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Uptake of Radium by barite under repository relevant conditons

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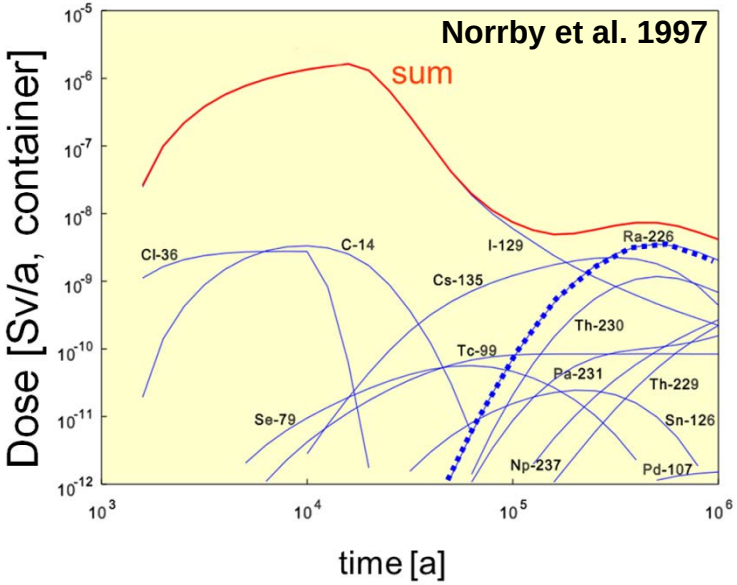
Radium in nuclear waste repositories

- In some scenarios of direct disposal of spent fuel, as a result of the ^{238}U decay chain ^{226}Ra dominates the dose during the late stages
- Possible Ba release during spent fuel corrosion → crystallization of barite ($BaSO_4$).
- Ra may be introduced into a system of barite in equilibrium with Ba^{2+} and SO_4^{2-}



Relevance of solid solution formation

Example: 0.1 n NaCl background electrolyte, 25 °C

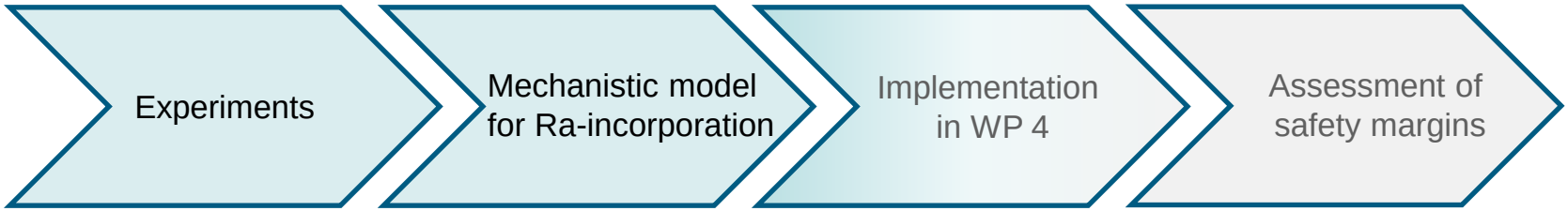
Solubility of pure $RaSO_4$ **$2 \cdot 10^{-5}$ mol/L**

Solid solution (0.5 g/L barite $a_0 = 0$)

Calculated Ra-solubility **$4 \cdot 10^{-8}$ mol/L**

Status of WP 2.1

- **Details about solid solution formation and barite recrystallization in the presence of Ra to be determined**



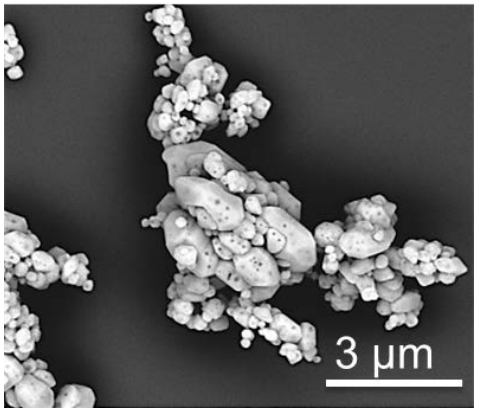
- **Status November 2013: experiments finished; results delivered to WP 4**

