Uptake of Radium during Barite Recrystallization

[1]F. Brandt, [1]M. Klinkenberg, [2]U. Breuer, K. Rozov, [1]D. Bosbach

[1]Institute of Energy and Climate Research – Nuclear Waste Management and Reactor Safety (IEK-6)
Research Centre Jülich GmbH, 52425 Jülich, Germany (m.klinkenberg@fz-juelich.de)
[2]Central Institute of Engineering, Electronics and Analytics, ZEA-3 Analytics, Forschungszentrum Jülich GmbH, Germany

Introduction & Objectives: The uptake of Ra by Barite via solid solution formation is an important process controlling the solubility of Ra in aqueous systems. Under nuclear waste repository relevant conditions, Ra may enter a system in which barite is in equilibrium with the aqueous solution. For the uptake of Ra by existing solid barite, previous macroscopic studies have suggested that barite may partially or fully recrystallize to radiobarite [1,2], i.e. Ra uptake is not limited to pure adsorption. In addition, recent atomistic simulations of the solid solution series $Ba_{1-x}Ra_xSO_4$ indicate the formation of a non-ideal solid solution with a Margules interaction parameter of $a_0 = 1.0 \pm 0.4$ (25 °C) [3]. (Fig. ❶). Here we present new macroscopic and microscopic results in order to quantify the uptake of Ra under ambient conditions and identify the spatial distribution of Ra after recrystallization.
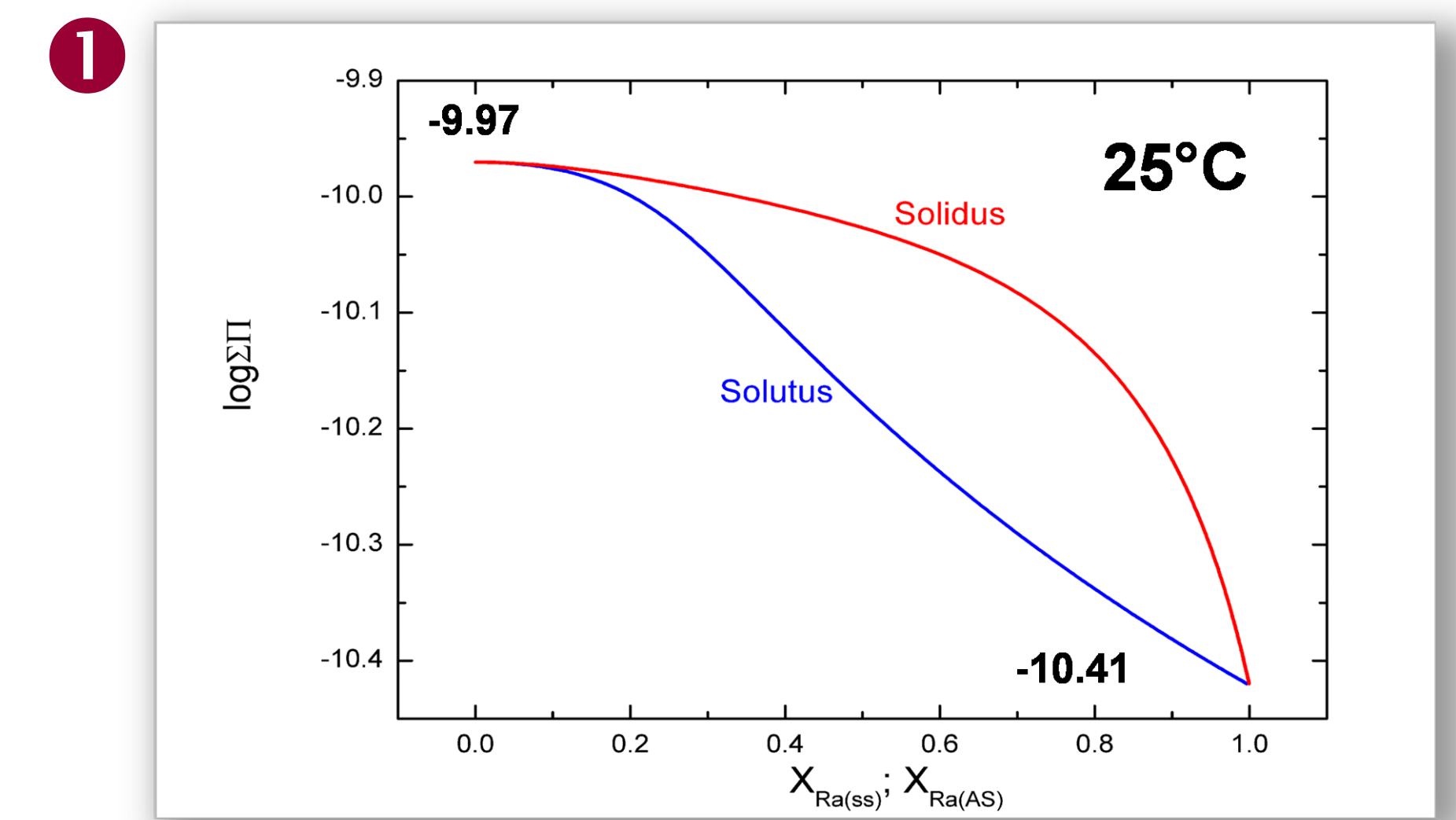
❶

