Natural Analogue Study Ruprechtov (CZ)

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Gesellschaft für Anlagen-
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Natural Analogue Study Ruprechtov (CZ)

An Experience Report

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Remark:

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The authors are responsible for the content of the report.

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Commemoration

For many years, Mirek Hercík has been a good friend and sedulous trouble-shooter of the Ruprechtov analogue study. He died on 29th June 2010 and we remember him and his work with this report.

Keywords

Geochemistry, Geology, Investigation Methods, Natural Analogue, Safety Case, Uranium

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1 Introduction

The preferred option for the long-term management of high level and long-lived radioactive waste is disposal in deep geological formations. The realization of such disposal concepts is based on both technical feasibility and long term safety. The latter requires a wide range of technical and scientific data for assessing the long term performance of disposal systems and sites. Fig. 1.1 gives a schematic example of the role of the different safety functions in the evolution of a disposal system for vitrified waste and spent fuel to be disposed of in a clay formation /OND 01/.

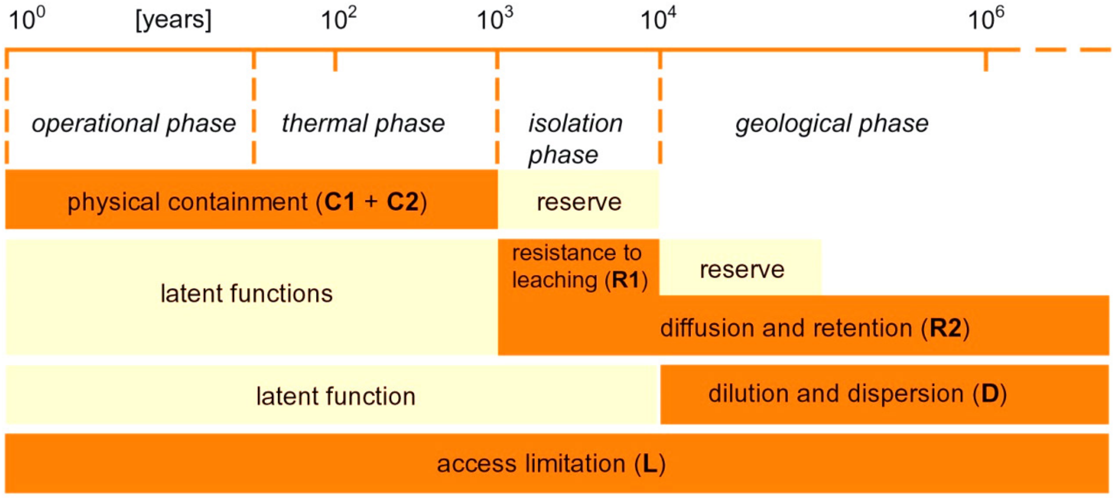

Fig. 1.1 The four phases in the normal evolution of a deep disposal system for the vitrified waste and spent fuel, and the corresponding long-term safety functions /OND 01/

Because of the complexity and the geological time frame to be considered, geological, hydrogeological and radiochemical data are of great importance. From this point of view deep insights into relevant “natural” geological processes may contribute substantially to system understanding and finally to the compilation of the so-called Safety Case, i. e. the overall assessment of all safety features. As in other countries, a compliance periode of 1 million years is required in Czech Republic and Germany. Such a long time span makes it difficult for predictive modelling to fully overcome the remaining uncertainties that accompany "short"-term lab experiments and field studies. This is particularly true for the geological phase as illustrated in Fig. 1.1, where geochemical processes in particular are relevant for fulfilling the safety functions. However, the comparison of such results with processes in nature, which show a reasonable similarity, may help in gaining greater confidence in those data as well as in the numerical models based on them. The respective natural, anthropogenic, archaeological or industrial systems which have some definable similarity with a radioactive waste repository and its surrounding environment, are usually denoted as natural analogues /MIL 06/.

The main value of natural analogue studies is to provide information about a geological system (evolution), i. e. the characteristics of processes occurring over very long time scales. In general, the direct use of quantitative information from natural analogue studies in a Safety Case has been mostly limited, because it is very difficult to extract hard numerical data from complex natural systems, where initial and boundary conditions cannot be fully defined. Indirectly this information could, however, be very valuable in a supportive sense. Therefore, natural analogues are an integral component of the Safety Case in national repository programmes /NAG 02/, /MIL 02/, /SMA 06/, /PUU 10/, /LOP 04/. Moreover, the regulatory authorities explictly require safety assessments to be supported by qualitative arguments for a system's long-term safety /NEA 13/.

At the time of initiation of the Ruprechtov natural analogue study, scant knowledge and ideas were available and the concept of a Safety Case had not yet been implemented. Therefore, in this respect parts of this report reflect the situation two decades ago.

Besides a brief overview on the different roles of analogues in national repository programmes and the evolution of analogue application in Safety Cases the intentions and objectives of this report are:

- Compile and critically discuss the decisions regarding the selection of the Ruprechtov site as a natural analogue;
- Classify the Ruprechtov site with regard to the type of uranium accumulation;
- Display the iterative steps, decisions and evolution of knowledge during the investigation of the site;
- Describe the experiences obtained, particularly in the selection and application of experimental laboratory and field methods;
- Outline the scheme by which these methods have contributed to understanding and characterizing the main features of the site;

- Illustrate the main findings relevant for a Safety Case for a radioactive waste repository, and
- Outline recommendations for future research and development (R&D) from the lessons learned.

The report structure displayed in Fig. 1.2 reflects the experimental / methodological approach applied in conducting the project. The existing knowledge at project start is compiled and discussed in Chapter 2. The methods applied and the key experiences are described in Chapter 3 (and the corresponding Annex A.2).

Chapter 4 describes how the key scientific issues have been investigated by applying different methods. The major results from the Ruprechtov project are summarized. During the duration of the project, new findings from R&D became available and are discussed in Chapter 5. On the basis of key Ruprechtov results and the new findings and information from R&D, the way in which system understanding can be increased and deepened is described in Chapter 6. In this framework, the geological evolution of the site and the interrelation of processes are described. Finally, it is discussed how these results could support the methodology of the Safety Case.

One key objective of this report is also to illustrate and include experiences gathered during the project which cannot always be found in technical or scientific reports. The findings and experiences laid out in this report are to a certain extent important for site characterization studies.

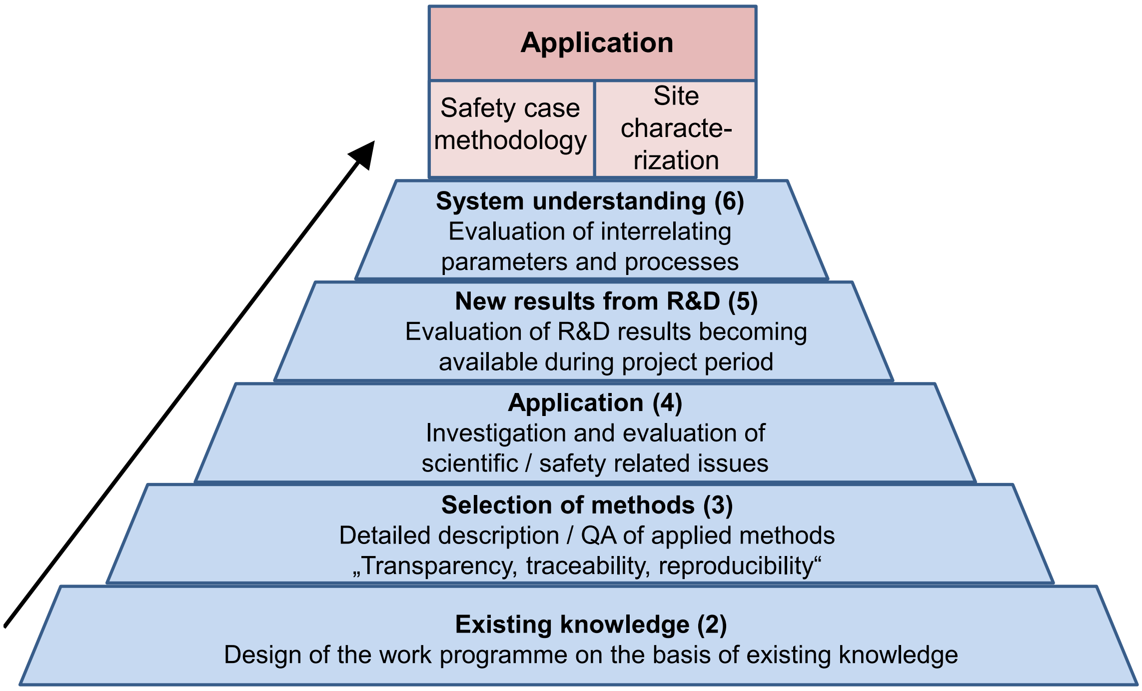

Fig. 1.2 Structure of the project steps and corresponding chapters of the report

1.1 General role of NA study application in a repository development programme

First analogue studies were started in the early 1980s. During the 1990s natural analogues became more and more relevant in many national and international repository research programmes. Emphasis was placed on providing proof of the long-term stability of engineered barrier materials in a natural / geological environment. For example, the long-term behaviour of artefacts (metals, glass, and bitumen) as well as the isolation properties of clay materials have been addressed. In addition classical analogues on the mobilization and immobilization behaviour of uranium in geological systems were still in the focus of research during this period.

The literature on analogue studies has been published in a large number of scientific journals and reports. In 1985 the international Natural Analogue Working Group (NAWG) was founded and since then 13 workshops have been conducted. The outcomes have been published in several reports by the European Commission and elsewhere, see /NAWG 14/. Sometimes analogues with their major characteristics have been assigned to safety relevant aspects of geological disposal. A good overview is given by /LOP 04/, reporting on the one hand on repository relevant materials and processes and on the other hand on a selection of well-known analogue studies. Forty-three analogues are here compiled and distinguished according to their relevance for long-term safety assessment into ten primary and thirty three secondary studies. The major categories are uranium deposits, clay analogues and analogues for alkaline conditions.

A more detailed review was conducted by an international expert team in the framework of an European project, reviewing more than 75 analogue studies /MIL 06/. These studies were similarly classified into a matrix with materials and processes in the subsystems “near field”, “far field” and the “near surface environment”. The application of the findings of performance assessment studies was evaluated. An important conclusion of this review was “*that natural analogues remain one of the most useful tools we have to increase our understanding of the processes that will control the evolution and safety of a repository over time. Analogue studies should, however, be considered as complementary to field, laboratory and modelling studies, rather than as isolated investigations. Implementing organizations should aim to integrate analogue studies fully into their research and development programmes. Their primary role is one of helping to understand processes and to develop and challenge conceptual models. Expectations should not be unrealistically high for the acquisition of quantitative data from future analogue studies for input to safety assessment models. The natural analogue community retains a deeply held belief that analogues contain information that is relevant when making a full Safety Case that employs multiple lines of reasoning*.”

In summary: Over recent decades, there has been considerable development in the consideration of the ways and means for the application of natural analogues. Early analogue studies often took the form of geochemical research projects intended to produce field data on processes (including their rates, where possible) that control radionuclide migration.

Meanwhile, there has been a paradigmatic change in-so-far as natural analogues can positively contribute to multiple lines of reasoning in a Safety Case, along with other kinds of information such as palaeohydrogeological findings and complementary indicators /NEA 12/. This change in the role of NA started with the analysis of the limitations of analogues. A strategy paper by Miller and Chapman pointed to the possibilities and constraints in investigating archaeological and industrial analogues /MIL 95/. Now it is widely accepted that there are multiple ways in which natural analogues can support a modern Safety Case for geological disposal systems, e. g. /MIL 06/, /NEA 14/.