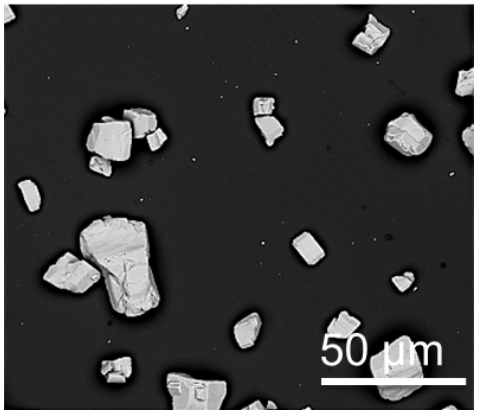
Ra uptake by $BaSO_4$: open questions

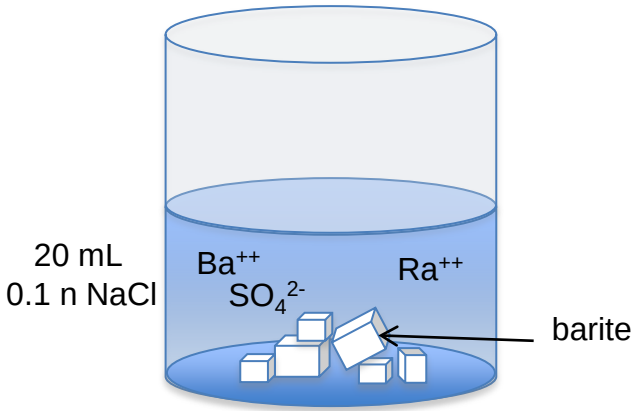
- Does barite take up Ra during recrystallization?
- Does barite completely recrystallize into a $Ba_{1-x}Ra_xSO_4$ solid solution in the presence of Ra?
- Spatial distribution of Ra within the solid?
- Influence of the presence of Ra on the recrystallization of barite?
- Influence of barite morphology and particle size distribution (PSD)?

Experimental setup

- Experiment: batch experiments with V = 20 mL
  $5 \cdot 10^{-6}$ mol/L $^{226}Ra^{2+}$
- Ionic strength: 0.1 n NaCl
- Solid/Liquid: 0.5 g/L, 5 g/L
- Variation of barite type Aldrich (AL) and
  Sachtleben (SL)
- Room temperature

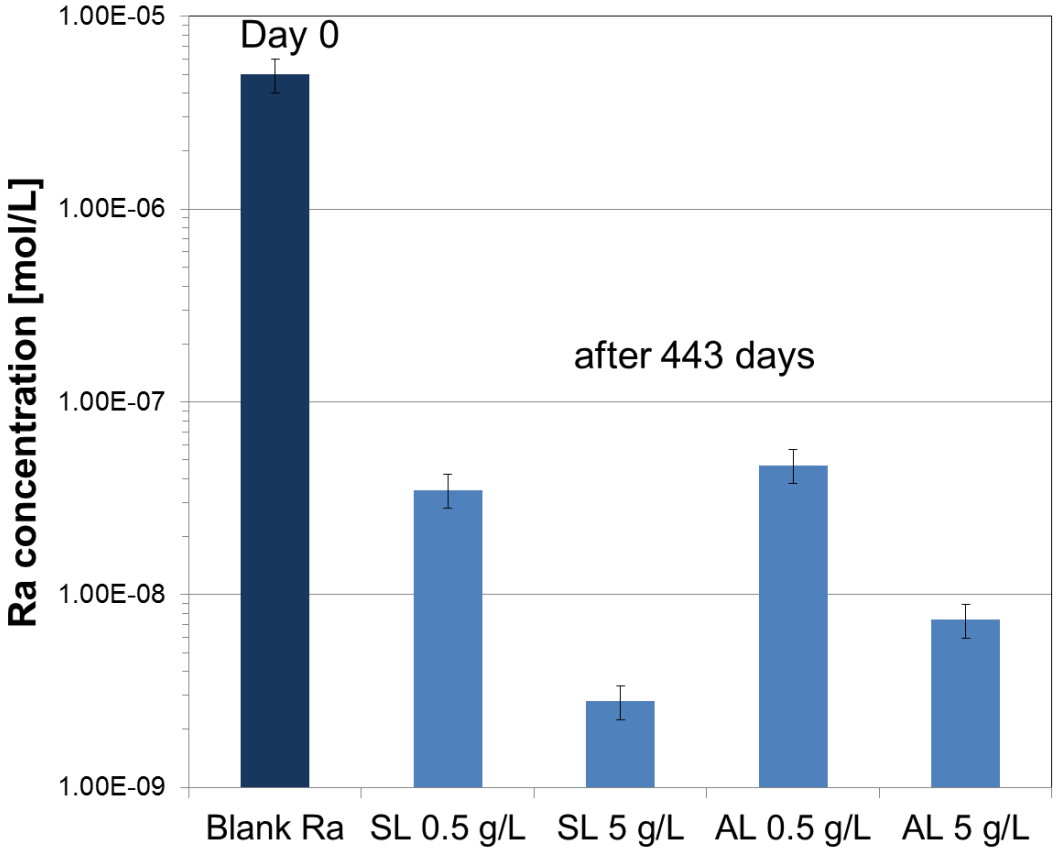






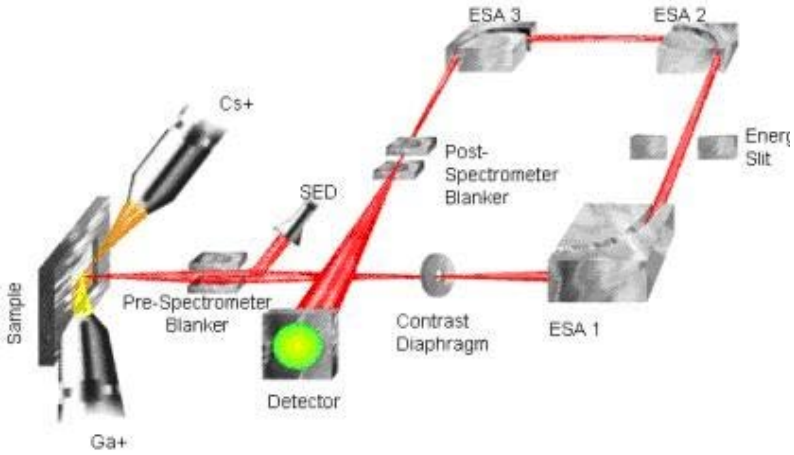
Ra uptake by barite – 5 g/L and 0.5 g/L at RT

