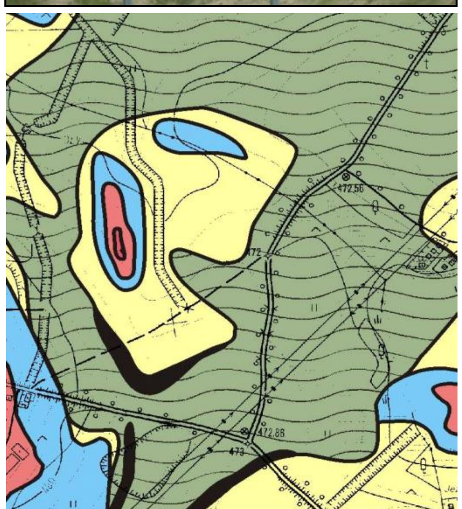
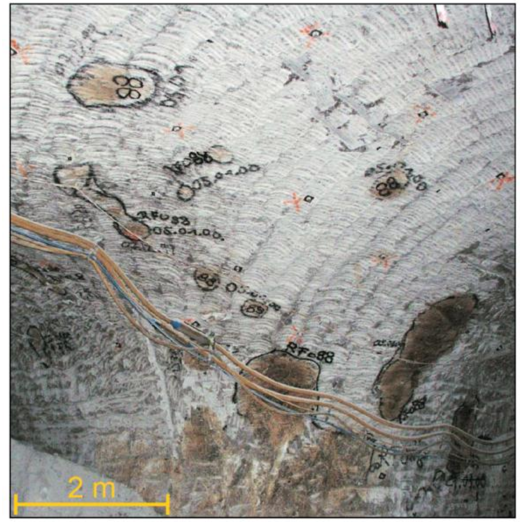
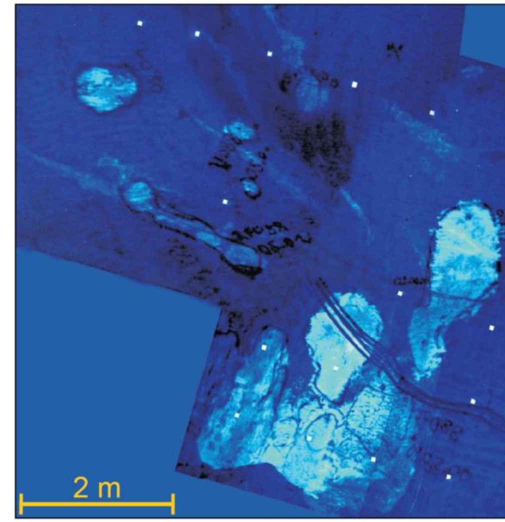






Results of the Salt Club Workshop: Natural Analogues for Safety Cases of Repositories in Rock Salt

U. Noseck, J. Wolf, W. Steininger

Salt Club Workshop:
Natural Analogues for Safety Cases of Repositories in Rock Salt

- 4. and 5. September 2012 in Braunschweig
- including visit of ERAM (6. September)
- hosted by PTKA-WTE, GRS
- 37 participants from 8 countries
  (Salt Club members + CH, CZ, F and UK)
  - research institutes
  - universities
  - regulators
  - federal institutes
  - engineering companies
  - salt mining and oil/gas storage industry

Salt Club Workshop:
Natural Analogues for Safety Cases of Repositories in Rock Salt

- part I: presentations
  - organised in 4 sessions:
    I. overview session
    II. integrity of rock salt
    III. long-term properties of technical barriers
    IV. chemical and microbial processes

- part II: workshop
  - working groups
  - wrap-up discussion

Part I: Presentations

R. Alexander: The changing role of natural analogues in waste disposal
C. Pescatore: Current activities of NEA-FSC

General aspects

N. Rempe: The current status of the geological disposal of radioactive waste in the USA
J. Janeczek: The current status of the geological disposal of radioactive waste in Poland
E. Verhouf: The current status of the geological disposal of radioactive waste in the Netherlands
W. Steininger, U. Noseck: The current status of the geological disposal of radioactive waste in Germany

Disposal programmes

J. Wolf: Overview on potential analogues for repositories in rock salt
N. Rempe: Geological analogues for hot waste and for radionuclide releases
J. Urai: Deformation mechanisms and constitutive behavior during long term creep of salt formations
M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience
J. Urai: Geological constraints on mobility of brines and hydrocarbons in salt
M. Mertineit: The mechanical behavior and geometry of anhydrite layers in rock salt: Thermomechanical experiments
J. Hammer: The mechanical behavior and geometry of anhydrite layers in rock salt: Observations from nature
M. Knauth, W. Minkley: Integrity of rock salt formation under static and dynamic impact
J. Urai: Geomechanical modeling of salt tectonics and structural evolution in salt

Integrity of rock salt

F. Crotogino: Experiences from Gas storage in salt caverns
V. Lukas: Experiences from salt mining and hazardous waste disposal

Long-term behaviour of technical barriers

V. Metz: Ra-Ba Co-precipitation in a Large Scale Evaporitic System: Field Study and Laboratory results
V. Havlova: Results from Ruprechtov Site as analogue for uranium retention in
G. Bracke: Properties and behavior of hydrocarbons in rock salt
A. Meleshyn: Analogues for microbial effects in rock salt

Microbial and chemical processes

Part II: Working Groups / Wrap-up Discussion

- working in 4 groups
  - What are the most important points you have learned?
  - What are the key unresolved issues?
  - What are your highest priority recommendations for future NA studies for salt?
  - Do you have any other thoughts you would like to recommend to the Salt Club?

- plenum
  - discussion of results
  - outlook

Results (I): General Aspects of NA

- NA are an essential part of the Safety Case portfolio (Finland, Sweden)
- “When is a study an analogue?
  Are there objective criteria?
  Laboratory studies $\rightarrow$ NA
  BE CAREFUL USING NA (overinterpretation)
  $\rightarrow$ there is now more realism about what NA studies can achieve

- How to apply NA in a Safety Case?
  NEA/RWM/FSC(2008)3: analogue, analogy, anecdote
- “Still too many bottom-up projects, driven by science, not SA or safety case (because science is sexy) – need to think about this over the next couple of days“ (Russell)
- Safety Case should lead NA, not vice versa
  How to document / communicate NA?