Fig. ❶: Lippmann diagram calculated for RT $a_0 = 1.0$.

Experimental setup:

♦ Batch recrystallization experiments at **room temperature** (Fig. ❷).
♦ **Sachtleben barite**: blocky crystals, particle size of > 10 μm, specific surface area **0.17 m²/g** (Fig. ❸).
♦ The **solid** (barite powder)/**liquid** (0.1 n NaCl) **ratio: 5 g/L** and **0.5 g/L.**
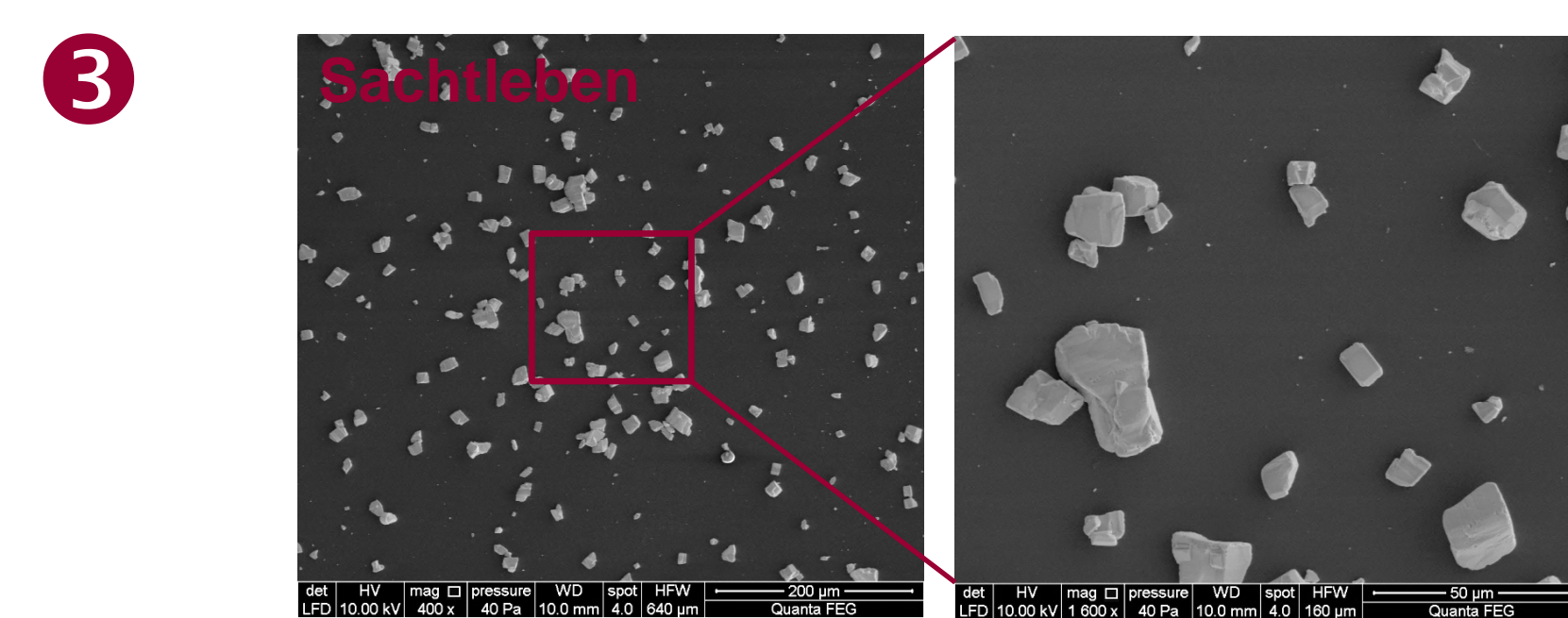♦ Initial Ra/Ba ratio of 0.3 (**5*10⁻⁶ mol/L Ra**).

