Ruprechtov Natural Analogue Site (CZ): Study of redox processes and O_2 influence on U migration in sedimentary formations

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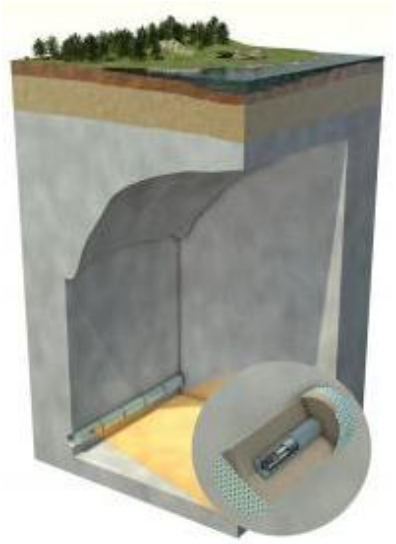
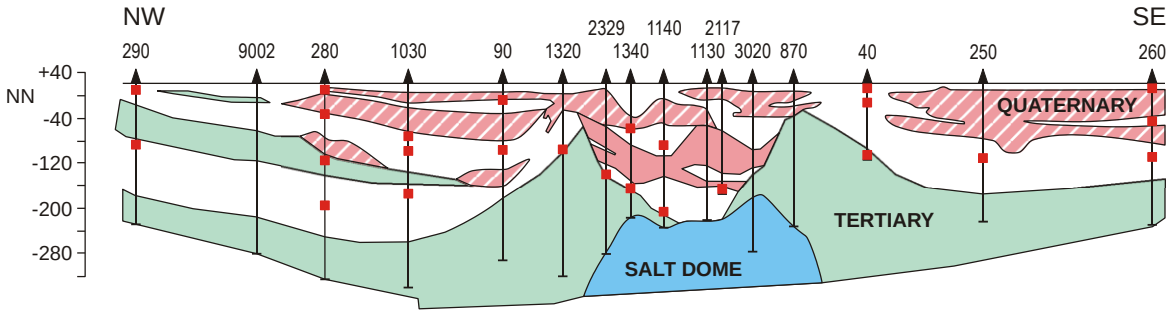
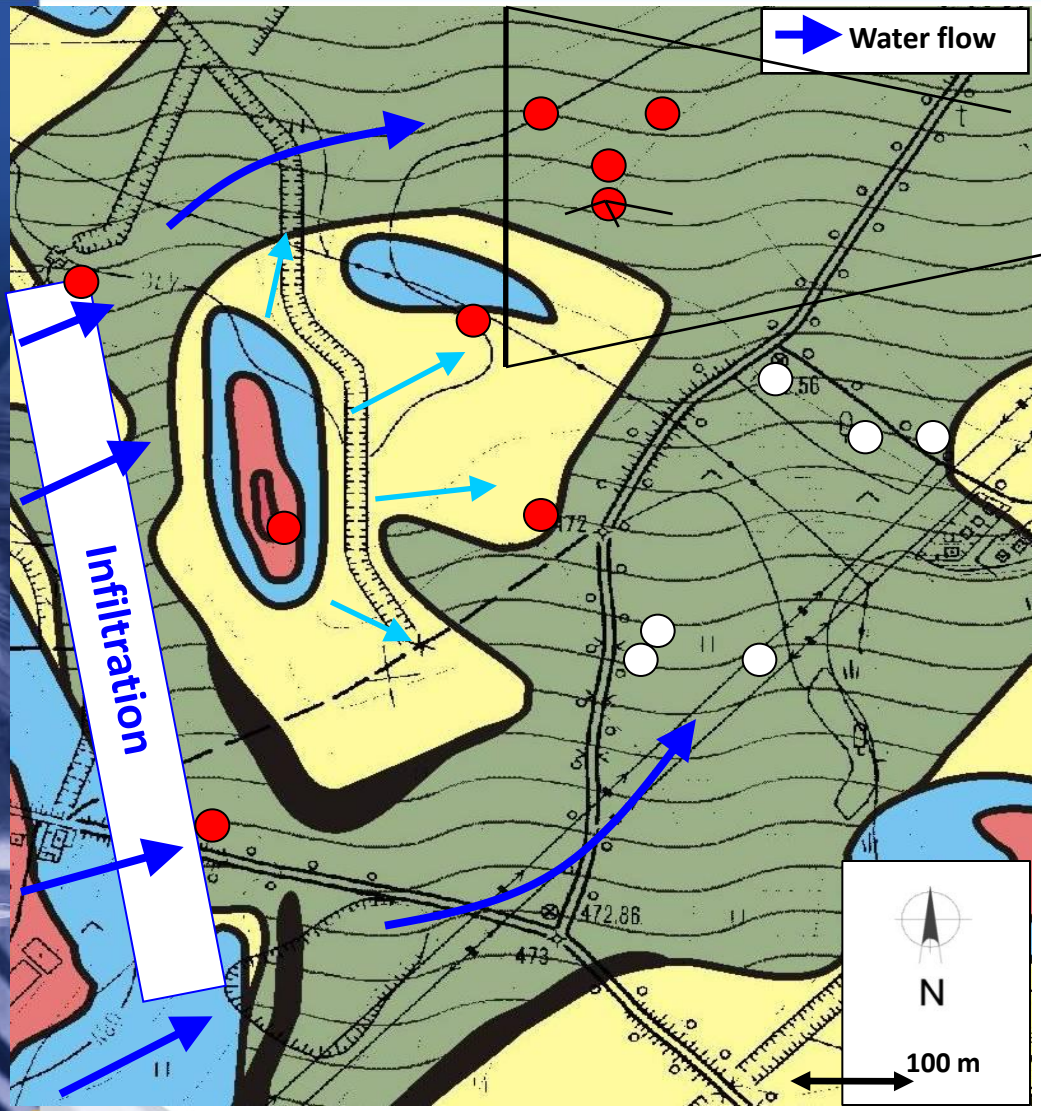
Aims

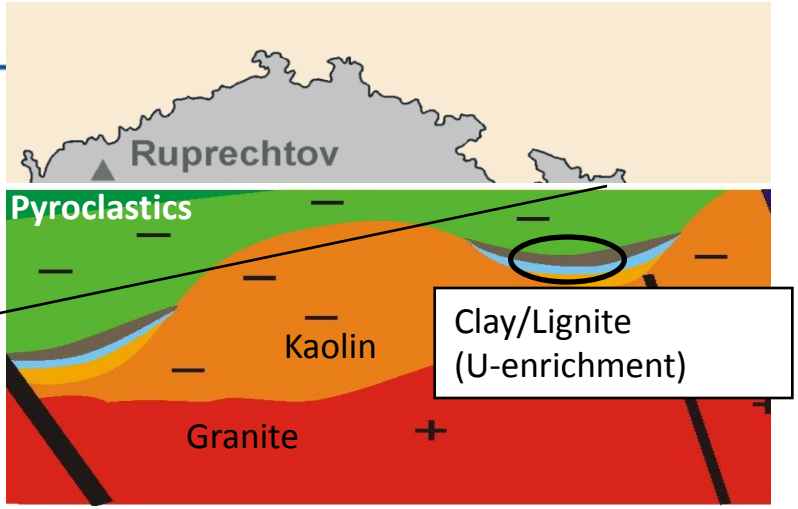
- Overburden of repository host rocks as additional barrier system
- Such formations are made up by quarternary and tertiary sediments
- Information about long-term stability of such formations and their role as a barrier for radionuclide (uranium) transport
- Natural analogue study: sedimentary argillaceous formation Ruprechtov, Cz