Analogues for the Integrity of rock salt

Relevant aspects for the integrity of the geological barrier

- Impact of subrosion and diapirism
- Transport pathways in the geological barrier
- Mechanical load capacity
  - Earthquakes
  - Competent rock formations
- Thermal load capacity
  - High temperatures (waste)
  - Low temperatures (glacials)

Water pathways in the geological barrier

German safety requirements (BMU 2010): It has to be shown that

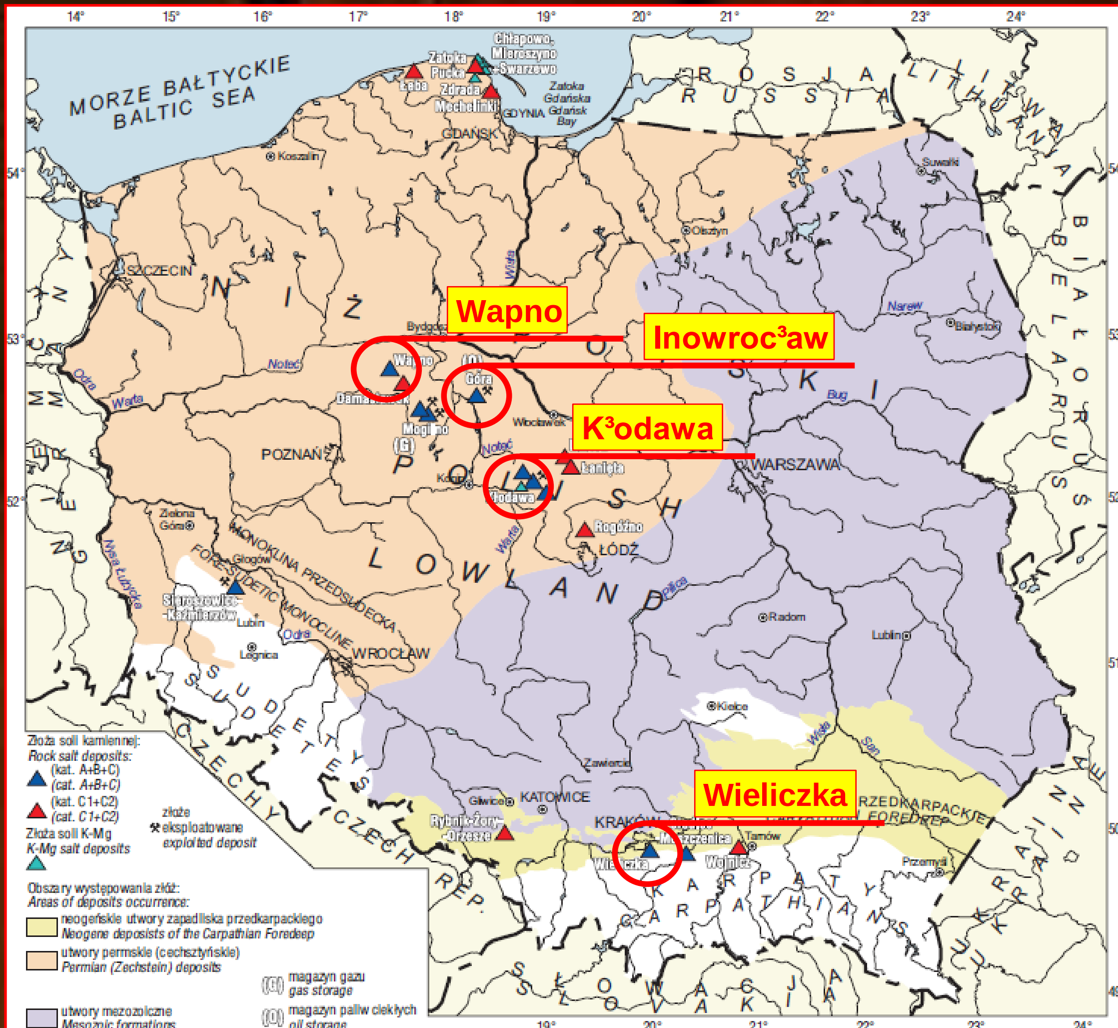
- *the formation of secondary water pathways, which might lead to in- or outflow of evtl. contaminated brines within the isolating rock zone can be excluded, and*
- *Any pore water that may be present in the isolating rock zone does not participate in the hydrogeological cycle outside of the isolating rock zone as defined by water legislation.*

Arguments that no fluids from adjacent formations intruded into the salt formation can be derived from Natural Analogues:

- Mechanical behaviour of rock salt → presentation Jens Wolf
- Chemical composition and isotope content of fluid inclusions (brines and gases)
- Trace element profiles (Br, Rb) in salt rocks

→ Presentation: M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience

Location of salt deposits in Poland



Czapowski G. & Bukowski K. Prz. Geol., vol.57, No. 9, 2009

M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience

Zechstein salts – deposited at the final stages of sea water evaporation, rich in Ca, Mg salts

Miocene salts – formed at the initial stage of sea water evaporation, dominated by halite

Isotopes routinely used in water hazard studies in salt mines

M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience

OXYGEN:

$^{18}R = {}^{18}O/{}^{16}O$

$$\delta^{18}O = \left(\frac{^{18}R_{sample} - {}^{18}R_{std}}{^{18}R_{std}} \right) \cdot 1000‰$$

DEUTERIUM:

