Nuclear Waste Management IEK-6
Institute of Energy and Climate Research

JÜLICH
FORSCHUNGSZENTRUM

Radionuclide solubility control in solid solution – aqueous solution systems: Radium solubility in the presence of barite

Dirk Bosbach, Felix Brandt, Martina Klinkenberg, Victor Vinograd, Konstantin Rozov, Juliane Weber, Uwe Breuer

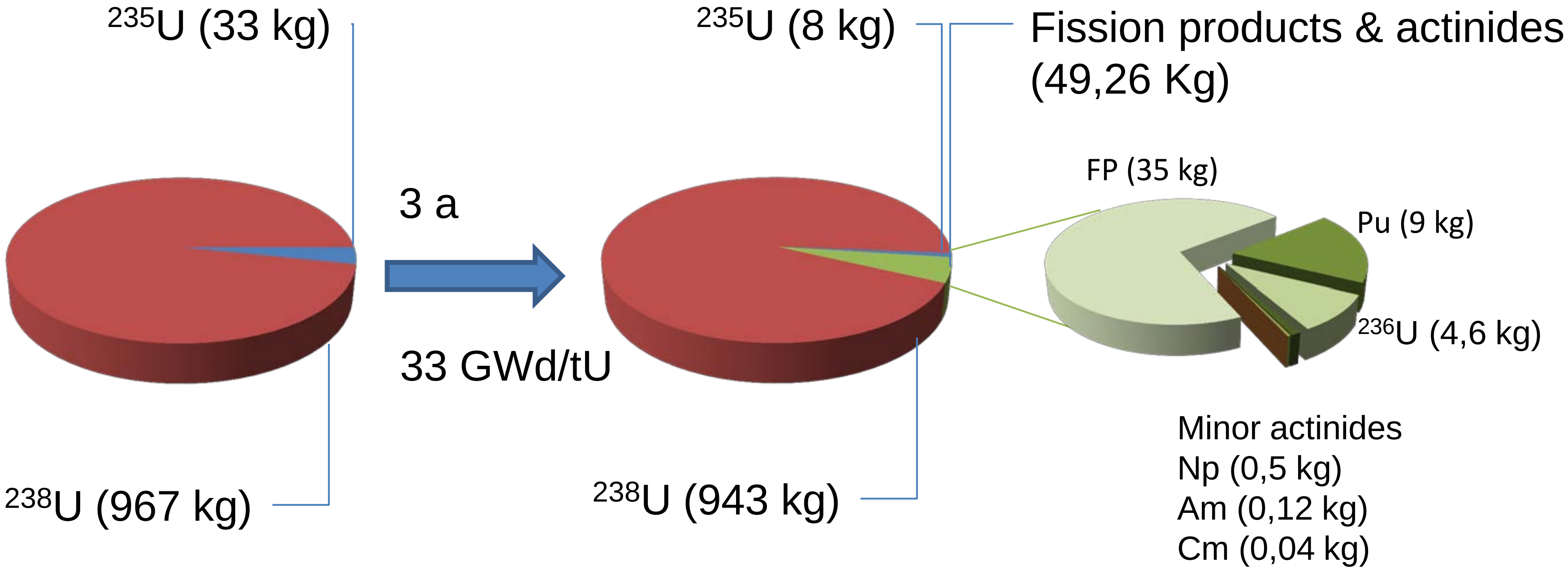
July 14/15, 2014

Heat-generating radioactive waste in Germany

	Volume / cask	Waste package volume [m^3]
HAW – glass (CSD-V)	3.719 canisters	ca. 670
MAW – glass (CSD-B)	600 canisters	ca. 110
Compacted waste (CSD-C)	4.104 canisters	ca. 740
Spent fuel elements		
Power reactors	11.133 tSM (in Pollux casks)	21.800
PKA/IKA	2.600 Mosaik II casks	3.400
THTR/AVR	4457 CASTOR casks	1.970
Research reactors	65 CASTOR casks	160
WAK Karlsruhe	ca. 900 200L drums	180
	Total	**29.030**

Source: Federal Office of Radiation Protection (Germany), Sep 2011

Spent / used nuclear fuel



^{235}U (33 kg)

^{238}U (967 kg)

3 a

33 GWd/tU

^{235}U (8 kg)

^{238}U (943 kg)

Fission products & actinides (49,26 Kg)

FP (35 kg)

Pu (9 kg)

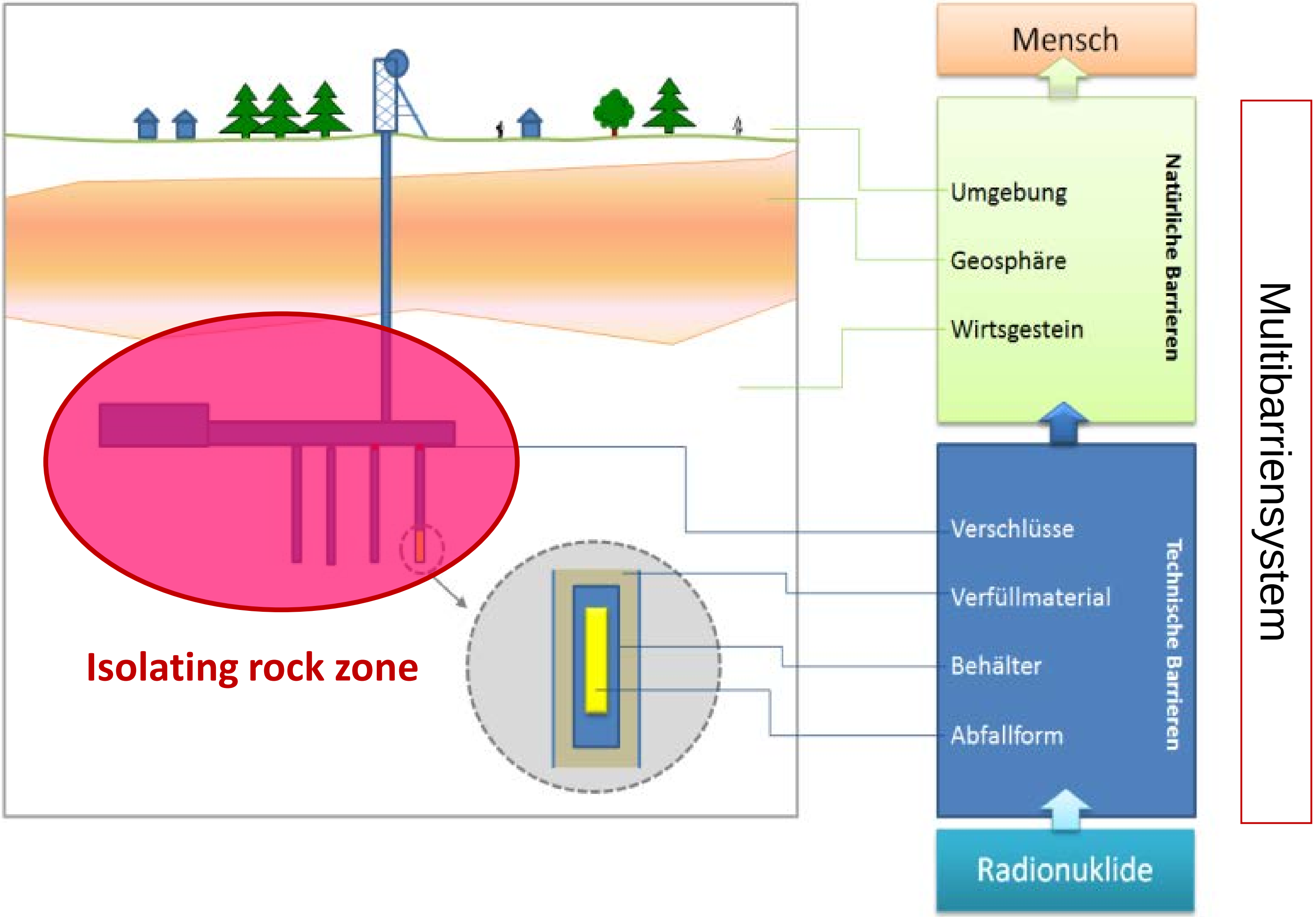
^{236}U (4,6 kg)

Minor actinides
Np (0,5 kg)
Am (0,12 kg)
Cm (0,04 kg)

Nuclear fuel

SF / UNF

Disposal of nuclear waste in a deep geological formation



Mensch

Umgebung

Geosphäre

Wirtsgestein

Natürliche Barrieren

Verschlüsse

Verfüllmaterial

Behälter

Abfallform

Technische Barrieren

Radionuklide

Multibarriensystem

Isolating rock zone

What is a Scenario?

- *A postulated or assumed set of conditions and/or events. They are most commonly used in analysis or assessment to represent possible future conditions and/or events to be modelled, such as possible accidents at a nuclear facility, or the possible future evolution of a repository and its surroundings.* [IAEA Glossary, 2007]

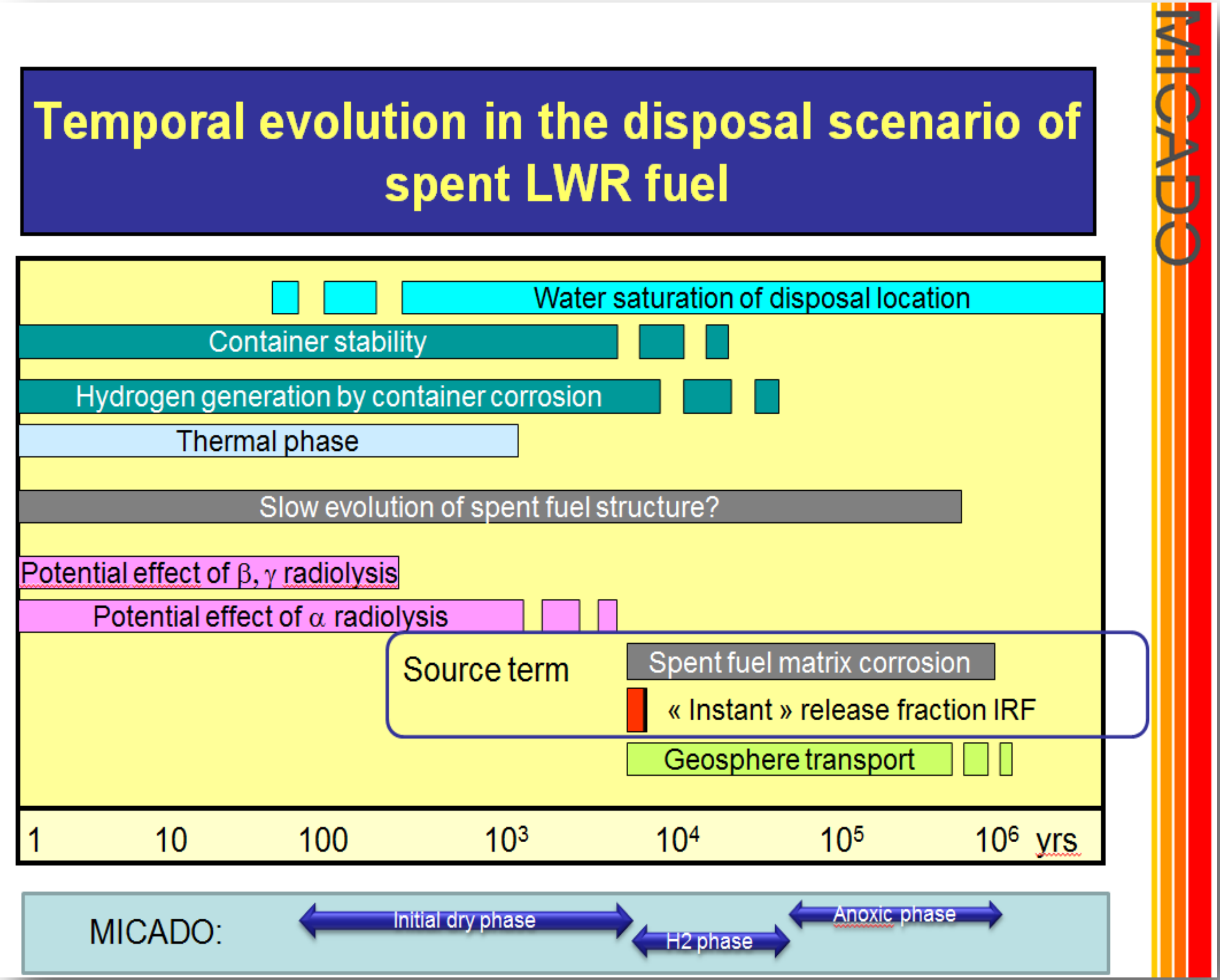
- *Scenarios are descriptions of alternative evolutions of the disposal system. Scenarios are used to identify and define assessment cases that are consistent with the assessment context. Each assessment case may represent or bound a range of broadly similar possible futures.* [IAEA Specific Safety Guide SSG-23, 2012]