Geological sketch of Ruprechtov site





Tertiary pyroclastic sediments

Kaolin

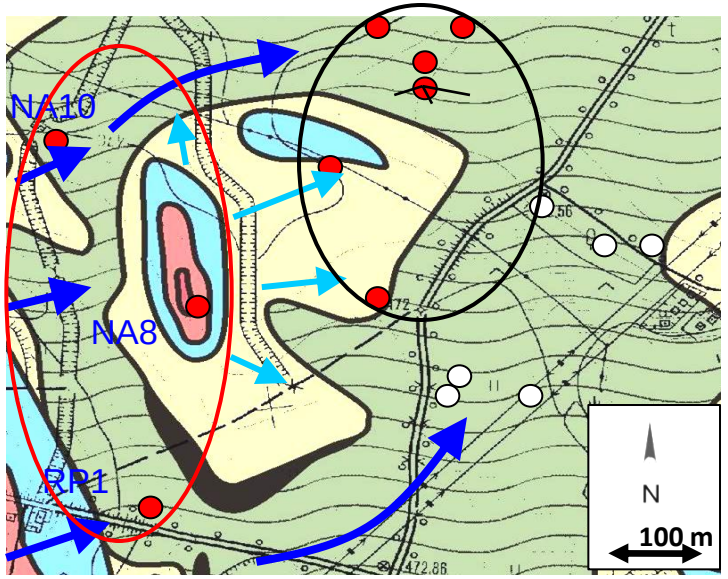
Granite

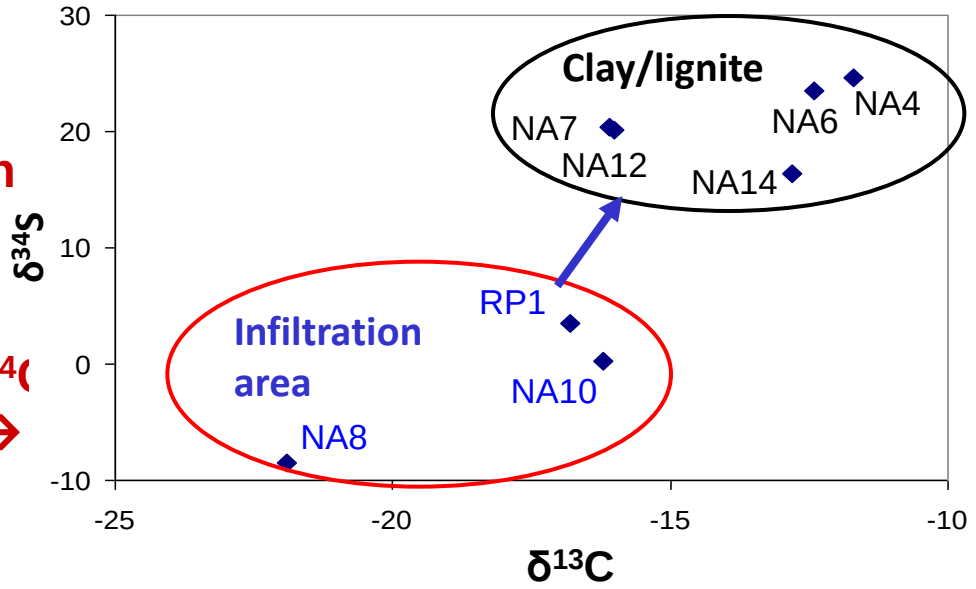
Conclusions of previous, namely FUNMIG IP research

- **Understanding of U immobilisation processes in a very complex system**
  - **Uranium is long-term immobilised in a reducing environment**
  - **U concentration dominated by amorphous UO_2 (ningyoite) and U(IV) phosphate mineral ningyoite almost reaches saturation.**
  - **U(IV) predominant redox state in the clay/lignite layers,**
    - **carbonato complexes can stabilise hexavalent uranium in solution even under reducing conditions**
    - **organic colloids do not play an important role for U complexation**
  - **Indication for long term stability of the immobile U phases in the clay/lignite horizon**
  - **Presence of organic matter a priori need not to mean increased U mobilisation (potential U complexation); in this case OM as a redox condition stabilisator**
  - **Role of microbes very important (OM degradation)**
- **Important for demonstration of the long-term (geochemical) stability of the formation**

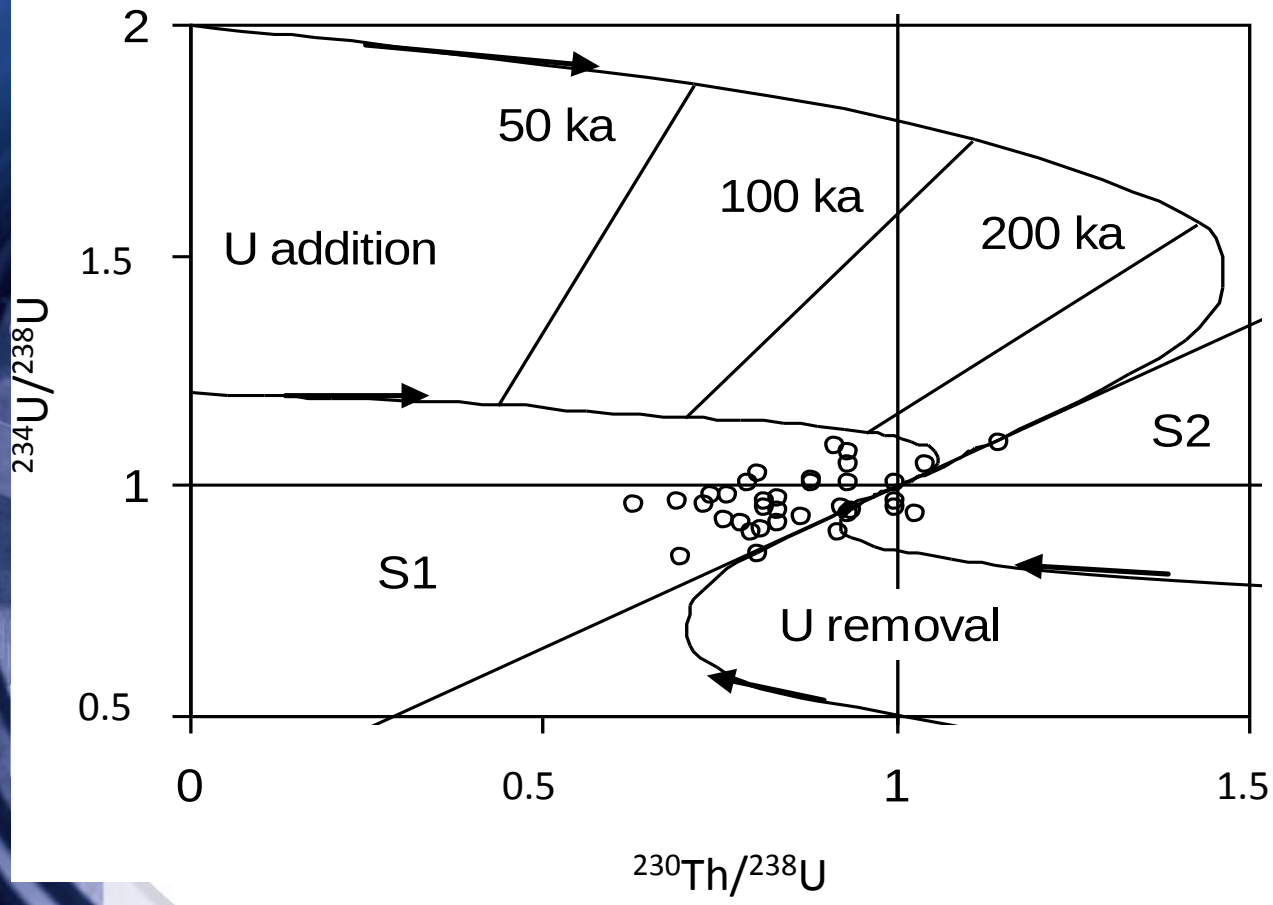
Other relevant features for uranium geochemistry

- **Generally important role of microbes in the clay/lignite horizon**
  - **Formation of framboidal pyrites in the geological past → FeAsS layers on pyrite surfaces**
  - **Autochthonous sulphate reducing bacteria identified**
  - **Sulphate reduction in the recent past shown by increased ^{34}S fraction in the clay lignite horizon → Redox conditions**
  - **Organic matter degradation and CO_2 formation by evolution ^{13}C, ^{14}C in DIC → increased CO_2 pressure**