Methods:

♦ The Ra and Ba concentration in solution were monitored via **Gamma spectrometry** and **ICP-MS.**
♦ **TOF-SIMS** measurements were performed in order to investigate the spatial distribution of Ra within the barite crystal.
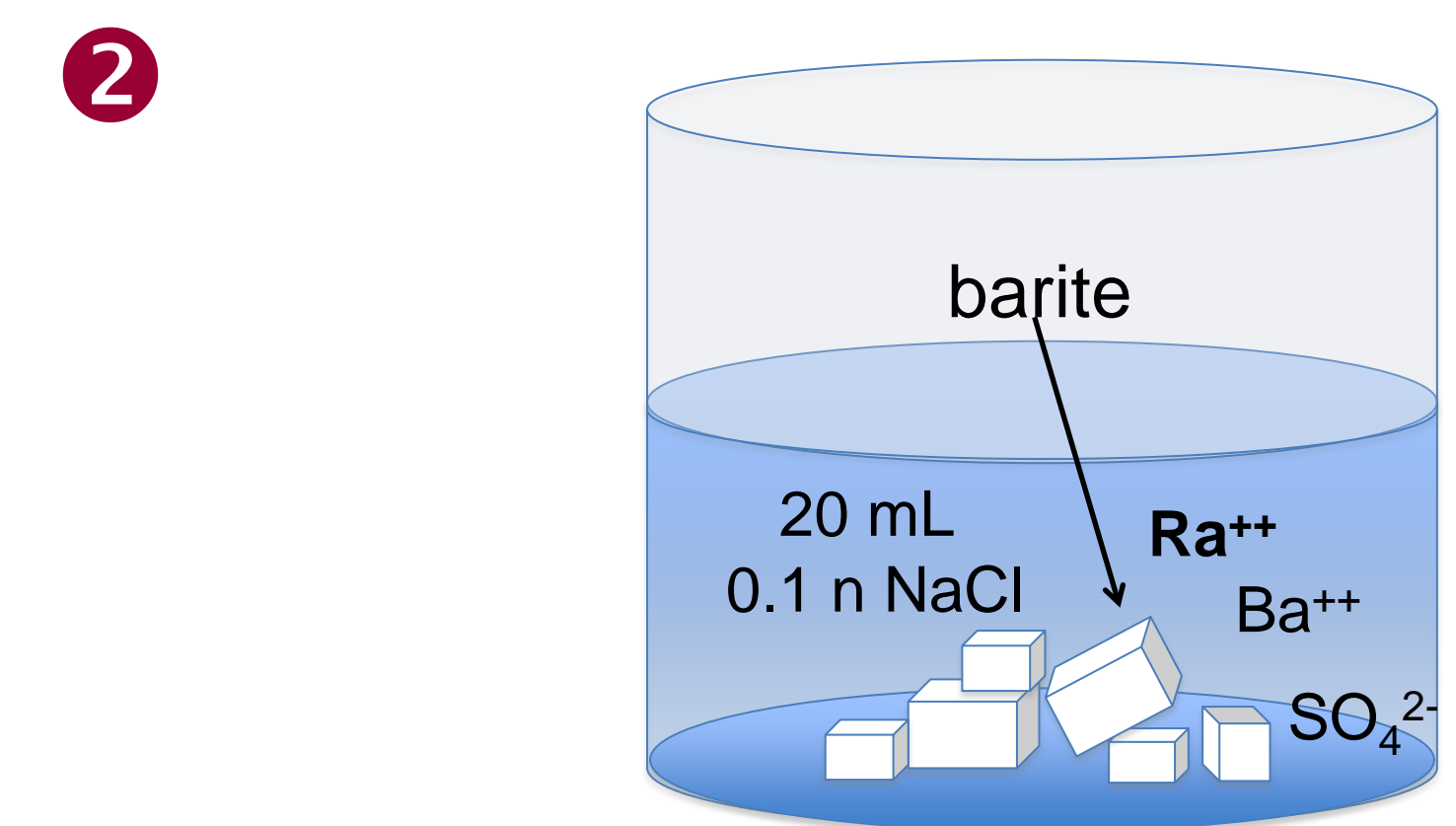
❷