- *In safety assessment for the post-closure period, the performance of the geological disposal system under the expected evolution and under certain specific, but less likely, evolutions and events is analysed.* [IAEA SSG-14, 2011]

➢ **The long-term safety of the repository system has to be demonstrated for a wide variety of relevant scenarios**

Types of Scenarios

- **Reference scenario (base case)**
  - expected (normal) evolution, combining an entity of probable events and processes describing a coherent range of expected developments
- **Alternative (disturbed) scenarios**
  - less likely evolutions, addressing, e.g.
    - intensified glaciation
    - tectonic disturbances
    - poor sealing, early canister failure
- **(Inadvertent) human intrusion scenarios**
  - developed on the basis of stylized representations of the nature of the intrusion
  - designed to provide illustrations of potential impacts
- **What-if scenarios**
  - highly unlikely events/processes but with potentially significant consequences, sometimes physically impossible
  - demonstration of robustness of disposal system



Temporal evolution in the disposal scenario of spent LWR fuel

Water saturation of disposal location

Container stability

Hydrogen generation by container corrosion

Thermal phase

Slow evolution of spent fuel structure?

Potential effect of β, γ radiolysis

Potential effect of α radiolysis

Source term

Spent fuel matrix corrosion

« Instant » release fraction IRF

Geosphere transport

B. Grambow, SUBATECH

Geological Disposal seems to be the best option

OECD NEA RWMC collective statement, 2008

- There is overwhelming scientific consensus world-wide that geological disposal is technically feasible

30+ years of R&D needed for the first license applications in Europe

- Sweden 76: March 2011 (35 yrs)
  operation 2029 (53 yrs)
- Finland 78: Dec. 2012 (34 yrs)
  operation 2022 (44 yrs)
- France 70's: 2015-2017 (35-40 yrs)
  operation 2025 (ca.50 yrs)

C.Davis, EC

Long-lived fission & activation products and actinides

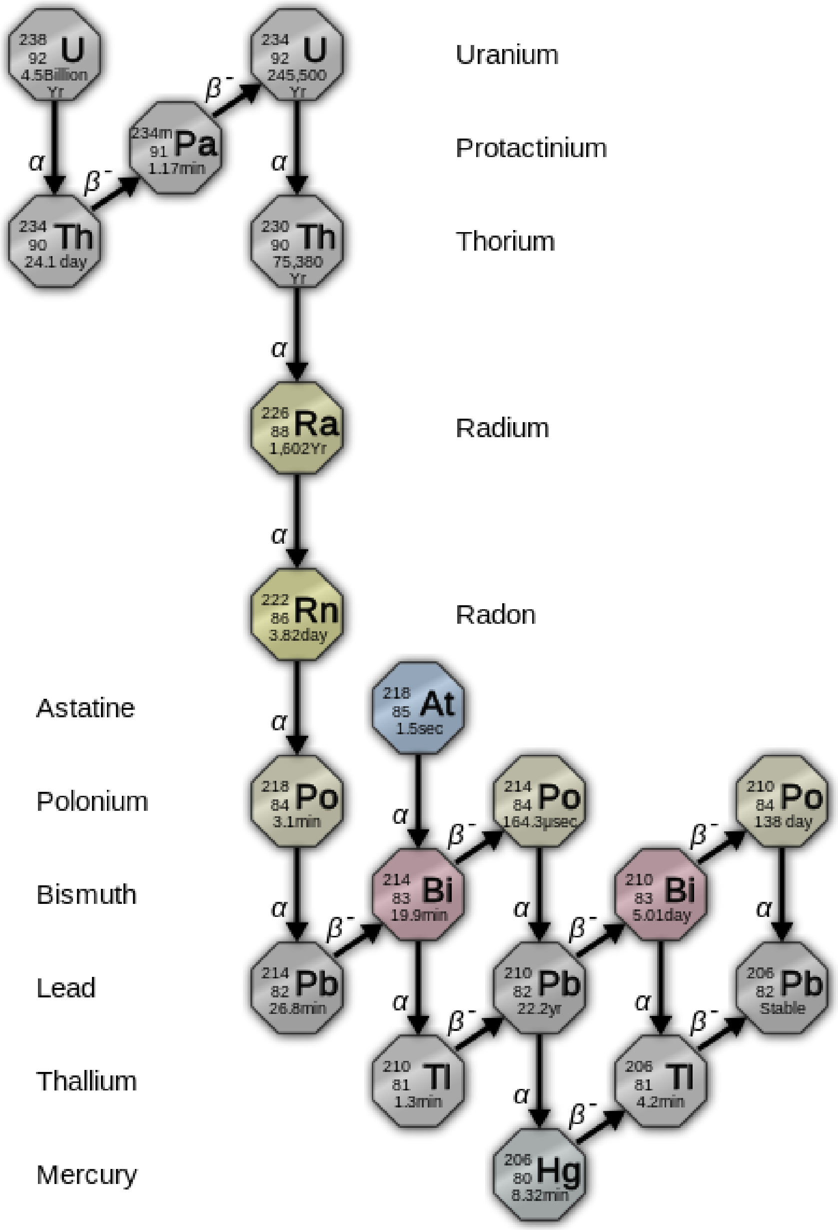
Long-lived fission and activation products (engl. MOFAPs)
C-14, Cl-36, Se-79, Tc-99, I-129, Cs-135
… because of their mobility within the repository system
(CAUTION: conservative assumption).

Actinides:
U, Np, Pu, Am, Cm
… because of their high radiotoxicity (alpha-emmitters!).

For certain scenarios:
Ra, …

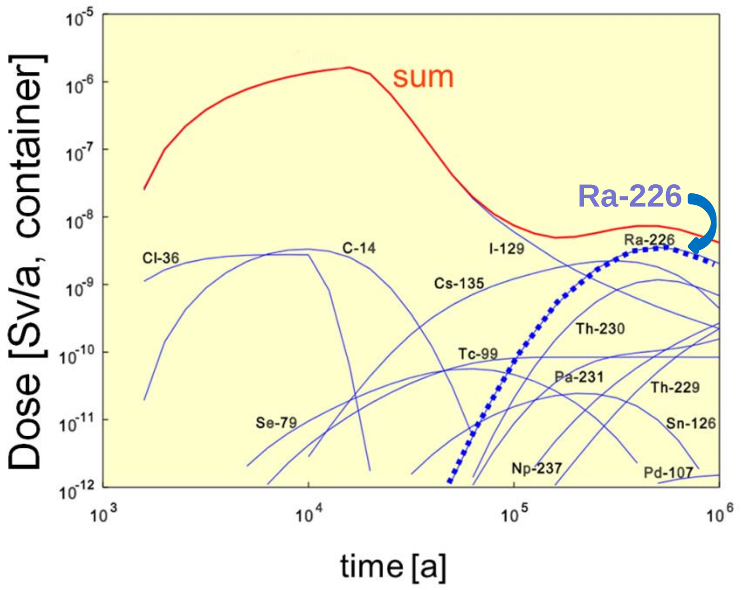
^{238}Uranium decay chain

The Radium series



Radium in nuclear waste repositories

- In some scenarios, 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 in which is barite in equilibrium with Ba^{2+} and SO_4^{2-}

(Norrby et al. 1997)

