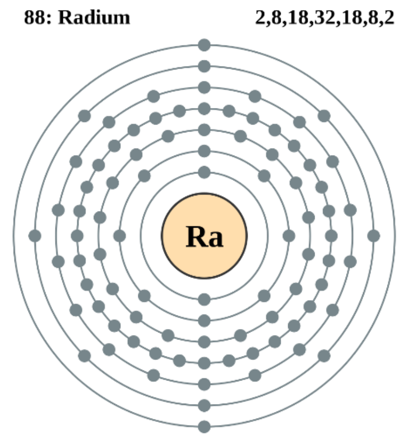


Radium sorption on crystalline rock

SYP2022 - Helsinki

Project overview 11/2022

EURAD Future 2.2/Uni Helsinki/Posiva/SKB

Otto Fabritius

Opening image source: https://commons.wikimedia.org/wiki/Category:Radium#/media/File:Electron_shell_088_radium.png

INTRODUCTION

Otto Fabritius, MSc (Chemistry)

University of Helsinki

- 2014-08 – 2018-07 BSc (UH)
- 2018-08 – 2020-06 MSc (UH)
  - ’Ra behaviour in geologic media; application to nuclear waste deposition’
- 2020-09 – present (compl. est. 2024-05) PhD
  - Topic **’Radium sorption and diffusion in crystalline rock’**

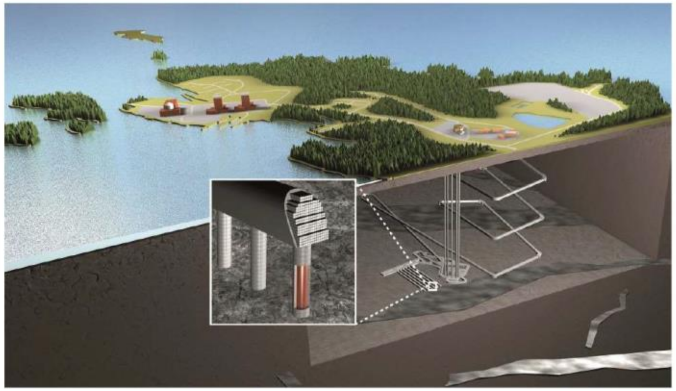
Areas of expertise

- Radium sorption and precipitation in deep groundwater conditions, SNF geological disposal, PHREEQC geochemical modeling

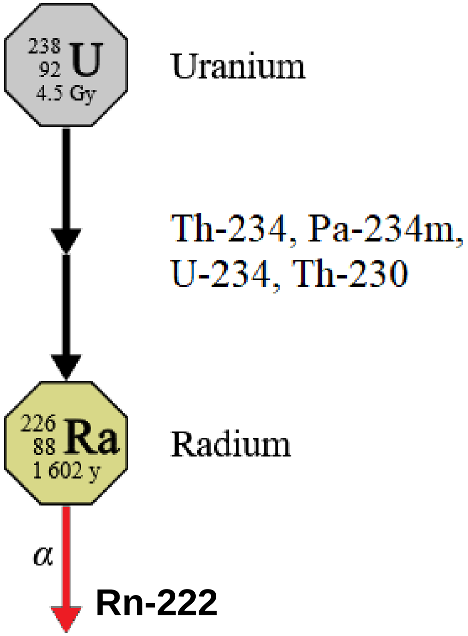
BACKGROUND

- In the safety case calculations of the Finnish and Swedish deep geological disposal plants, Ra-226 is recognized as one of the **most safety-relevant** waste-borne radionuclides

- Enriched in the waste as a daughter of U-238 (8.6-9.3 × 10^{10} Bq of Ra-226 **per canister**) + notable potential for mobility in bedrock** → **risks for biosphere!**



KBS-3*

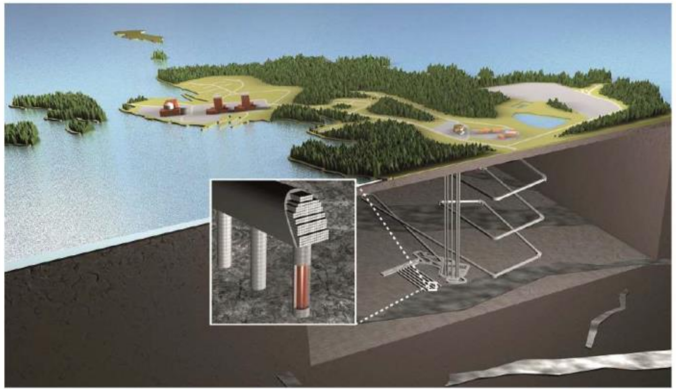


*Posiva Oy (2017), POSIVA 2017-02.
**Jaremalm et al. (2013) SKB TR-13-28.