$^{2}R = {}^{2}H/{}^{1}H$

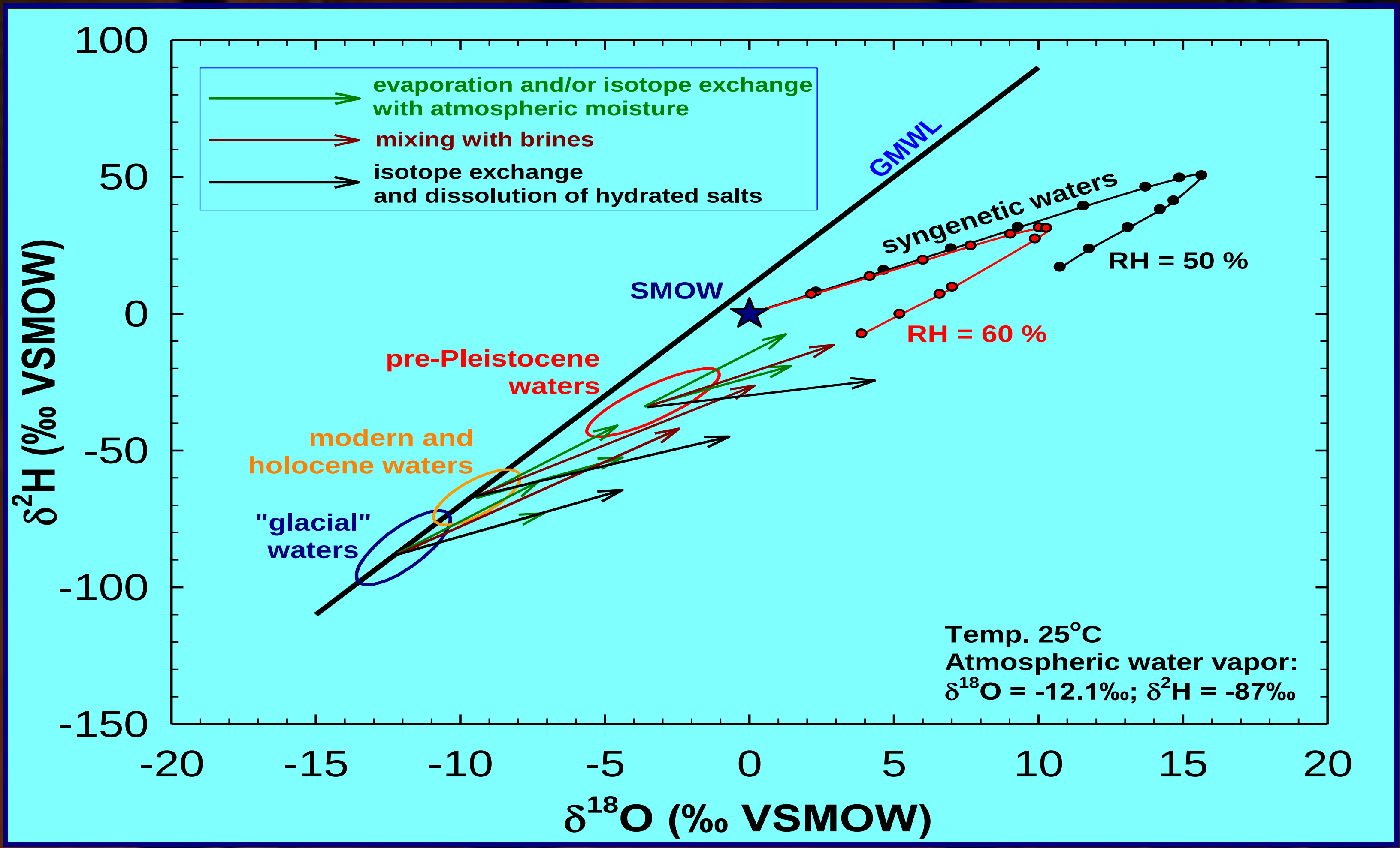
$$\delta^{2}H = \left(\frac{^{2}R_{sample} - {}^{2}R_{std}}{^{2}R_{std}} \right) \cdot 1000‰$$

Standard: Vienna Standard Mean Ocean Water (VSMOW):

$\delta^{18}O = 0$ ‰ ; $\delta^{2}H = 0$ ‰ ***by definition***

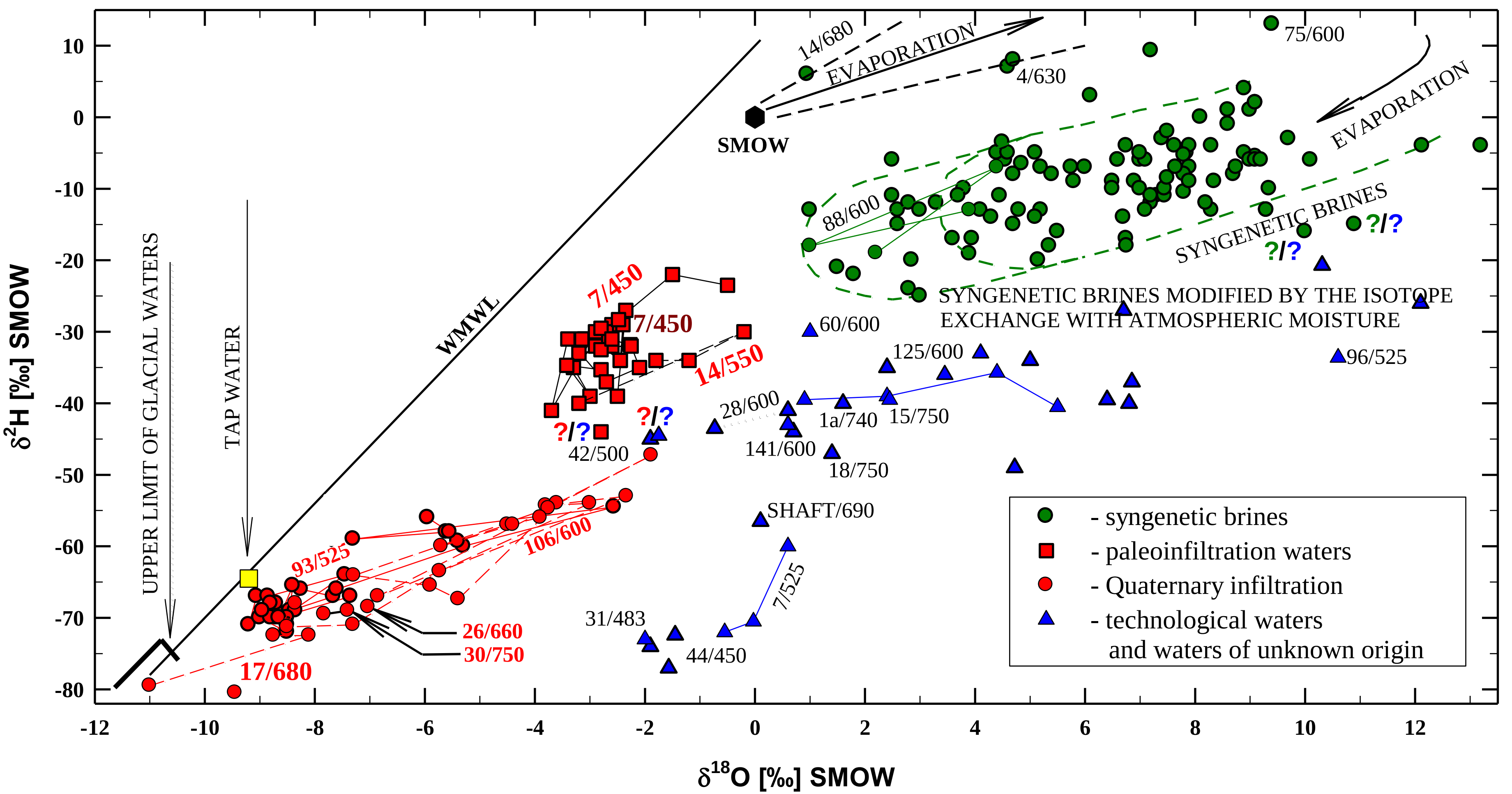
Stable isotope composition of groundwaters in the vicinity of the Polish salt mines

