# DATA GAPS RELATED TO THERMODYNAMICS IDENTIFIED IN EURAD-FUTURE PROJECT

EURAD2 – annual event 1, Bologna

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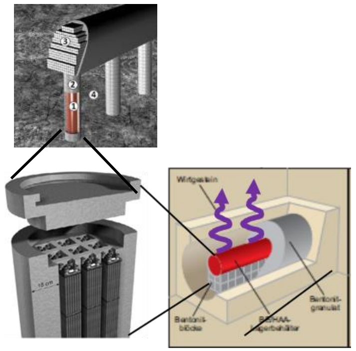
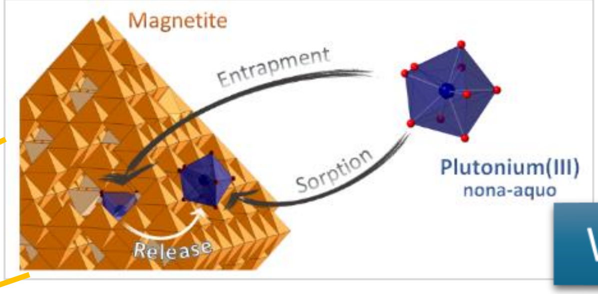
# FUNDAMENTAL UNDERSTANDING OF RADIONUCLIDE RETENTION

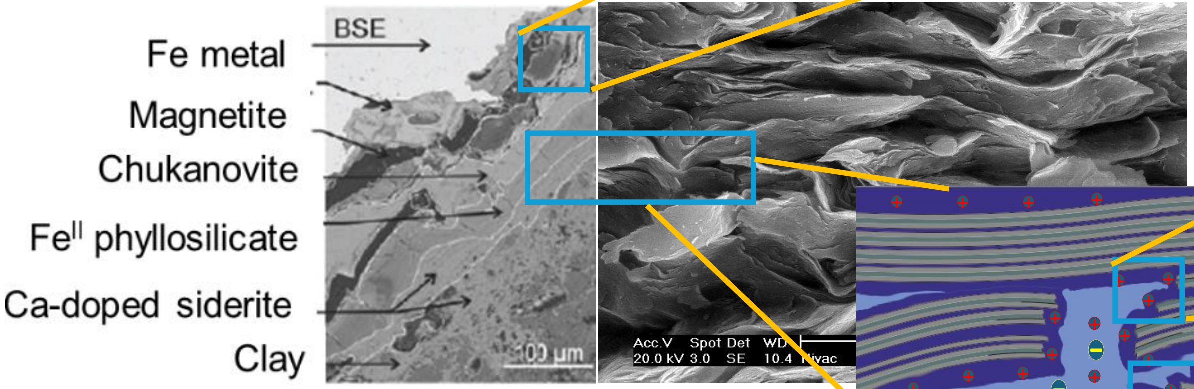
## Pillars of RN transport and retention