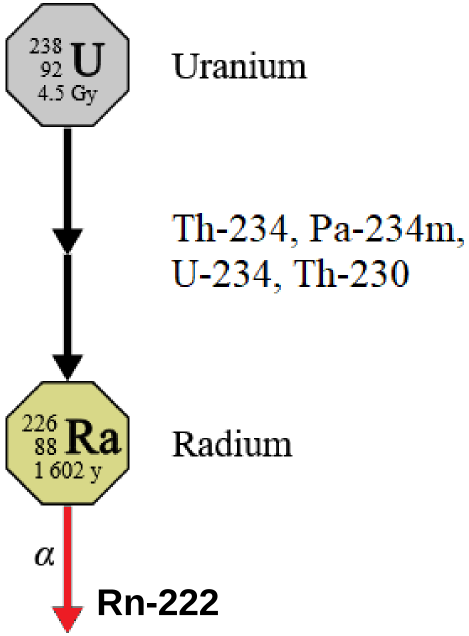
BACKGROUND

- Radium migration in the bedrock surrounding the disposal facility needs to be understood for the safety assessments and dose models in case of a waste containment failure

- Distribution coefficient data for the safety case calculations in FIN & SWE and mechanistic understanding of retardation by modeling with PHREEQC



KBS-3*



*Posiva Oy (2017), POSIVA 2017-02.

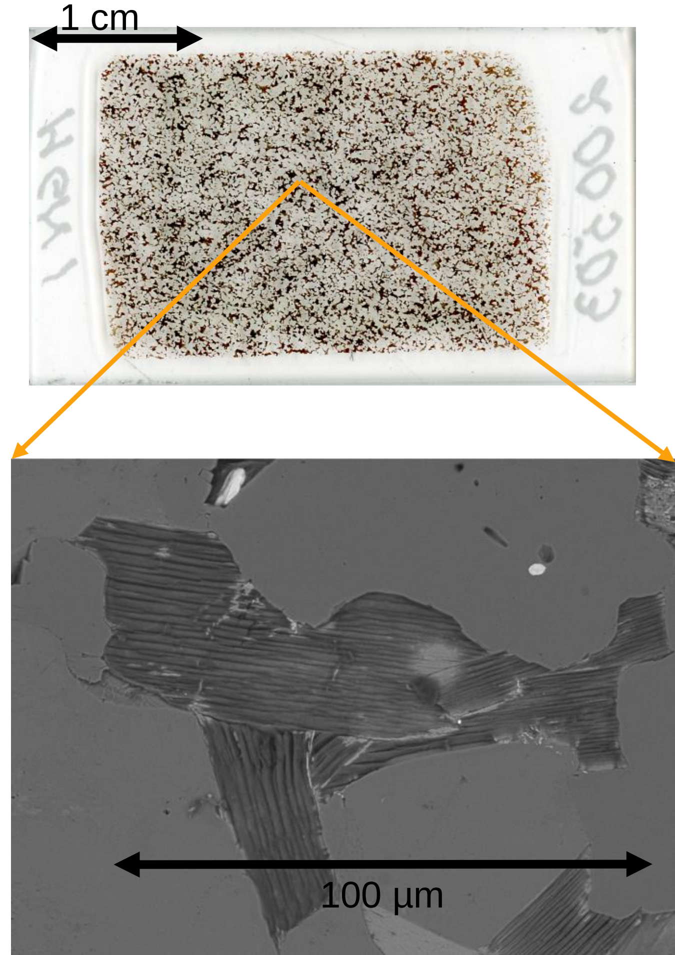
MATERIALS & METHODS

- Rock types and biotite from Olkiluoto (4) and Forsmark (4)
  - Metatexitic gneiss, mica gneiss, diatexitic gneiss, granite pegmatoid; granodiorite, monzogranite, tonalite (alt. zone) & granodiorite (alt. zone)
  - Batch sorption samples (0.071-0.3 mm Ø) and thin section samples
- Groundwater references from Olkiluoto (3) & Forsmark (6)
  - Fresh, brackish & saline waters