M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience



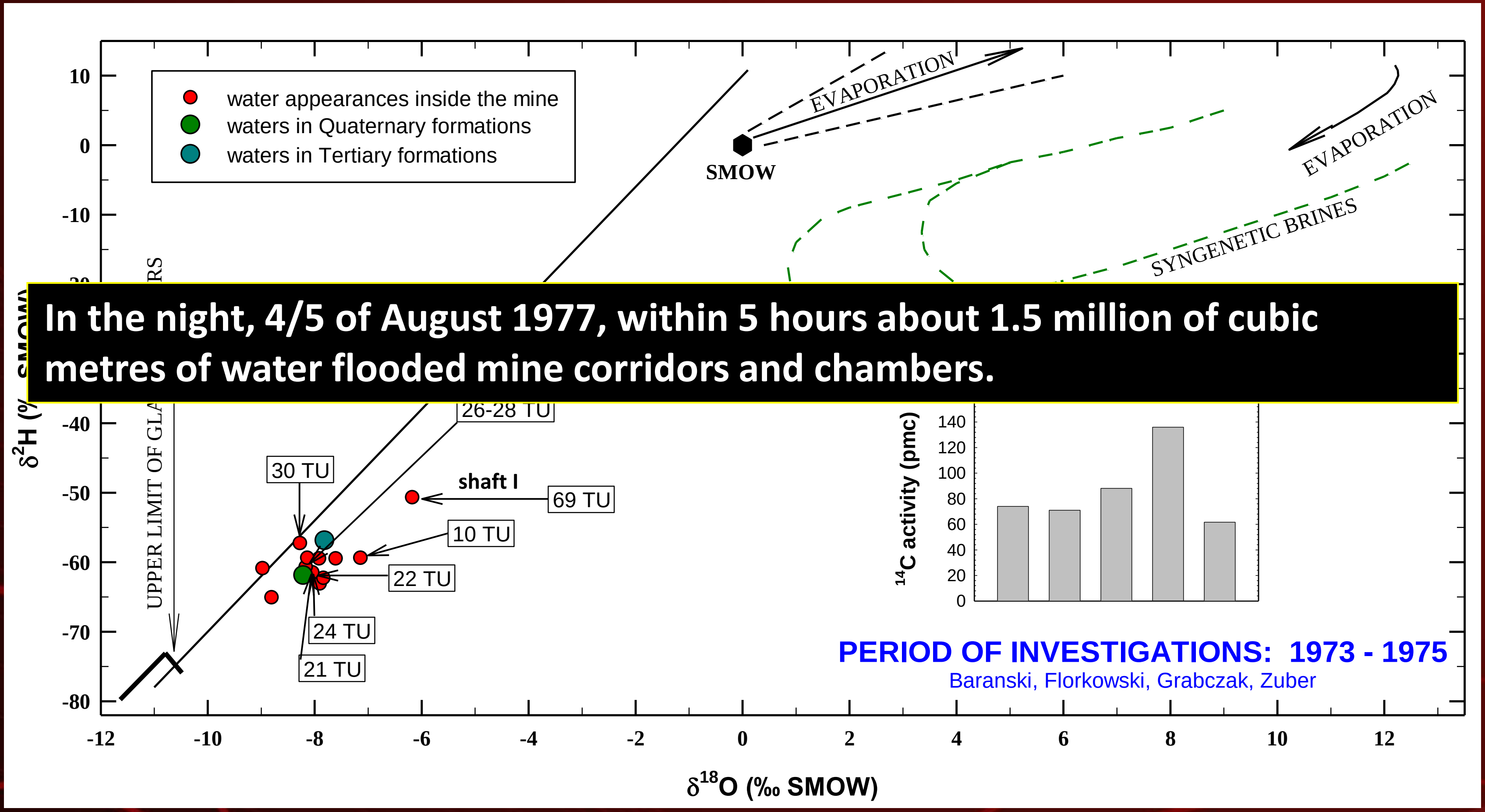
Stable isotope composition of brines in the Klodawa mine

M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience



Stable isotope composition of waters in the Wapno Salt Mine

M. Dulinski: Isotope monitoring of water appearances in salt mines: the Polish experience

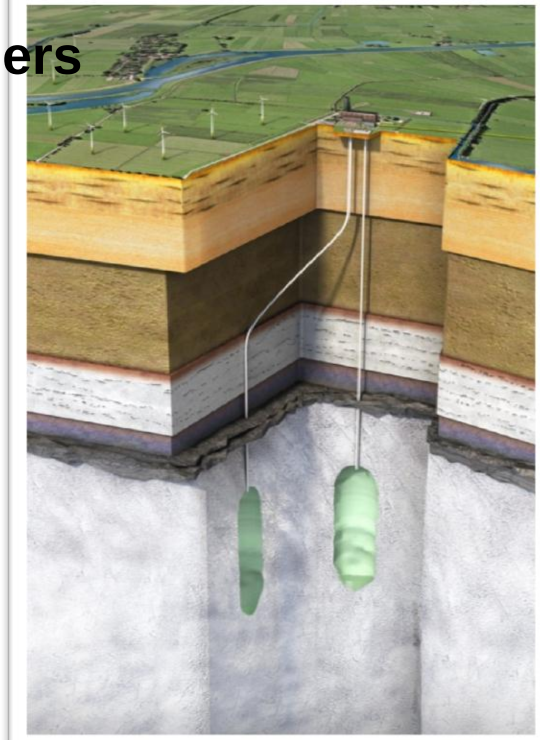


In the night, 4/5 of August 1977, within 5 hours about 1.5 million of cubic metres of water flooded mine corridors and chambers.

Potential of isotope analyses for demonstrating the integrity of salt formations

Method	Objective
$\delta^{18}O$ and $\delta^{2}H$ in brines of Zechstein rock salt	distinguish between meteoric or marine origin of formation waters
$\delta^{37}Cl$ in Zechstein rock salt	Amount of evaporation, input of seawater, re-dissolution of salt
$\delta^{34}S$ and $\delta^{18}O$ in sulfates of Zechstein rock salt	indicate changes in the inflows, restriction conditions, redox reactions, and biogenic processes
$\delta^{13}C$ and $\delta^{18}O$ in carbonates	post-sedimentation transformation of carbonates due to a contact with meteoric waters
$^{87}Sr/^{86}Sr$ in rock salt	modifications of brine chemistry by interaction processes with deep hydrothermal fluids or adjacent rocks
Micro-thermometry of fluid inclusions	Homogenization temperature → temperature during formation of fluid inclusion