Discovery of Radium: 1898

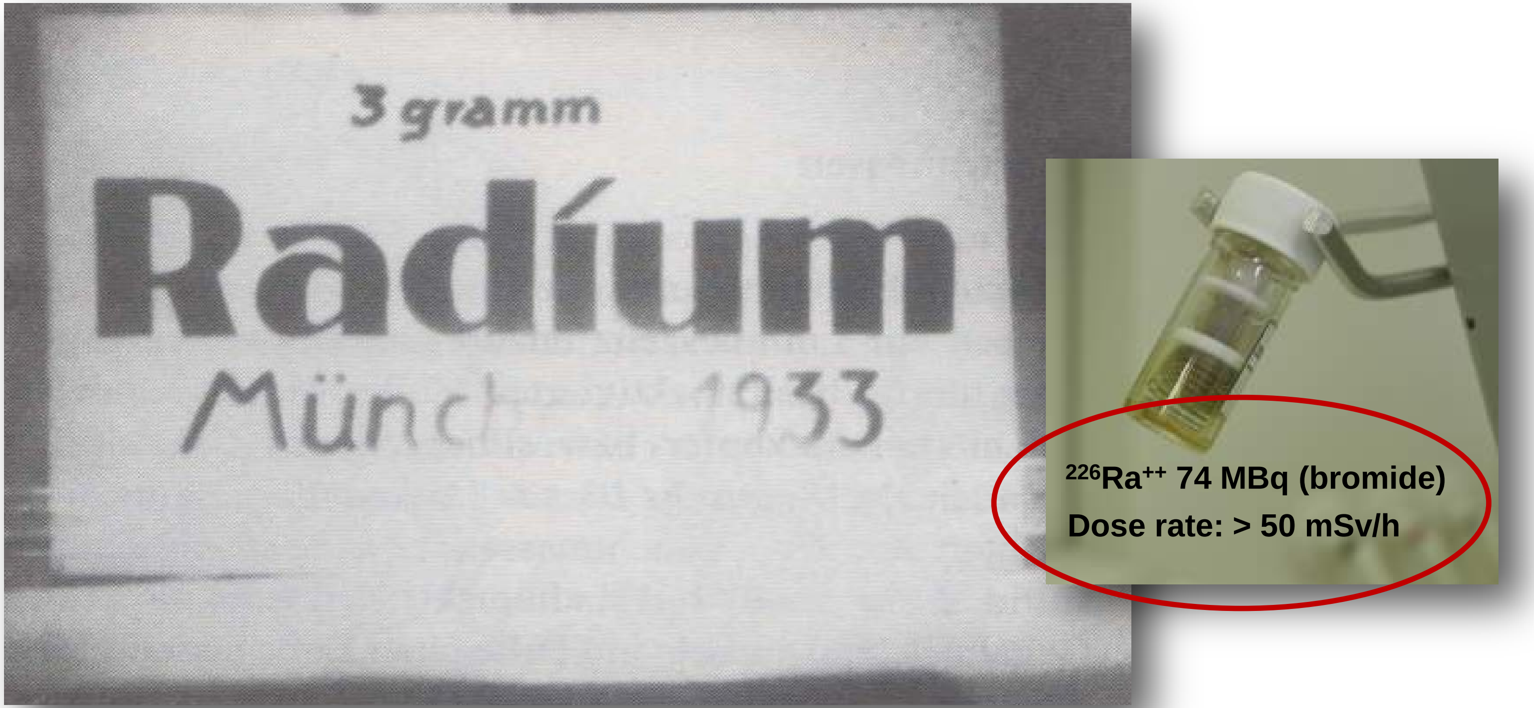
Marie und Pierre Curie

Discovery of Thorium, Polonium and Radium

Noble Prize in Physics 1903 - "in recognition of the extraordinary services they have rendered by their joint **researches on the radiation phenomena** discovered by Professor Henri Becquerel."

Noble Prize in Chemistry 1911 - "in recognition of her services to the advancement of chemistry by the **discovery of the elements radium** and polonium, by the isolation of radium and the study of the nature and compounds of this remarkable element."

Radiation induced lumincescence - 3 g $RaBr_2$



$^{226}Ra^{++}$ 74 MBq (bromide)

Dose rate: > 50 mSv/h

O. Hönigschmid & R. Sachtleben

Radium for the consumer (in the early 1900s)


Das erste Radium-Bad im Jahr 1906


Radiumbiere

sowie Pilsner Gambrinus

in Flaschen

liefert

Karl Kraus.

Bestellungen in der Bürgerlichen Brauerei
St. Joachimstal.

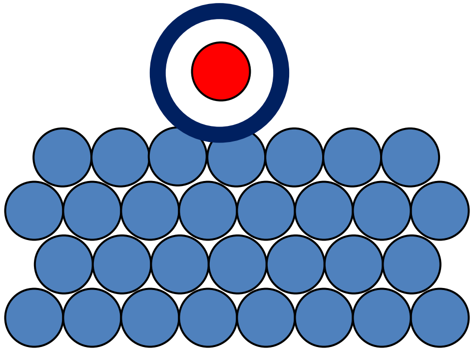
Important publications on Radium

Experimental data on Radium are rare!

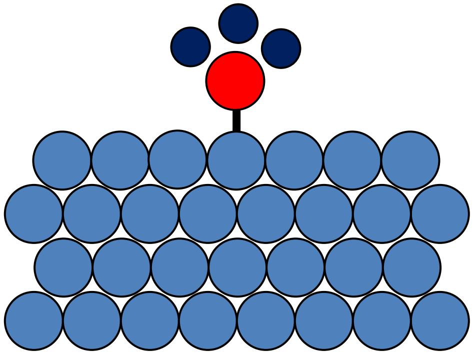
- Lowson, R. T. The Thermochemistry of Radium Thermochimica Acta, 1985, 91, 185-212
- Langmuir, D. & Riese, A. The thermodynamic properties of radium Geochimica et Cosmochimica Acta, 1985, 49, 1593-1601
- Lind, S. C.; Underwood, J. & Whittemore, C. F. The solubility of pure radium sulfate The Journal of the American Chemical Society, 1918, XL, 465-472
- Nikitin, B. & Tolmatscheff, P. Article on the validity of mass effect law. II. Quantitative determination of solubility of radium-sulfate in sodium-sulfate solutions and in water. Zeitschrift für physikalische Chemie – Abteilung A – Chemische Thermodynamik Kinetik Elektrochemie Eigenschaftslehre, Akademische Verlagsgesellsch. Geest & Portig, 1933, 167, 260 -277
- Kirby, H.; Salutsky, M.; Grace, W. & Al., E. The Radiochemistry of Radium Radiochemistry, National Academy of Sciences, National Research Conucil, 1966, 213

Immobilisation reactions for dissolved radionuclides

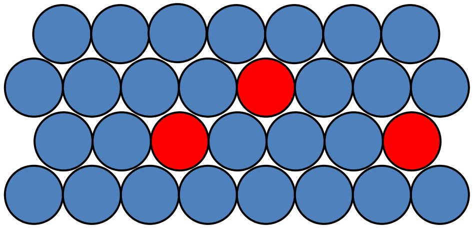
1. Electrostatic Adsorption



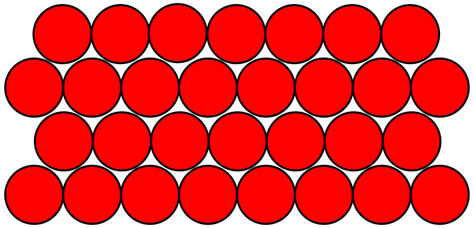
2. Chemical Adsorption



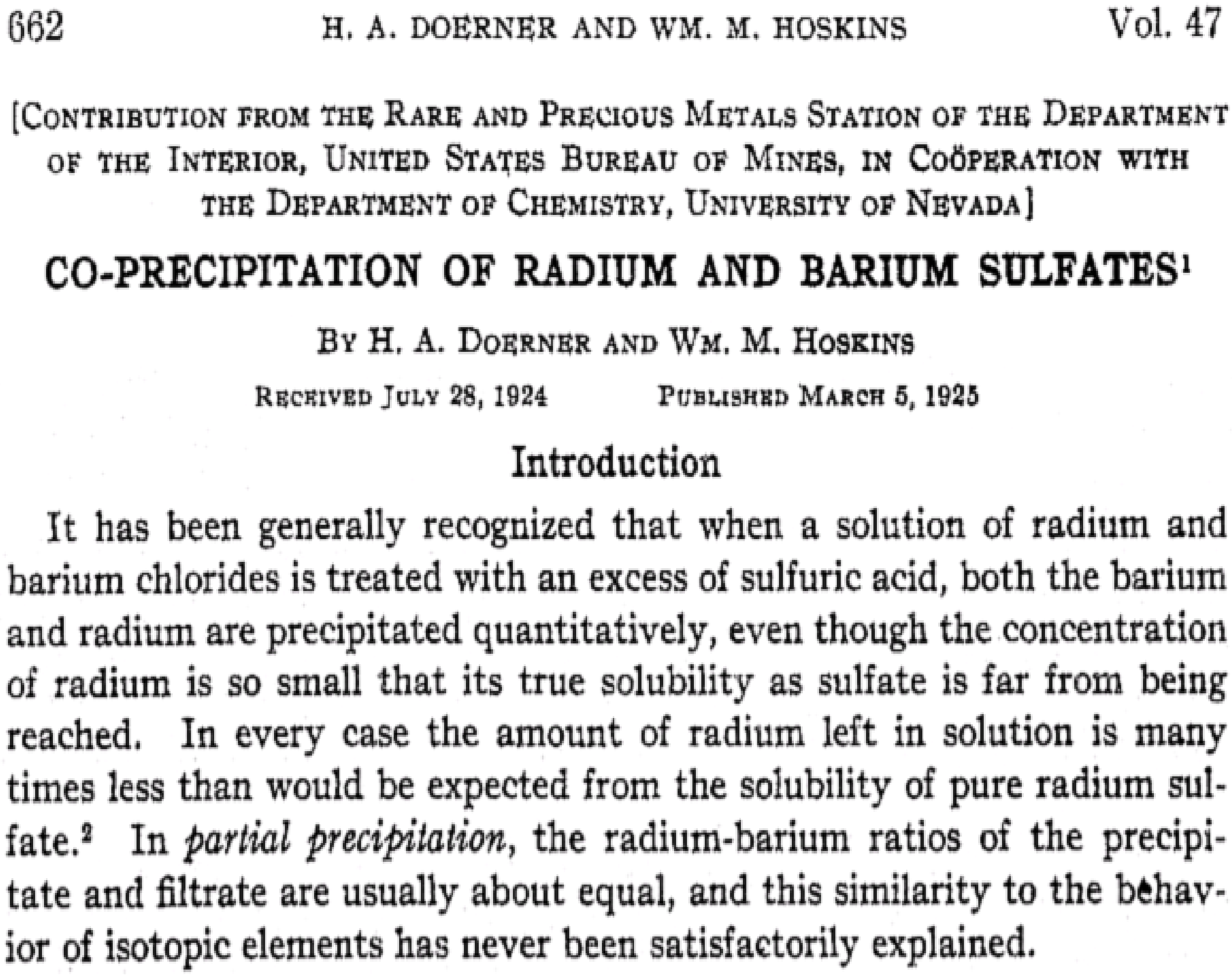
3. Coprecipitation/Solid Solution



4. Precipitation



Radium uptake by barite



[CONTRIBUTION FROM THE RARE AND PRECIOUS METALS STATION OF THE DEPARTMENT OF THE INTERIOR, UNITED STATES BUREAU OF MINES, IN COÖPERATION WITH THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEVADA]

CO-PRECIPITATION OF RADIUM AND BARIUM SULFATES[1]

By H. A. DOERNER AND WM. M. HOSKINS

RECEIVED JULY 28, 1924 PUBLISHED MARCH 5, 1925

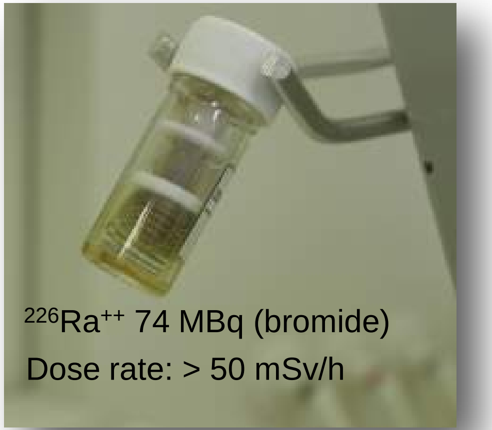
Introduction

It has been generally recognized that when a solution of radium and barium chlorides is treated with an excess of sulfuric acid, both the barium and radium are precipitated quantitatively, even though the concentration of radium is so small that its true solubility as sulfate is far from being reached. In every case the amount of radium left in solution is many times less than would be expected from the solubility of pure radium sulfate.[2] In *partial precipitation*, the radium-barium ratios of the precipitate and filtrate are usually about equal, and this similarity to the behavior of isotopic elements has never been satisfactorily explained.