MATERIALS & METHODS

- Batch sorption experiments
  - 50 g/L solid-to-solution
  - Spiked 200 Bq of Ra-226 per sample
  - Ba (Ra analog) conc. isotherm 10^{-9} to 10^{-3} M
  - 1 + 2 weeks agitation periods
- PHREEQC modeling and expr. results interpretation
  - Thermodynamical calculations, DFT biotite sorption site density and energy calculations
- Thin section sorption studies
- FE-SEM-EDS studies on sorption samples

Mica gneiss thin section sample (samples by GTK)



HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

MATERIALS & METHODS

- PHREEQC geochemical and thermodynamical modeling
  - Ba used as an analog of Ra in the modeling (more data on Ba)
  - Sorption in the model represented as a combination of ion exchange with the K^+ layer and surface complexation 'above' the mineral sheet edges
  - Ra coprecipitation with Ba as $BaRaSO_4$ and $–CO_3$, atmospheric CO_2 taken into account
  - LLNL database

$$M-K+1/2\ Ba^{2+}\leftrightarrow 1/2\ Ba-M_2+K^+$$

Part 1: Binary ion exchange, with M- representing the cation exchange sites

$$S\_sOH + Ba^{2+} \rightleftharpoons S\_sOHBa^{2+} \quad \mathrm{Log}\,K = -5.47$$

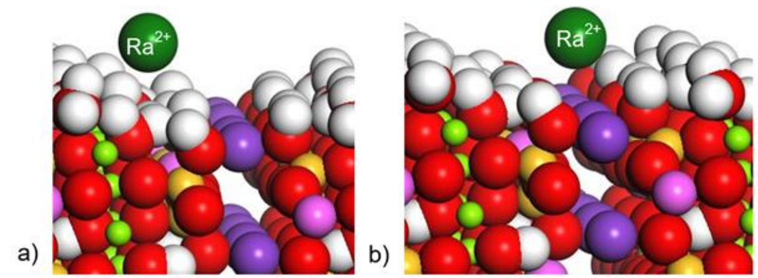
$$S\_wOH + Ba^{2+} \rightleftharpoons S\_wOBa^{2+} + H^+ \quad \mathrm{Log}\,K = -5.85$$

Part 2: Surface complexation, sorption on strong sites and weak sites (from DFT)

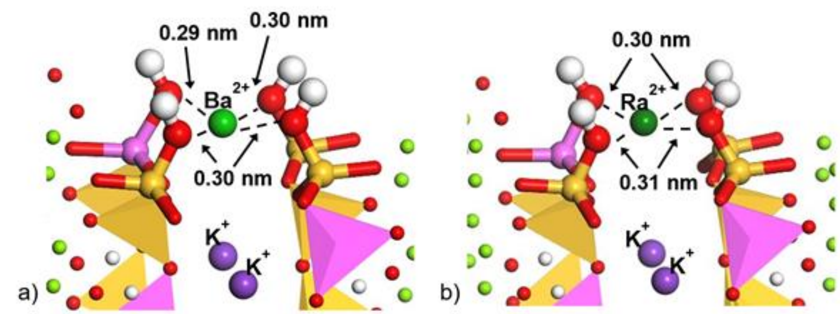
Part 3: Model parameter optimization with Python coupled Iphreeqc iterator tool (Microsoft COM)

MATERIALS & METHODS

- DFT model* suggests that Ra (and Ba) sorb most energetically favorably on the sheet edge sites (FES) of the biotite lamellars -> broken edges and cracks, easy access to exposed K^+ layer
  - More surface area -> more sorption sites -> higher sorption affinity
- Ra (and Ba) easily replaced on these edge K^+ sites by smaller and lighter Na^+ and Ca^{2+} -> site saturation -> Ra left in the sorption solution



Optimal surface complexation positions of Ra^{2+} on biotite a) cut surface, and b) above edge site. Edge site energetically favored