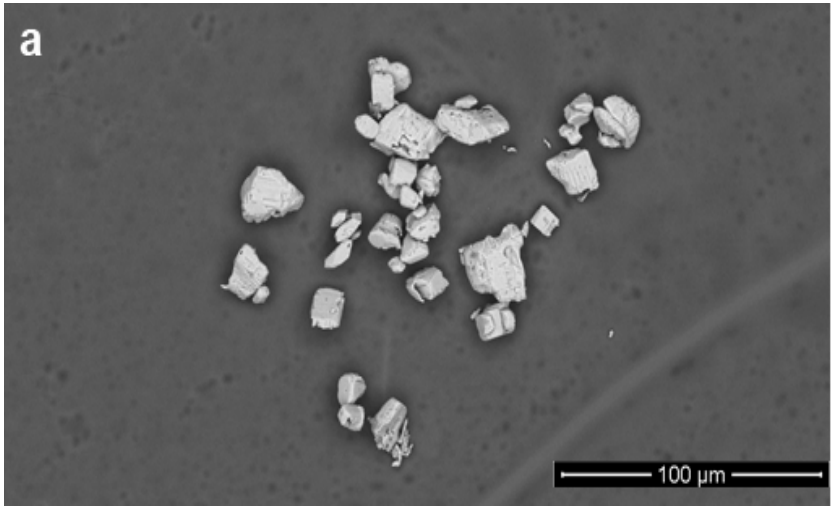
- Mass balance calculations give a final **Ra/Ba** ratio of
- **~ 2.5 x 10^{-4}** for 5 g/L barite at RT
- **~ 2.5 x 10^{-3}** for 0.5 g/L barite at RT



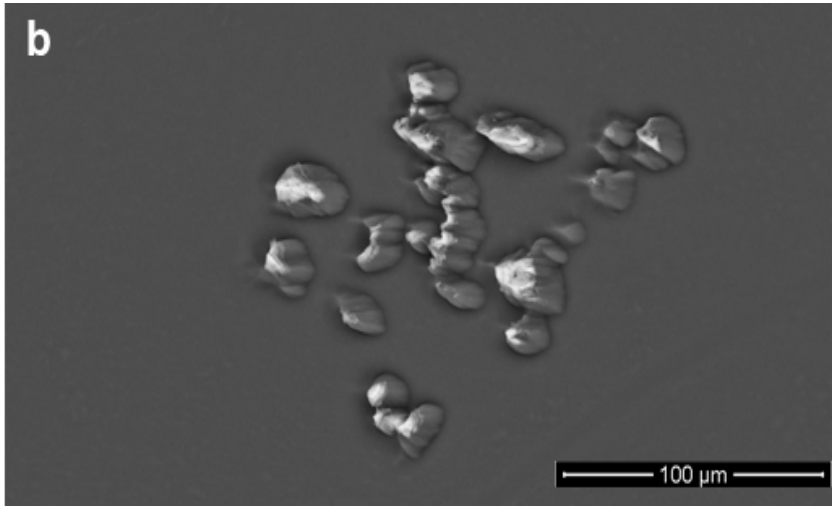
Does barite take up Ra?

- Determination of Ba and Ra content and distribution
- Time of flight secondary ion mass spectroscopy (ToF-SIMS)
- Sachtleben barite 0.5 g/L
- Analysis of complete grains