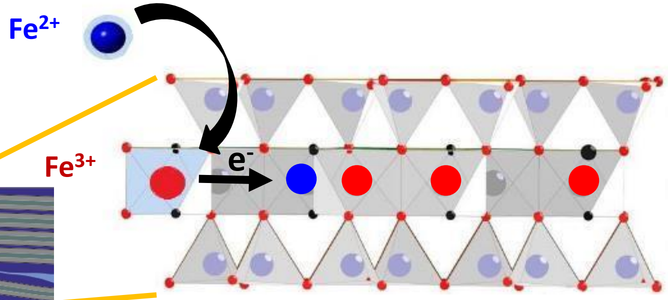


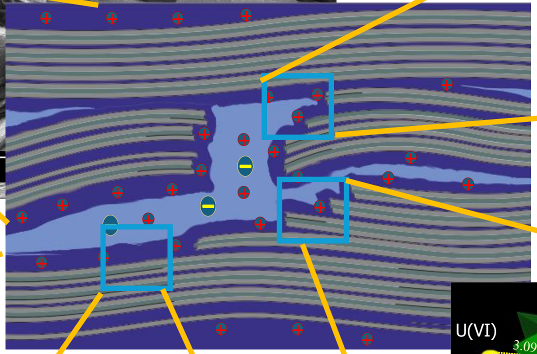



**WP 3.0 REDOX**

**Argillaceous Rocks**

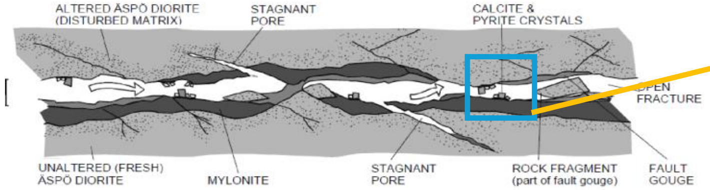


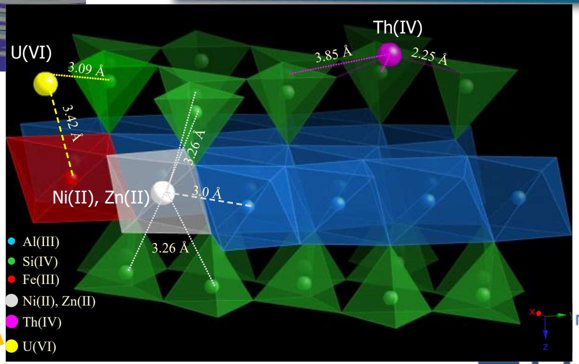



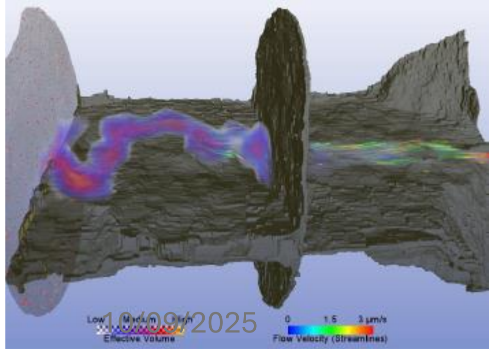



**WP 2.3 SORPTION REVERSIBILITY**

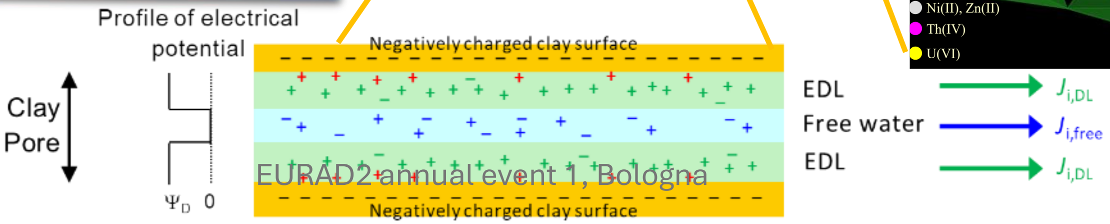
**Crystalline Rocks**



**WP MOBILITY: 2.1 Clay & 2.2 Crystalline**



## AIM OF FUTURE:
## *DELIVER SOLID SCIENTIFIC KNOWLEDGE ON RN MOBILITY TO SUPPORT SAFETY ASSESSMENT*

- ❑ **Obtain mechanistic understanding of radionuclide mobility and retention w.r.t.**
  - ❑ **EDL effects**: anion exclusion, enhanced flux in EDL for cations
  - ❑ **microstructural effects** (water saturation, pore heterogeneity and connectivity, grain boundaries)
  - ❑ **Chemical aspects** of pore water composition (pH, IS, competing elements)
  - ❑ **Interplay of transport regime and chemical boundary conditions** in fractured crystalline rocks

- ❑ **Understand the nature of the long-term retention mechanisms i.e. adsorption reversibility**
  - ❑ Adsorption versus incorporation (surface precipitation, neo-formation), competitive adsorption, solid solutions

- ❑ **Quantify/Characterize redox controlled retention and mobility processes**
  - ❑ Interaction between redox–sensitive radionuclides and relevant Fe-bearing minerals (clays & oxides)
  - ❑ Structural constraints on availability of redox active elements in the system: e.g. total Fe content, structural location and molecular scale surface speciation