Long-term properties of barriers



Not much analogue information at the workshop

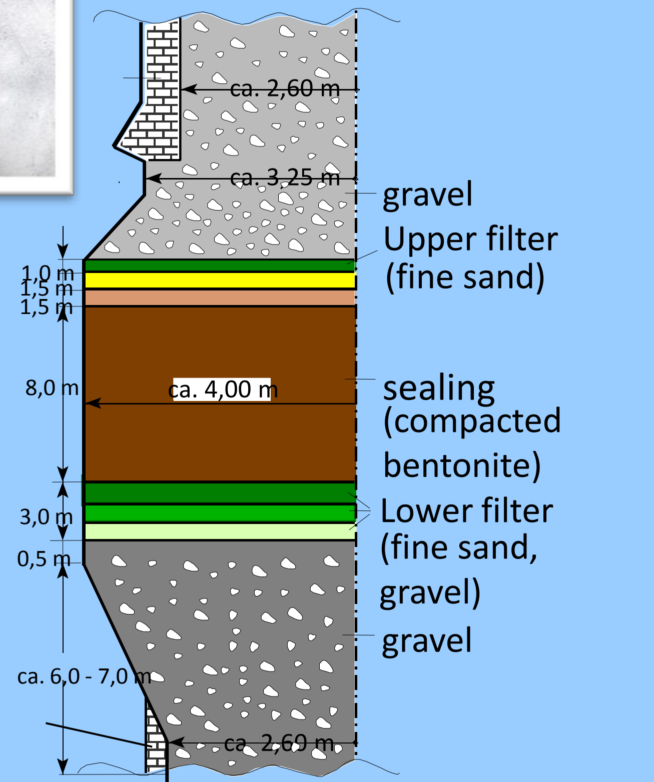
- experiences from salt mining and hazardous waste disposal
- provide very useful practical information on aspects such as design of tunnel backfills, plugs and seals

F. Crotogino: Experiences from Gas storage in salt caverns,

V. Lukas: Experiences from salt mining and hazardous waste disposal

Potential fields for investigations

- performance confirmation monitoring of the seals in hazardous waste repositories over several decades into the future
- Density of H_2 filled gas storage caverns
- More thoughts needed



Analogues for chemical and microbial processes

Processes mainly relevant in case of radionuclide release scenarios

- solubility and sorption of naturally occurring radionuclides

→ V. Metz: Ra-Ba Co-precipitation in a Large Scale Evaporitic System: Field Study and Laboratory results

- hydrocarbons

- microbial activity

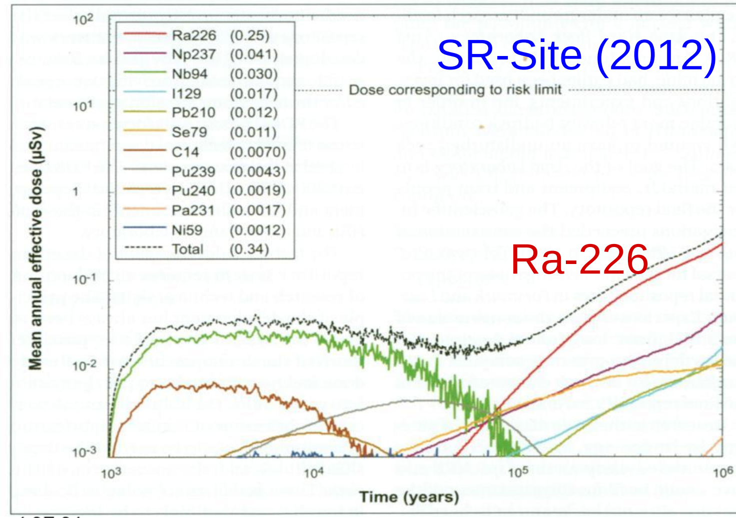
→ A. Meleshyn: Analogues for microbial effects in rock salt

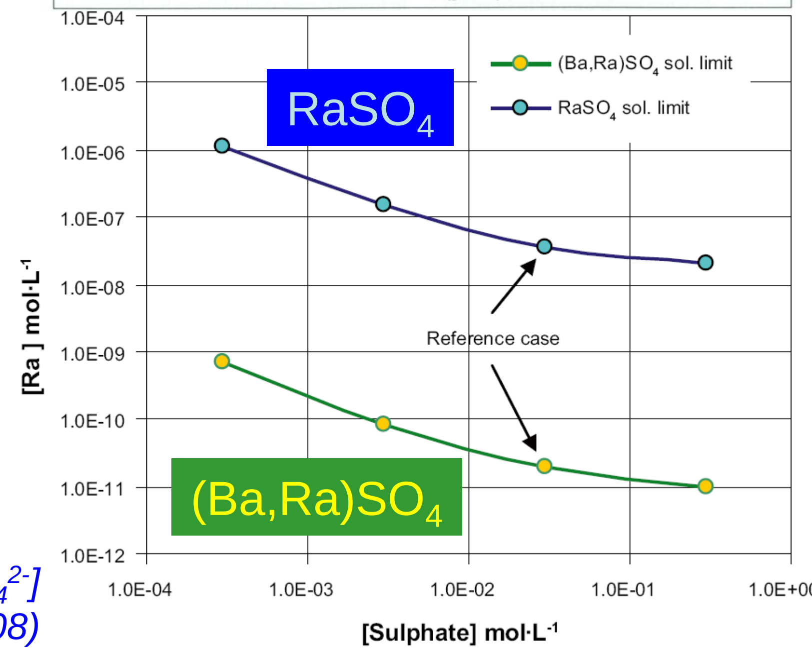
$RaSO_4$(s) solubilities vs. (Ba,Ra)SO_4(s) solubilities

V. Metz: Ra-Ba Co-precipitation in a Large Scale Evaporitic System: Field Study and Laboratory results

- Though Ra readily forms solid solutions with barite, most safety assessments for ^{226}Ra in nuclear waste repositories assume that its solubility is limited by pure $RaSO_4$(s)

- It is expected that (Ba,Ra)SO_4(s) solid solution limits Ra concentration by several orders of magnitude lower than $RaSO_4$(s) (e.g. Grandia et al. (2008) SKB TR-08-07)