For example, natural analogues can be useful for

(i) Identifying and understanding features, events and processes (FEP), and therewith checking the completeness of a FEP catalogue;

(ii) Underpinning FEP illustrating long-term safety (but not used in safety assessment), therewith contributing to multiple lines of reasoning;

(iii) Scenario development by identification of the relevance of FEP for a specific site;

(iv) Model development and qualification (i. e. evaluation of completeness of the considered processes and the check / validation, if model assumptions are plausible and reasonable), up-scaling issues, reducing data uncertainties, exploring bandwidth of data ranges and adaption of databases to natural observations, understanding spatial and temporal variations and process interactions and increasing confidence in conceptual models;

(v) Method development and testing, especially methods to be used for site-characterization and/or for the experimental programme as part of a Safety Case;

(vi) Confidence building, in a broader sense, for experts and laypersons by illustrating safety concepts, relevant FEP and assessment results to stakeholders.

1.2 Investigation of the Ruprechtov site: objectives and intentions

The Ruprechtov project was initialized in 1995. At that time the preferred options for the disposal of heat-generating radioactive waste were repositories in a salt dome in Germany and in granitic rock in the Czech Republic.

For the German repository programme, at the beginning 0f the 1990s a national expert group discussed the relevance and application of natural analogues for the assessment of the long-term safety of a radioactive waste repository and identified major topics for their use. One of seven identified topics concerned nuclide retardation in the overburden, especially the interaction of radionuclides (uranium and thorium) with Quaternary and Tertiary sediments under central European climate conditions /STE 96/. Based on existing knowledge of the sedimentary basin in Northern Germany, specific questions have been raised about the function of the overburden as a barrier for radionuclides, the corresponding processes such as dispersion, sorption and precipitation, as well as the role of organic matter, colloids and microbes. The objective was to increase the understanding of fundamental transport and retardation processes under complex natural conditions. These questions were key to starting the search for a suitable and appropriate analogue site (see Chapter 2.4.2 for more details).

In the 1990s, the intention arose to integrate natural analogues into the new developing Czech programme for a deep geological repository for spent nuclear fuel and high-level radioactive waste. In 1995, several sites with a natural occurrence of uranium mineralization were identified to be used as a potential natural analogue /HAN 95/. In 1997, the Atomic Act established a state organization (SÚRAO), which took over the competences and responsibilities regarding radioactive waste management in the Czech Republic. The study of natural analogues was subsequently incorporated into the Czech programme and elaborated in detail /HAV 98/. During that time several sites were proposed as potential natural analogues. One of the main objectives was to investigate argillaceous material, because bentonite plays an important role as a barrier in the near field of repositories in granite. Therefore, the analogue site should allow for the study of the behaviour of relevant radionuclides such as uranium and thorium in clay sediments. Similarly to the German approach, Tertiary and Quaternary geological sequences represent to some extent the overburden or the far field of potential granitic host rocks in the Czech Republic.

Various international analogue studies on the mobilization and immobilization of uranium in natural environments were conducted in the 1990s, e. g. /BLO 00/, /CRA 94/, /GAU 00/, /DUE 92/. One example of such investigations is the analogue study at Alligator Rivers /AIR 87/. The main relevance of this study lies in the illustration of uranium transport in natural porous systems over a million years, including processes of uranium retardation by sorption on Fe-oxyhydroxides and partly subsequent fixation in crystalline iron minerals. However, this and most other analogue studies have addressed very different rock formations or boundary conditions compared to the Tertiary and Quaternary sediments mentioned above.

The decision to use the Ruprechtov site as a research site was taken on the following:

- Sediments representing characteristics of the overburden of potential host rocks;
- Occurrence of organic rich material and uranium enrichment in the formation;
- Occurrence and quality of bentonite;

- Availability of geological information on uranium accumulation;
- Occurrence of uranium mineralization within an app. 40 m depth (for practical purposes: no mining work required);
- Accessibility of the site in terms of ownership and mining regulations.

In Germany, a site near Heselbach, with uranium-bearing Tertiary sediments was investigated using some drillings. It was proved that several lignite[1] seams within the basin were deposited in clayey sediments and overlayed with a sandy-silty horizon. Uranium was concentrated in lignite seams and clays at a depth of down to 0.5 – 8.0 m below surface with content up to 1,100 ppm. The hydrological situation and the former flow system at the site have changed due to coal mining in the close neighbourhood during the last two centuries. Today the location is an industrial site covered by a concrete pavement and other materials containing hydrogen carbonates with a strong influence on the geochemical conditions of the system. The latter fact particularly affected the investigations such that it was decided to stop the investigations. Therefore, further work was focused on the Ruprechtov site in the Czech Republic.

The site is located In the southern foreland of the Krušné Hory (Ore Mountains / Erzgebirge), part of the Ohře-Rift. Uranium accumulations have been mined in the nearby Hájek deposit which is located app. 5 km NNE of Karlovy Vary. Moreover, the predominant part of the Sokolov basin contains brown coal seams, but the Hroznetin sub-basin containing the Ruprechtov site has not been affected by any coal mining. The schematic geological cross-section (Fig. 1.3) gives a first impression of the situation of the area showing a sequence of mainly pyroclastic sediments overlaying a granitic basement. Uranium mineralization occurs in the direct vicinity of lignite seams. The close proximity to the underlying granite gave rise to an assumption about the suitability of the site for detailed studies. Consequently, an initial work programme for the confirmation of the geological situation and the occurrence of uranium was set up (see Chapter 2.3).

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[1] The term *lignite* is used in this report synonymously with the term *brown coal*

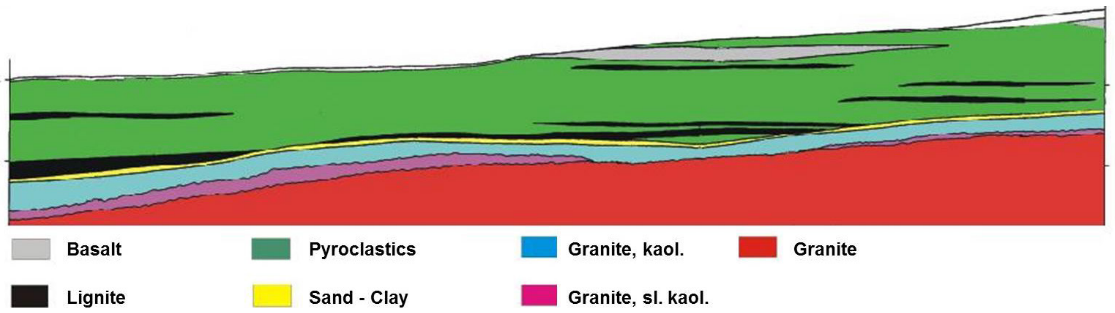

Fig. 1.3 Schematic geological cross-section of Hájek South deposit (from /NOS 02/, modified after unpublished ÚJV-documents)

A similar outline of the knowledge concerning geological situation at that time can also be found in /FRA 82/ (see also Fig. 2.8).

2 Knowledge about uranium deposits and natural analogue studies at the beginning of the Ruprechtov project

Potential concepts and the relevant properties of geological repositories for long-lived and high-level radioactive waste have been investigated since the 1960s. After the main technical issues had been clarified, aspects related to geology and mineral deposits were also increasingly taken into account and researched within the framework of more sophisticated safety considerations in the 1980s and especially in the 1990s. On the one hand, these related to the mechanical and geohydraulic properties of potential host rocks such as granite, argillaceous rocks and rock salt formations. On the other hand, they concerned the geochemical behaviour of the relevant radionuclides and here, in particular, of uranium in the geosphere, including the genesis of natural uranium deposits. Of utmost interest are the mineralogical and geochemical changes undergone by such deposits due to geological and geohydraulic processes /OECD 82/ as experienced during decades of uranium mining and uranium prospection worldwide. Some of these processes create so-called “natural analogues” not only for their long-term retention of uranium but also because they show similarities to radioactive waste repositories planned in comparable geological environments. Studied in depth, such analogues can provide a better conceptual understanding of safety assessment models including the most relevant data and processes /EUC 06/.

The first and most widely known example was the investigation of the Oklo uranium deposit in Gabon where nuclear fission reactions occurred under natural conditions about 2 billion years ago whose products, surrounded by argillaceous rock, still exist today /LOU 97/, /LOP 04/. It has been shown that in terms of the long-term behaviour of geological repositories, geochemical processes under various temperature and pressure conditions are important. The stability or solubility of the minerals depends on the Eh and pH conditions, in particular during the formation of uranium-bearing mineral phases. For this reason research on natural analogues focused on geochemical issues.

In parallel with the scientifically oriented work on various natural analogue projects, expert groups of the OECD/NEA and the IAEA underlined the importance of the accumulated knowledge as a significant contribution to demonstrating the long-term safety of repositories /NEA 04/, /NEA 99/. Today, there is broad consensus that, due to the longevity of high-level radioactive waste, geochemical processes are of great importance for demonstrating the safety of geological repositories. Realizing this, the term “natural analogue" was adopted from the research at an early stage, e. g. in the framework of the Natural Analogue Working Group (NAWG) and introduced as standard terminology and scientifically substantiated in scientific-technical guidelines /IAEA 99/.

The findings of mineral deposits research have thus provided important input for safety research on geological repositories in two ways. Firstly, the observations, measurements and experience undertaken in practice have provided a large amount of data whose evaluation and assessment clearly indicates the migration or isolation of uranium in geological systems. Secondly, knowing the safety relevance of geochemical and geohydraulic processes, assessments of the long-term properties of repository systems are carried out today on the basis of numerical models. Thus, knowledge, methods and techniques in the field of waste disposal research have been further developed during the project period to a considerable degree.

In view of the various concepts of repositories and their features having an impact on the geochemical system, scientific and technical working groups have identified the main safety-relevant processes at an early stage and assigned natural and archaeological analogues to them (Tab. 2.1) /MIL 94/. The vast majority of the scientific literature on this subject was published in the 1990s.

This was also the period during which the Ruprechtov research project commenced, where additional issues were taken into consideration. This concerns, as part of the repository system, the overburden with the processes taking place within it, which was included in the safety analyses and assessments of that time. The consideration of "far-field processes" was relatively new in the context of research on natural analogues, since previous work dealt more or less with processes in the near field of a repository. This aspect was taken up by the German expert panel (SKE) on “Research and Development” (R&D), particularly in view of the performance of covering strata as barrier formation for deep geological repositories /PTE 94/, /STE 96/. The Ruprechtov site provided the opportunity for the more detailed study of processes in the so-called far field and characterizing the physico-chemical processes in porous low-permeability rocks and formations, which considerably contribute to the long-term confinement of radioactive waste in a geological repository system.

Tab. 2.1 Key geochemical processes for which natural analogue information has been provided /MIL 94/

Process	Analogue
Container corrosion	Industrial and archaeological artefacts, native materials
Waste form breakdown	Uraninite ores, natural glasses, archaeological artefacts and cements natural CSH compounds / minerals, natural bitumens, cellulose
Radionuclide solubility	High natural decay series waters (e. g. ore bodies), hyperalkaline springs
Radionuclide transport	Ore bodies, geochemical discontinuities in sediments, sub surface bomb tests, accidental discharges, natural colloids
Redox front processes	Natural redox fronts in uranium ore bodies, in recent turbidities, and in reduction spots
Matrix diffusion	Fracture zones in / around mineralized veins

The assumed geology of the location, important for the selection, was as follows: The granite "basement" with different types of uranium mineralization and the overlying argilized volcano-detritic sediments with significant montmorillonite content, which in part also contain uranium, form a geological system in which the occurrence of uranium is bound to various geological events. Taking into account past and present environmental conditions, there are clear indications regarding the mobility and fixation of uranium in surficial formations. These and previous findings from uranium mining in the area and from other analogue projects were considered in the development and implementation of the research programme.