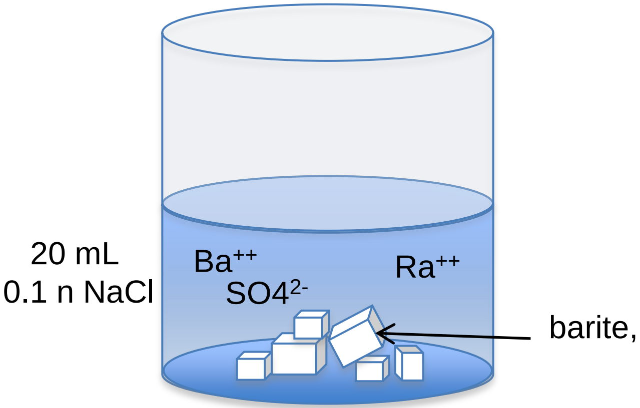
Curie et al., 1898, Doerner & Hoskins, 1925, Hahn, 1936, Jucker & Treadwell, 1954, Gordon & Rowley, 1957, Langmuir & Riese, 1985)

Experimental setup

- **Stock solution:** 8.8 x 10^{-4} mol/L $^{226}Ra^{2+}$
- **Experiment:** batch experiments with V = 20 mL
  5 x 10^{-6} mol/L $^{226}Ra^{2+}$
- **Ionic strength:** 0.1 n NaCl
  solubility of pure $RaSO_4$ at 0.1 n NaCl: ~ 2 x 10^{-5} mol/L
- **Solid/Liquid:** 0.5 g/L, 5 g/L
- **Variation of** barite type


$^{226}Ra^{++}$ 74 MBq (bromide)

Dose rate: > 50 mSv/h



Relevance of solid solution formation

- **Example calculation (GEMS-PSI)**

  Solubility of pure $RaSO_4$:

  0.1 n NaCl background electrolyte, 25 °C

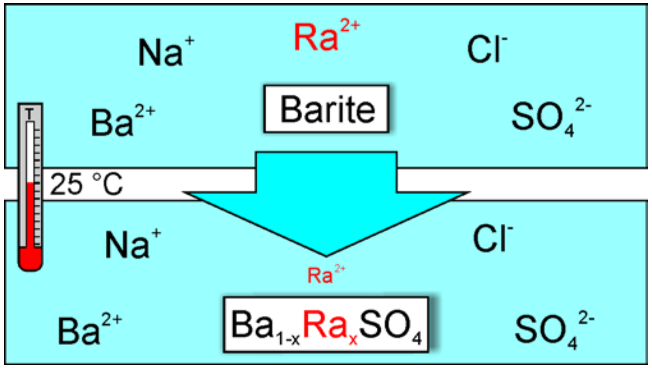
  c(Ra)aq in equilibrium: **$2 \cdot 10^{-5}$ mol/L**

  Solublity of Ra in equilibrium with a

  $(Ba,Ra)SO_4$ solid solution

  (0.5 g/L barite; $a_0 = 0$)

  $c(Ra)_{aq}$ in equilibrium: **$4 \cdot 10^{-8}$ mol/L**



What do we need to know …

… in order to describe the Ra solubility in the presence of barite?

The recrystallization process

- Will pure $BaSO_4$ recrystallize to a $Ba_{1-x}Ra_xSO_4$ solid solution?
- Spatial distribution of Ra within the solid?

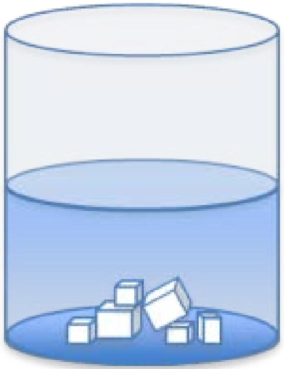
Thermodynamics of the system Ra - Ba - SO_4 - H_2O

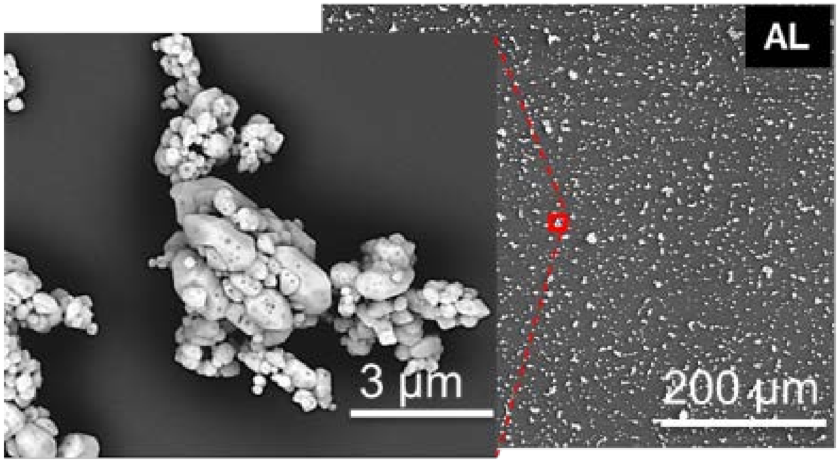
- Aqueous speciation
- Solubility of end-members
- Thermodynamic data of mixing

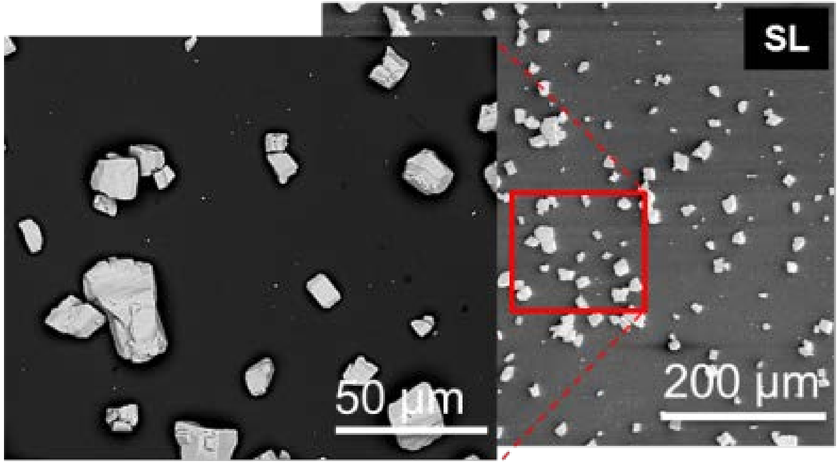
Recrystallization experiments: setup

Starting conditions

- $5 \cdot 10^{-6}$ mol/L $^{226}Ra^{2+}$
- Ionic strength (NaCl): 0.1 n
- Solid/Liquid: 0.5 g/L, 5 g/L
- Temperature: ambient conditions
- pH ~ 5.0

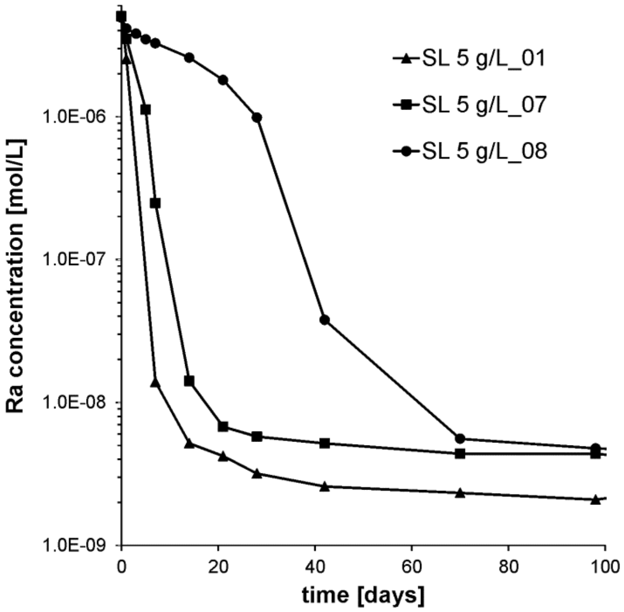


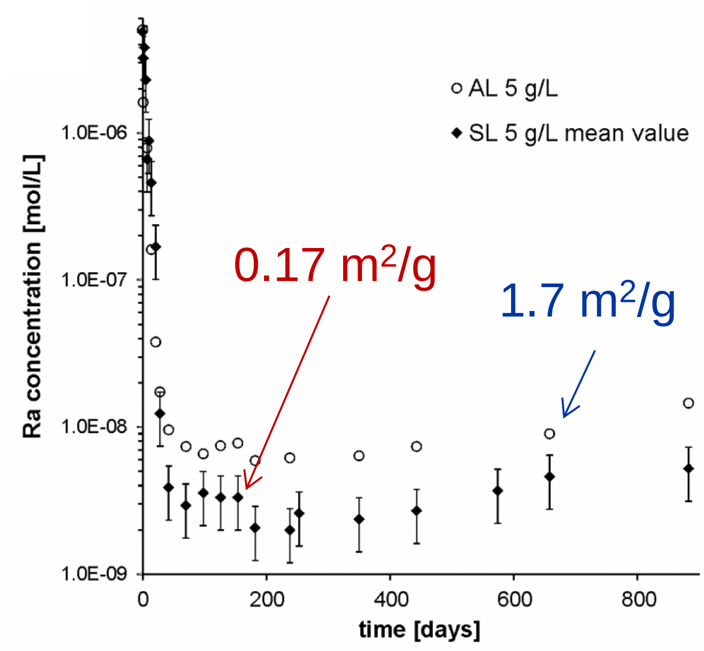




Solubility of pure $RaSO_4$ at I = 0.1 n (RT):
~ $2 \cdot 10^{-5}$ M

Ra uptake by barite at ambient conditions (5 g/L)