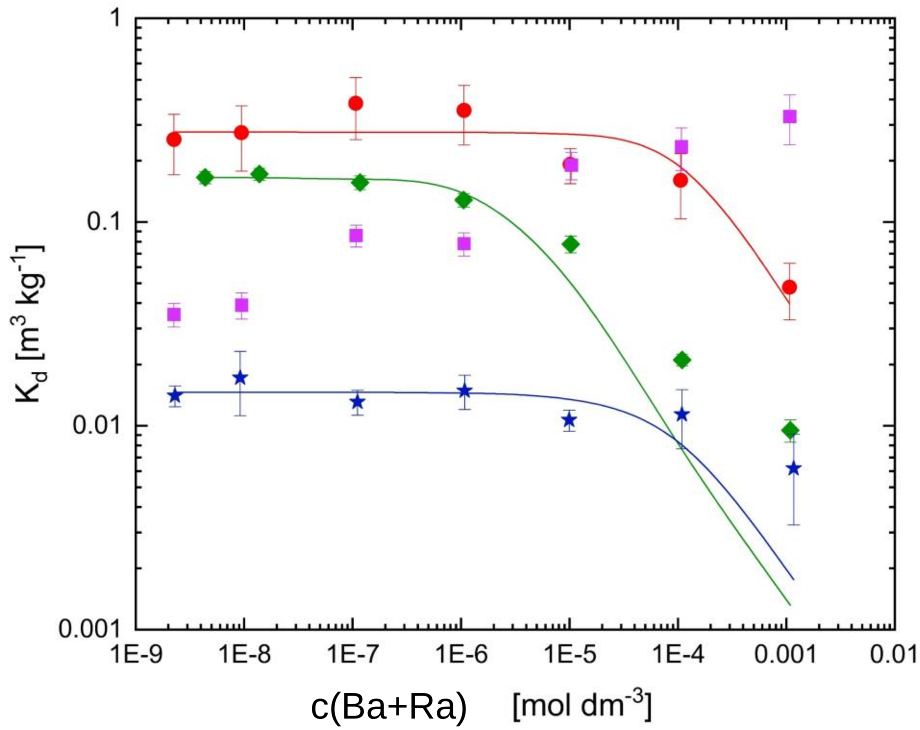


Ion exchange positions of Ba^{2+} and Ra^{2+}, outermost cation layer K^+ replaced

*Fabritius et al., (2022) *Appl. Geochem.*, 140, 105289.

RESULTS & DISCUSSION

- Mass distribution coefficients of Ra-226 on Olkiluoto biotite in four SGWs
- PHREEQC model, parameters optimized with expr. results via Iphreeqc
  - DFT sorption site density, coprecipitation of Ra as $BaRaSO_4$ or $-CO_3$, atmospheric CO_2



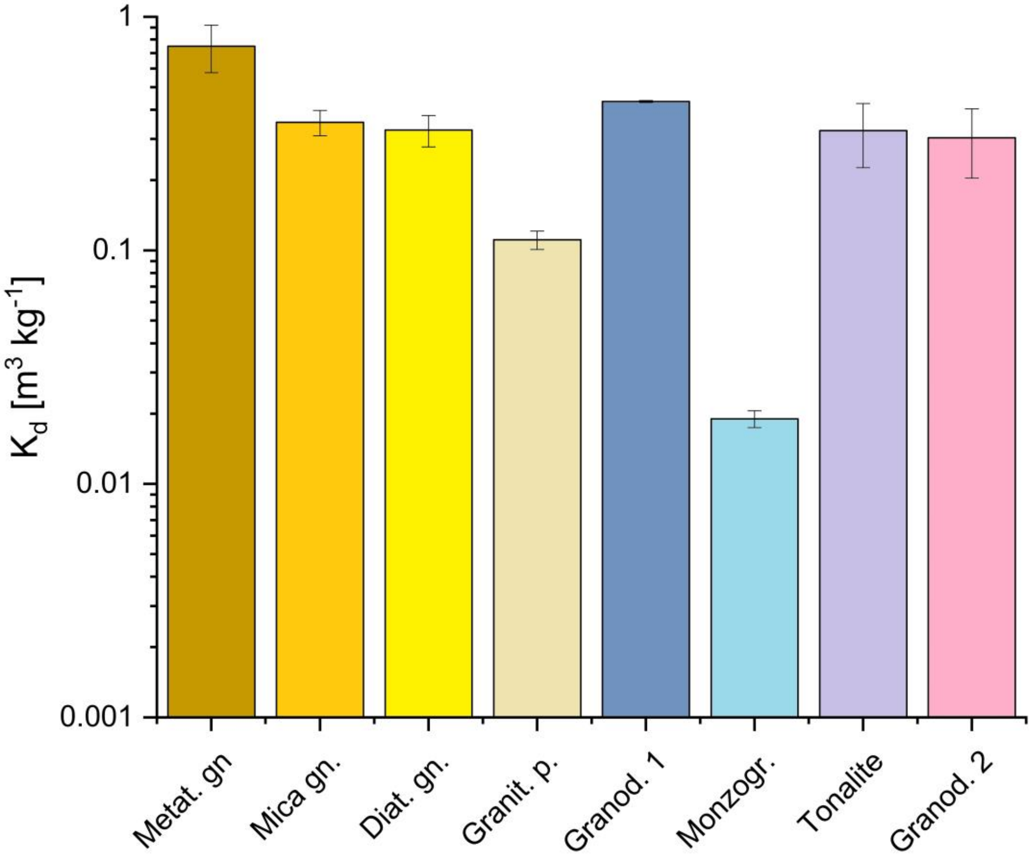
Fabritius et al. (2022) Radium sorption on biotite; surface complexation modeling study. *Appl. Geochem.*, **140**, 105289.