Uranium immobilisation in the geolgical past

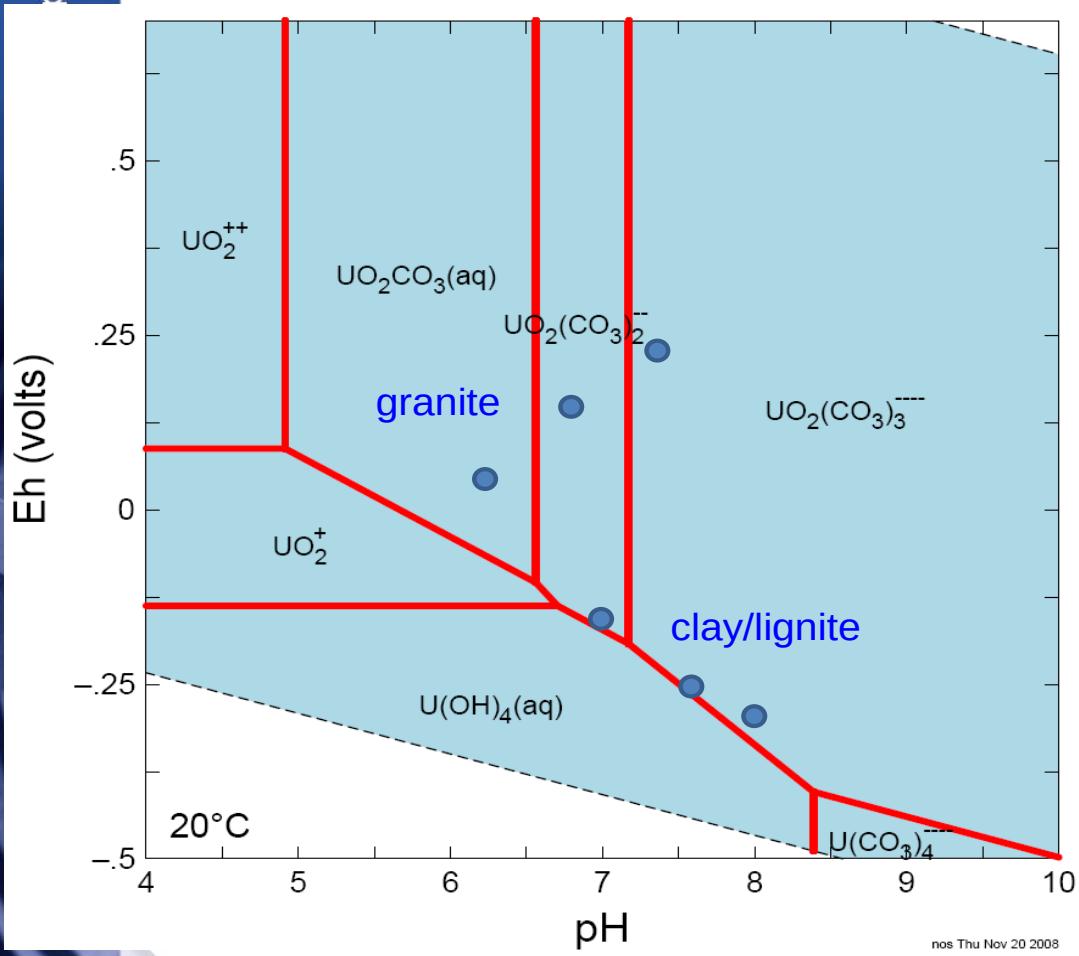


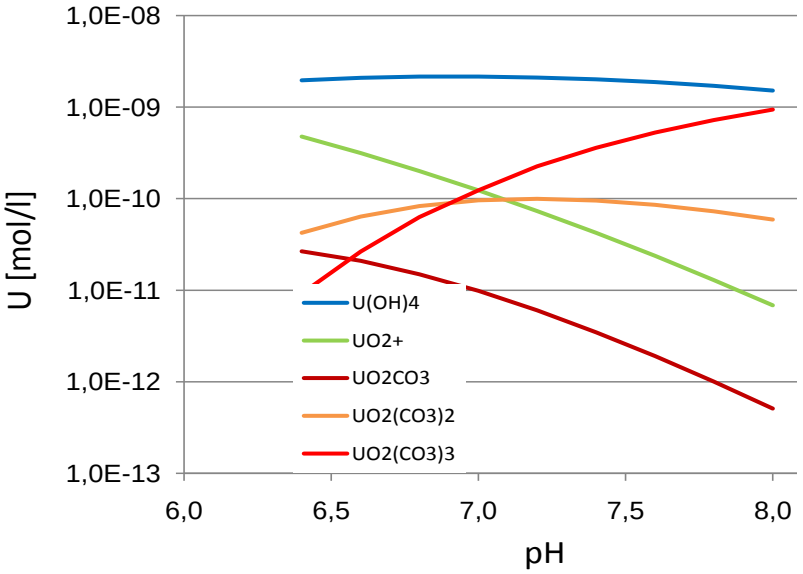
U-disequilibrium series

Bulk sample analysis indicate uranium deposition

Segment S1: open system from which ^{234}U has been selectively removed

Geochemical speciation of uranium





- **Calculation by GWB and NEA-TDB**
- **In clay/lignite water: speciation dominated by tetravalent $U(OH)_4$**
- **U(VI) carbonato complexes $UO_2(CO_3)_3^{4-}$ with increasing pH**

FUNMIG Publications

- Noseck U., Laaksoharju M., Suksi J., Havlova V., Denecke Melissa., Buckau G., Tullborg E. (2010): Real system analyses/ Natural Analogues. Applied Geochemistry, In preparation

- Cervinka R., Stamberg K., Havlova V., Noseck U. (2010): Humic substances extraction, characterization and interaction with U(VI) at Ruprechtov site (CZ). Radiochim. Acta 99, 1–12 (2011) / DOI 10.1524/ract.2011.1806.

- Noseck U, Rozanski K, Dulinski M, Havlova V, Sracek O, Brasser Th, Hercik M, Buckau G (2009): Characterisation of hydrogeology and carbon chemistry by use of natural isotopes – Ruprechtov site, Czech Republic. Applied Geochemistry, Volume 24, Issue 9, 1765-1776.

- Noseck U, Brasser Th, Suksi J, Havlova V, Hercik M, Denecke MA, Förster HJ (2008): Identification of Uranium enrichment Scenarios by Multi-Method Characterization of Immobile Uranium phases. Phys. Chem. Earth, 33, 969-977.

Objectives of new project (2009-2012)

(1) Model verification / validation

- The kaolin mining at Ruprechtov offers the unique possibility to check the most relevant parameters of conceptual model in the three-dimensional opening

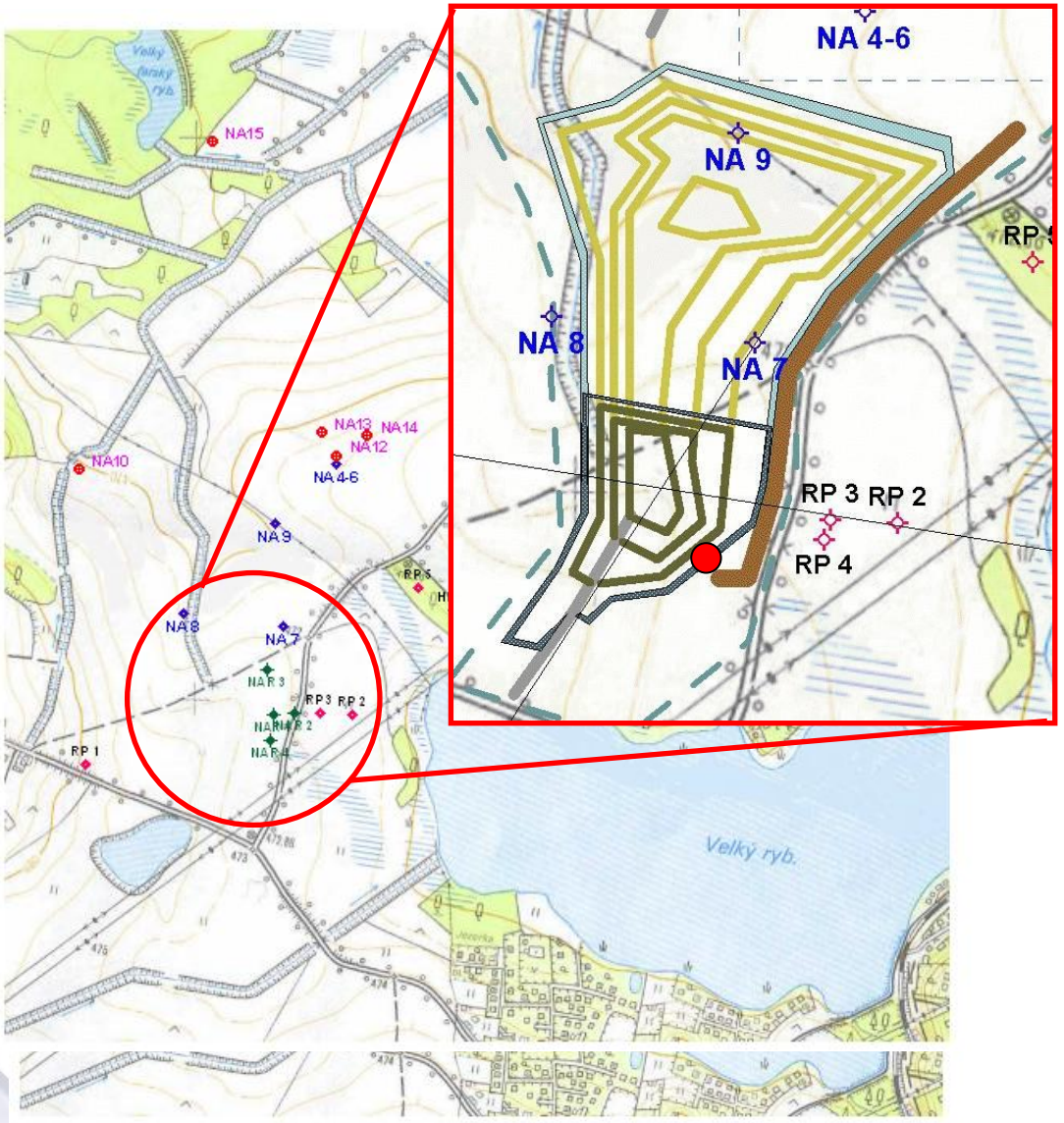
(2) Redox processes

- An additional (unique) aspect arises from the decrease of the groundwater level over a wide area. This causes
  - changes in hydrochemical conditions,
  - in particular increase of redox potential.
- Investigation of changes in geochemical (redox) conditions and its consequences in a natural system
- Increase understanding of REDOX processes

Work programme: Model verification/validation

- 3D Analyses of the openings with regard to
  - General stratigraphical conditions
    - Tertiary layers, Base of the Tertiary, Location and extension of lignite rich and water bearing layers
  - Location of fault zones (hydraulic connections to the underlying pre-tertiary rocks)
  - Spatial and structural distribution of uranium enriched zones
  - Characterisation and verification of uranium-bearing minerals
    - Identification of uranium enriched locations
    - Detailed microscopical analyses (ASEM, Microprobe)
    - Comparison with U(IV)/U(VI) and $^{234}U/^{238}U$ ratio