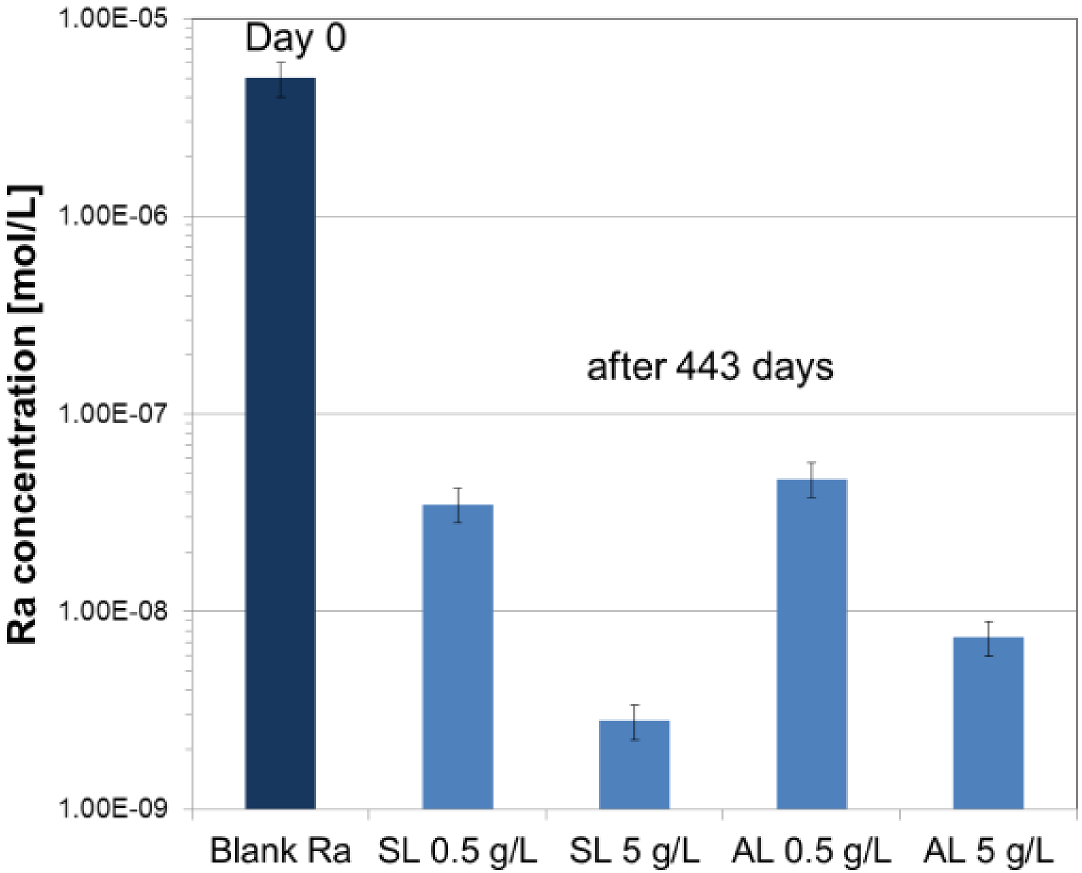


0.17 m^2/g

1.7 m^2/g

- Ra concentration reduced by more than 99% in the presence of barite
- Ra decrease with time is not directly related to barite surface area

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



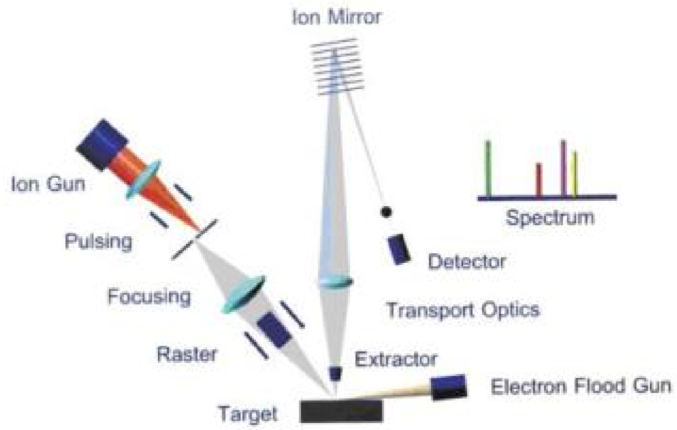
- Mass balance calculations give a final **Ra/Ba** ratio of

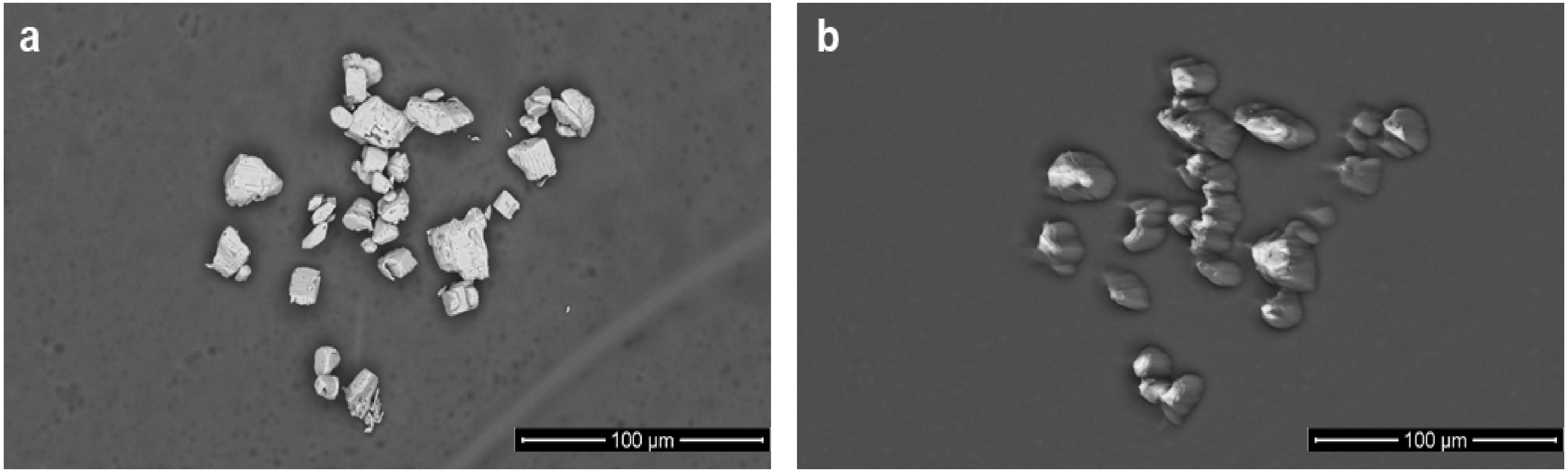
  2.5×10^{-4}
  for 5 g/L barite at RT

  2.5×10^{-3}
  for 0.5 g/L barite at RT

Spatial distribution of Ra?

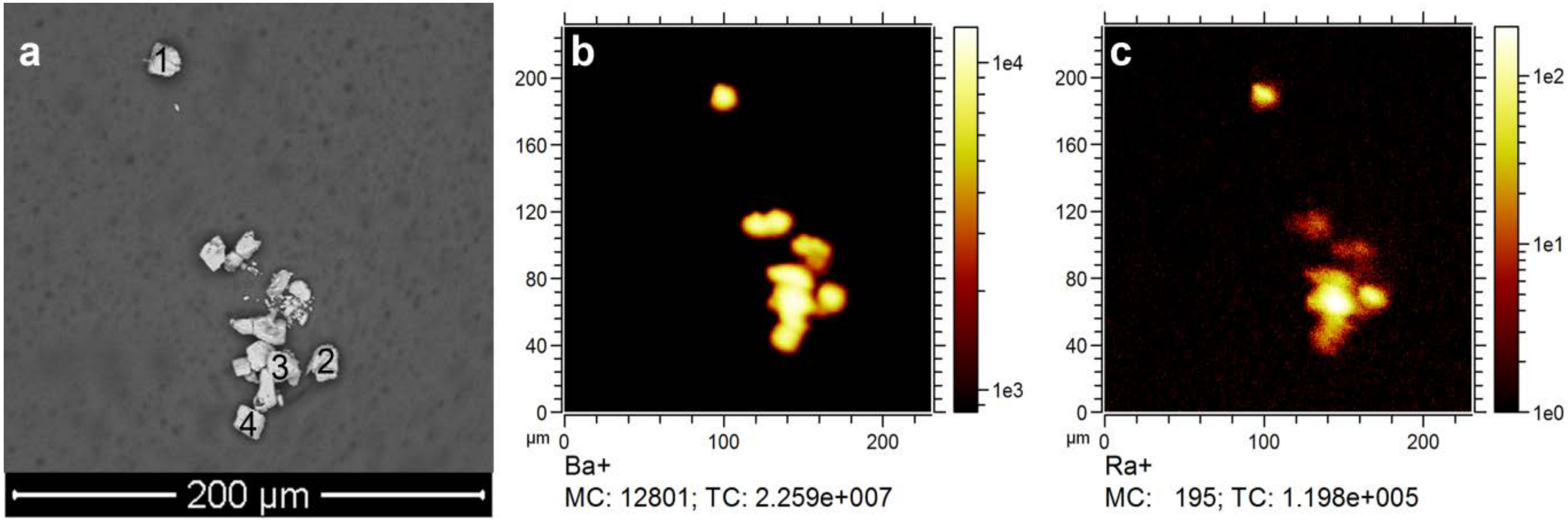
- ToF-SIMS
  - Sachtleben barite 0.5 g/L
  - Analysis of complete grains
  - Determination of Ba and Ra distribution





Does barite take up Ra?

- Optimization of the spatial resolution → Identification of individual barite grains
- Integrated intensity distribution of the Ba and Ra signal



All grains contain Radium in similar concentrations

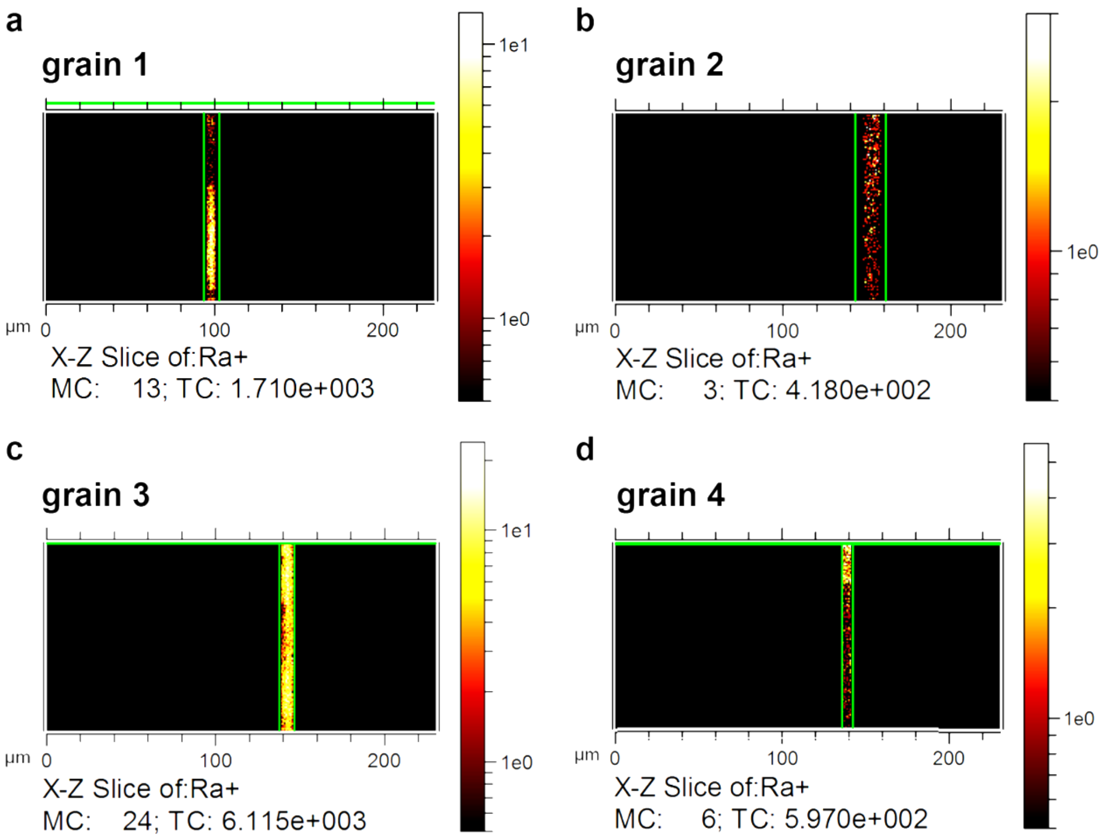
Compositional homogeneity of radiobarite ?