RESULTS & DISCUSSION

- K_d results comparison (fresh granitic reference water)
  - Olkiluoto (MTG, MGN, DGN, GP)
  - Forsmark (granodiorites, monzogranite, tonalite

'Natural' E-7 M Ba

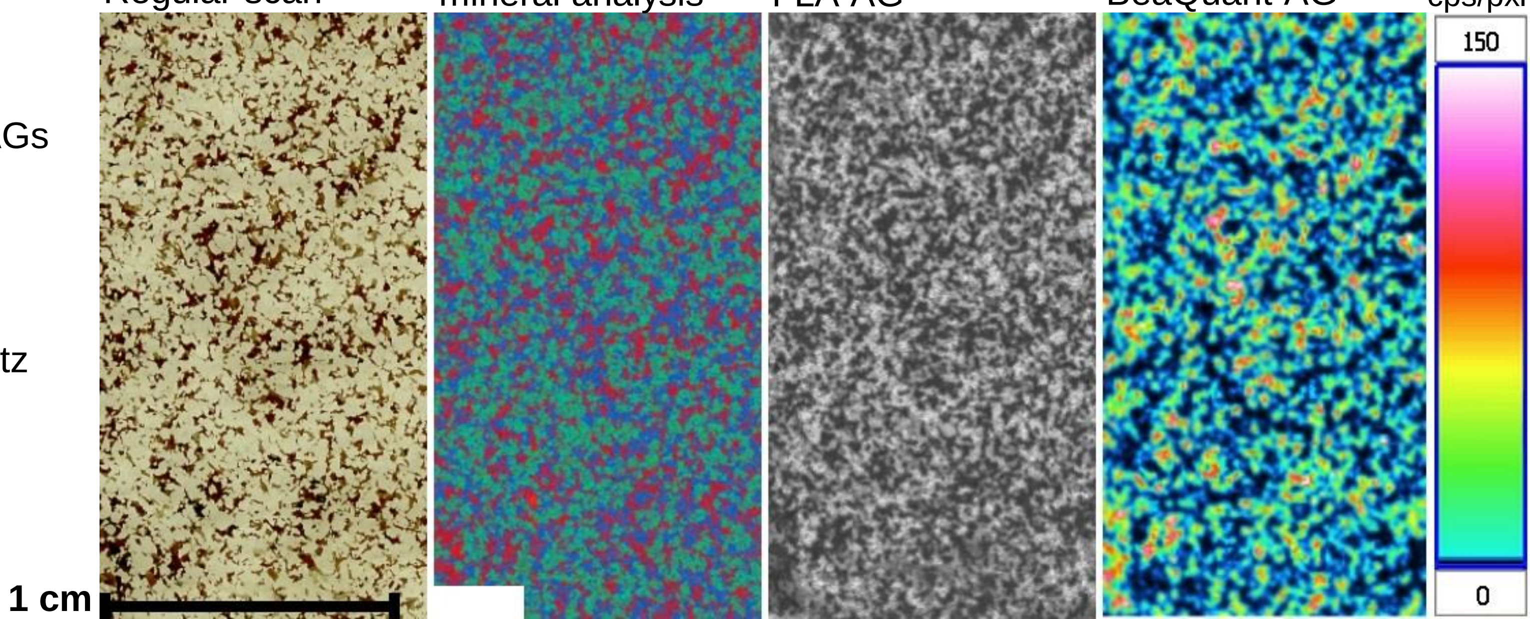
- Olkiluoto:
  - K_d lowest in GP due to low mica and low SSA
- Forsmark:
  - K_d lowest in monzogr. due to low mica and very low SSA
  - Tonalite: high K_d even though low mica, altered zone effect?