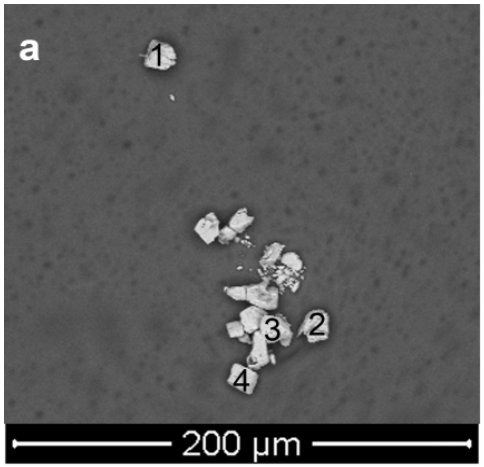
before measurement

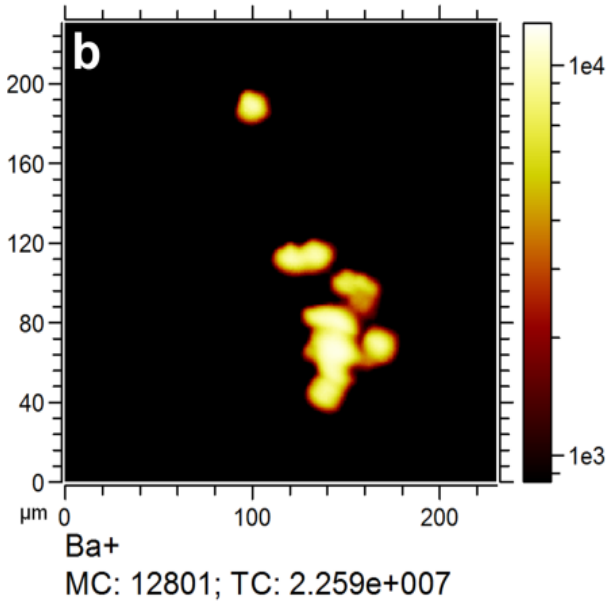


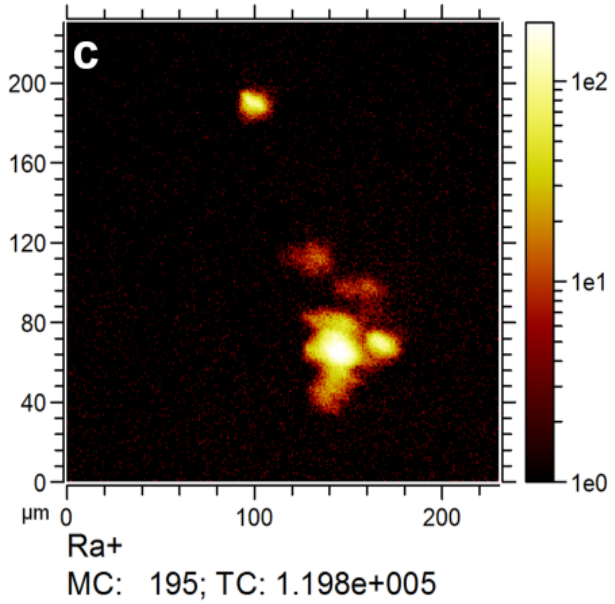
after measurement

Does barite take up Ra?

- **Optimization** of the spatial resolution ➔ Identifcation of individual barite grains
- Integrated intensity distribution of the Ba and Ra signal
- All grains contain Ra

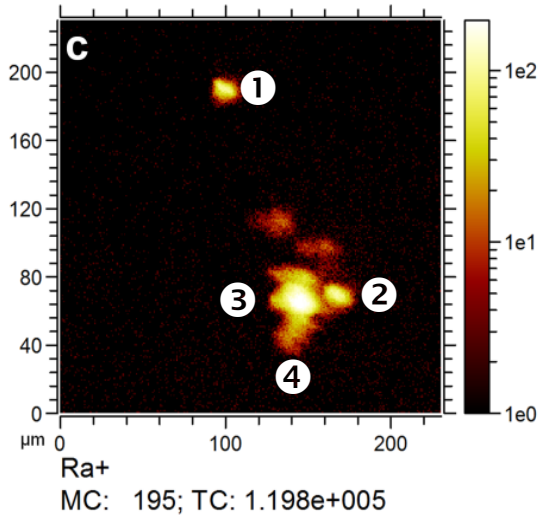




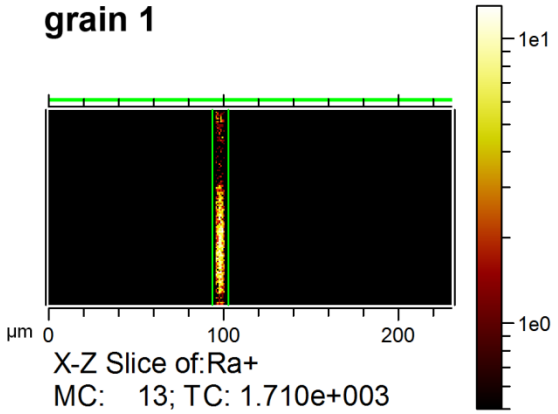


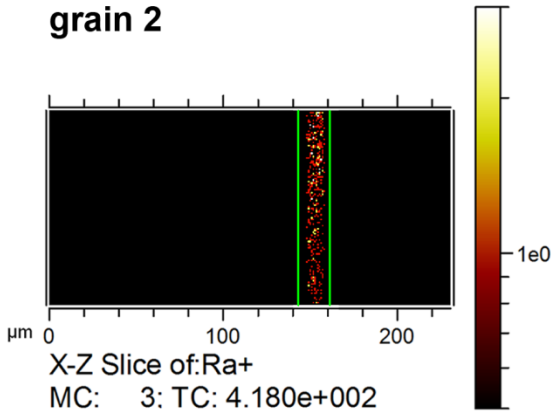
Compositional homogeneity of radiobarite ?