Kaolin opening and new boreholes drilled



Výzkumná oblast Ruprechtov

Lokalizace vrtů

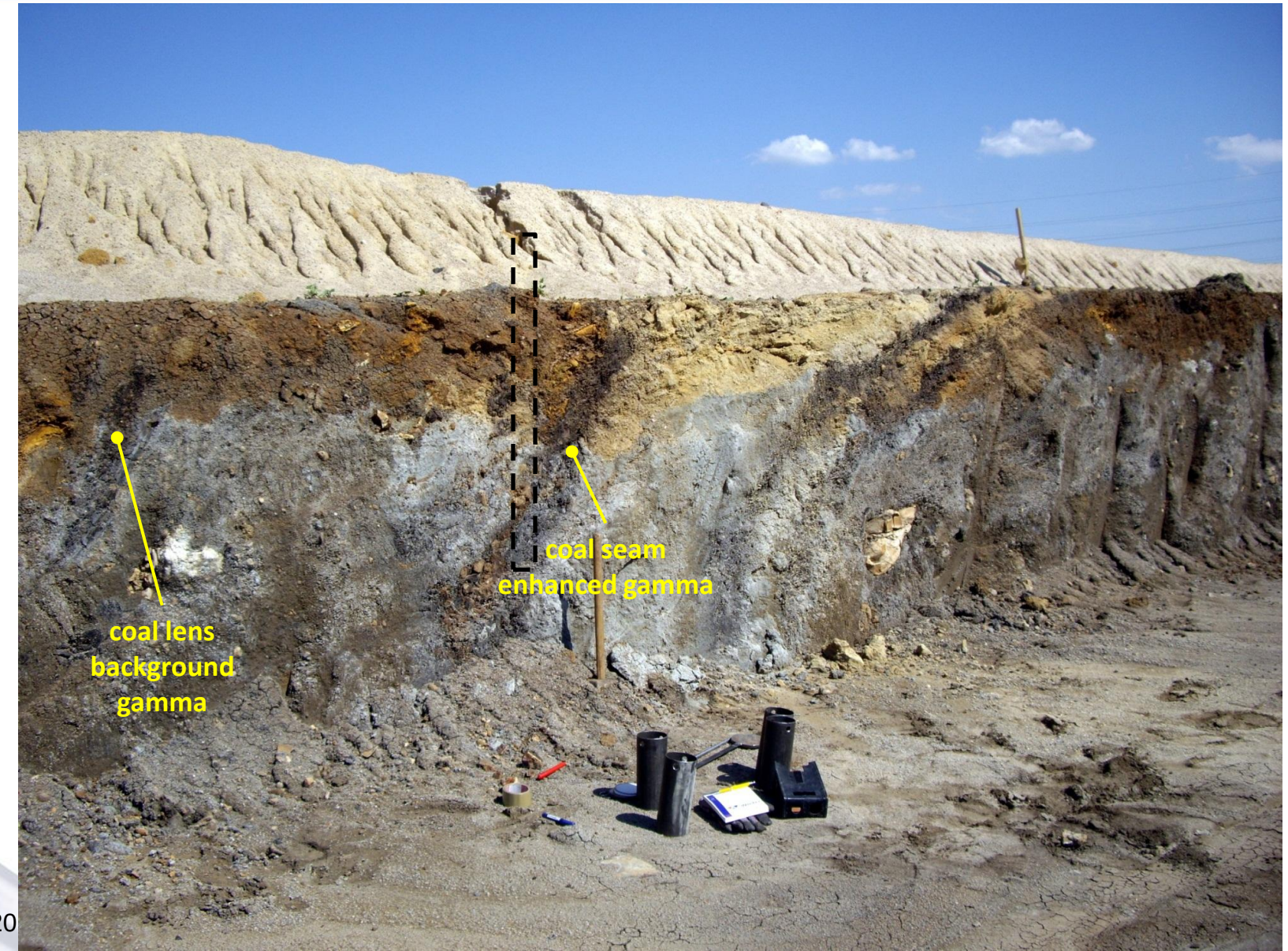
Legenda :

- vrtná kampaň 1999, 2002 (NA 4 - NA 9)
- monitorovací vrty pro důlní těžbu Gekon 2003 (RP 1 - RP 5)
- starší průzkumné hg. vrty (HR 4, PR 4)
- vrtná kampaň 2003 (NA 10 - NA 15)
- vrtná kampaň 2009, 2010 (NAR 1 - NAR 3, NAR 4)

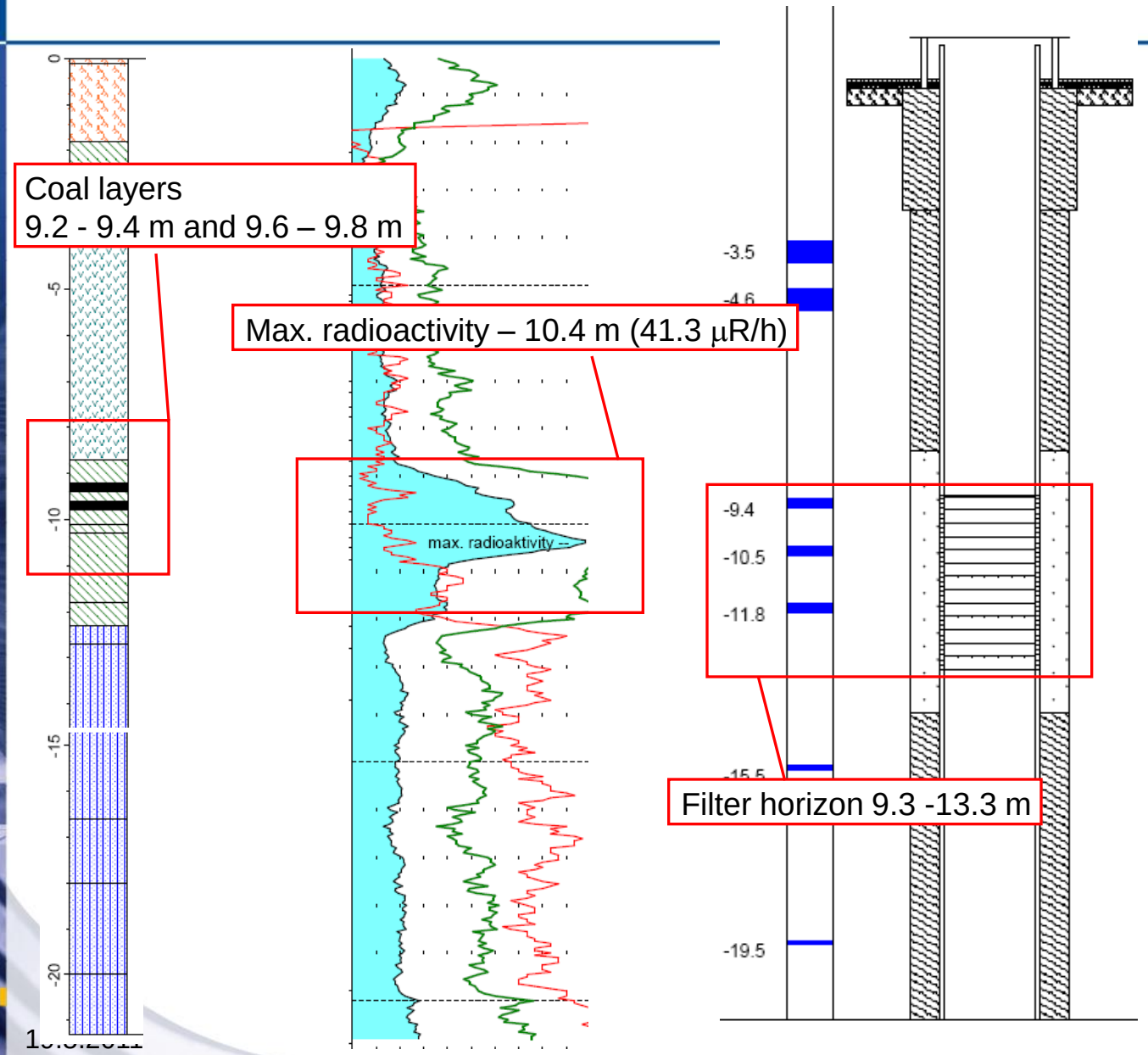
M 1 : 10 000

M 1 : 10 000

Research on the kaolin opening and surrounding



Research on 4 new boreholes



NAR 4 [21.3 m]

Drilling time:
19.7. - 23.7.2010

Location:

S- JTSK	Balt
849877.27	472.00
1004064.11	472.97

Geology:
Coal at 8.66 to 8.7 m, 9.2 to 9.4 m and 9.6 to 9.8 m

Gamma log:
Logging – max. 10.4 m = 41.3 µR/h

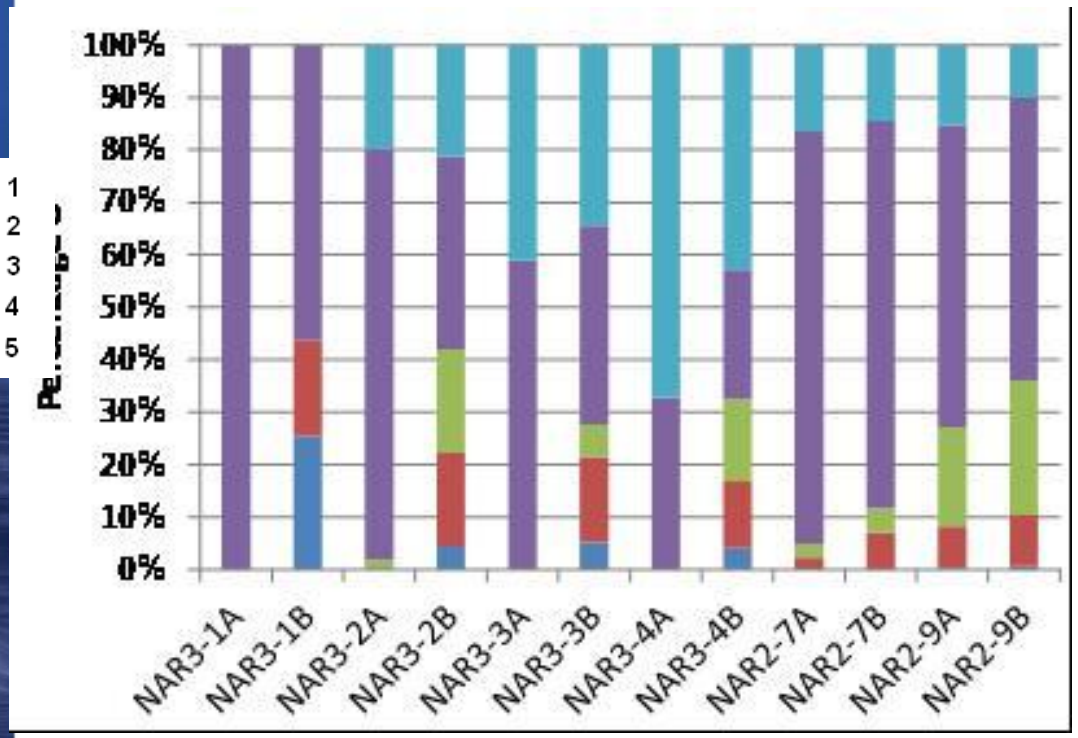
Main inflow:
3.5 and 4.6 m
9.4; 10.5; 11.8; 15.5; 19.5