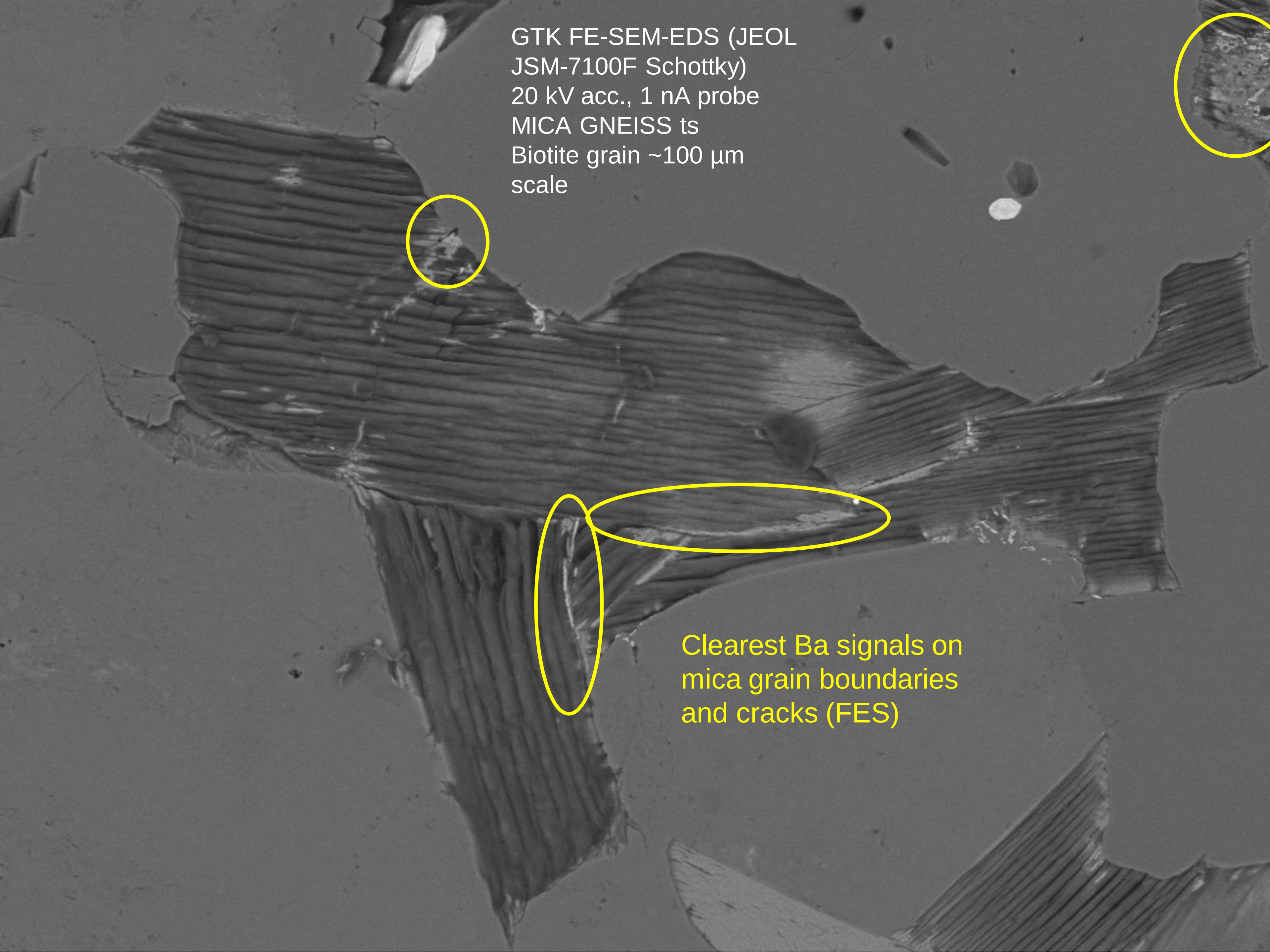


RESULTS & DISCUSSION

- Thin section studies with Ra-226 on rock samples
- Spatial distribution of Ra, on which minerals Ra sorbs with highest affinity
- Autoradiography studies to measure Ra distribution quantitatively (from FLA AG to BeaQuant™ digital AG cps/pxl → Bq/pxl)

3 'levels' of Ra sorption visible in AGs
-High affinity (mica minerals)
-Mid (plagioclases, feldspars)
-Low sorption (quartz etc.)