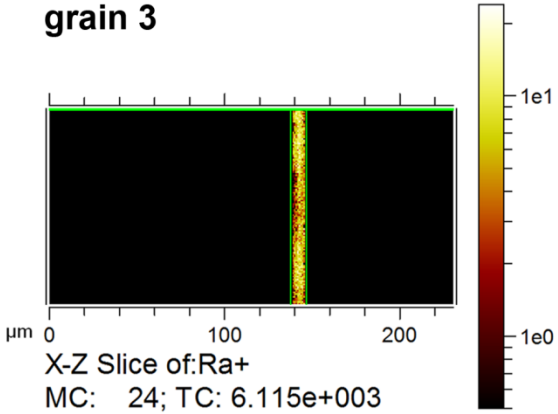
- Spatial distribution of Ra within the barite particles
- Depth resolution: ~ 0.1 µm
- All particles contain Ra
- Indication of a complete recrystallization of barite into a $Ba_{1-x}Ra_xSO_4$ solid solution

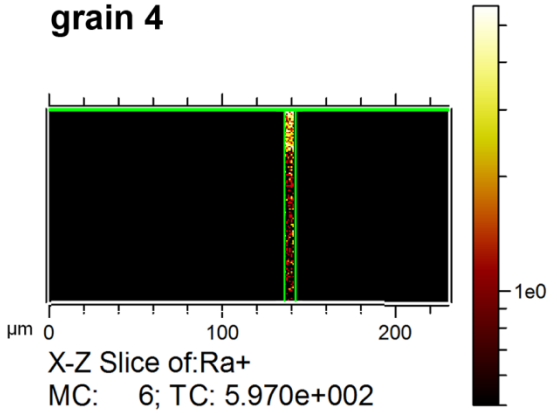


Depth profiles of integrated Ra signals

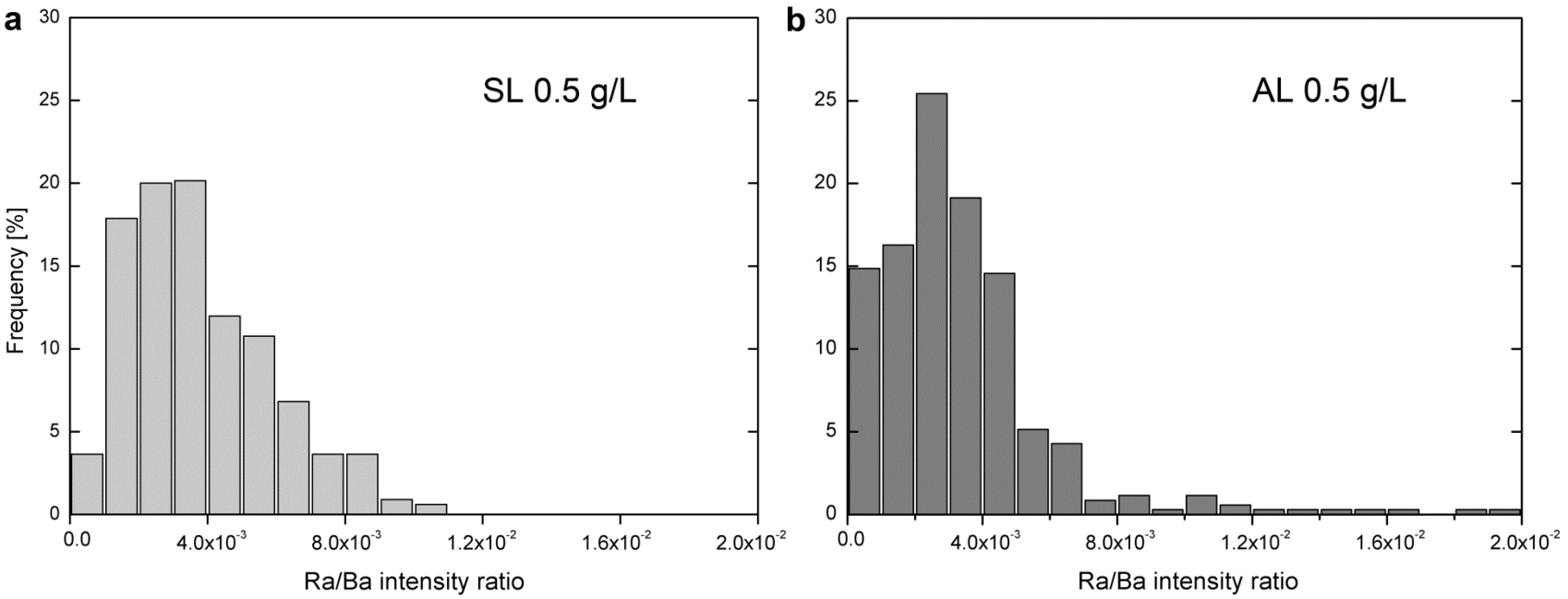








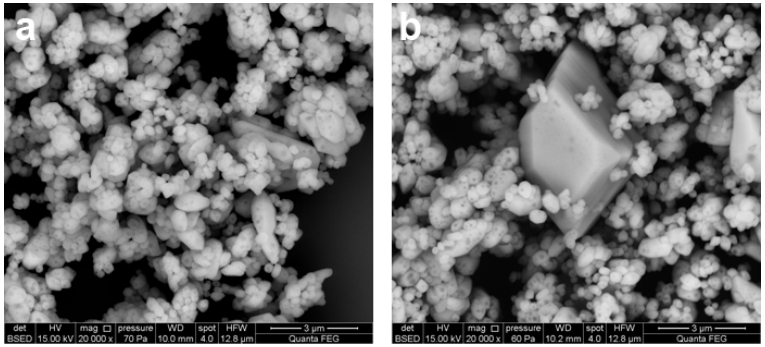
Ra/Ba ratio derived from ToF - SIMS measurements



Mass balance calculations give a final **Ra/Ba** ratio of **2.5×10^{-3}** for 0.5 g/L barite at RT.