For the preparation of this report it seemed to be important to compile a basis focussed on geological and deposit-related aspects to enable the better characterization of the location (genesis, evolution, etc.). For this purpose, around 300 scientific papers and book contributions from international research programmes with relevance for the Ruprechtov project as well as relevant publications of the IAEA and OECD/NEA were compiled in a knowledge database /SWI 14/. In some cases, more recent literature on economic geology and on the topic of "natural analogues" was also considered. In addition, the various project reports were summarized in a separate subfolder. In structuring the database, the main topics were chosen, as shown in Tab. 2.2.

Tab. 2.2 Database structure of project-relevant literature

Topic No.	Topic title
1	Natural uranium ore deposits
2	Projects on natural analogues
3	Data from natural analogues
4	Transport phenomena
5	Environmental issues
6	Collection of field data (Ruprechtov project)
7	Miscellaneous
7.1	Waste management issues
7.2	Geological disposal concepts

2.1 Natural uranium-containing systems

Worldwide, more than 200 minerals containing uranium are known from a variety of geological formations and deposits that differ in their chemical composition, crystalline structure and genetic origin. Primarily, uranium originates from the upper part of the Earth's crust where it accumulated through igneous differentiation and due to its strongly lithophile character. Uranium is present in almost all igneous rocks as a trace element. Values in acidic (granitic) rocks can typically reach up to 4 g/t.

During their formation, intrusive rocks such as granites cool down slowly, so uranium concentrates in residual solutions and can subsequently precipitate in pegmatites, hydrothermal veins and adjoining rocks (impregnation) in specific mineral phases. Extrusive rocks with their volcanic rocks and lavas, however, cool down rapidly which, under certain conditions, will prevent the escape of residual solutions and volatile heavy metal compounds, which may also lead to a higher uranium content in the rock /DYB 62/.

The distinct oxidation behaviour and the related high solubility of oxidized (hexavalent) uranium species are the reason for its relatively large mobility in the geological system. So, uranium is dissolved and transported relatively easily in contact with groundwater and surface water. The consequences are, on the one hand, strong dilution in the aquatic systems or, on the other hand, due to reducing physico-chemical conditions, the formation of solid mineral phases and in special cases "secondary" accumulation in rocks. As some types of deposits show, weathering processes are of great importance in this context.

Normally, the uranium content of river water is very low with values between 1 and 3 µg/L. Groundwater samples from different sediments and rock formations in Germany in some cases produced mean concentrations of up to 15 µg/L U /DIE 12/. In the Czech Republic the average in groundwater sources is 4.4 µg/L U /STA 96/. In Western Bohemia, where mineralized waters are used for spa purposes, the typical U content is 1-2 µg/L with a maximum of 32.8 µg/L in Františkovy Lázně (cold mineralized groundwaters) and between 16 and 25 µg/L in Jáchymov (radioactive thermal groundwaters). Some high U content springs occur also in this area with a maximum concentration of 788 µg/L in Poustka - Horní Žandov /KOL 79/. Compared to this, the uranium content in seawater is much lower and ranges between 1.5 and 3.5 µg/L, although rivers have delivered significant amounts over geological time scales. Reducing conditions in deeper marine areas are stated as being decisive for this "balance" which promotes large precipitation and deposition of uranium in the sediments. Black shale formations and the formation of marine phosphorites with higher uranium contents are regarded as exemptions /DYB 62/.

The geochemical cycle of uranium in the geosphere and the environment, as schematically shown in Fig. 2.1, is largely known, e. g. /LAN 78/, /LAN 97/. The most common mineral phase occurring in nature is uraninite (UO_2). At usually low temperatures in surficial areas, the reduced, tetravalent uranium form is immobile. However, highly mobile uranyl ions (UO_2^{2+}) may be generated as a result of oxidation to higher valence (uranium VI); bacteria also contribute to this process /EWI 99/. Conversely, such solutions may form many complex mineral phases entering a reducing environment, depending on the pH value and the material content. The minerals uraninite, coffinite and brannerite are particularly common /FIN 99/.

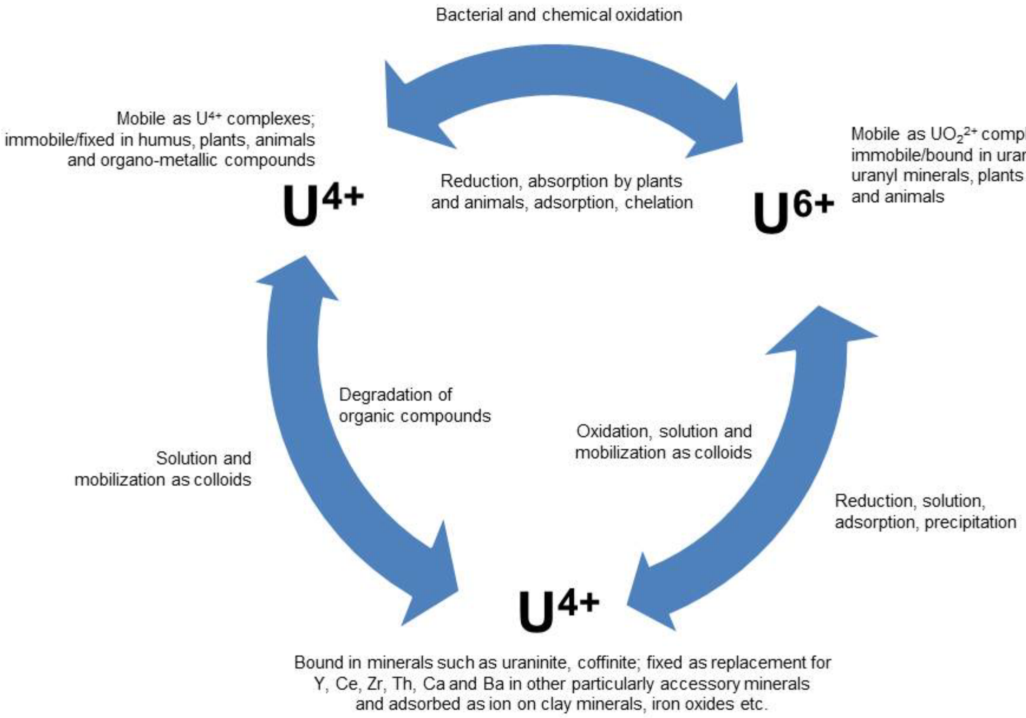

Fig. 2.1 Interconversion cycle of tetravalent (U^{4+}) and hexavalent (U^{6+}) uranium in nature (modified after /BOY 82/)

2.1.1 Uranium accumulation in geological formations

In many cases, the mineral phases occurring in uranium deposits give indications of their genesis. In addition, knowledge is available on the genesis and facies of the rocks forming the deposit with their tectonic overprint. A general distinction can be drawn between magmatic (primary) and sedimentary (secondary) deposits. Besides these, there are also deposits (Tertiary) whose facies and mineral contents have been significantly changed by metamorphic overprint of rocks (pressure and temperature loads), possibly in combination with geodynamic activities.

Against the background of being able to distinguish between uranium deposits on the basis of geological, genetic, geochemical and geochronological criteria, it is understandable that typing into main groups and subgroups is a complex matter. In his standard work “Uranium Ore Deposits", /DAH 93/ mainly divided uranium deposits according to their geotectonic evolution or according to the host rock type. In total, a distinction is drawn between sixteen main types and up to forty subtypes and classes. The classification is based on principle criteria and metallogenetic aspects. Thanks to the complexity of the ores and geneses, some overlaps are unavoidable. In 2009, the IAEA also presented a catalogue of deposit types /IAEA 09/ which, in principle, is based on the same criteria and thus largely correlates with that of Dahlkamp. In total, the pricipal characteristics of 14 main types are described, and the corresponding world's largest deposits with their production rates are assigned to these types.

In the following discussion, four main types which can be related to the geological conditions in and around Ruprechtov to some extent are presented with regard to the Ruprechtov project:

1. **Unconformity-related deposits:** These deposits are associated with crystalline rocks of the Proterozoic, which are unconformably overlain by clastic sediments of the Early Proterozoic. Uranium accumulations are either found along fault zones in crystalline rock, or in the area of the unconformity bound to clay, or in directly overlying sandstones. In a recent publication, C.W. Jefferson et al. /JEF 07/ illustrate the diversity of this type of uranium deposit as being very important for uranium mining. Unconformity-related deposits constitute more than 33 % of the world’s known resources and are mainly found in Canada and Australia. Fig. 2.2 shows a schematic geological profile presenting the main components of these deposits.

   In view of the complex processes governing not only mobilization but also precipitation, fixation and sorption of uranium in a geological environment, it must be pointed out that the more global term “unconformity” is, among others, related to three essential aspects in geology, i. e. the development of rock formations over time, stratigraphic conditions and structural formation as a result of tectonic events and orogenic phases. First and foremost, an unconformity marks a period of time during which no sediments were deposited and the existing mainland was exposed to the influence of weathering and erosion. Compared to contemporaneous depositional environments, there is a gap in the rock sequence which may represent many millions of years. Major hiatuses are easily recognizable by means of different geological criteria. In particular, the structural changes in the subsurface often associated with unconformities are an indication of movements in the earth's crust, mountain uplifts, tectonic shifts and often also volcanic activity.

   From a deposit-related point of view, this results in a complex pattern of parallel or tilted rock units, partly having very different mineral contents. This type of deposit requires the presence of uranium in the older rock formations (Proterozoic, Phanerozoic) which, due to the unconformity, have been exposed to weathering over a long period of time. The deposits have formed subsequently in the vicinity of these unconformities and they differ in their configuration, rock type and composition and in the amount of ore that is contained. Fracture-bound deposits in metasediments have formed immediately below unconformities. Their mineralization is mainly monometallic, with average uranium content (0.3 – 1 % U_3O_8). Clay-bound deposits are found in rocks that were immediately deposited on unconformities. They are polymetallic (U, Ni, Co, As) and associated with bitumen. Their ore grades are very high (1 – 14 % U_3O_8). The principal mineral phases in both ores are pitchblende and uraninite /DAH 93/.

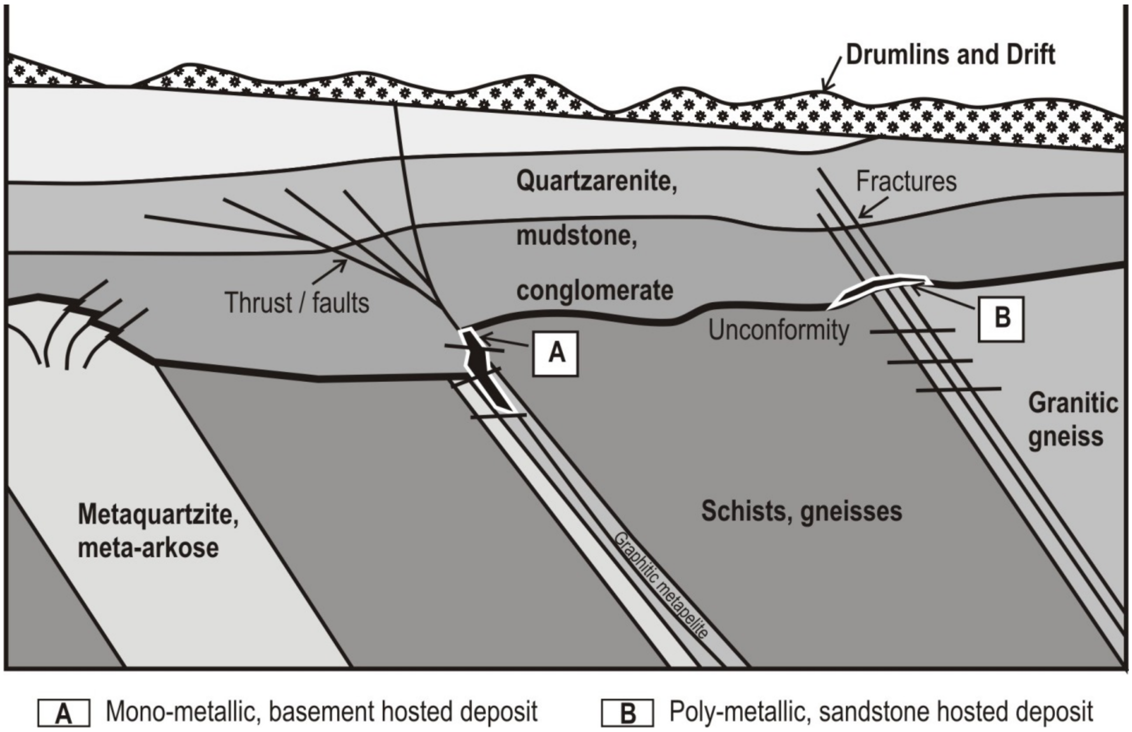

Fig. 2.2 Generalized geological elements of mono- and poly-metallic unconformity-associated U deposits in the eastern part of the Paleoproterozoic Athabasca Basin

This is an empirical geological framework model illustrating two end-member styles of ore, between which a complete spectrum of styles are known, even within single deposits and deposit groups (modified after /JEF 07/).