Fig. ❷: Experimental setup.

❸

Fig. ❸: SEM images of initial equilibrated Sachtleben barite.
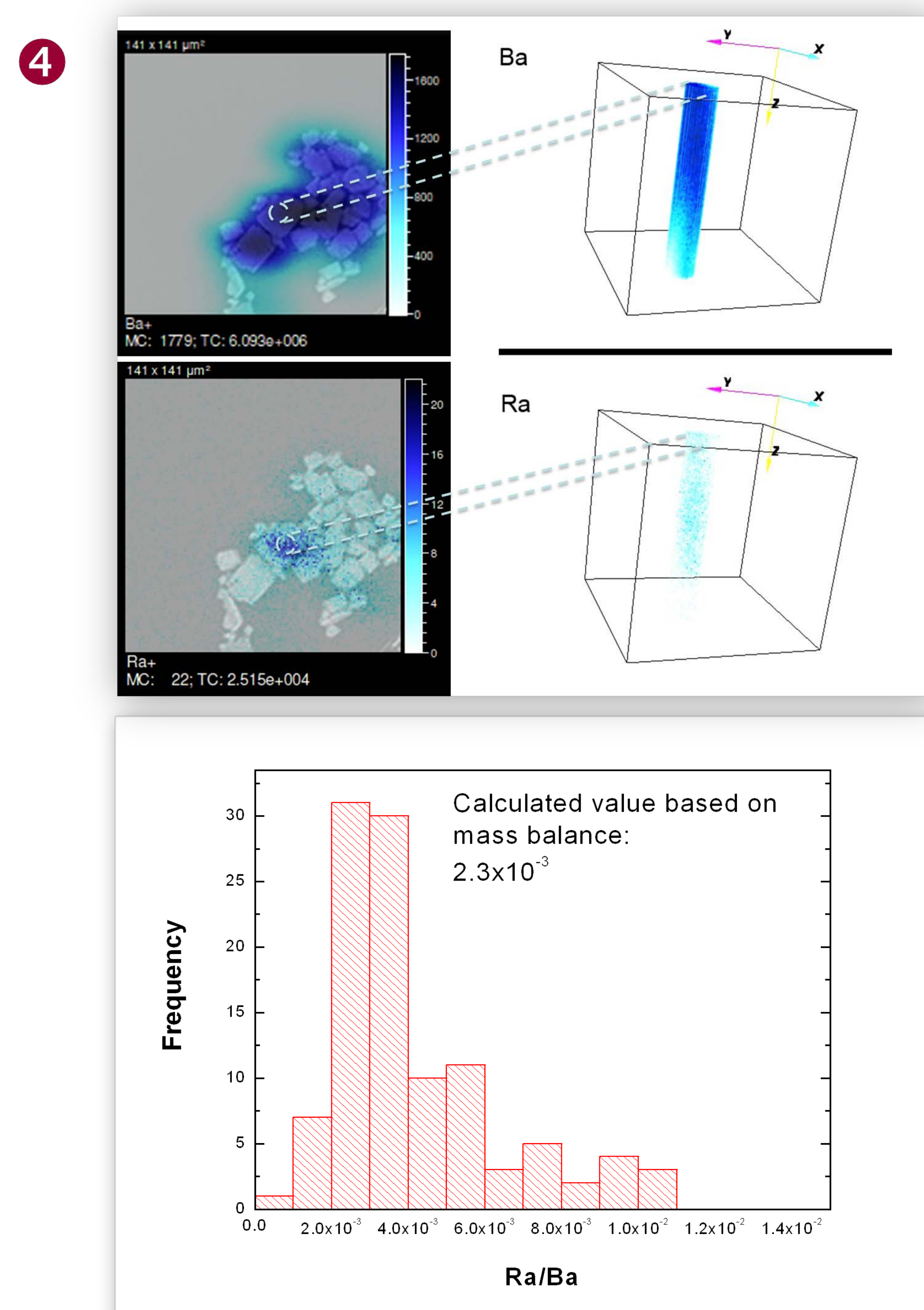
Results & Discussion:

❹

Fig. ❹: top: SEM and TOF-SIMS analysis of 0.5 g/L sample after 350 days. Bottom: distribution of Ra/Ba ratios based on profiles taken from the TOF-SIMS analyses above.
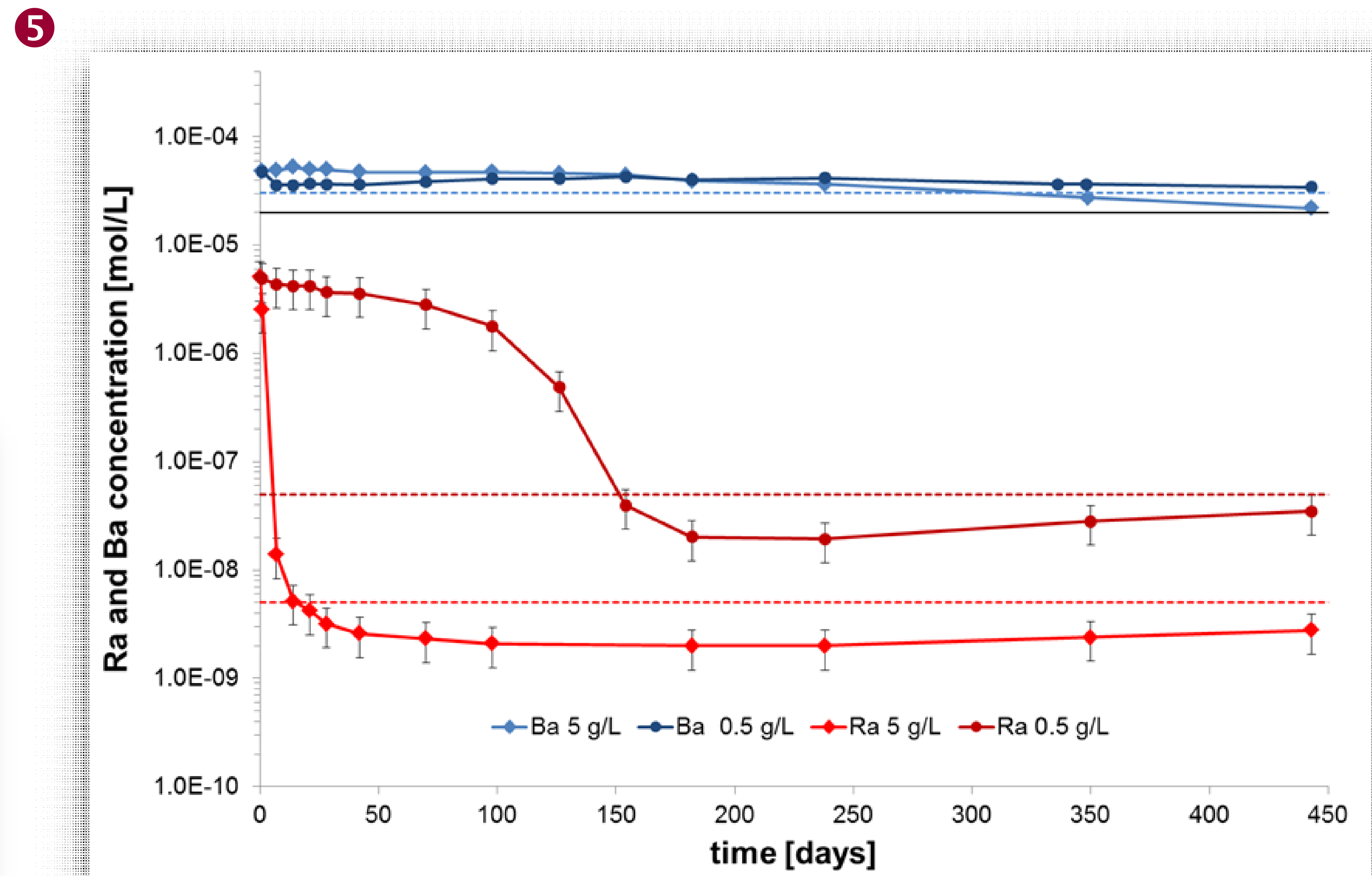
❺