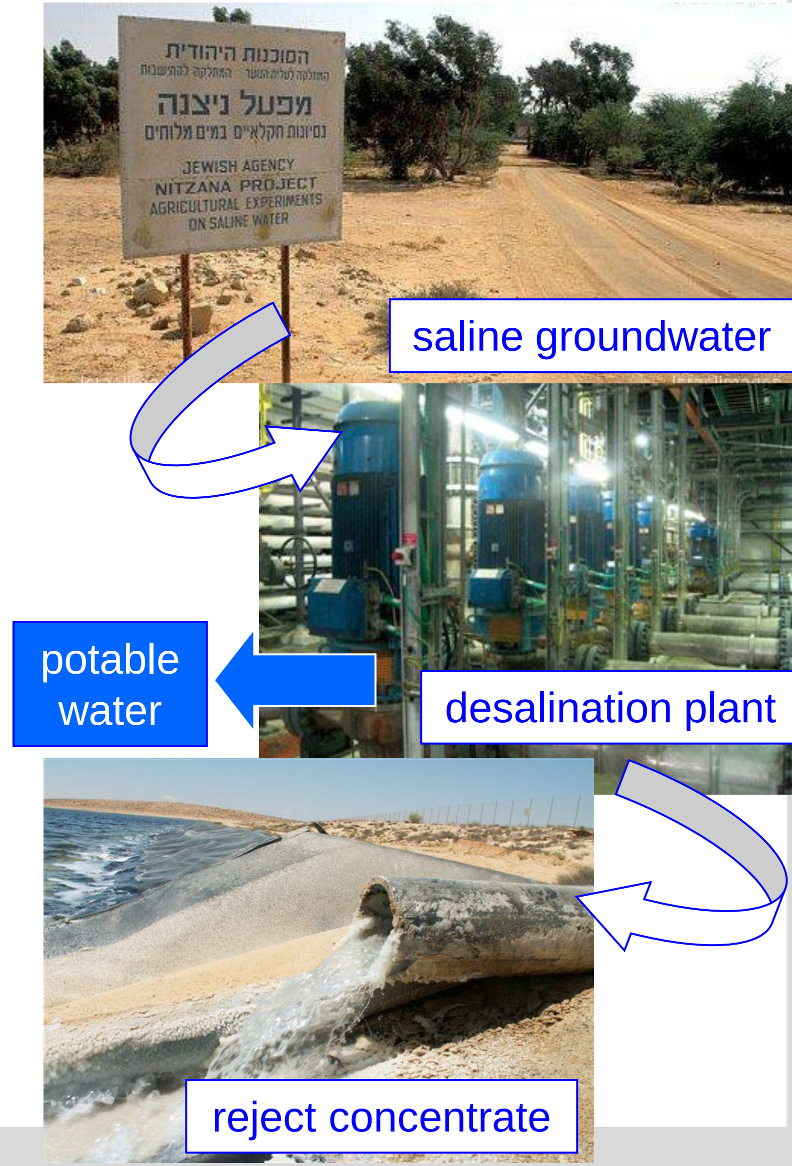
Ra solubility limit as function of [SO_4^{2-}]
Grandia et al. (2008)

אוניברסיטת בן-גוריון בנגב
Ben-Gurion University of the Negev

$(Ba,Ra)SO_4$ formation : Ketziot field study

Karlsruhe Institute of Technology

- Mediterranean Coastal Aquifer becoming contaminated with salts, nitrate, boron
- Ketziot desalination plant (Negev, Israel) desalinizes groundwater (~3.7 Mio m^3 per year)
- residual reject brine contains ^{226}Ra (12 $Bq \cdot kg^{-1}$)
- $(Ba,Ra)SO_4(s)$ co-precipitation determined in field study and laboratory experiments



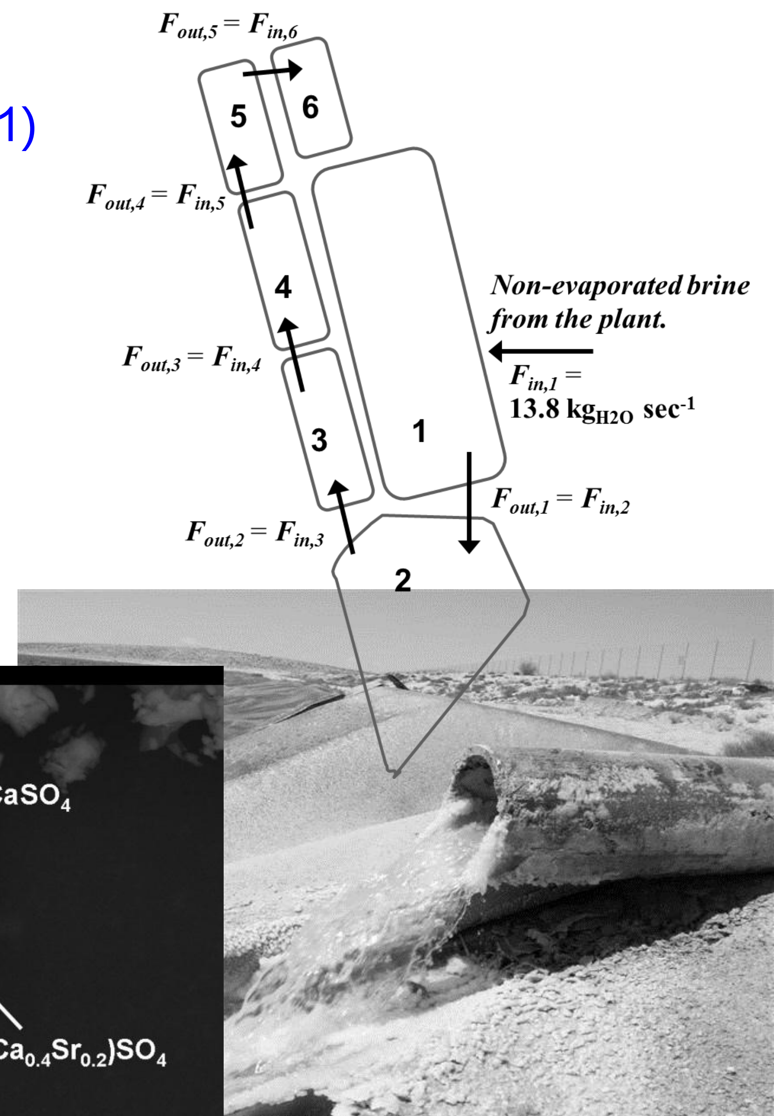
Rosenberg et al., Geochimica et Cosmochimica Acta 75, 5403-5422 (2011b).
Vengosh, Water on the Gaza Strip. Geolog. Soc. America Annual Meeting, November 2003.

(Ba,Ra)SO_4 coprecipitation in Ketziot

- residual reject brine supersatured with respect to sulfates (saturation degree Ω_{barite}= 16.7, Ω_{gypsum}= 2.1)
- reject brine conveyed to evaporation ponds
- due to evaporation gypsum, halite and Ca-/Sr-/Ba-sulfates co-precipitate

$$y\mathrm{Ba}^{2+} + z\mathrm{Sr}^{2+} + w\mathrm{Ca}^{2+} + \mathrm{SO_4}^{2-} = (\mathrm{Ba}_y\mathrm{Sr}_z\mathrm{Ca}_w)\mathrm{SO_4(s)}$$

- Ra^{2+}(aq) removal from brines corresponds to retention by Ra / barite solid solution with determined in laboratory evaporation experiments



Rosenberg, Metz, Oren, Volkman, Ganor, Geochimica et Cosmochimica Acta 75, 5403-5422 (2011b). Rosenberg, Metz, Ganor (submitted) Ra-Ba co-precipitation in a large scale evaporitic system. Geochimica et Cosmochimica Acta

Summary and conclusions

Applicability of $(Ra_xBa_{1-x})SO_4(s)$ solid solution formation in aqueous systems under nuclear waste repository relevant conditions depends on the availability of

(i) a molecular level understanding of the mixing mechanisms (e.g. regular solid solution model),

(ii) appropriate Pitzer parameters for calculating γ_{Ra2+} (established by Rosenberg et al., 2011a),

(iii) thermodynamic data for the end-members and

(iv) information on kinetic limitations.