As stated previously, the processes of uranium mineralization, transport and redeposition are decisive for the formation of these high-grade uranium accumulations. Basically, however, these mechanisms also apply to younger rock formations with unconformities. The "Koongarra" (Australia) and "Cigar Lake" (Canada) deposits have been intensively investigated and assessed under technical aspects of disposal with regard to the behaviour of high-level radioactive waste. Important findings on the transport and sorption of uranium have been derived from the investigations at Koongarra; whereas the stability of uranium ore under reducing conditions and the formation of a bentonite-bearing “clay halo” make Cigar Lake an analogue for the long-term isolation of waste in deep geological formations.

2. **Sandstone deposits:** Depending on the morphological conditions and the characteristics of former river beds, uranium deposits usually occur at preferred locations in medium- to coarse-grained sandstones. In addition to factors such as flow directions and velocity, the presence of reducing agents such as carbonaceous material, sulfides, hydrocarbons and ferro-magnesium minerals have played a role in the formation of such deposits. Sandstone uranium deposits can be divided according to their physical properties and the nature of the reducing environment into four subtypes "roll front deposits", "tabular deposits", "basal channel deposits" and “tectonic / lithologic deposits” /IAEA 09/.

   Sandstone deposits are common in the USA, Kazakhstan and Niger. They constitute around 18 % of the world’s known uranium resources. In the Czech Republic, the "Hamr-Stráž" p. Ralskem (abandoned uranium mine) uranium deposit belongs to the subtype "tabular deposits". Also known is the Tono Mine in Japan where Tertiary rocks have been opened up down to a depth of 130 m. Uranium mineralization is found in lacustrine sediments with significant amounts of organic material and secondary pyrite, immediately overlying a uranium-bearing Cretaceous granitic complex. The sequence of Tertiary sediments comprises conglomerates, sandstones and tuffites, which were deposited in extensional basins and "paleochannels” in the former granite surface /YOS 90/.

   More recent studies describe in more detail the deposit conditions in so-called "paleochannels" or "paleovalleys" in areas in Australia and the USA /JAI 10/. Large-scale prospecting shows that uranium deposits often occur at confluences and prominent river bends. Factors that promote the formation of deposits are contacts (excavations) of the river bed with underlying rocks, coarse-grained sediments, and the presence of abundant organic material. The example from the Painted Desert Valley (Utah), shown in Fig. 2.3 illustrates the incision of the meandering river bed in the underlying Moenkopi Formation and the filling with coarse sandstones and gravels of the Chinle Formation in the Upper Triassic (about 250 Ma ago). In the lowest stratigraphic unit, the Shinarump Member, the uranium was deposited at preferred locations. In these depressions, the uranium was obviously less exposed to oxygen-rich water so it could not be released again and transported. In particular, overlay with more argillaceous rocks may have contributed to this.

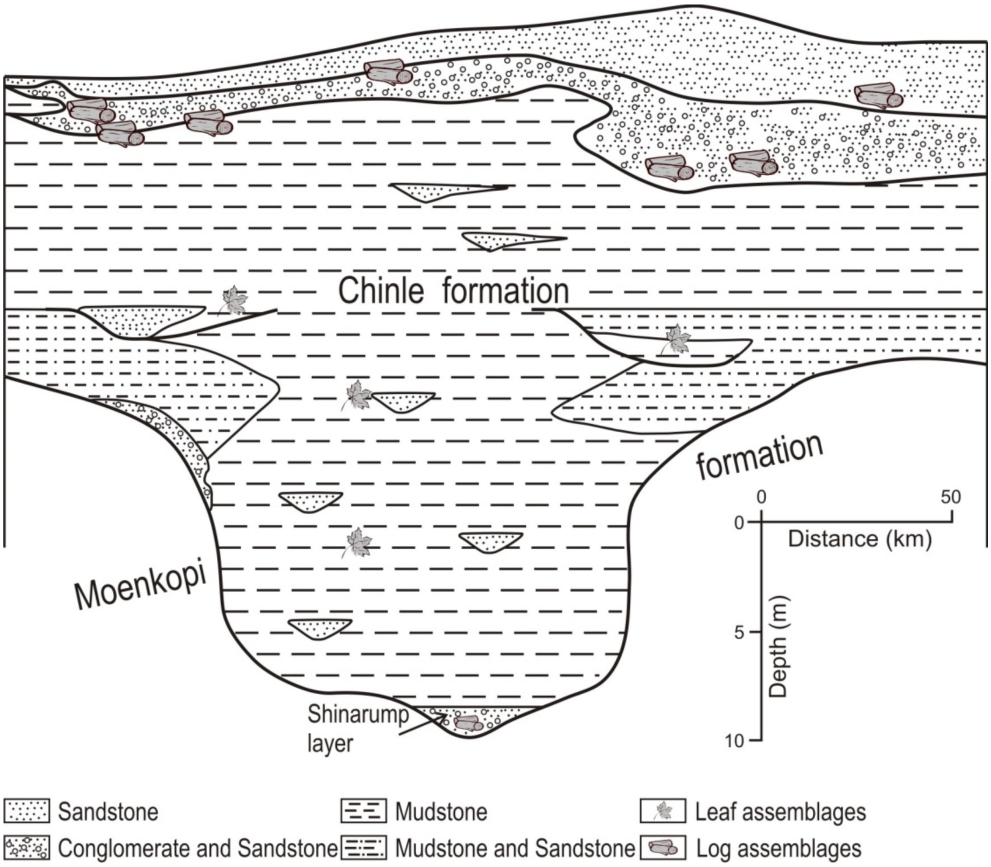

Fig. 2.3 Schematic cross-section of the Painted Desert paleovalley showing the stratigraphic relationships of layers of the Chinle formation

Uranium mineralization is located predominantly in the Shinarump layer (modified after /DEM 03/).

3. **Volcanic and caldera-related deposits:** These deposits are formed in the immediate vicinity of volcanic complexes or in the sunken caldera areas after the magma chambers have emptied. These calderas are filled with volcanic material and clastic sediments. Here, uranium mineralization is often bound to structures / faults /PET 04/. Stratabound mineralization often occurs in areas outside the caldera, usually bound to tuffitic material overlying the local sediments or intercalated with them. The sources of uranium are first and foremost volcanic rocks which are exposed to weathering by meteoric waters as well as to the influence of volcanic activities such as hot springs and fumaroles. Through such processes, the uranium becomes strongly dissolved and is largely transported away from its "primary" site of deposition by surface waters and groundwaters. With favourable conditions, it

may also precipitate again epigenetically in close proximity to various rocks /DYB 62/. Indications of volcanic origin are also given by the accumulation of trace elements, such as Mo, Sn, W, Hg, As, Sb and Li, in the primary rocks.

The volcanic deposit type is often "masked" by an overprint resulting from increased hydrothermal activities and diagenetic processes, which complicates its assignment to possible subtypes and classes /DAH 93/. Most of these deposits show characteristics which can also be found for other types, such as the occurrence of uranium mineralization in faults and fissures or as surficial deposits or accumulation in stratified sandstones. The latter type, however, is not directly related to volcanogenic processes. In general, the formation of ore deposits (not only uranium) associated with effusive volcanism is often complex and takes place in many ways /DSO 68/ and economically exploitable deposits do not occur often.

Recent scientific studies on Mesozoic ignimbrites of the Tulukuevskoe deposit (Siberia) show, regardless of the primary mineral supply, the complex remobilization and redeposition processes by alterations in the vadose (water-unsaturated) zone in combination with a change from reducing to oxidizing conditions (and vice versa). There are indications that in the volcano-sedimentary environment, hydrothermal processes have also contributed to the formation and distribution of organic material important for the sorption of uranium /PET 04/.

4. **Surficial deposits:** Surficial uranium deposits are often referred to as Tertiary or recent deposits, since uranium mineralization is predominantly bound to young sediments or soils. This type frequently occurs in sand- and gravel-containing calcareous crusts (calcretes) which have been formed by precipitation of calcium carbonate in pore spaces or by the release of CO_2 from carbonate solutions. Surficial deposits often occur in the immediate vicinity of the primary host rocks of uranium, such as deeply weathered granites. Such sediments are preferably formed in arid and semi-arid regions and are deposited in alluvial channels or in evaporation pans.

   Other forms of this type mainly originated in a humid environment and are usually bound to clay-rich sediments with abundant vegetable-organic matter. In the Flodelle Creek deposit in Washington State (USA), uranium is found in solidified peat, whose formation has been controlled by the topography and the local water regime. It is underlaid by granodiorites with above-average uranium contents. Strikingly, mineralizations do not occur such that under such conditions either uranoorganic complexes are formed or the uranium is adsorbed onto the organic material. Moreover, often there are no daughter products of uranium due to the young age /DAH 93/. In Broubster (Scotland), significant uranium deposits are found in post-glacial peat, whose metal content was released from neighbouring Devonian sandstones and transported with the groundwater. The uranium predominantly occurs in the form of fulvate/humate complexes which have cationic character at pH-values < 6 in the peats and are therefore efficiently bound to the sediments /HOO 94/.

In addition to the described types of deposits, there are a number of others, some with great economic importance. These are, among others, uranium deposits in hematite-rich breccias and quartz-pebble conglomerates. Another type is vein deposits in granitic rocks (see Chapter 2.1.2.2) and metasedimentary rocks with their different facies. The most prominent deposit of this type in the Czech Republic is the Příbram uranium deposit. Deposits associated with different intrusive rocks, such as granite, monzonite, carbonatites and pegmatites, should also be mentioned but are not dealt with here since they are not directly related to the Ruprechtov project.