- Spatial distribution of Ra within the barite particles

- Depth resolution: ~ 0.1 µm

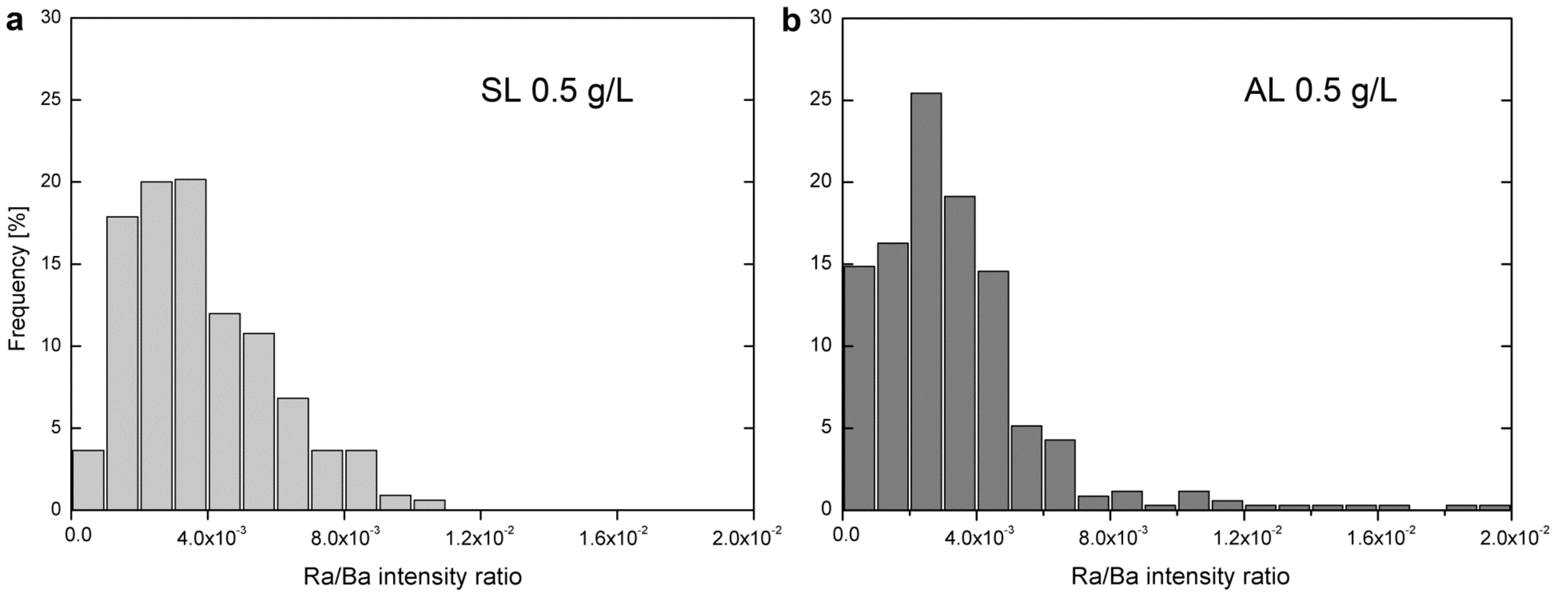
- Indication of a complete recrystallization of barite to a $Ba_{1-x}Ra_xSO_4$ solid solution

Depth profiles of integrated Ra signals



Klinkenberg, Brandt et al. (2014) ES&T (accepted)

Ra/Ba ratio derived from ToF - SIMS measurements



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

Klinkenberg, Brandt et al. (2014) ES&T (accepted)

What do we need to know …

… in order to describe the Ra solubility in the presence of barite?

The recrystallization process

- Will pure $BaSO_4$ recrystallize to a $Ba_{1-x}Ra_xSO_4$ solid solution?
- Spatial distribution of Ra within the solid?

Thermodynamics of the system Ra - Ba - SO_4 - H_2O

- **Aqueous speciation**
- **Solubility of end-members**
- **Thermodynamic data of mixing**

Thermodynamic Properties of Radium

The Nagra/PSI TDB 01/01 is one of the reference data bases for geochemical modelling of nuclear waste repositories.
In the Nagra/PSI TDB 01/01 all thermodynamic constants for Ra are taken from Langmuir & Riese (1985).

The Ra phases and species included in TDB 01/01 are
- Ra(s)
- Ra^{2+}
- $RaOH^+$
- $RaCl^+$
- $RaCO_3$(aq), $RaCO_3$(s)
- $RaSO_4$(aq), $RaSO_4$(s)

Geochimica et Cosmochimica Acta Vol. 49, pp. 1593–1601
© Pergamon Press Ltd. 1985. Printed in U.S.A.
0016-7037/85/$3.00 + .00

The thermodynamic properties of radium

DONALD LANGMUIR
Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401

and

ARTHUR C. RIESE
Atlantic Richfield Company, Corporate Technology, 515 South Flower Street, Los Angeles, CA 90071

(*Received June* 27, 1984; *accepted in revised form April* 17, 1985)

Abstract—The enthalpy, Gibbs free energy, and entropies of aqueous radium species and radium solids have been evaluated from empirical data, or estimated when necessary for 25°C and 1 bar. Estimates were based on such approaches as extrapolation of the thermodynamic properties of Ca, Sr, and Ba complexes and solids plotted against cationic radii and charge to radius functions, and the use of the Fuoss or electrostatic mathematical models of ion pair formation (LANGMUIR, 1979). Resultant log K (assoc) and ΔH^0 (assoc) (kcal/mol) values are: for $RaOH^+$ 0.5 and 1.1; $RaCl^+$ −0.10 and 0.50; $RaCO_3^0$ 2.5 and 1.07; and $RaSO_4^0$ 2.75 and 1.3. Log Ksp and ΔH^0 (dissoc) (kcal/mol) values for $RaCO_3$(c) and $RaSO_4$(c) are −8.3 and −2.8, and −10.26 and −9.4, respectively.

Trace Ra solid solution in salts of Pb and of the lighter alkaline earths, has been appraised based on published distribution coefficient (D) data, where $D \simeq (mM^{2+})(N_{RaX})/(mRa^{2+})(N_{MX})$ (m and N are the aqueous molality and mole fraction of Ra and cation M in salt X, respectively. The empirical solid solution data have been used to derive both enthalpies and Gibbs free energies of solid solution of trace Ra in sulfate and carbonate minerals up to 100°C. Results show that in every case D values decrease with increasing temperature. Among the sulfate and carbonate minerals, D values decrease for the following minerals in the order: anhydrite > celestite > anglesite > barite > aragonite > strontianite > witherite > cerussite.

INTRODUCTION

THE GEOCHEMISTRY of radium in the environment is of considerable interest because of the potential danger the element poses to human and animal health. Radium activities in excess of the U.S. ENVIRONMENTAL PROTECTION AGENCY (1977) limit of 5 pCi/l for Ra-226 plus Ra-228 in drinking water are found in ground waters from uraniferous rocks and in waters associated with uranium mining and mill tailings, and can be expected in waters that have contacted low or high level nuclear wastes.

To accurately model and predict the environmental behavior of radium in any of these situations, we need a reliable and complete thermodynamic data base for radium. Such a data base does not exist. Nearly all of the thermodynamic data for radium given by the National Bureau of Standards (WAGMAN *et al.*, 1982) has been estimated (PARKER, 1984, oral commun.). Such estimation is based on smoothly varying and known (usually) properties of the other alkaline earth aquo-complexes and solids. Of all the aqueous species and solids listed by WAGMAN *et al.* (1982), only Ra^{2+} ion and $RaSO_4$(c) are likely to have any significance in the environment. On the other hand, $RaCO_3$(c) as a solid solution component, and the complexes $RaOH^+$, $RaCl^+$, $RaCO_3^0$ and $RaSO_4^0$ should influence radium mobility in some waters. However, no thermodynamic data are available for these entities.

THERMODYNAMIC DATA FOR PURE RADIUM SOLIDS AND AQUEOUS SPECIES

In this study, several approaches were used to estimate the thermodynamic properties of radium solids and aqueous species. The increase in cation radius of the divalent alkaline earths from Ca to Sr and Ba to Ra suggests that the bonding between these cations and common ligands should be more ionic or electrostatic for Ra than for Ba, Sr or Ca. Thus, plots of the thermodynamic properties of the alkaline earth sulfate complexes, for example, against the cation radii should approach Fuoss or electrostatic model behavior as one moves from Ca towards Ra (see LANGMUIR, 1979). The comparison is, however, best made among cations likely to have the same coordination number with a given ligand. For Ra, the coordination number is 8 or 12 in its solids (SHANNON, 1976). In a few instances, as in aragonite, Ca exists in 8-fold coordination (radius 1.12 A); however, the best comparison is between Sr, Ba and Ra in 8-fold coordination, with effective radii of 1.26, 1.42 and 1.48, respectively (SHANNON, 1976).

Examination of ΔG^0 and ΔS^0 of association of the alkaline earth sulfate complexes, plotted against a charge to radius function (LANGMUIR, 1979), shows that the ΔG^0 data approach pure electrostatic behavior from $CaSO_4^0$ to $BaSO_4^0$. Similar behavior is evident for ΔS^0 of complexation. This suggests that if the empirical ΔG^0 of formation of a complex can be accurately modeled with the electrostatic model, then

Solubility and mixing model

- **Solubility products** $BaSO_4$ $\log(K_{SP}) = - 9.97$ to 9.98
  $RaSO_4$ $\log(K_{SP}) = -10.26$ to -10.41

- **Regular solid solution proposed in literature, parameters of the solid solution $Ra_xBa_{1-x}SO_4$**
  $a_0 = 0.35$ (Zhu et al.) - 2.5 (Curti et al.)

