600; 602 – 605)	**602 – 605 nm**	**602 – 605 nm**
Feldspar:	**599 – 604 nm** (599 – 600; 601 – 604)	**602 – 605 nm**	**602 – 605 nm**
Mica:	**598 – 605 nm** (598 – 601; 602 – 605)	**603 – 604 nm**	

- Tendency of **weaker sorption** strength at **lower pH**
- Sorption **primarily** occurs on **hot spots** (mica)
- Almost no sorption on feldspar and quartz (compared to granite/gneiss) except for high roughness regions

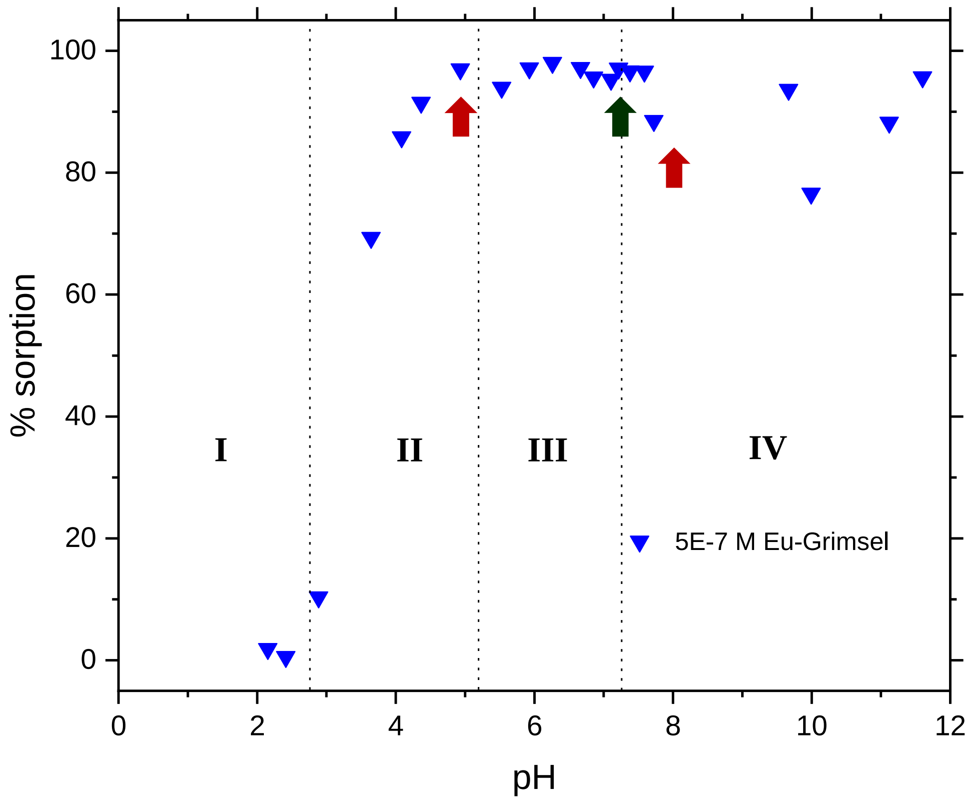
Planned: Cm(III) sorption on Grimsel sample

WIP: Cm(III) sorption on Grimsel sample

I = 0.0012 M NaCl
[Cm(III)] = $5 \cdot 10^{-7}$ M

pH = 7.30
t = 7 d

Most likely granodiorite/mylonite/fault gouge



I = 0.0012 M

Two pH values on same sample:

1.) pH 5.0

2.) pH 8.0

Effect of pH dependent change of sorption preference and speciation

Strong buffering effect shifted **pH from 5.0 to 7.3** (low ionic strength?)

