



**Deliverable No. D5.1**

**REDOX PROCESSES IN RADIONUCLIDE TRANSPORT IN CRYSTALLINE ROCK**

**REDOX PHENOMENA CONTROLLING SYSTEMS**

**ReCoSy**

**COLLABORATIVE PROJECT (CP)**

Submitting organizations: University of Helsinki

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Actual submission: 47 Project Months

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| Project co-funded by the European Commission under the Seventh Framework Programme of the European Atomic Energy Community (Euratom) for nuclear research and training activities (2007 to 2011) |  |   |
| Dissemination Level  |  |   |
| <b>PU</b>  | Public   | X |
| <b>RE</b>  | Restricted to a group specified by the partners of the project |   |
| <b>CO</b>  | Confidential, only for partners of the project                 |   |



## Objectives

The objective of the last period of the project (months 36-45) was to finalize and summarize all the work related to (1) development of wet chemical method to study U oxidation states in geomaterials, (2) application of U series study to derive information of past redox-perturbations at the Olkiluoto site, Finland and (iii) collaborations with the University of Cyprus (#19) and Institute of Isotopes, Hungarian Science Academy (#20).

## Status and results

### *1 Development of wet chemical method to study U oxidation states in geomaterials*

Most of the work was done to get a better insight into redox-interferences that can occur during U dissolution. It was known that iron dissolved during U dissolution can modify original U redox-state during the extraction of U. Also the possible role of radiation induced defects in modifying U redox-state was studied using an annealing test. Significant amount of such defects are formed if sample material contains a lot of U and Th. The results show that radiation induced defects can affect  $U^{4+}/U^{6+}$  ratio during U extraction. For the first time the results from the wet chemistry and XANES were compared. The comparison shows good agreement.

### *2 Application of U series study to derive information of past redox-perturbations*

U series disequilibrium in fracture surface material always refers to recent water-rock interaction. Disequilibrium is formed when U moves relative to its daughter  $^{230}\text{Th}$ . When U is seen to have mobilised it is fair to assume that there has been a change in redox-conditions. U series disequilibrium was observed in most of the samples taken from infiltration area in Olkiluoto manifesting that sample material has been taken from an open water-conducting fractures. From the nature of disequilibrium one can derive information of geochemical conditions prevailed when disequilibrium was created. In steady-state flow conditions (normal meteoric recharge) where oxygenated water recharges into the anoxic bedrock and turns to anoxic U series behaviour model presented figure 1 (left) is obtained. Activity ratios derived from the model can be presented in a plot diagram on the right. Activity ratios plotting in the upper right sector (forbidden for steady-state) can not be found in the steady-state model on the left figure. Significant part of the samples plot in this “forbidden” sector suggesting that respective fractures have experienced a hydrological event other than normal recharge. These non-steady-state disequilibria were interpreted to have formed as a result of U remobilisation. U remobilisation is possible if flow conditions have changed in which case redox-conditions may have changed as well. U series disequilibria obtained in the outcrop samples, i.e. from oxidising conditions, clustered in the diagram in the upstream side of the redox-front as is expected (Fig. 1). An interesting observation was that U mobilisation was observed in fractures where pyrite was present.

U series study in connection with other hydrogeochemical tools offers a powerful tool to study redox-perturbations. The non-steady state disequilibria will be modelled as a part Posiva's paleohydrogeological investigations.

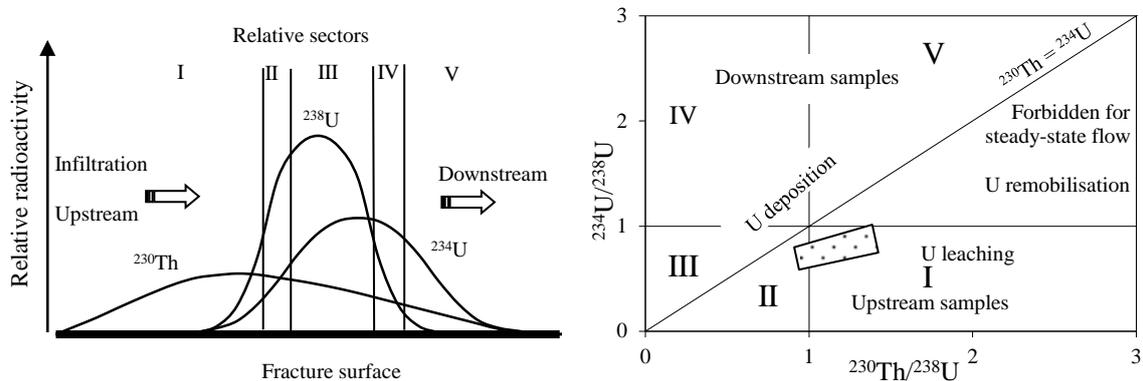


Figure 1. Left: U series disequilibrium model under steady-state flow. U leaching characterises sector I and deposition sectors II-V. Relative radioactivity in y-axis delineates the development of radioactivity of the three longest-lived U series nuclides on fracture surface when infiltration advances along fractures. Right: Plotting diagram of U series disequilibrium data according to the model. Outcrop samples are indicated by dotted area.

Collaboration with the University of Cyprus concerned U series and U oxidation state analyses of samples taken from phospho-gypsum stack. Enrichment of U was observed in organic material containing phospho-gypsum. Whether the enrichment was due to U reduction remained unclear.

Collaboration with Institute of Isotopes (Hungarian Academy of Science) concerned post-mortem analysis of U in Boda Clay bore core samples. Strong sorption of uranyl ions was demonstrated on the bore core samples in break through experiments. From the combination of results (U oxidation states) it was concluded that the sorption of uranium is not correlated with simultaneous redox processes, i.e. the  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  and  $\text{U(VI)} \rightarrow \text{U(IV)}$  processes are not simultaneously coupled at the strong sorption.

## Dissemination

The summary and final results were presented in the 4<sup>th</sup> ReCoSy Annual Workshop in Karlsruhe in oral presentation and poster. S&T contribution concerning wet chemistry in determining U oxidation states was submitted to the 4<sup>th</sup> AWS proceedings. Two manuscripts, (i) the application of U series study in studying past redox-changes and (ii) wet chemistry in studying U oxidation states in solid materials are under preparation to be submitted to scientific journals. A technical report of the U series studies in the groundwater infiltration area in Olkiluoto will appear in the Posiva technical report series.

## Further activities

No further activities have been planned.