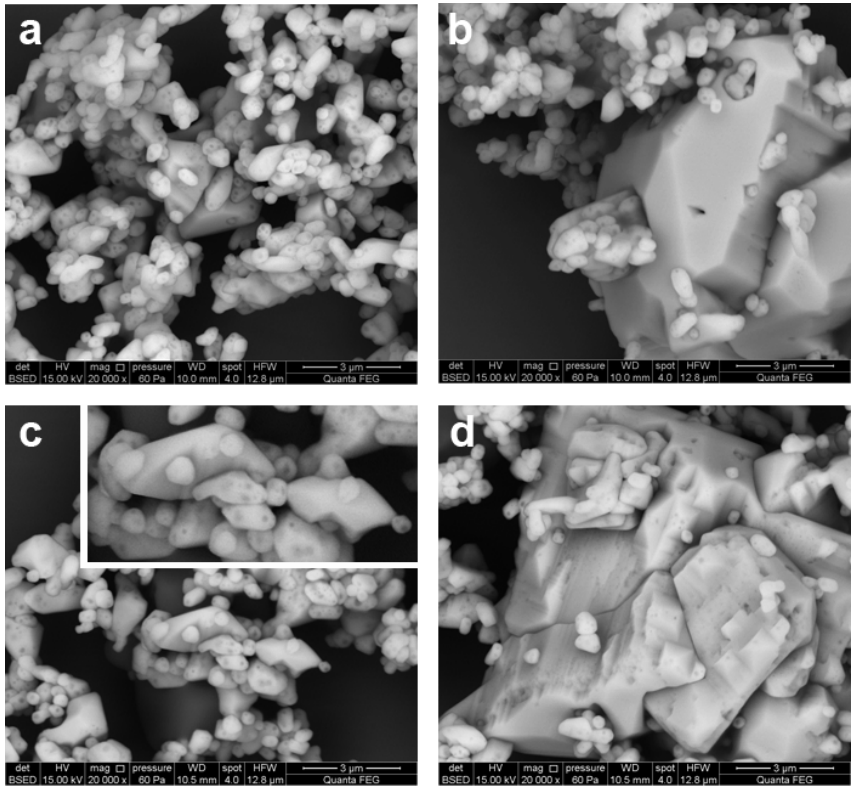
Evolution of the morphology of AL barite

Reference day 0 and 443



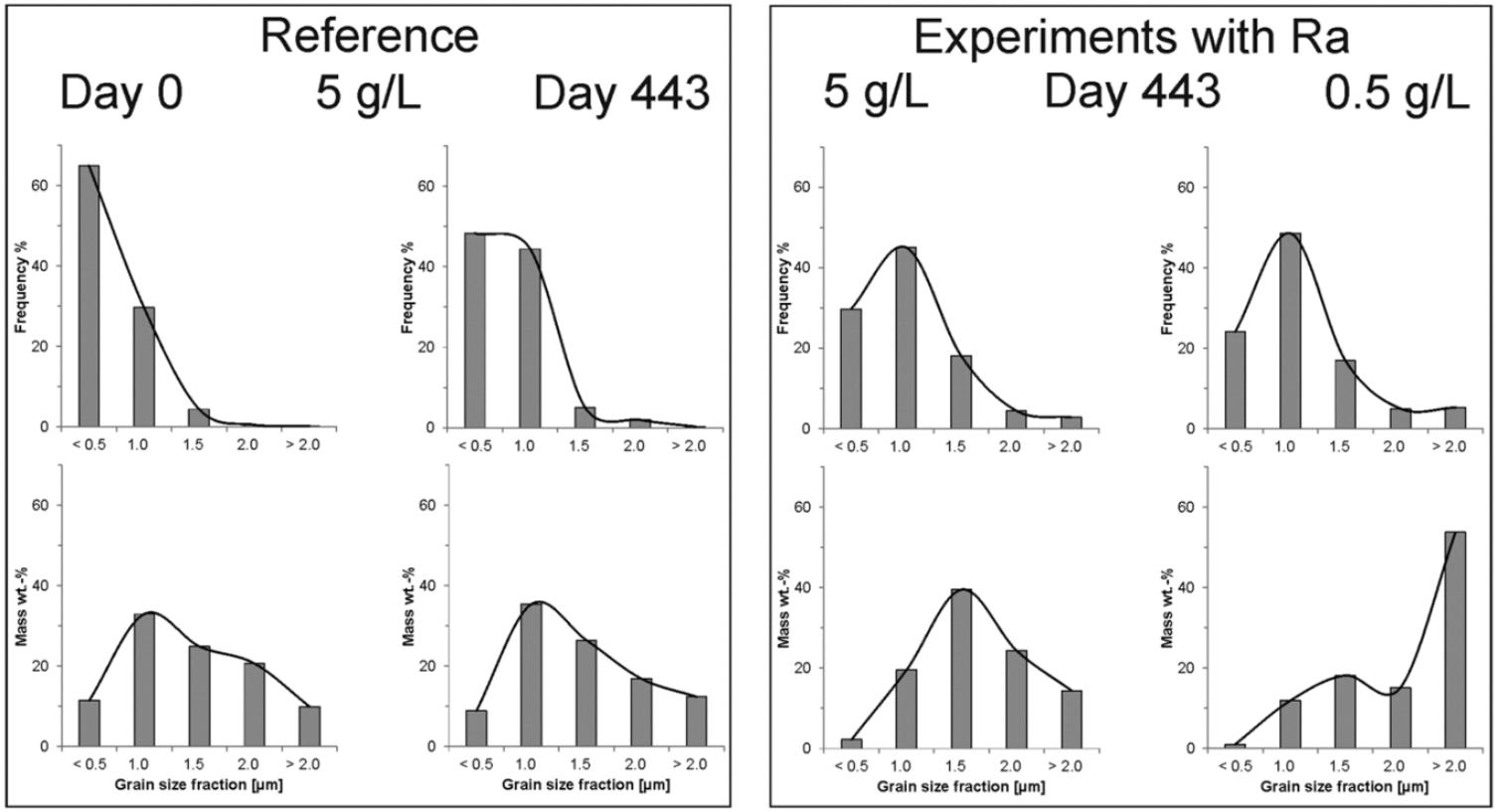
- Newly formed idiomorphous, large particles
- Particle coarsening
- Ostwald ripening
- Shape: less round, sharp edges, less pores on the surface
- Effects more distinct with Ra