# HOW IS THIS ACHIEVED?

- **Systems Studied:**
  - Model systems: Pure clay minerals (Ill, MoMo,…), fracture filling materials (calcite, chlorite,…) & Fe-bearing clays&minerals (Notronite, magnetite, green rust,…)
  - Natural systems: argillaceous (COx; OPA, Boda) and crystalline rocks (Bukov, Onkalo)
  - Weakly, moderately and strongly sorbing + redox sensitive radionuclides

    (I, Se, Ra, Ba, Co, Ni, Zn, Tc, Re, U, Np, Pu, Am,…)

- **Experiments**
  - Sorption experiments (disperse/compacted) under highly controlled conditions
  - Transport experiments (different scales) under highly controlled conditions
  - (Cutting edge) Spectroscopy (Mossbauer, XPS, synchrotron-XAS techniques, ATR-FTIR, LA-ICP-MS, TOF-SIMS/rL-SNMS, AMS, 14C-autoradiography, PET)

# THERMODYNAMIC DATA IN FUTURE – ROLE AND IMPACT?

- ❑ ***No explicit focus*** **on gathering or validating thermodynamic data - focus on process understanding**
  - ❑ Experimental conditions (often) tailored towards this goal:
    choice of RN, material, availability of (thermodynamic) data…

- ❑ ***Implicit use*** **of thermodynamic data**
  - ❑ Design of experiments e.g. speciation calculations, predictive calculations, controlling conditions,…
  - ❑ Modelling of sorption(interaction) experiments
  - ❑ Reactive transport modelling of transport experiments
  - ❑ Interpretation of spectroscopic data

→ **high quality thermodynamic data were key to the success of the FUTURE project**

# BIRD EYE CONCLUSIONS AND OUTCOME OF THE PROJECT

- ❑ **Validity of *bottom up* approach for sorption is broadly confirmed but not always straigthforward … as all underlying mechanisms and parameters must be known:**
  - ❑ From dispersed systems to compacted systems -> **straightforward if system chemistry is well known**
  - ❑ From single mineral to complex systems -> **straightforward**
  - ❑ From single RN to RN mix (competition) –> **remains challenging** and **needs further studies**
- ❑ **New/missing sorption data became available and included into sorption models**
- ❑ **Sorption reversibility should not be taken for granted… often some irreversibility is observed but mechanisms are difficult to unravel**
- ❑ **Mechanistic sorption models are applicable in the interpretation of transport experiments (but PW chemistry should be accounted for)**
- ❑ **Mechanistic understanding of anion exclusion and surface diffusion has matured**
- ❑ **Development of spectroscopic techniques helped to:**
  - ❑ Push detection limits for concentration measurements by several orders of magnitude
  - ❑ Provide detailed zoom into surface properties
  - ❑ Revealed quantitative information about the RN speciation in aqueous phase, in solids and at interfaces

# GAINED UNDERSTANDING (DATA AND MECHANISMS) HELPS TO IMPROVE MODEL DESCRIPTIONS DESCRIBING RADIONUCLIDE TRANSPORT AT DIFFERENT SCALES SUITABLE FOR SA PURPOSES

- Extending datasets for sorption and diffusion on rocks and compacted minerals
  - → **Support for the selection and scientific justification of (Kd, De…) values in the SA**
- Clear evidence for enhanced cation diffusion in clay systems (surface diffusion)
  - → **Must be considered in generalized SA**
- New data for anions transport and anion exclusion: divalent anions, particle orientation, partial saturation, ….
  - → **current SA model can be refined**
- Significant improvement in understanding the mechanisms of redox processes in which iron bearing phases and clays can promote sorption-reduction reactions
  - → **Redox controlled uptake in the vicinity of wastes by corrosion products should be considered in SA**
  - → **Effect of redox-mediated processes on radionuclide mobility needs further investigations.**
- Limitations of current retention/diffusion models (leading to overestimation and underestimation) are clearly identified:
  - → **Competition, slow kinetic process, sorption onto non-clays minerals, solid solution formations**

# KNOWLEDGE GAPS RELATED TO THERMODYNAMICS

- **Kinetic data**
  - Redox processes
  - Retention mechanisms other than reversible sorption

- **Completeness of thermodynamic databases**
  - Scarcity of data for some elements (experimental difficulties of all kinds)
  - Incomplete data for some elements
  - Internal consistency

- **Thermodynamics in confined systems**

- **Solid solution thermodynamic aspects**