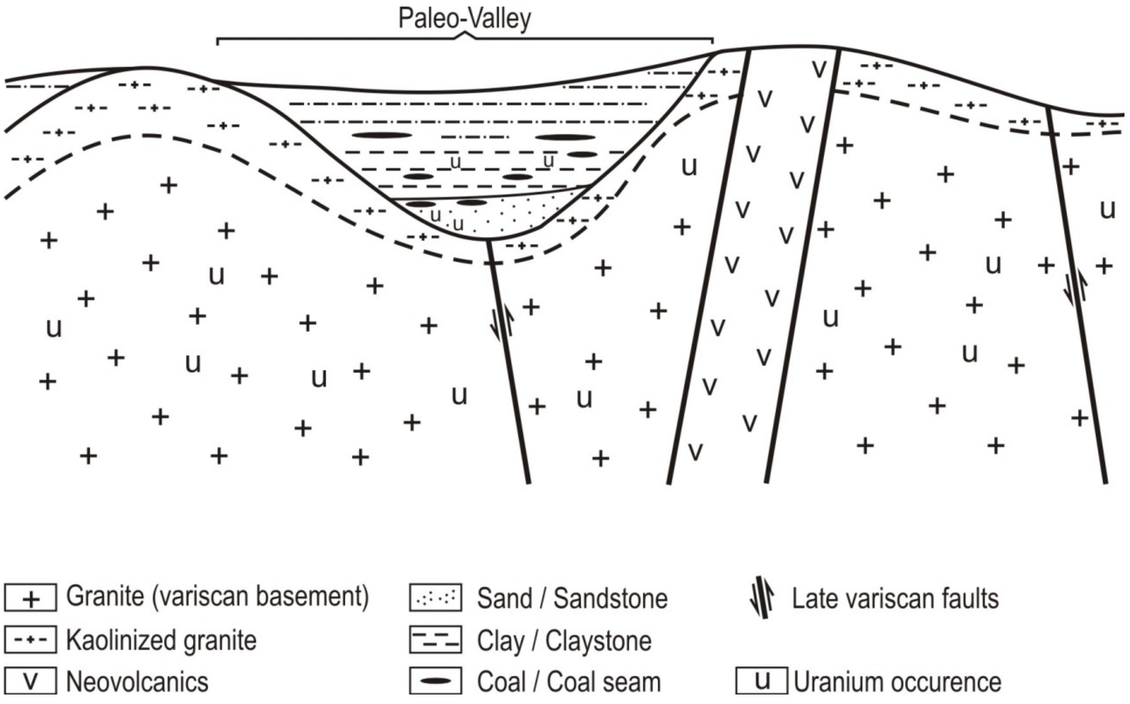

Fig. 2.4 Schematic cross-section showing the main geological features of the Ruprechtov area including the occurrence of uranium in granite (broadly disseminated) and in Tertiary sediments (locally accumulated in layers)

The types shown here are characterized by petrographic features and geochemical processes which in part and/or with certain restrictions can be found in the Ruprechtov deposit with its locally concentrated uranium contents in Tertiary sediments. The findings from the known deposits have helped in planning the research project as regards contents, in identifying the main "deposit-forming" processes more precisely by means of the investigations carried out and in determining their genetic type.

2.1.2 Uranium deposits and mining in the Czech Republic

During the period 1946-2000 a total of 164 uranium deposits and uranium mineralization occurrences were explored in the Czech Republic of which 86 deposits and occurrences were mined. All of the mined deposits fall under the following three types as defined by /DAH 93/, /IAEA 09/:

- Vein deposits, granite related (72.1 % of total uranium production from 1946 to 2000);
- Sandstone deposits, tabular type (27.1 % of total uranium production from 1946 to 2000);
- Surficial deposits (uraniferous coal and lignite deposits) (0.8 % of total uranium production from 1946 to 2000).

2.1.2.1 Uranium mining

Uranium mining in the Czech lands commenced in the first half of the 19th century. Pitchblende from the Jáchymov deposit was used for the production of dyes for the glass and ceramics industries. Radium extraction commenced at the beginning of the 20th century. Prior to the First World War, Jáchymov was the world leader in terms of radium production. It has been estimated that uranium production in the period 1853 to 1944 amounted to 469.5 t. For details see Annex A.1.

From 1946 onwards there was a significant acceleration in the exploration and mining of uranium deposits in the Czech Republic, whereas no uranium production is reported for 1945 and 1946, approximately 500 t of U (metal) was produced in 1951, in 1952 nearly 1,000 t and in 1955 a remarkable 2,000 t (circa 10 % of worldwide annual production). The development of the production of U in the period 1946 – 2013 is shown in the Annex in Fig. A.1. Annual production reached a maximum in 1960 at more than 3000 t (circa 6 % of worldwide annual production) /IAEA 09/. Production fell dramatically at the beginning of the 1990s and, since 2000, uranium has been mined only at the Rožná mine. For details see Annex A.1.

2.1.2.2 Vein-type deposits

Vein-type deposits (granite-related) are the most common and important type of uranium deposit in the Czech Republic as well as across the Bohemian Massif as a whole. However, vein deposits are not relevant to the Ruprechtov project, in terms of its geological and mineralogical properties.

Vein type deposits are defined as fractures of highly-variable thickness, generally significant extension along the strike and filled with mineralization /IAEA 09/. Examples of vein deposits in the Czech Republic consist of “typical” veins, both monometallic (pitchblende and gangue minerals) found at Příbram and polymetallic (with other minerals such as Co, Ni, Ag, Pb, Zn in economic quantities) at Jáchymov and partly at Příbram, as well as stockworks, columns and narrow cracks filled with pitchblende.

Both subtypes of granite-related deposits, which are defined based on their spatial relationship to granitic plutons or the surrounding host rock, are present in the Czech Republic; however, the perigranitic subtype (veins in metasediments and contact-metamorphic rocks) strongly predominates. Examples of this subtype include the Příbram, Jáchymov and Rožná deposits. Deposits of the endogranitic (intragranitic) subtype, although rare in the Czech Republic, include for example the Vítkov II (West Bohemia) deposit in the Bor Pluton of Variscan origin and a few relatively insignificant deposits in the Central Bohemian Pluton.

2.1.2.3 Sandstone deposits

In terms of economic importance sandstone deposits (see Chapter 2.1.1) make up the second most significant type of deposits in the Czech Republic. They provide more than 27 % of total uranium production.

Uranium mineralization of this type was discovered in the sediments of the Czech Cretaceous Basin in the mid-1960s. All of the deposits explored are very similar in terms of their stratigraphical position, lithology, form of uranium-bearing body and average uranium content. Uranium accumulations are present in freshwater (river and lake) sediments of Cenomanian age and principally in the basal part of Cenomanian marine sediments near the transgression boundary (unconformity). Uranium-bearing sediments consist of various types of sandstone and siltstone. Uranium is bound to sediments with a high content of organic substances and pyrite as well as to significant changes in lithology. The shape of the uranium-bearing bodies is predominantly tabular, less commonly lenticular, and the thickness of individual bodies varies from several decimeters to 8 meters. Uranium mineralization is predominantly present in the form of matrix impregnations; the average content of uranium is 0.1 %. For more details see Annex A.1.

2.1.2.4 Surficial deposits

Surficial deposits (uraniferous coal and lignite deposits) are rare in the Czech Republic and of negligible economic significance. This type is characterized by elevated uranium content in lignite/coal and in clay and sandstone immediately adjacent to lignite. Uranium grades are typically very low (20 – 60 g/t) and only a small percentage of layers have a uranium content in excess of 0.1 %.

A few small uranium deposits of Carboniferous and Permian age have been explored and mined in the Intra-Sudetic Basin (northern part of the Czech Republic). Uraniferous coal has been found to be present in the form of irregular lenses with a maximum thickness of 0.25 m in coal seams and has been mined together with energetic coal at a number of deposits (Svatoňovice).

The economic importance of this type of deposit in the Czech Republic has been historically negligible, making up a mere 0.5 % of total uranium production.

Small deposits and occurrences of uranium mineralization of the same type have been found in the Tertiary sediments of the Hroznětín section of the Sokolov Basin; however, the economic importance of these accumulations was even less than those mentioned above, i. e. just 0.3 % of the total uranium production of the Czech Republic.

The importance of this type of mineralization lies in the fact that the Ruprechtov natural analogue is made up of this type of uranium accumulation. A more detailed description of the stratigraphic position of the uranium accumulation in the Hroznětín section of the

Sokolov Basin is presented in Chapter 5.1; a description of individual uranium deposits, including a geological sketch map, can be found in Annex A.1.

2.1.3 Main genetic phases of uranium formation and accumulation in the north-western part of the Bohemian Massive

The rocks of the greater region are predominantly of Proterozoic and Palaeozoic age, were folded during the Variscan orogeny 340 to 270 Ma ago and are partially characterized by high-grade metamorphic overprint. To a significant degree, they form the basement of the ancient land mass, known as the "Bohemian Massif", /CHL 78/. The massif is divided into southern (Moldanubian), central (Bohemian) and northern (Saxothuringian) parts (see Fig. 2.5, after /STR 86/). The central Bohemian part mainly consists of metamorphic rocks into which acid granitoid magmas intruded during a Late Variscan phase. These are classified according to their petrochemical characteristics, drawing a distinction between older and younger granites. Older Late Variscan granites formed during the Lower Carboniferous are predominantly found in the western Krušné hory (Erzgebirge), the Vogtland and the area around Karlovy Vary. Younger Late Variscan granites were formed during the Lower Permian and frequently occur as small intrusions. From the metallogenetic point of view, they are of special importance due to their Li, F, P, Th, Yb, Ba, and U content /BAU 00/. A modern view on the greater area is available /CHA 10/ but it does not have any impact on the interpretation of the Ruprechtov findings.

Tectonic processes also play a role in the formation of uranium deposits. So, for example, two large NE-SW striking tectonic junctures in the north-western part of the Czech Republic (Central Bohemian lineament, Ohře valley lineament) and a deep-reaching NW-SE striking fault (Jáchymov Fault) determine the structural pattern of the overall faulting system originating in the post-Variscan phase. In the vicinity of these zones and at their cross-cutting areas are known uranium deposits, e. g. the Jáchymov and Příbram vein deposits. Not far from the Ruprechtov study area, the Jáchymov fault cross-cuts the SW-NE trending alignment of Tertiary volcanics with the Doupovské mountains in the intersectional area.

In the post-Variscan phase, Permo-Carboniferous sediments (arkoses, shales, coal bands) were deposited in local basins of the "Bohemian Massif". Until the beginning of the Upper Cretaceous, the entire massif was a land surface which was levelled by erosion. This was followed by deposition of sandstones and marls in epicontinental shallow water areas in many parts of northern Bohemia and Moravia. Because of the nearness of the granites to the surface and partly promoted by hydrothermal veins, these were intensively exposed to weathering. Under humid climatic conditions, siallitic decomposition of feldspars led to the formation of large kaolin deposits that either sedimented eluvially (at the place of their origin) or were swept away alluvially and redeposited close by. Deep-seated deposits are particularly bound to the chemism of the waters prevailing beneath and, as in the region around Karlovy Vary, to the occurrence of thermal CO_2-rich groundwaters /SAN 80/, /WIL 95/.