$a_0 = W/RT$
a_0 Guggenheim interaction parameter
W enthalpy interaction paramter, W is independent of temperature

Solid-solution aqueous solution equilibria: Lippmann

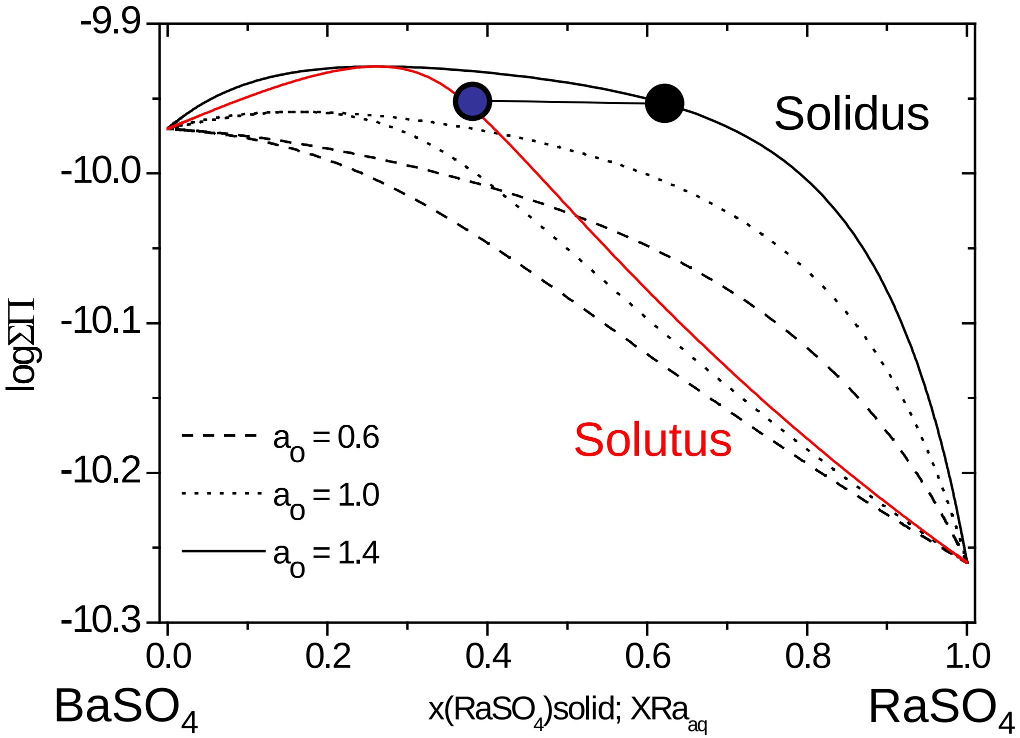
Total solubility product

$$\Sigma\Pi = [A^-]\,([B^+] + [C^+])$$

$$\ln(f_i) = a_0\,(1 - X_i)^2$$

Solidus $$\Sigma\Pi_{eq} = K_{BA}x_{BA}f_{BA} + K_{CA}x_{CA}f_{CA}$$

Solutus $$\Sigma\Pi_{eq} = 1 \Big/ \left(\frac{x_{B,aq}}{K_{BA}f_{BA}} + \frac{x_{C,aq}}{K_{CA}f_{CA}}\right)$$



Relevant parameters: interaction parameter and endmember solubilities

(F.Lippmann, 1977)

Determination of the interaction parameter: the Single Defect Method (SDM)

Regular solid solution model $\Delta H_{mix} = x_A x_B W$

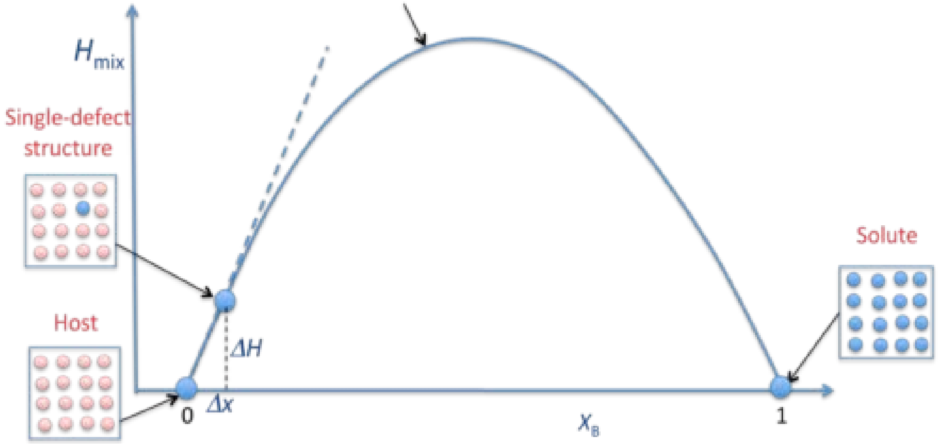
In very dilute solid solutions:

$$W = \left.\frac{dH_{\text{mix}}}{dx_{\text{B}}}\right|_{x_{\text{B}}=0} \approx \frac{\Delta H}{\Delta x}$$

W enthalpy interaction paramter

$a_0 = W/RT$

a_0 Guggenheim interaction parameter



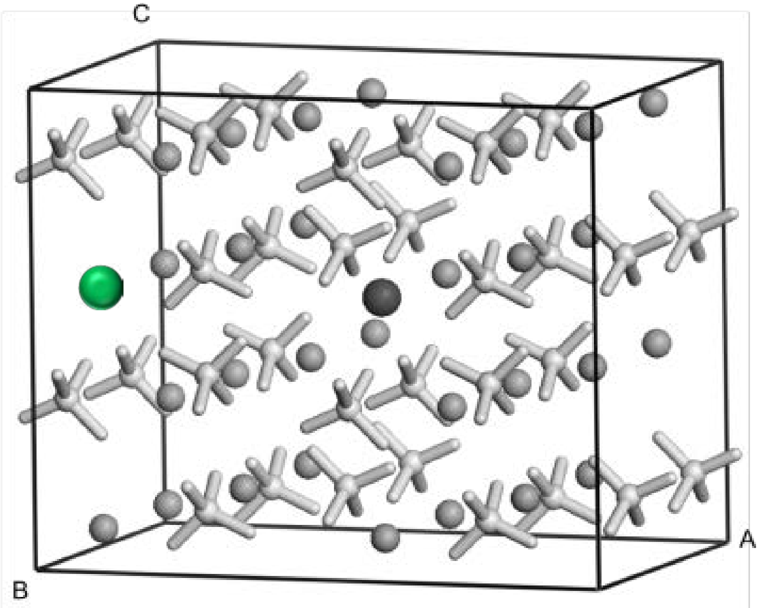
ΔH is computed ab initio as the excess energy of a supercell with a single defect (Δx is the mole fraction of the solute component in the supercell)

(Sluiter & Kawazoe, 2002)

The SDM calculations for a 2 x 2 x 2 supercell of barite

$Ba_{31}RaS_{32}O_{128}$

- DFT calculations with CASTEP (Clark et al. 2005)
- Exchange-correlation functional of Wu & Cohen (2006)
- Ultra-soft OTFG pseudopotentials (Materials Studio 6, Accelrys)
- Plane wave cutoff 910 eV



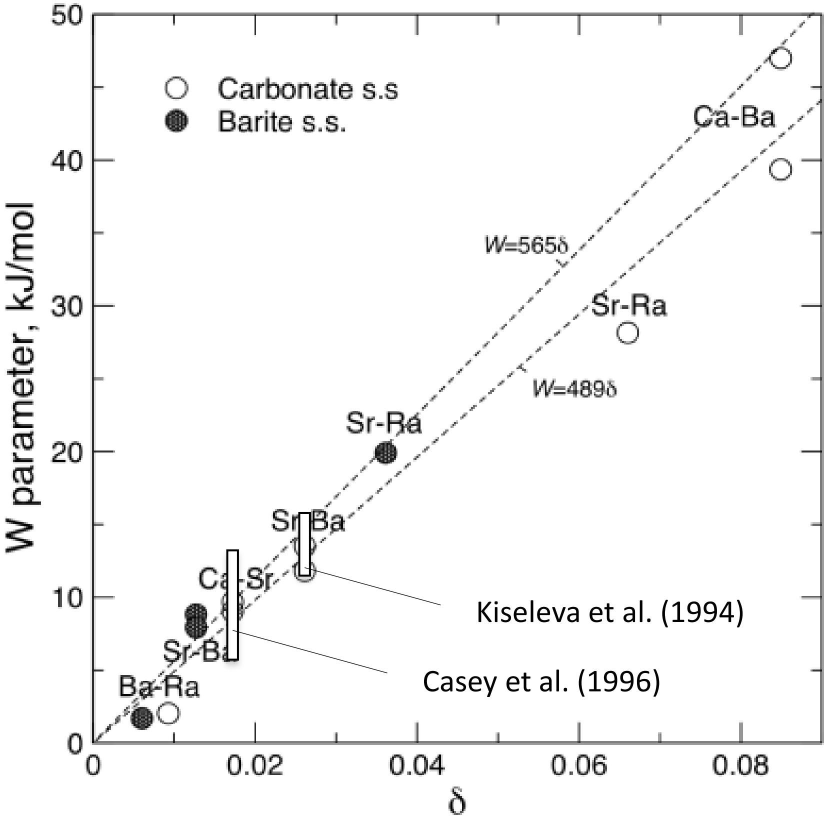
Vinograd, Brandt et al. (2013), GCA

Verification of the structure model

	BaSO$_4$ XRD (Hill et al., 1977)	GGA-WC	RaSO$_4$ XRD / EXAFS	GGA-WC
a	8.884	8.865	9.07 1)	9.099
b	5.456	5.433	5.52 1)	5.507
c	7.157	7.142	7.28 1)	7.294
Ra/Ba - O	2.952	2.940	2.996 2)	3.006
S - O	1.475	1.480	1.485 2)	1.481
Ra/Ba - O - S	133.9°	133.3°	127° 2)	135°

1) Weigl et al. 1968; 2) Ekberg et al. 2012

Verification of SDM interaction parameters: results for carbonate and barite solid solutions



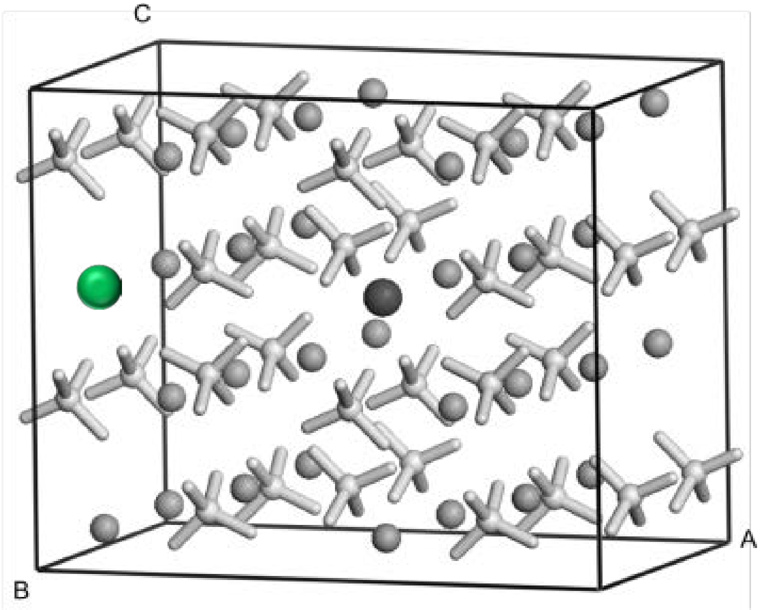
Kiseleva et al. (1994)

Casey et al. (1996)

The predicted *W* values correlate linearly with $\delta = \left(\Delta V / \overline{V}\right)^2$, the relationship is expected from atomistic solid solution theories, e.g. Davis & Navrotsky 1983