GTK FE-SEM-EDS (JEOL JSM-7100F Schottky)
20 kV acc., 1 nA probe
MICA GNEISS ts
Biotite grain ~100 µm scale
Clearest Ba signals on mica grain boundaries and cracks (FES)

RESULTS & DISCUSSION

- SEM-EDS of dried MMA treated batch sorption sample
- Strong signals of Ba and S on biotite or feldspar (II) sandwiched between quartz grains (I & III)
- Evidence of $BaSO_4$ precipitation in sorp. exp.
  - Ra c. too low for signal
  - High auxiliary Ra removal, Ra most probably with $BaSO_4$

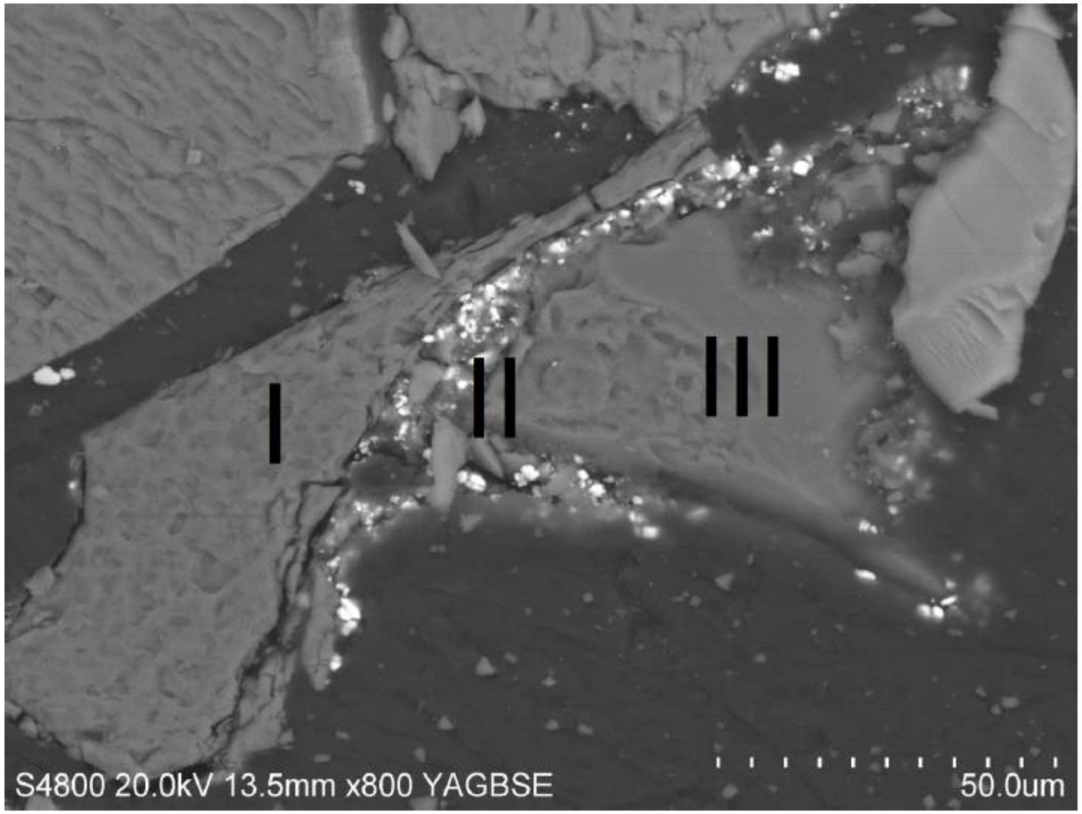


Fig. 4-16. Backscattered electron image of PMMA coated Typ1_Prov_A (granodiorite) Ra batch sorption sample.

RESULTS & DISCUSSION

Conclusions

- Ra^{2+} is a weak contender in sorption reactions against lighter and smaller Na^{+} and Ca^{2+}

  → Ra migrates onwards in areas of high salinity
- Ra is strongly retained in areas of high SO_4 due to (co)precipitation as $RaSO_4$ and $BaRaSO_4$

  → implications for the disposal safety cases
- Ra sorption can be accurately modeled

  → usable and valuable data for the safety cases

ACKNOWLEDGEMENTS

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FUTURe

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GTK

THANK YOU