Aldrich with Ra day 443



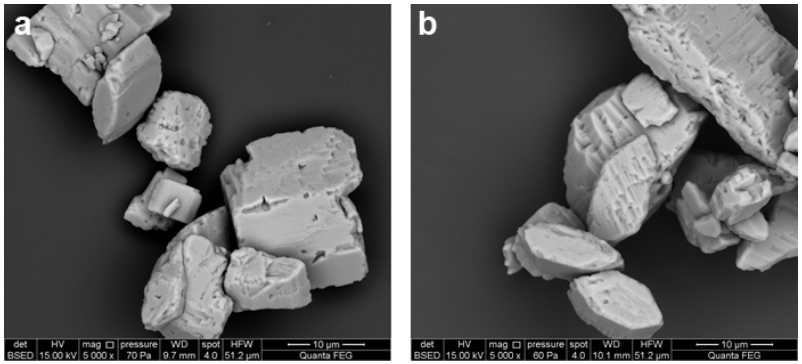
Evolution of the particle size distribution of AL barite

- Statistical information by image anlaysis
- Wide PSD
- Particle coarsening
- Additional influence of Ra



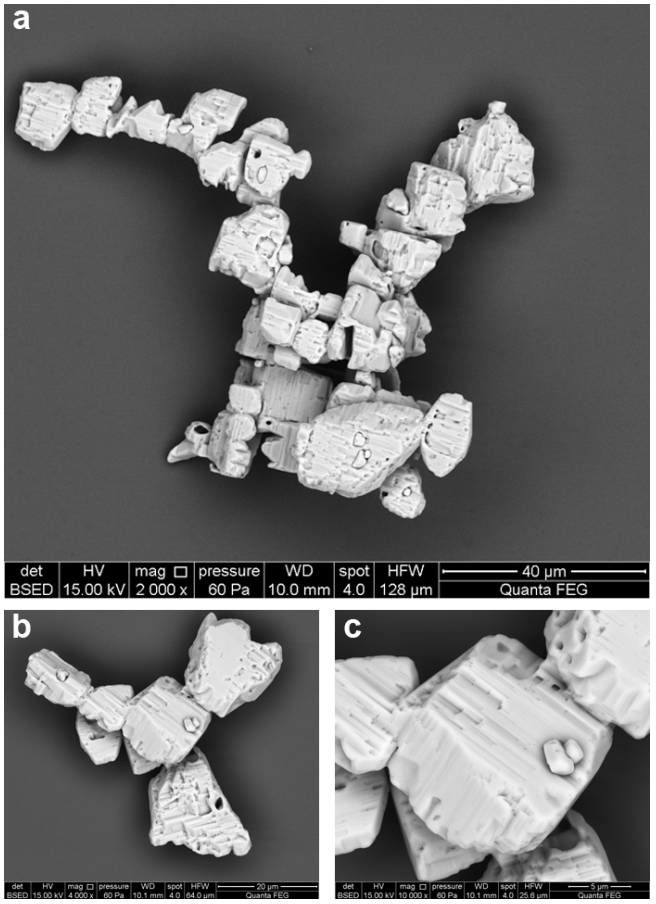
Evolution of the morphology of SL barite