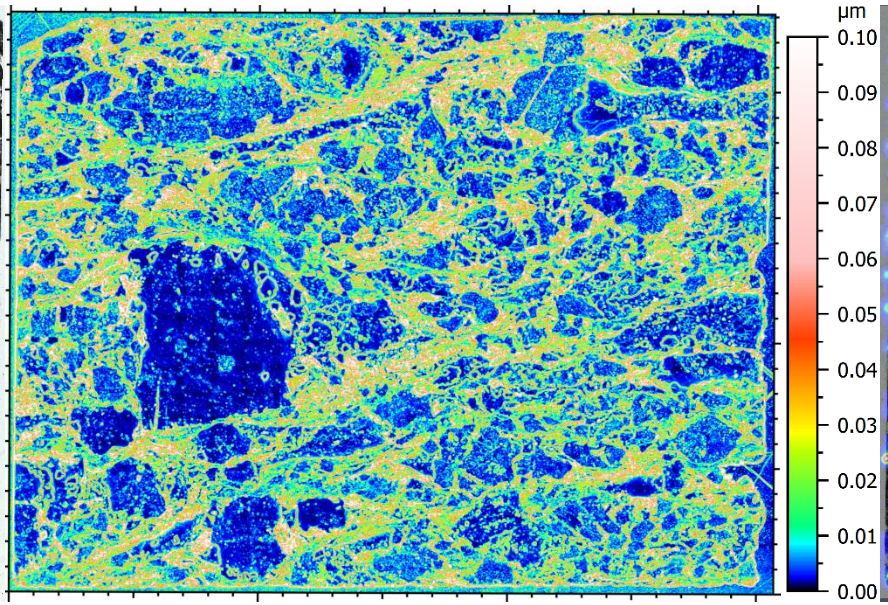
WIP: Cm(III) sorption on Grimsel sample

I = 0.0012 M NaCl
$[Cm(III)] = 5 \cdot 10^{-7}$ M

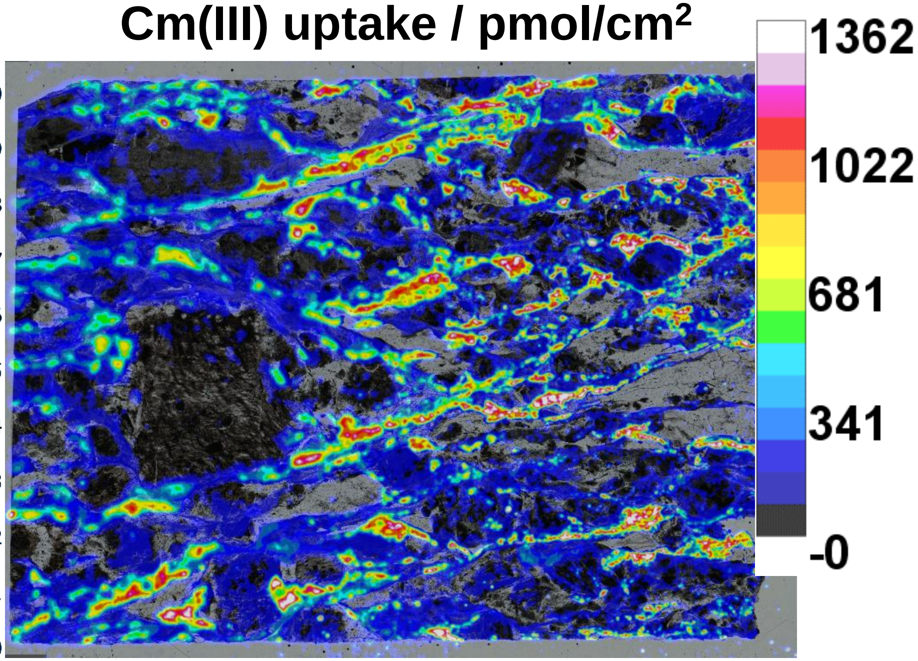
pH = 7.30
t = 7 d

Mineral composition

Surface roughness



Cm(III) uptake / pmol/cm²



Preliminary results:

- Major sorption preference on black mineral phases (so far identified as different mica)
- Little sorption on feldspar
- Almost no sorption on quartz

pH dependent Cm(III) sorption studies on granitic pegmatite and Grimsel rock

pH dependent Cm(III) sorption studies on crystalline rocks

	Granitic pegmatite pH 6.83	Granite pH 8	Gneiss pH 8
Quartz:	**598 – 605 nm** (598 – 600; 602 – 605)	**602 – 605 nm**	**602 – 605 nm**
Feldspar:	**599 – 604 nm** (599 – 600; 601 – 604)	**602 – 605 nm**	**602 – 605 nm**
Mica:	**598 – 605 nm** (598 – 601; 602 – 605)	**603 – 604 nm**	

- Tendency of **weaker sorption** strength at **lower pH**
- Sorption **primarily** occurs on **hot spots** (mica)
- Almost no sorption on feldspar and quartz (compared to granite/gneiss) except for high roughness regions
- Speciation dependency on surface roughness:

  Quartz > Feldspar > Mica

Cm(III) uptake / pmol/cm²