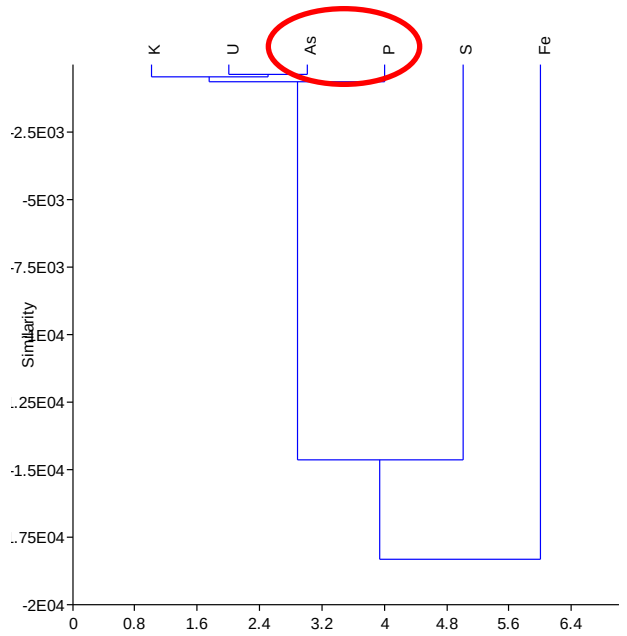
Casing:
145 mm Diam.
9.3 – 13.3 F

Analyses

- Identification of U enriched parts
- Element content (including U)
- Mineralogical and petrological analyses (ASEM, microprobe)
- Uranium forms: Sequential extraction (SE)
- $^{234}U/^{238}U$ activity ratios

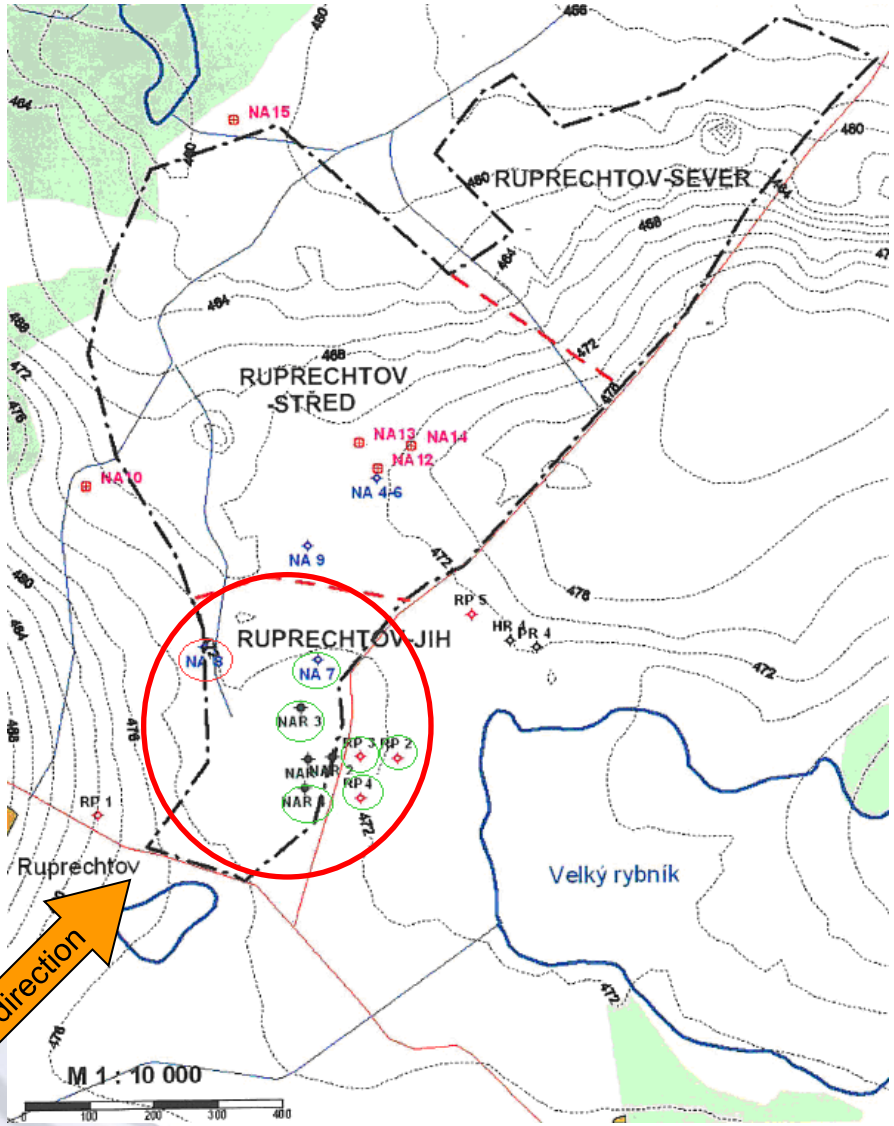
Borehole research: The very first results I.





- Sequential extraction: U is present predominantly in U(IV) form in fresh samples from boreholes with positive corelation of U with **As** and **P**
- The other experimental results are under evaluation

Borehole research: The very first results I.

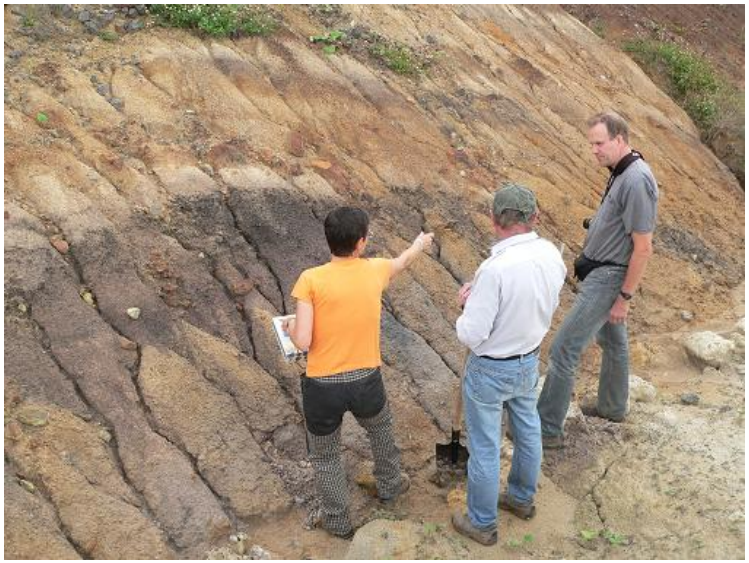


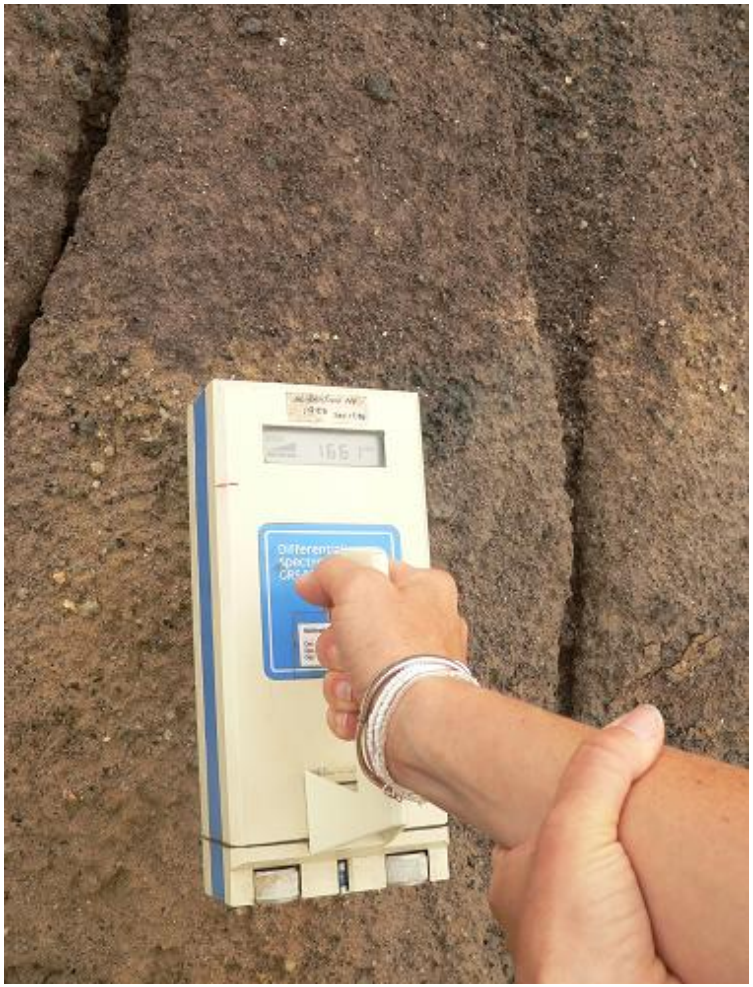
- GW regime change due to mining
  - wells close to mine (NA7B, RP2, RP3, RP4, NAR1, NAR2, NAR3) have faster response of gw level on rainfall, large gw level oscillation
  - Mining does not significantly affect the decrease of groundwater levels in monitoring wells – still above uranium layers
  - Significant changes can be attended during mining operation on Ruprechtov-center and Ruprechtov-north deposits