- Both, in coprecipitation and (re)precipitation experiments aqueous Ra concentrations are controlled by solubilities of $(Ra_xBa_{1-x})SO_4(s)$ solid solutions and are many orders of magnitude below respective solubilities of pure $RaSO_4(s)$
- Ra removal via coprecipitation observed in the Ketziot large-scale evaporitic system is in agreement with Ra removal measured in laboratory evaporation experiments

Doerner, Hoskins, JACS 47, 662-675 (1925), Rosenberg et al., Geochim. Cosmochim. 75, 5389-5402 (2011a)

Microbial occurrence in ancient halite deposits

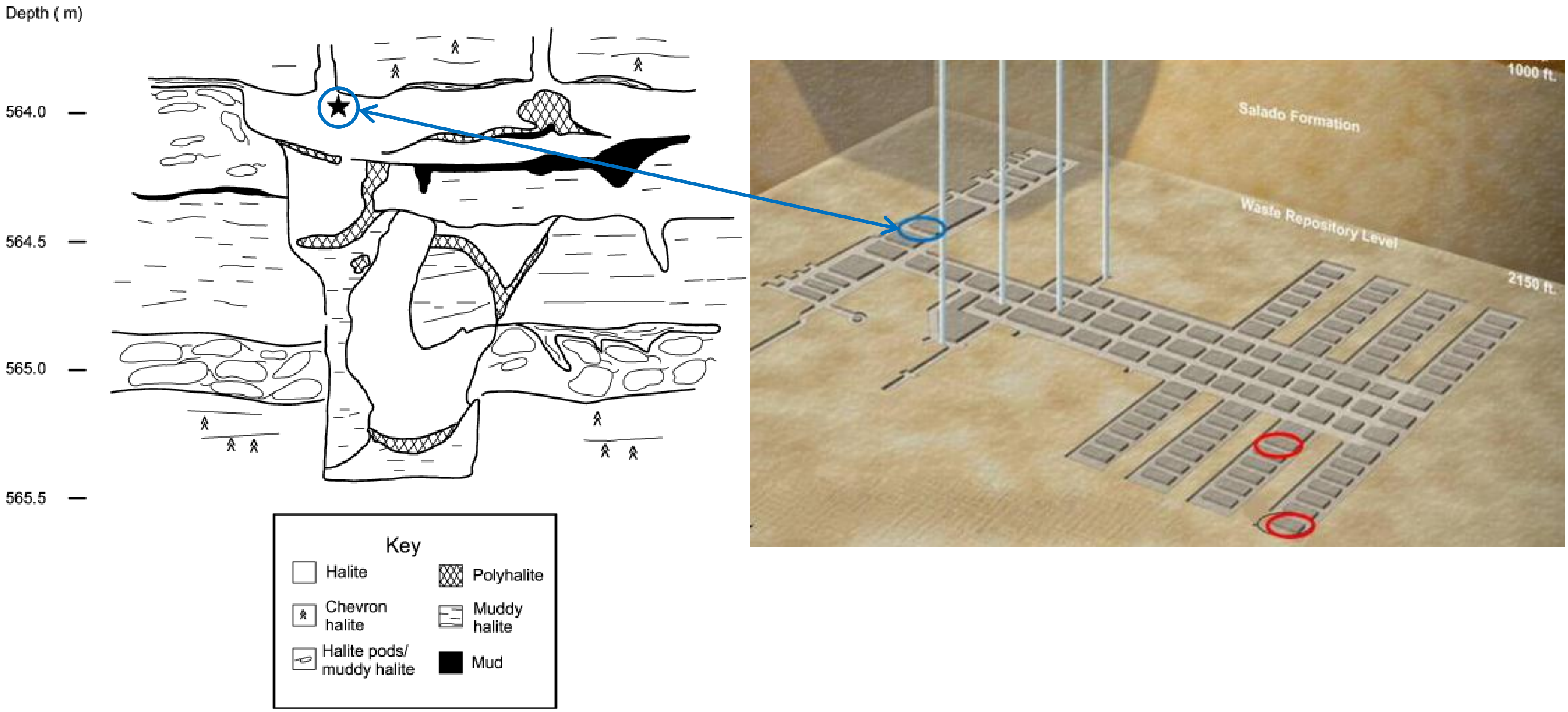
- As late as 1981 mined rock salts were described as microbe-free by microbiologists. This perception of salt mines as sterile environments is still widespread, although there is no doubt any more that ancient halite deposits support substantial populations of halophilic bacteria and haloarchaea /Grant, 2004/.

- E.g., G-Seep brine from the WIPP underground workings contained 7×10^4 to 3×10^6 cells ml^{-1} /Francis and Gillow, 1993/, brines from Winsford salt mine (UK) contained up to 4×10^7 cells ml^{-1} and from Boulby salt mine (UK) ~2×10^6 cells ml^{-1} /McGenity et al., 2000/.
  - Estimates of numerical abundance of microbes in natural saline environments may be substantially underestimated due to populations of newly discovered Nanohaloarchaea (~0.6 µm diameter), which have eluded previous detection /Narasingarao et al., 2012/.

- There are few negative controls in studies of ancient evaporites. E.g., no microbes were recovered from salts that had been subjected to burial temperatures of ~160 °C. Similarly, no microbes were found in a brine that had originated from a highly deformed potash seam within a salt diapir, which had previously been deeply buried and heated to at least 80 °C /McGenity et al., 2000/.

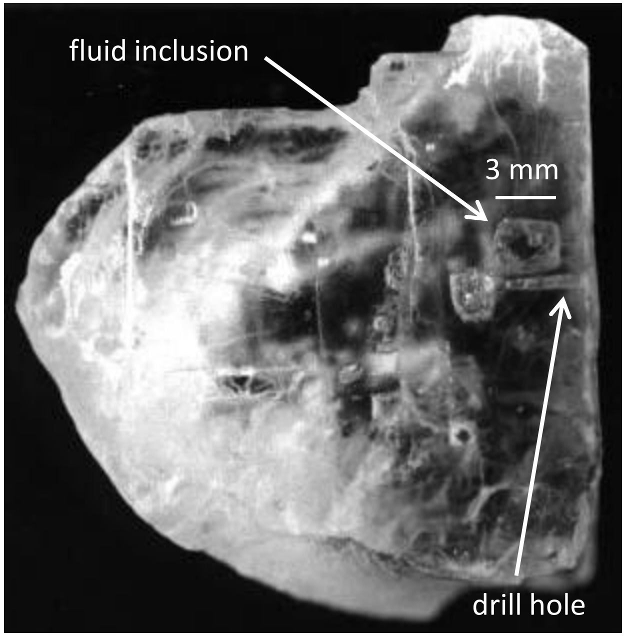
Microbial survival in ancient halite deposits