Fig. ❺: Temporal evolution of the Ra and Ba concentrations with 5 g/L and 0.5 g/L of barite. Dashed lines indicate predicted concentrations for Ba, Ra 0.5 g/L and Ra 5 g/L, using an interaction parameter $a_0 = 0.6$ and $logK_{sp}(RaSO_4) = -10.41$.

♦ After 350 days, Sachtleben 0.5 g/L and 5 g/L barite contains **Ra in the crystal volume;** TOF-SIMS results indicate no zoning of Ra: indication of complete recrystallization of barite to radiobarite (Fig. ❹, top).
♦ Ra is reduced by more than 99% in the presence of barite (Fig. ❺). The ratio of Ra/Ba intensities in TOF-SIMS analyses corresponds well with the calculated Ra/Ba concentration ratio of the solid phase based on mass balance calculations
♦ Ba concentrations in aqueous solution indicate near to equilibrium conditions with the barite end-member after ~ 1 day.

♦ A plateau of the Ra concentration is reached at **3.5*10⁻⁹ to 7*10⁻⁹ mol/l** for experiments with **5 g/L** within the first 50 days.
♦ A slower decrease of the Ra concentration to **2*10⁻⁸ mol/L** is observed after 180 days for experiments with **0.5 g/L.**
♦ Solubility of pure $RaSO_4$ at 0.1 n NaCl: ~ 2 x 10⁻⁵ mol/L (black line Fig. ❺).
♦ The final Ra concentrations agree reasonably well with predicted values, when $a_0 = 0.6$ and $logK_{sp}(RaSO_4) = -10.41$ are used.

Outlook:

Spectroscopic and microscopic (e.g. TEM) studies will be carried out to achieve a nanoscopic system understanding of the micro structural evolution and Ra incorporation into the barite crystal as well as its spatial distribution in the crystal.

Acknowledgement:

References:

[1] Bosbach, D.; Böttle, M. & Metz, V. (2010) Waste Management, Svensk Kärnbränslehantering AB
[2] Curti, E. et al. (2010) Geochimica et Cosmochimica Acta, **74**, 3553-3570
[3] Vinograd, V.L., Brandt, F., Rozov, K., Klinkenberg, M., Refson, K., Winkler, B., Bosbach, D., Solid-aqueous equilibrium in the BaSO₄-RaSO₄-H₂O system: first-principles calculations and a thermodynamic assessment, Geochimica et Cosmochimica Acta (2013), doi: http://dx.doi.org/10.1016/j.gca.2013.08.028

Mitglied der Helmholtz-Gemeinschaft