Work programme: Redox processes (2)

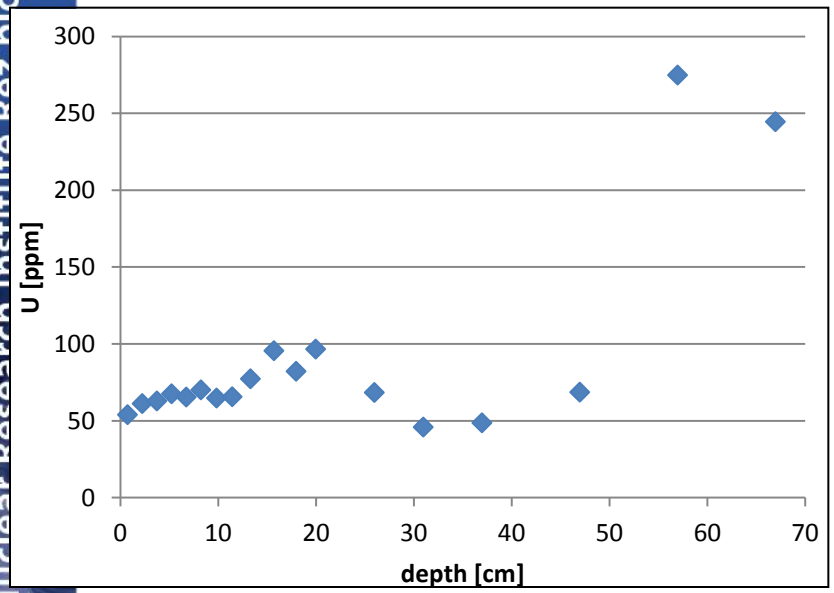
- **Investigations in the natural system:**
  - **Drilling of 2-3 boreholes at the site**
  - **Study of sediment profile on U accumulated point: study of U forms behaviour in dependence of distance from the surface**
  - **Changes in hydraulic conditions (water levels) in selected boreholes**
  - **Groundwater properties in disturbed/undisturbed wells (5 probing campaigns) in 3-4 boreholes**
  - **Sediment samples from disturbed/undisturbed uranium-bearing horizon:**
- **Accompanying Laboratory experiments**
  - **Extended sequential extraction of Uranium forms in rock**
- **Interpretation and modeling of changes in redox potential and other groundwater and sediment properties and impact on U mobilization**
  - **Thermodynamic model: speciation, reaction path modelling**
  - **Coupled model: transport and geochemistry**