- Extraction and cultivation of a 250-million-year-old halotolerant bacterium from a brine inclusion in a halite crystal from WIPP Site (Salado Formation) were claimed in a more recent report /Vreeland et al., 2000/, which has received significant publicity because of the extreme sterilization techniques used to avoid contamination by modern microorganisms:



Microbial survival in ancient halite deposits

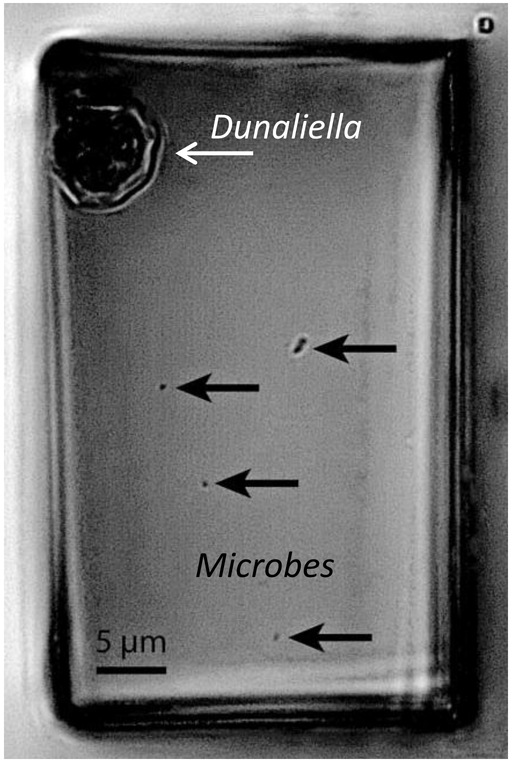
- Critics questioned this claim by arguing that large, single-crystal nature of the sampled halite is not typical of primary halite deposition, so that the fluid inclusion and the viable bacterium in them may represent much more recent features /Hazen and Roedder, 2001/.
  - However, the disputed fluid inclusions were found to contain evaporated Permian seawater /Satterfield et al., 2005/.



- Based on an evolutionary rate of 1.5 nucleotide substitutions per 100 bases in 16S rDNA per 50 million years and the observation that the 250-Myr-old bacterium from WIPP Site is 99% identical to a modern bacterium from the Dead Sea, critics argued that the extracted bacterium must be a modern one /Nickle et al., 2002; Hebsgaard et al., 2005/.
  - However, observations of extreme similarity of haloarchaea in 23-, 121-, and 419-Myr-old salts from Spain, Brazil and USA suggested that salt formations represent a natural gene bank for Earths biosphere through dissolution and re-precipitation of salt depositions as a result of the active water cycle and tectonic processes /Park et al., 2009/.

Microbial survival in ancient halite deposits

- Further critics concerned the issue of DNA stability over long periods of time and lacking independent replication of the observation /Willerslev and Hebsgaard, 2005/.
  - However, the same authors later succeeded in evidencing DNA repair and bacterial survival for 0.5 Myr in permafrost /Johnson, Hebsgaard et al., 2008/.
- The metabolic activity – even a very low one – such as DNA repair requires an *in situ* energy source. This poses a further question on the mechanism of microbial survival in fluid inclusions.
  - Microbes in fluid inclusions from Death Valley were often observed to be co-trapped with the *Dunaliella* algae, which contain up to 7 M glycerol, $C_3H_5(OH)_3$, in their cytoplasm and release it into brine /Schubert et al., 2010/.
  - Although virtually all hypersaline lakes contain large amounts of dead plant material, the Salado formation contains no sign of fossilized organics but detectable populations of cellulose-degrading microbes /Vreeland et al., 1998/.



Microbes in a 12000-year-old inclusion from Death Valley

Conclusions on microbes

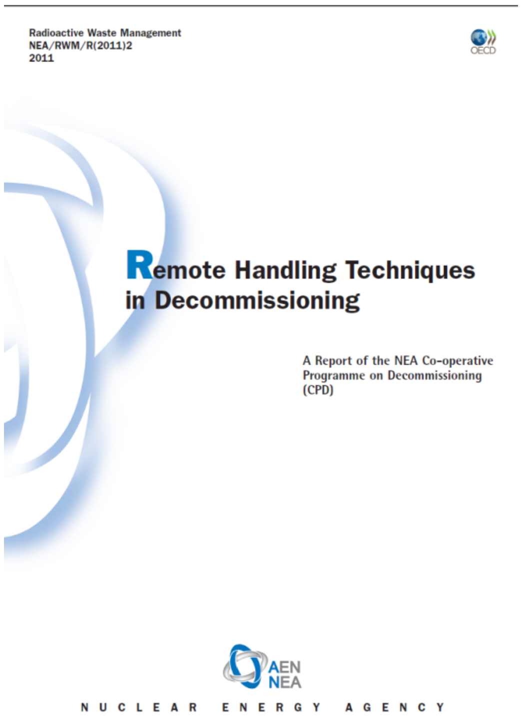
- Microbes capable of exerting negative impact on the long-term performance of a radioactive waste repository are indigenous to rock salt.
- Rock salts can contain electron donors and acceptors in amounts sufficient for microbes to remain active for very long periods of time.
- Additional sources of electron donors and acceptors will inevitably be added to the repository system as a result of repository excavation as well as placement of radioactive waste, backfill and sealing materials.
- A microbiological exploration of repository environments in rock salts, an evaluation of the maximum microbial effect in long-term performance assessments, and an evaluation of possible measures to inhibit or impede microbial activity in a repository in rock salt appear to be necessary.

Results (II) from working groups: Aspects of NA specific to Salt

- NA are focused on the integrity of salt (main barrier for containment)
- more NA on (geo)technical barriers required
  - compaction of crushed salt → Presentation from Jens Wolf
- further topics of high interest for NA
  - microbial activity in salt
  - deformation of anhydrite
  - fluid inclusions
  - gas storage
- open discussion of radwaste community with other scientific fields and industry

Further activities

- Proceedings to be published as NEA-R report
- Initiation of joint international projects
  - Salt Club
  - US/German Cooperation
- Prioritization → Assessment scheme
- Identification of further analogues
- Workshops focused on single aspects



Radioactive Waste Management
NEA/RWM/R(2011)2
2011

OECD

Remote Handling Techniques in Decommissioning

A Report of the NEA Co-operative Programme on Decommissioning (CPD)

AEN NEA
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ご清聴ありがとうございました