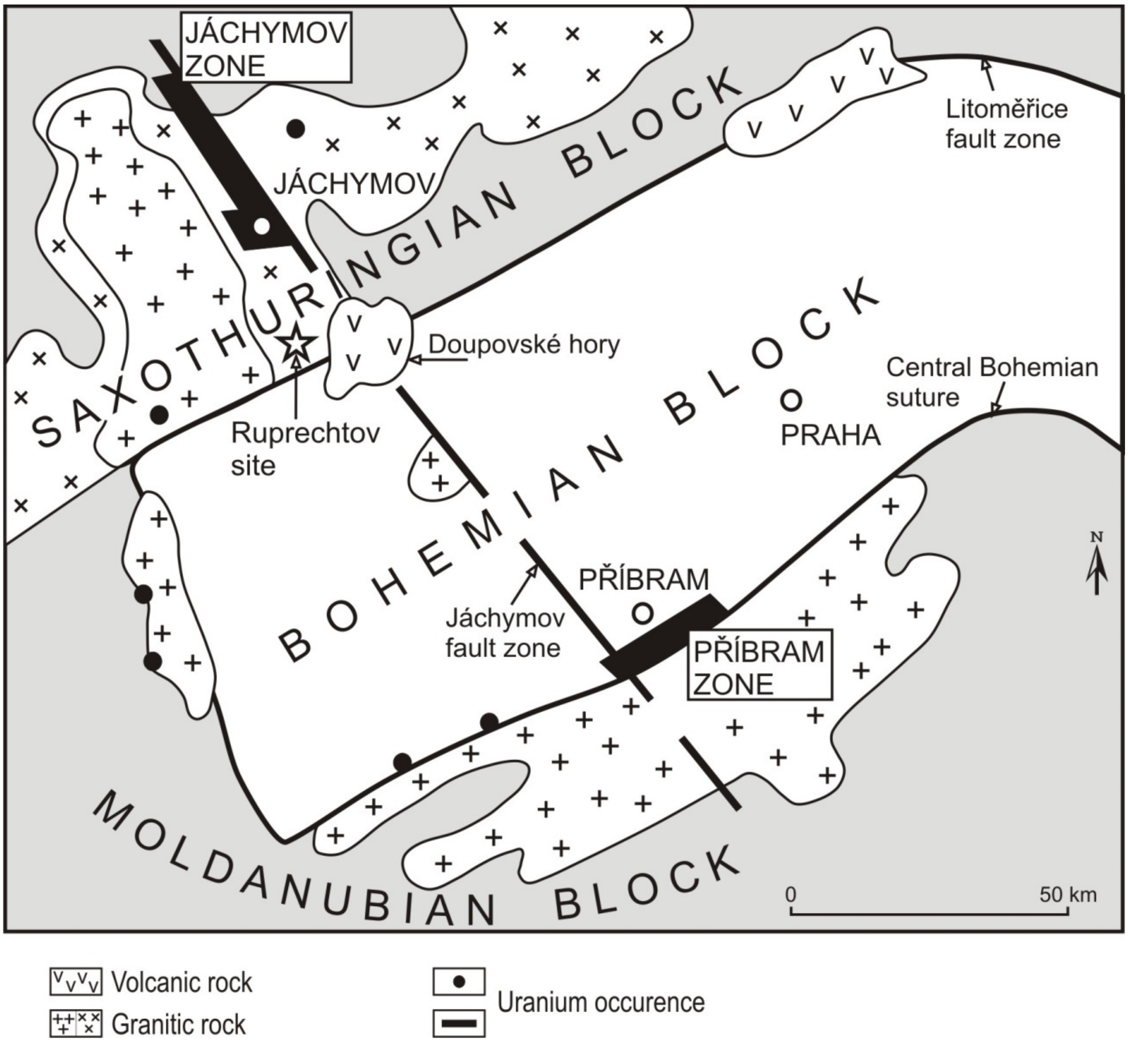

Fig. 2.5 Sketch of the structural setting of the Jachymov and Příbram U-vein zones within the north-western part of the Bohemian Massif (modified after /STR 86/)

During the Tertiary, the Krušné hory (Erzgebirge) was lifted by about 1,000 m during the Alpine tectogenesis and the formation of horst and graben structures took place, while falling obliquely to the NW /BAU 00/. As described above, older fault systems were partly rejuvenated. The occurrence of basalt and phonolite volcanoes in different regions of the Krusnehory and the Ohře valley graben is also bound to the tectonic processes.

In the western part of the Ohře valley graben (Sokolov Basin), sediments with a thickness of 400 m were deposited on the Variscan rocks /ROJ 04/. At the Eocene-Oligocene boundary, the original basin was filled with fluvial sediments of the Staré Sedlo Formation, followed by the Nové Sedlo Formation with mainly tuffitic material. This marks the beginning of tectonic movements and the onset of volcanism. The younger Sokolov Formation mainly consists of lignite with some tuffitic strata covered by a sequence of argillaceous sediments, indicating the end of the endogenous phase. In the geological profiles of P. Rojik, three unconformities in the strata sequence give indications of the interaction of dynamic processes and volcanic activities.

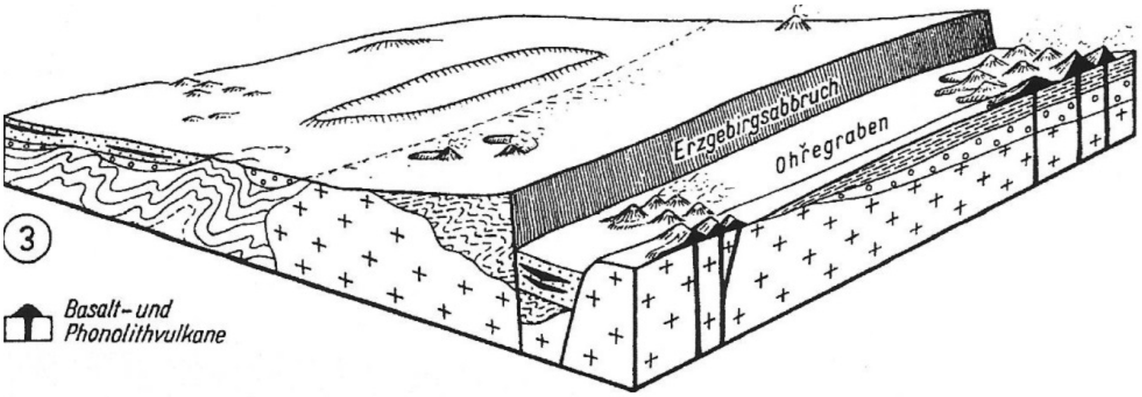

Fig. 2.6 Major structural features at the Krušné hory with the Ohře Rift Valley (extracted from /WAG 90/)

An important indicator of the impact of climate-dependent factors in the alteration and new formation of minerals is the formation of bentonites due to argillitization of volcanic rocks. Autohydrothermal alteration of the hot volcanic material in an aqueous-swampy environment is regarded as one of the most common reasons for this phenomenon /FRA 82/. Locally, hydrothermal solutions may also contribute to the disintegration of the pyroclastic rocks. Rapid subsidence of the sedimentary basins and permanent overlay by additional tuffites has led to large thicknesses of bentonite.

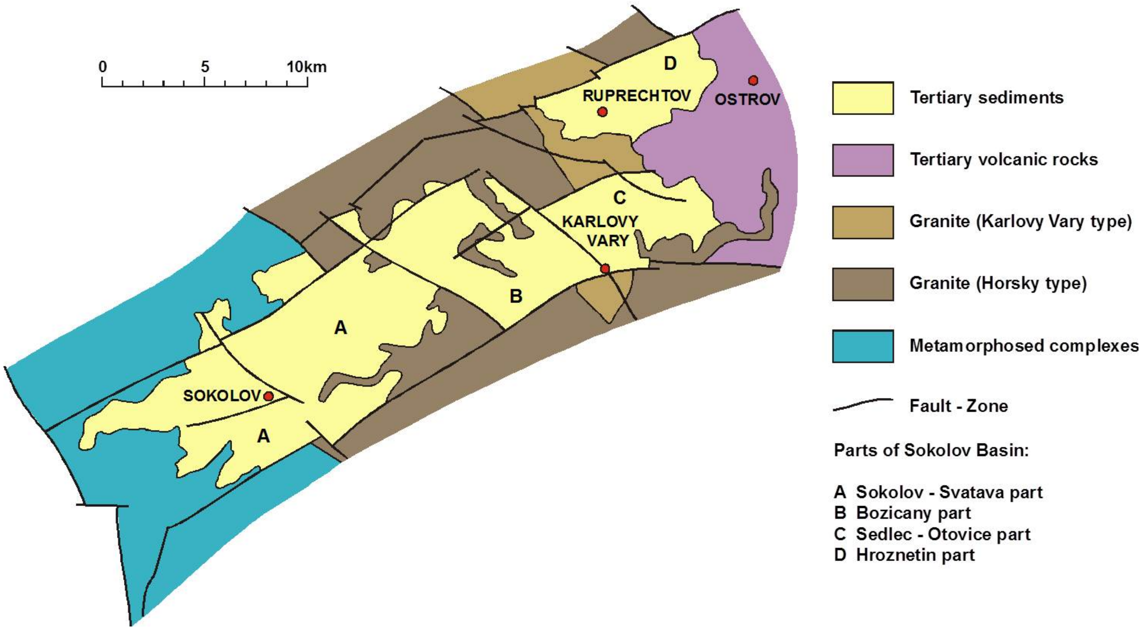

Fig. 2.7 Geological sketch map of Sokolov Basin; the Hroznětín section with Ruprechtov site in the NE is marked by letter "D" (from /NOS 02/, modified after unpublished ÚJV-documents)

Not far from the Ruprechtov study area and near the village of Hroznětín is found the bentonite deposit of Velký Rybník described in the literature. Here, a volcanic rock sequence with a thickness of 70 m is exposed. The basis is kaolinitized granite overlaid by tuffogenic clays, partly mixed with volcanic material. The lowest strata are derived from basaltic tuff. Several siderite precipitations indicate reducing conditions in the water-bearing depression areas where the glowing, pyroclastic material was altered into bentonite through autohydrothermal decomposition. Moreover, sharp-edged ejecta show the proximity to the volcanic crater /FRA 82/.

Such rock-forming conditions and processes can also be considered to have occured at the Ruprechtov locality due to its close proximity. There, however, the topography of the deposition area seems to have been somewhat less homogeneous than in the Hajek deposit due to several granite bulges (see Fig. 2.8).

In the immediate vicinity (about 2 to 2.5 km) is the former kaolin mine Hájek where uranium was also mined (see Annex A.1). Some documentation is available on the mineral deposits in the region, particularly focussed on the stratigraphic conditions, the quality of the raw material and economic issues of mining. Scientific treatises mainly deal with aspects of the regional geology and genesis. The essential facts about the geological situation at the Ruprechtov site have been summarized by ÚJV Řež, a. s. in 1996 in brief documentation /SKO 96/.

2.1.3.1 Geology of the Hroznětín area

The Hroznětín section of the Sokolov Basin originally formed an integral part of the uniform Sokolov Basin from which it recently became separated by denudation. The Sokolov Basin and the Cheb and Most Basins make up the Tertiary sedimentary filling of the Ohře rift.