Outcrop profile research

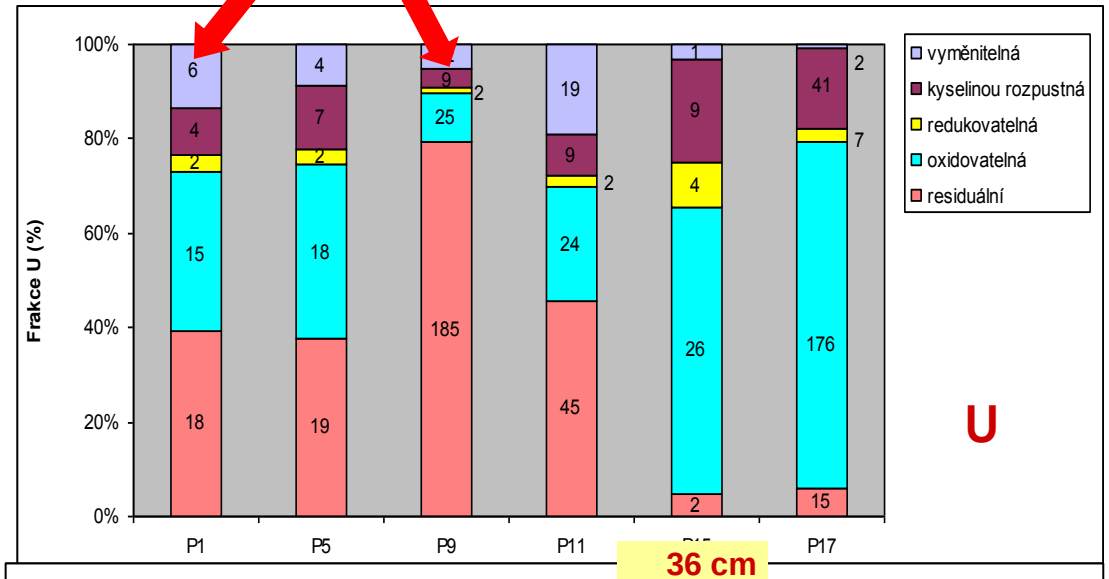




Outcrop profile research (OC-B): Sequential extraction

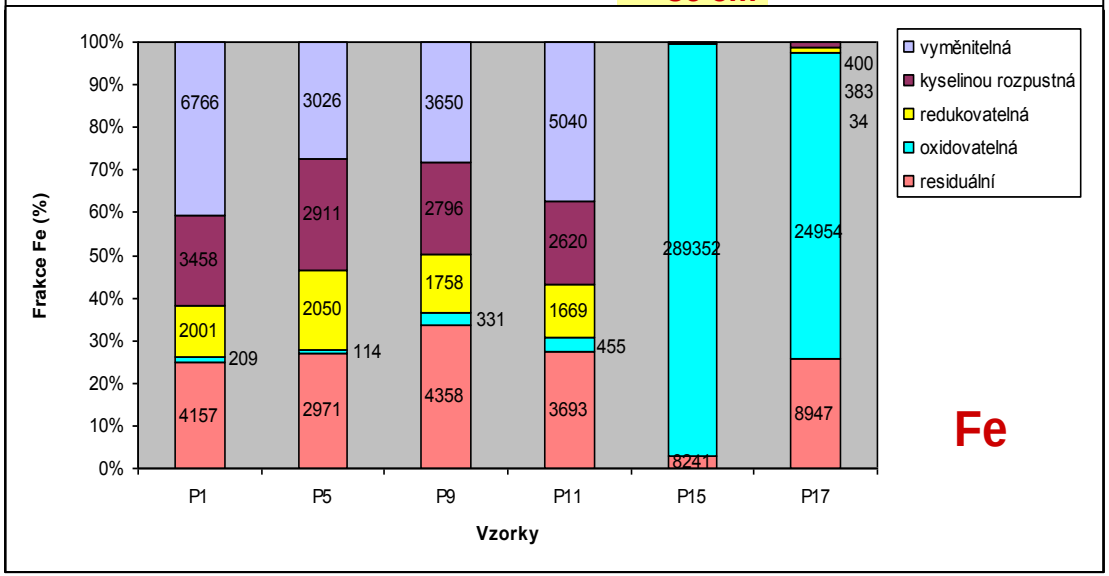


Low content of exchebgeable form: leaching



U

36 cm



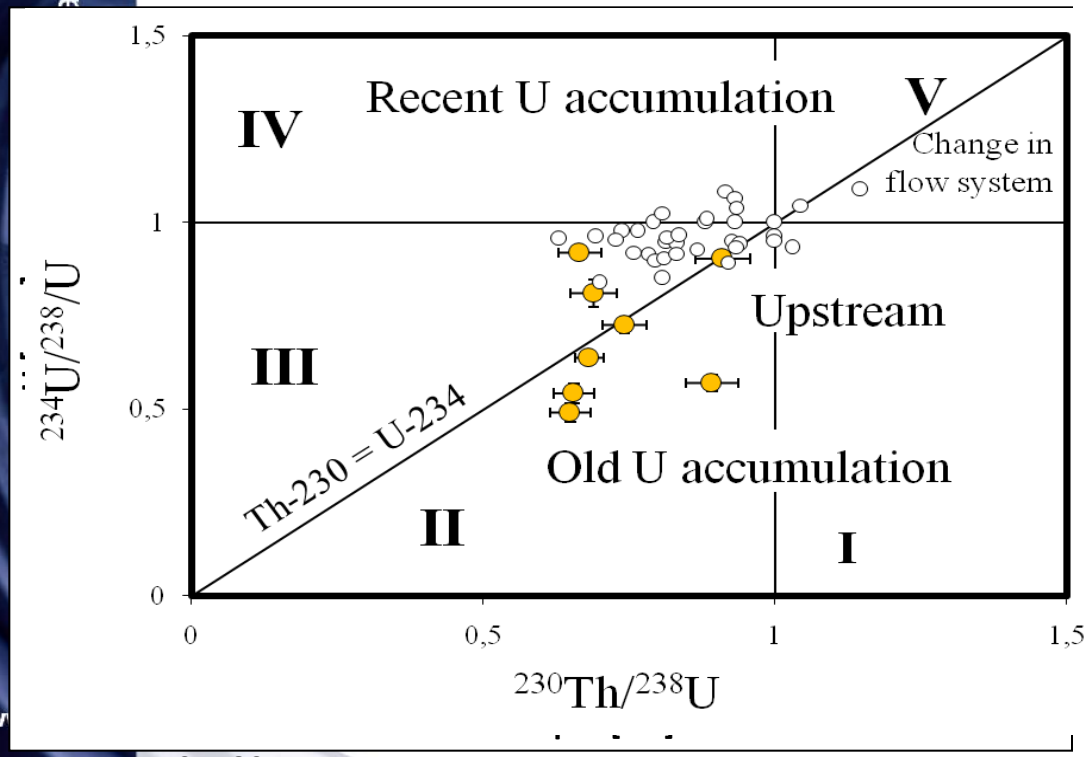
Fe

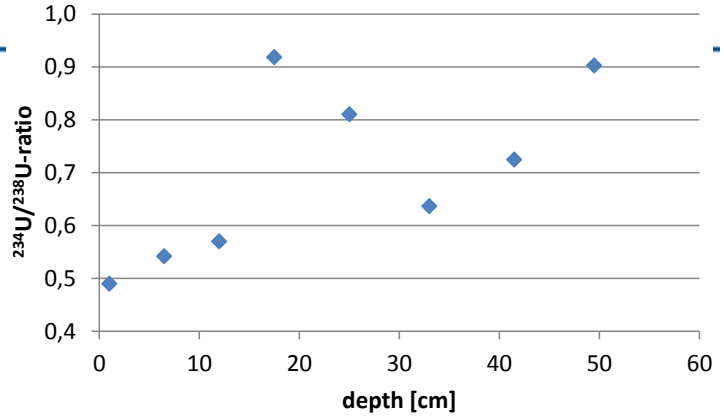
RESULTS:

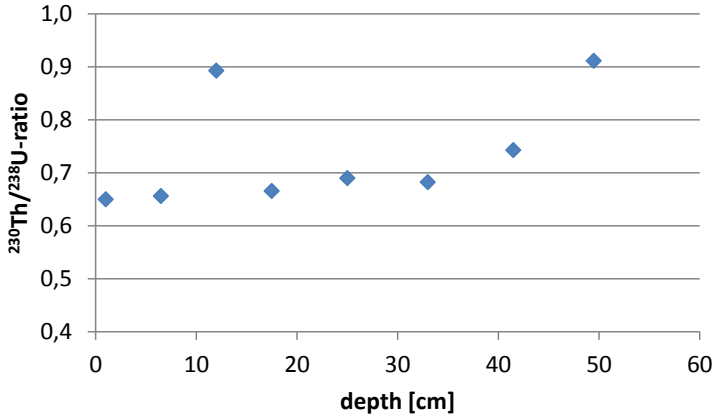
30cm of clay sediment is enough to protect U from oxidising conditions that can arise potential to oxidation and thus migration

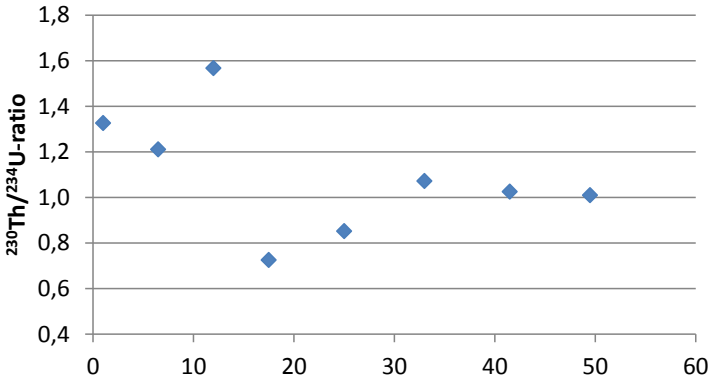
2. Outcrop profile research: AR ratios in OC-A

Question: different behaviour for OC as for NA(R) samples → indication for alteration/leaching









Study of U form change due to Samples NA13 and NA14 (cont. FUNMIG)

Aim: to study changes in U forms in sediment with time (2006 – 2009) under O_2 contact