Sachtleben day 0 and 443



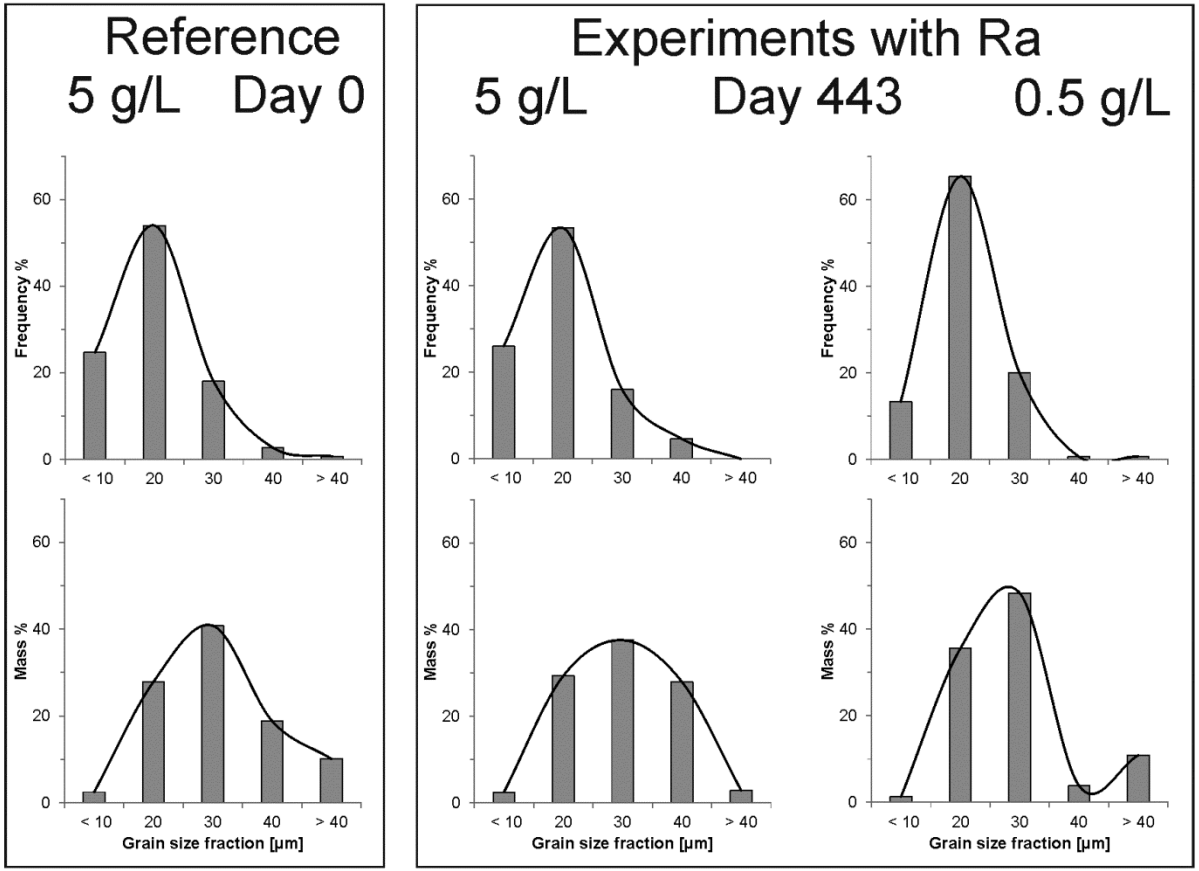
- No significant change of the morphology
- Smoother crystal faces
- Grains are grown together and form large aggregates

Sachtleben with Ra day 443



Evolution of the particle size distribution of SL barite

- Narrow PSD
- Slight increase of coarse particles



Evolution of morphology and grain size distribution

- Particle coarsening due to Ostwald ripening after recrystallization
- Significant additional effect due to the presence of Ra

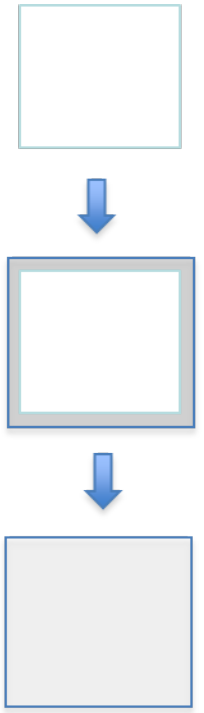
➔ Ra enhances the recrystallization of barite

	Mean value	
	Frequency based	Equ. mass based
	[µm]	[µm]
AL Reference at the beginning	0.50	0.69
AL Reference 5 g/L after 443 days	0.58	0.82
AL 5 g/L after 443 days	0.80	1.15
AL 0.5 g/L after 443 days	0.86	1.26
SL Reference at the beginning	15.00	18.62
SL 5 g/L after 443 days	15.28	18.79
SL 0.5 g/L after 443 days	14.99	18.33

Conclusion

- Efficient Ra uptake by barite
- Ra could be found in all barite particles after recrystallization
- Complete recrystallization of barite into $Ba_{1-x}Ra_xSO_4$ solid solution

➔ Ra enhances the recrystallization



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Thank you for your attention!