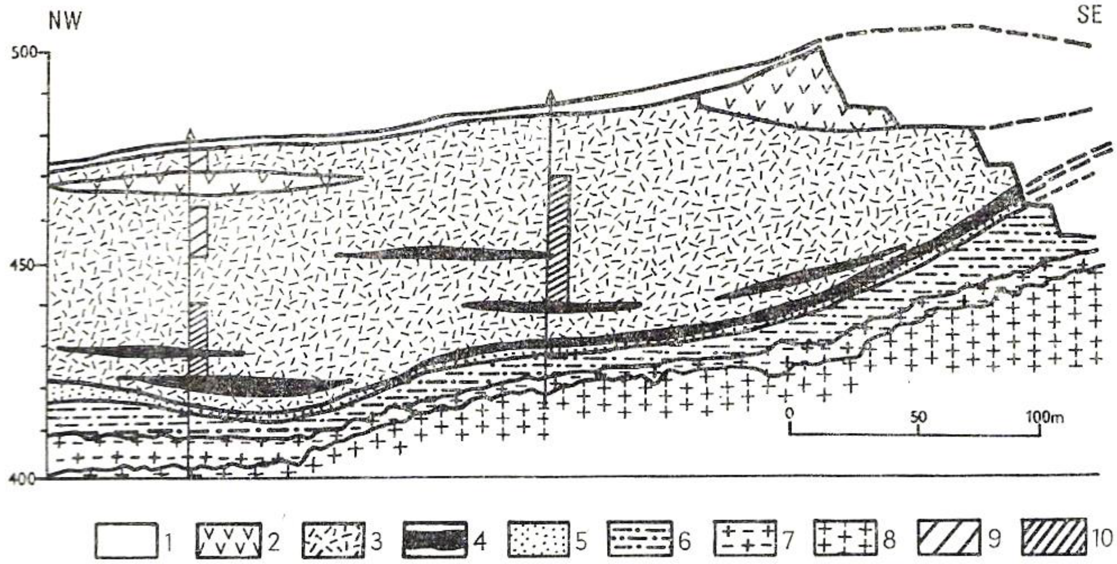

Fig. 2.8 Schematic geological cross-section through part of the Velký Rybník bentonite deposit (close to Hájek kaolin mine)

1: quaternary sediments, 2: basalt, 3: tuffs, tuffites, tuffitic clay (volcano-detritic rock sequence), 4: coal, carbonaceous clays amidst of volcano-detritic rock sequence, 5: kaolin in-situ, 6: kaolin in-situ with imperfect decomposed feldspars, 7: granites, kaolinized, 8: Granite, undecomposed, 9: bentonite, quality 450 (not balanced), 10: bentonite, quality 550 and higher (translated, from /FRA 82/)

The base of the Tertiary sediments of the Hroznětín section is made up of Karlovy Vary-Eibenstock composite pluton of Variscan age (predominantly Krušné Hory granite, less often the Horský granite suggested by previous authors) /KLO 10/. The western and south-western boundaries of the recent extent of the basin consist of the aforementioned granite, while the south-eastern and eastern limits are defined by the Doupov Hory volcanic complex. The northern limit of the basin is formed by the Krušné Hory Fault, the direction of which is WSW-ENE in the area described. Geophysical investigation has proved the presence of approximately perpendicular faults running NW-SE to NNW-SSE. The identification of individual faults on the basis of drill core analysis is practically impossible due to the lack of correlation horizons in the Tertiary sediments.

The granite below the Tertiary sediments is deeply kaolinized locally to a depth of up to an average of 30 – 40 m. The deepest known incidence of kaolinization is at a depth of 100 m /BOS 04/.

2.1.3.2 Uranium mineralization in the Tertiary formations of the Hroznětín area

The Hroznětín section of the Sokolov Basin, recently totally separated by denudation from the main part of the basin in the west is the only part of the Bohemian Massif where uranium mineralization bound to Tertiary sediments has been present in a minable amount. Historically, 10 indications of uranium mineralization were explored in the Hroznětín section of the basin while an additional 4 indications were explored in isolated relics of Tertiary sediments outside the Hroznětín section. Five small deposits (A-E in Fig. 2.9) were subsequently mined in the Hroznětín section of the basin as the result of geological exploration.

The extreme horizontal and vertical variability in terms of both the thickness of the uranium-bearing layer and the uranium content led to a large discrepancy between the estimated reserves and the actual amount of ore mined; in some cases this led to the premature termination of mining activities /KLE 71/. A detailed description can be found in Annex A.1.

Five small deposits were subsequently mined in the Hroznětín section of the basin as the result of geological exploration; their geographical position is shown in Fig. 2.8.

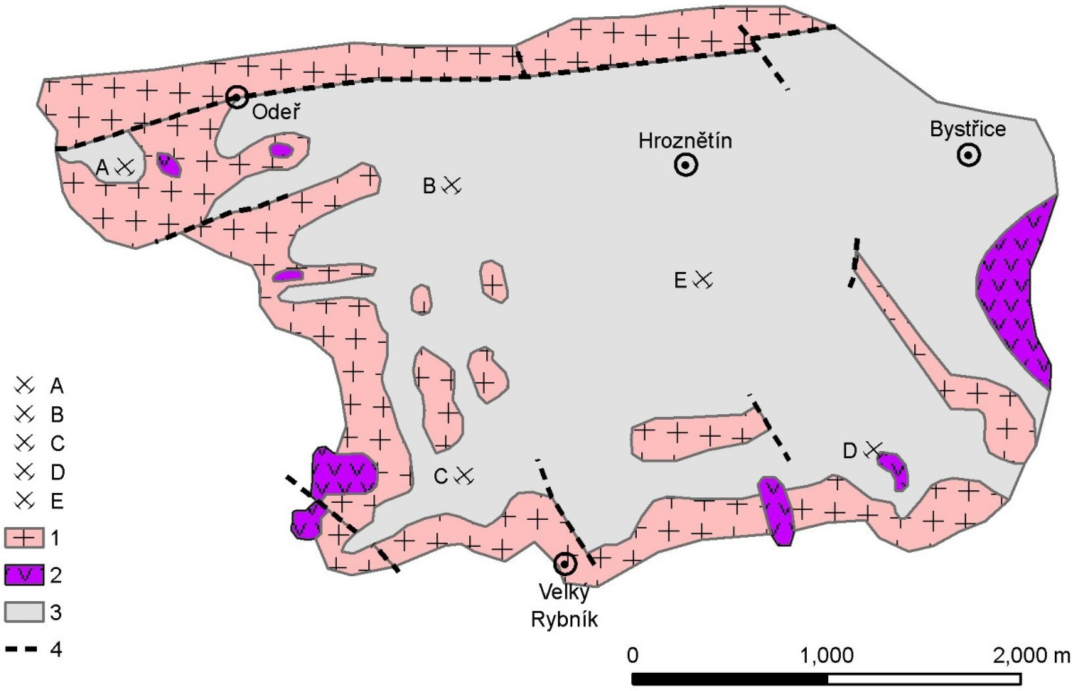

Fig. 2.9 Geological sketch map of the Hroznětín section of the Sokolov Basin with location of mined deposits (modified after /KAF 03/)

Deposits: A Odeř; B Ruprechtov North; C Ruprechtov South; D Hájek South; E Hájek North; Geology: 1 Granite of Karlovy Vary - Eibenstock composite pluton; 2 Tertiary basalts; 3 Tertiary sediments; 4 Main faults

The **Hájek South** deposit located near the recent southern limit of the Hroznětín section makes up the most important deposit in the area. This deposit (together with Hájek North deposit) is situated in a trough running NNW-SSE. The sedimentation of the Nové Sedlo Formation begins with a sequence of grey tuff with an organic admixture as well as with thin layers of organic-rich clay and thin seams of coal with a total thickness of up to 9 m; four uranium-bearing layers are also present in this sequence the thickness of which varies from 1 m to 2 m. The predominant uranium mineralization is bound to coal seams and organic-rich clay. Uranium mineralization is present in a finely dispersed form and the uranium minerals uraninite and coffinite have been discovered. In addition, uranium blacks are also present.

The **Hájek North** deposit located in the middle part of the Hroznětín section is very similar in its Tertiary sediment lithology and stratigraphy to that of the Hájek South deposit. Three uranium-bearing layers heve been discovered in this deposit; the lowermost lies in the sediments of the Staré Sedlo Formation (according to the interpretation of uranium geologists) and consists of a wavy sheet varying in thickness from 0.15 m to 2.77 m.

At the **Ruprechtov I** deposit situated in the proximity of the SW corner of the Hroznětín section uranium mineralization has been bound to the basal part of the Nové Sedlo Formation, which is made up of tuff, partly argilitized, with abundant intercalations of organic-rich clay and a thin coal seam /KLE 71/. The type of mineralization is not described in the afore-mentioned report, but it is not unreasonable to assume that it is the same as that of the Hájek South deposit.

The **Ruprechtov III** deposit located some 700 m NW of the village of Ruprechtov consists of an accumulation of uranium in the form of uranium blacks in fractured limonitized zones of granite /KLE 71/. The upper part of the accumulation has been mined using the open pit method; however, to extract the main part of the reserves, a shaft of 81.5 m depth was sunk and a crosscut bored beneath the expected reserves. During the construction phase only a small amount of low quality ore was discovered.

The **Odeř deposit** situated between the villages of Ruprechtov and Odeř, was exceptional in terms of the uranium deposits in the Hroznětín section of the basin due to its tectonic position, the presence of mineralization in a thick coal seam and the presence of uranium mineralization in a Quaternary peat bed. The deposit was found to be bound to a deep depression in kaolinized granite of NNW-SSE direction. The depression is tectonically predisposed and its north rim is the Krušné Hory Fault; the depression is approximately 1 km^2 in area. The development of this depression was different to that of the rest of the basin. Movements along the Krušné Hory Fault led in the area to a deepening of the depression and, consequently, to a thicker sequence of Tertiary sediments. The maximum thickness of the Tertiary filling is 290 m /OBR 71/. The Tertiary sedimentation commences with talus (diluvium according to uranium geologists) which is made up of boulders and blocks of granite, followed by sand and gravel tthen sandstone and a conglomerate with kaolin cement. Fragments of coal and volcanic material are also present. The sequence continues with sapropelite sedimentation and a coal seam with an average thickness of 13.5 m. The total area of the coal seam is 250 m x 400 m and it has a maximum thickness of 50 m. The Quaternary age peat bed developed only in the central part of the depression and has a maximum thickness of 4.5 m. Four uranium-bearing layers were discovered during the exploration stage: one layer in the talus, two layers in a coal seam and a further layer in peat.

2.2 Understanding of the Ruprechtov geology before the start of the project

More than 100 geological reports from the Hroznětín section of the Sokolov Basin are stored in the archive of the Czech Geological Survey. The majority of the reports are concerned with geological exploration for building purposes and hydrogeological exploration for the construction of local water wells.

Coal was never mined in the Hoznětín section of the basin which has a strong impact on the contents of the reports. Reports containing detailed lithological, stratigraphical, sedimentological and paleontological studies are not available. Studies covering the westernmost section of the Sokolov Basin, which is important in terms of brown coal production, highlight the difference between the two sections. At the same time the mineable brown coal seams were deposited in Sokolov basin, when volcanic activity started to limit the formation of greater amounts of organic matter close to the volcanic centre of Doupovské Hory.

A number of reports concerning granite, the Staré Sedlo Formation and, in part, the Nové Sedlo Formation contain information on the exploration and estimations of reserves of kaolin. Indeed, the Hroznětín area has large reserves of kaolin which is used in the production of china. Exploration commenced in the 1950s and the first report on the subject was published in 1956 /KUK 56/, followed by a further eight detailed reports concerning kaolin deposits in the Ruprechtov area up to 1988; the final report was /RAU 88/. The sediments of the Nové Sedlo Formation (volcanodetritic formation) were only described in brief in the reports concerning kaolin deposits; the sediments made up the overburden of kaolin, thus thickness and mechanical properties were the major factors covered. A number of basic bentonite tests were also included in the reports; indeed, the majority of the sediments was determined to be low-quality bentonite. From the archive available, it is impossible to reconstruct the presence and extent of the layers and lenses of organic-rich clay and coal seams in the sediment sequence.

For the purposes of delimiting the area of interest, data from core-less boreholes gathered by DIAMO during uranium exploration in the Hroznětín section of the basin was essential. The results from these boreholes are stored in a special database and provided in a report on exploration activities in 1969 /CSU 70/. The most important information includes the coordinates of individual boreholes and the gamma log which allowed identification of the area for pilot drillings. The successful drillings unequivocally supported the drafting of a research programme with exploration boreholes.

With regard to reports on uranium exploration and mining, if they are accessible, a detailed description of Uranium-bearing horizons is lacking in many cases. Moreover, both the distance of the uranium deposits from the studied area and the substantial horizontal variability are too large to allow a detailed comparison.

The starting point for the research program at the Ruprechtov site has been a rather simple geological situation as expected from the Hájek deposit (cf. Fig. 1.3). This assumption has also been confirmed by a schematic cross-section of the Ruprechtov site itself.