Samples taken in 2006; clay/lignite horizon

NA 13 – borehole depth 54,87 m

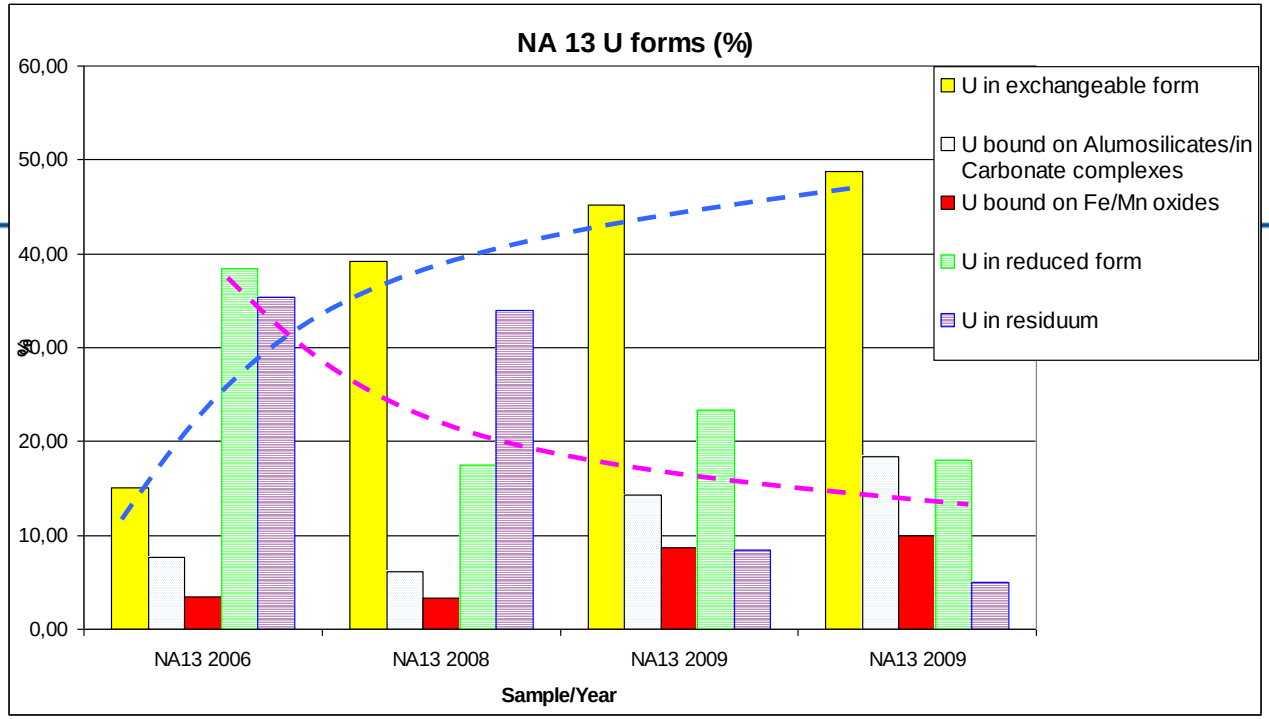
NA 14 – borehole depth 60,69 m

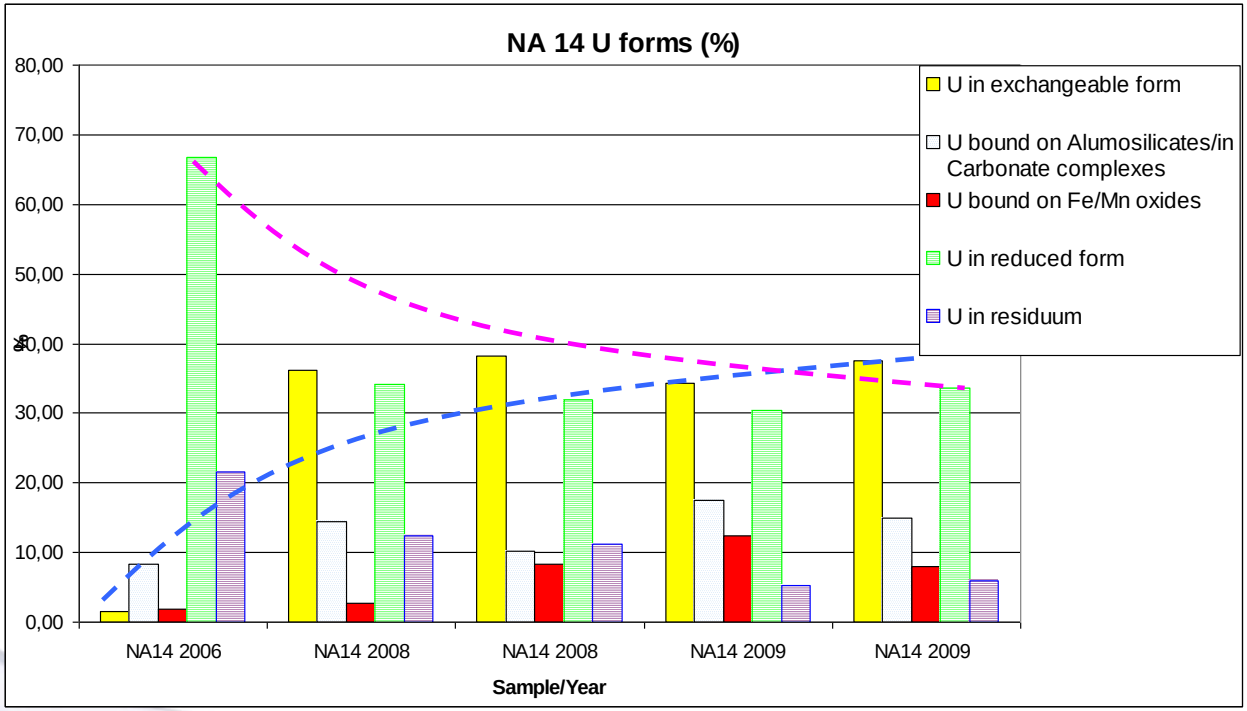
Samples ground and sieved

Fractions: - under 300 μm

- 300 – 500 μm

Used for SE within 4 years + AR measurements

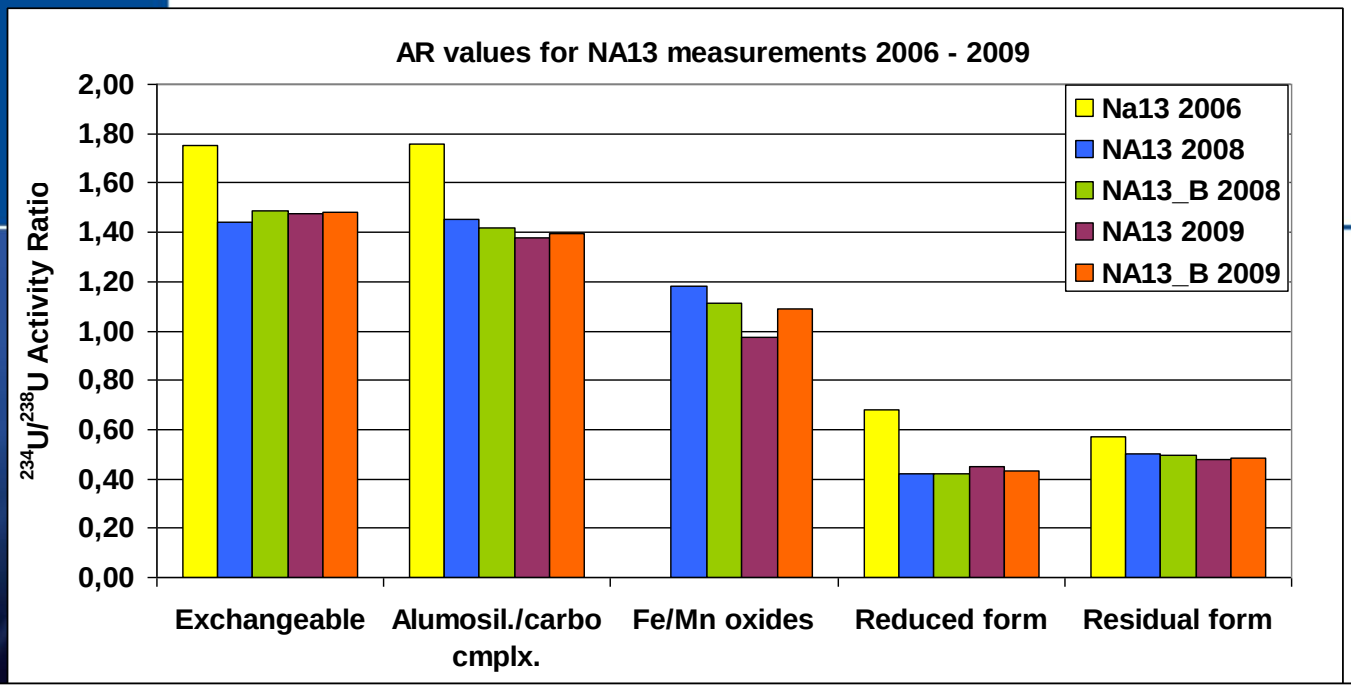

NA 13 U forms (%)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
%
NA13 2006
NA13 2008
NA13 2009
NA13 2009
Sample/Year
U in exchangeable form
U bound on Alumosilicates/in Carbonate complexes
U bound on Fe/Mn oxides
U in reduced form
U in residuum

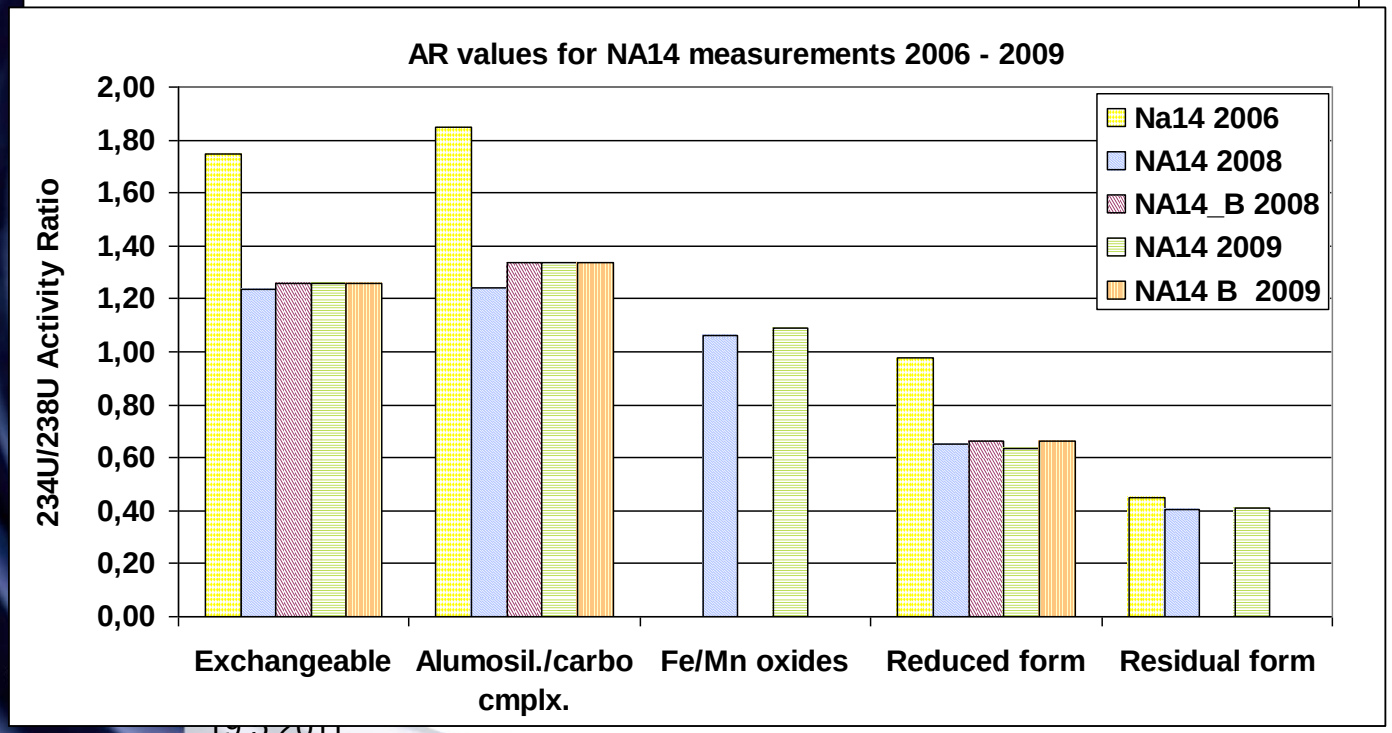

NA 14 U forms (%)
80,00
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
%
NA14 2006
NA14 2008
NA14 2008
NA14 2009
NA14 2009
Sample/Year
U in exchangeable form
U bound on Alumosilicates/in Carbonate complexes
U bound on Fe/Mn oxides
U in reduced form
U in residuum

SE results (II.):
Mass transfer of U forms betweem 2006 - 2009

	NA13 change in %	NA14 change in %
Exchangeable	+ 33.7	+ 32.9
Alumosilicates/Carbonate complexes	+ 10.7	+ 9.2
Fe/Mn oxides	+ 6.5	+10.6
U in reduced form	- 20.5	- 36.3
Residuum	- 30.4	- 16.4

SE results (I.)





Activity ratios (AR) 2006 - 2009

SE for „aged“ samples

- SE was performed for aged samples NA13 and NA14 (4 year time serie)
- U content in easily exchengeable fractions increases with time on the account of redused and residual fraction
- AR values in good agreement with SE results:
  - Easily accessible forms: AR > well above 1, i.e. by the U(VI) form
  - U in Reduced form (Step IV) and in Residual form (Step V): more or less around 0,6
- Shift in AR values due to oxidation (ageing): decrease for almost all fractions

- **Explanation:** low accessible U with ARs below unity is altered and moves into an accessible U form, thereby lowering the AR in the accessible fractions

CONCLUSIONS

- Activities on Ruprechtov NA site would continue at least until 2012
- Broad range activities in order to characterite redox processes under different conditions
- Many activities on-going and under evaluation
- Computation and modelling also included: U speciation in GW and penetration of O_2 rich water

Thank you for your attention

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