Determination of a_0 for Ra-Ba-SO_4

$Ba_{31}RaS_{32}O_{128}$

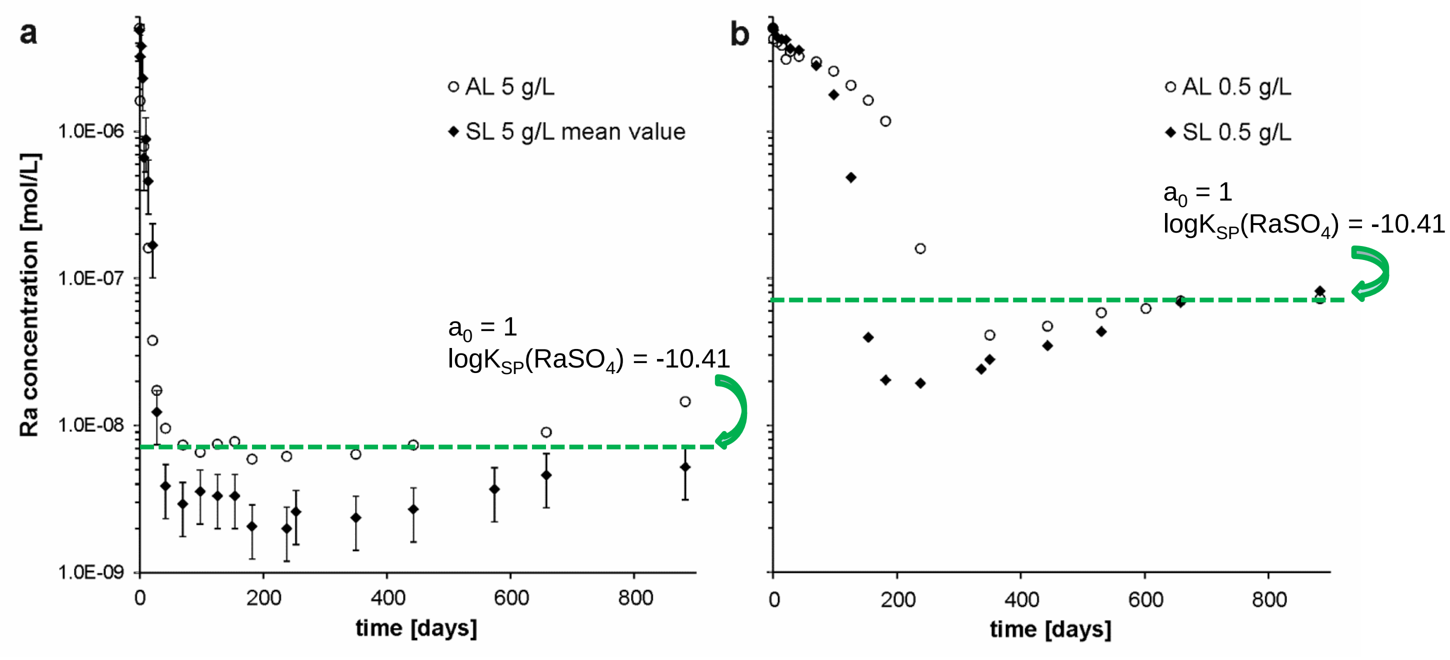


$W_{BaRa} = 2.43 \pm 1.0$ kJ/mol

$a_0 = 1.0 \pm 0.4$

Vinograd, Brandt et al. (2013), GCA

Ra uptake by barite at ambient conditions



- Good agreement with thermodynamic prediction at $a_0 = 1.0$ and $\log K_{sp}(RaSO_4) = -10.41$

Brandt, Klinkenberg et al. (2014), GCA, in preparation

Conclusions

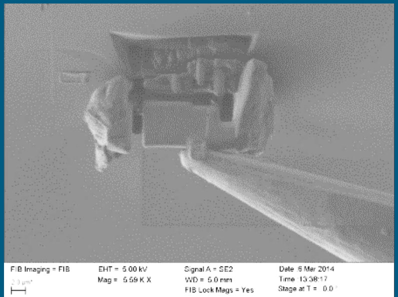
The recrystallization process

- Pure $BaSO_4$ recrystallized to a $Ba_{1-x}Ra_xSO_4$ solid solution within weeks to months depending on the S/L ratio and the type of barite

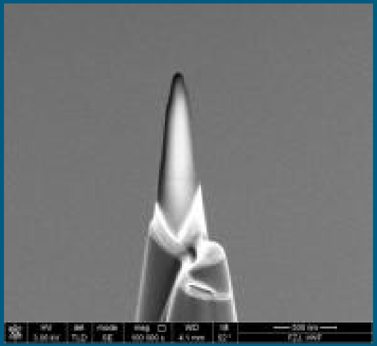
The solubility of Ra in equilibrium with a $Ba_xRa_{1-x}SO_4$ solid solution

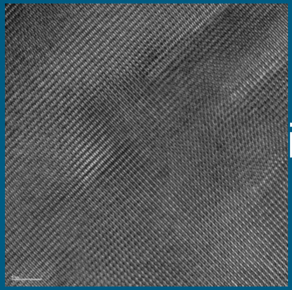
- According to atomistic modelling, the molecular level mixing model is slightly non-ideal with a_0 in the range of 0.6 to 1.4; a_0 is narrowed down from a range in the literature between 0.35 and 2.3
- A best fit between experimental data and thermodynamic predictions achieved with $a_0 = 1.0$ and $\log K_{sp}(RaSO_4) = -10.41$
- To observe the complete recrystallization, experiments longer than 800 days are necessary

Uptake of Radium by $BaSO_4$ - Outlook

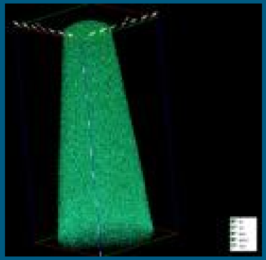


Sample preparation
by
Focused Ion Beam





Structural
information
TEM



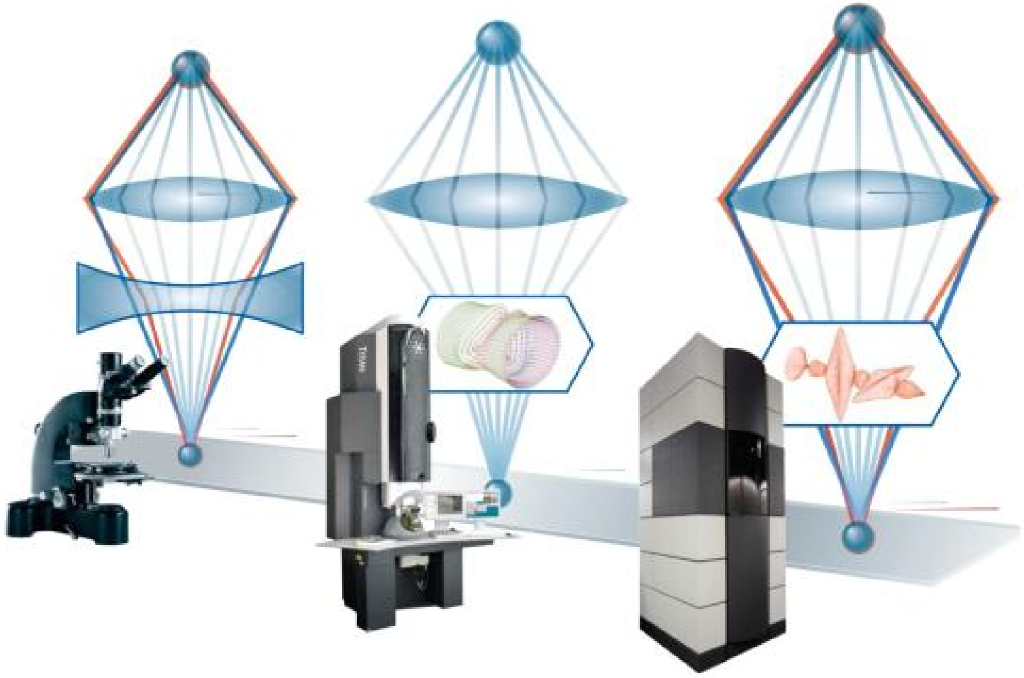
Chemical
composition
LEAP

Development
of a model for
Ra uptake

High resolution TEM

FEI Titan T:

- ❖ Acceleration voltage: 80 kV to 300 kV
- ❖ Information limit: 80 pm
- ❖ Spherical aberration correction unit

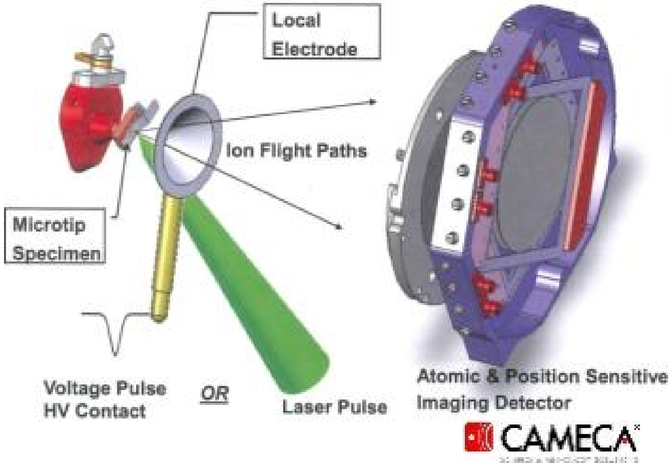


FEI Titan T, spherical abberation corrected

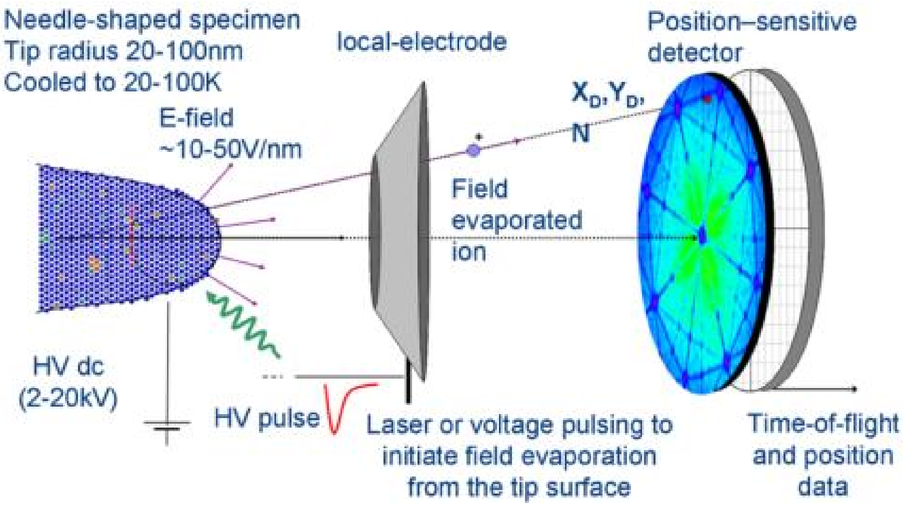
FEI Pico, spherical and chromatic abberation corrected

All images: www.er-c.org

LEAP Local Electrode Atom Probe



Cameca LEAP 4000X HR system



University of Oxford

Thank you for your attention!

The research leading to these results has received partial funding from the German Federal Ministry of Education and Research (BMBF) ImmoRad project.

Federal Ministry
of Education
and Research

The research leading to these results has received partial funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement n° 269688

SKIN

EURATOM

The research leading to these results has received partial funding from the swedish Svensk Kärnbränslehantering AB, SKB

SKB
Svensk Kärnbränslehantering AB