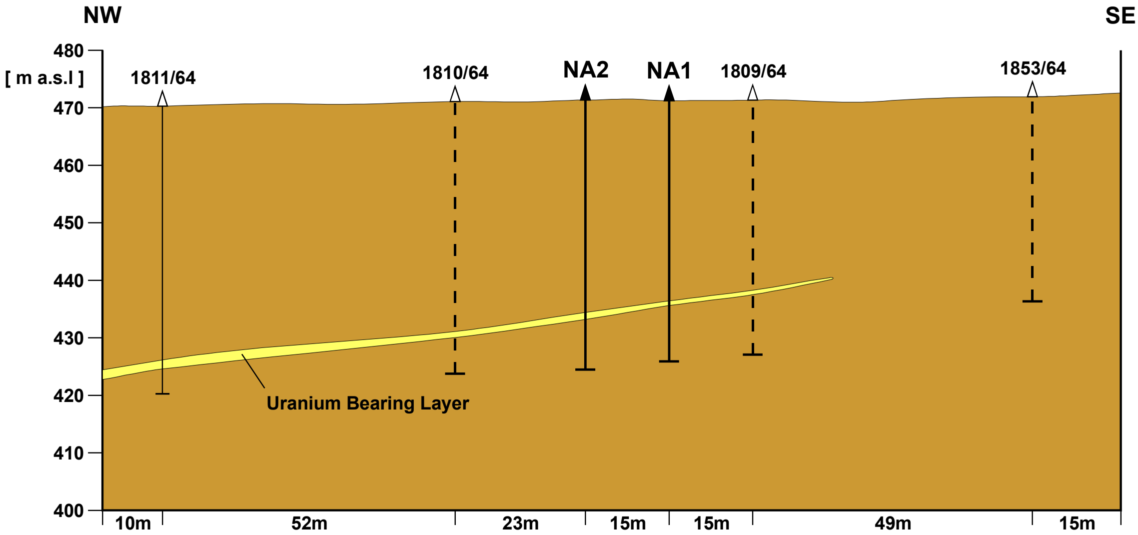

Fig. 2.10 Schematic cross-section of the Ruprechtov site with assumed position of main U-bearing layer and location of first exploratory wells NA1 and NA2 (from /BRA 98/, after unpublished ÚJV-document)

According to earlier information, the origin of the uranium enrichment in the Hájek and Ruprechtov area was supposed to lie in the surrounding (and subjacent) granite which has a relatively high content of this element. Referring to literature available at that time, /NRI 95/, /NRI 97/ described very favourable climatic conditions for leaching and migration of uranium during the Miocene, when the pyroclastic sediments – so-called volcano-detritic formation – (with intercalations of coal and carbonaceous clay) were deposited. High temperature and high humidity caused a second stage of kaolinization. The decomposition of organic material enriched the water with humic acids that could support dissolution of uranium from the weathered granite. The uranium then migrated in the form of complexes (bound to humics, carbonates or sulfates) and was deposited primarily in layers with higher organic matter content. At both locations, uranium has been identified as occurring as uranite, uraninite and coffinite and bound to immobile humic substances (/NRI 95/, /NRI 97/). This report already points out that all uranium mineralization is macroscopically invisible.

Based on rather sparse information at Ruprechtov site, uranium was expected primarily in the southern part of its kaolin deposit. The thickness of the covering pyroclastic sediments was known to vary between 0 and 10 m in the southern part and to increase in the northern part (near the town of Hroznetín) up to app. 120 m. During the course of earlier investigations at the Ruprechtov site, three uranium-containing layers were identified, the most important being the basal layer, mainly composed of lignite and lignitic clay. Two overlaying layers have been built up by tuff with a significant amount of organic material.

Only very little qualitative information on the uranium content of the sediments was available for the Ruprechtov site at that time. In previous reports, the only findings were around the strong variability of the uranium content and the thickness of the uranium-bearing layers, often in the form of lenses. In general, however, similar concentrations as in the Hájek deposit could be expected.

In order to check the suitability of the Ruprechtov site for further investigation, the aim of the first drilling campaign (NA1, NA2, see Fig. 2.10) was solely to prove the assumptions, described above, mainly uranium accumulation in the relevant depth. So far, this general check has ended positively (Fig. 2.11), verifying the main U-accumulation in the lowermost part of the Tertiary at a depth of 33 to 36 m.

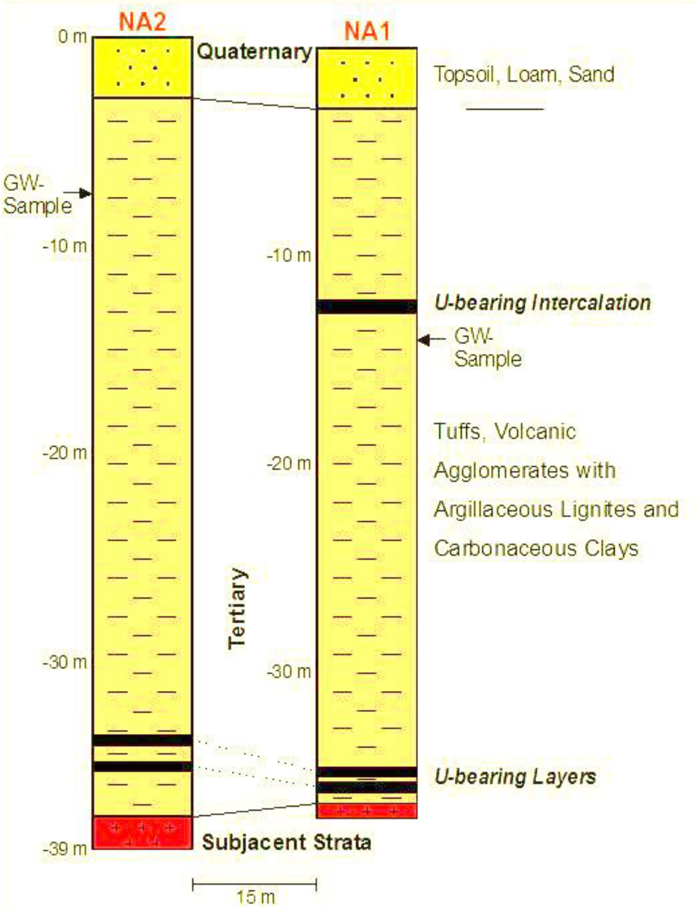

Fig. 2.11 Basic results from first core drills NA1 and NA2, verifying main U-accumulation in the lowermost part of the Tertiary (volcano-detrital) formation ("U-bearing layers") (from /BRA 98/, slightly modified)

2.3 Stepwise site investigation for overall system understanding

The entire Ruprechtov analogue project has been performed in a stepwise matter, starting with a basic study to clarify, whether uranium was really present at the proposed site and at a suitable depth from a) the scientific point of view, i. e. in sufficient depth to represent the analogue conditions needed, and b) the technical point of view, i. e. not at too great a depth so that standard drilling equipment could be used.

The steps of the investigation strategy are associated with the drilling campaigns as described in more detail in Chapter 3.1 (see also Fig. 2.12).

- Step 1 (1996 – 1998[2]) was the basic verification of uranium accumulations at the Ruprechtov site, which also gave a first overview of the stratigraphy, lithology, mineralogy and chemistry of the local Tertiary sediments at the most promising location in the area. The verification could already be undertaken through bulk analyses of drill cores from NA1 and NA2. NA3 was drilled roughly two years later to enable sediment analyses with spatially higher-resolution.
- Step 2 (1999) was still restricted to the small-scale area as dealt with in step 1. Two additional boreholes made it possible to investigate the relevant sediments in more detail. However, the greatest advance was the construction of groundwater monitoring wells to investigate the groundwater chemistry at the relevant depths.
- Step 3 (2002) with a total of four supplementary boreholes included a larger area and provided additional information on a) the underlying kaolin and granite as well as outcropping granite representing the uranium source rocks, and b) the Tertiary sediments with similar general stratigraphy as in the first two steps but at a different location. Since all of the new boreholes were constructed as groundwater monitoring wells, Step 3 also made it possible to investigate groundwater chemistry in a larger area, to differentiate between different aquifers and to obtain first ideas concerning the hydraulic regime in the area.
- Step 4 (2005) included six new boreholes over a significantly expanded area (covering granite, kaolin and, uranium anomalies in sediments). This step was particulary necessary to understand the groundwater flow field in the area and the pathway of uranium from its source rock to its present enrichment in distinct layers of the Tertiary sediments.
- Step 5 (2009 – 2010) was added to the investigation programme later. Open pit kaolin mining in the area of Steps 1-4, with deep excavation of overlaying sediments and kaolin itself has caused a major alteration of the natural conditions at the Ruprechtov site, including the overall hydrogeological situation. The main aim of Step 5 has therefore been to study the influence of kaolin mining on groundwater levels and its potential impact on the geochemical milieu (oxidation), especially the mobility of uranium.

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[2] Time frame is charcterized here by the associated drilling campaign

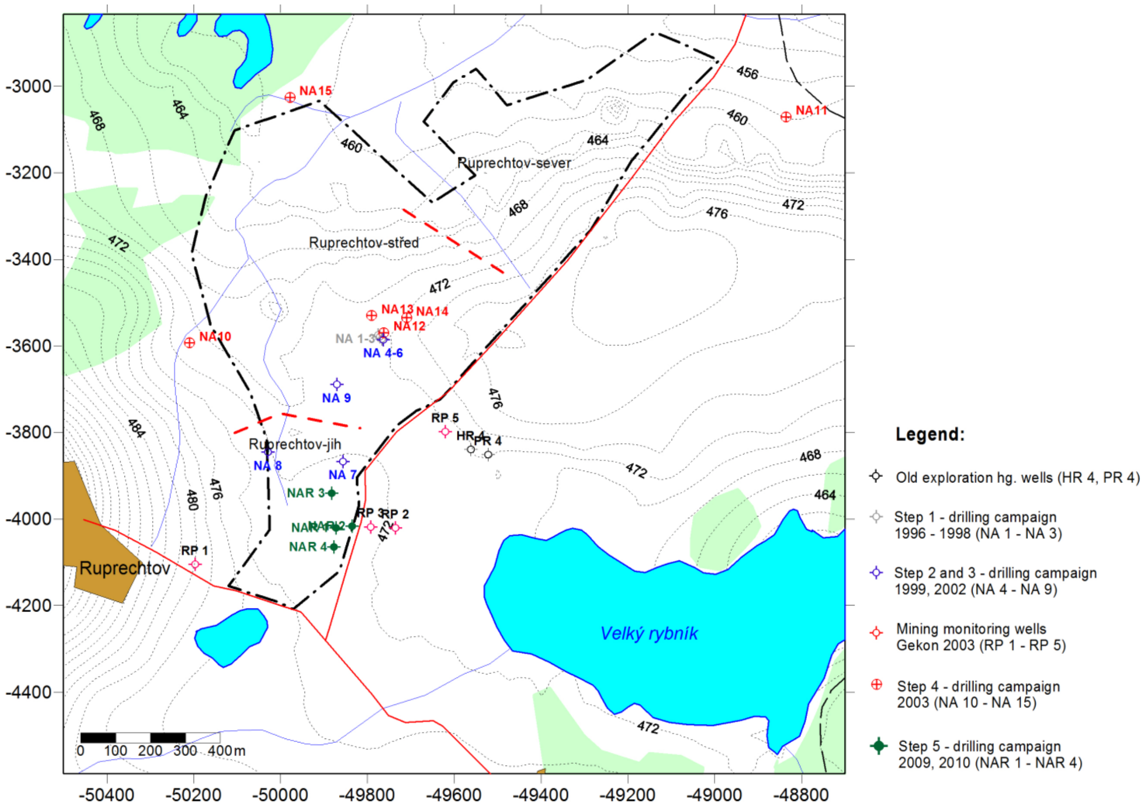

Fig. 2.12 Schematic map of the Ruprechtov site with boreholes and wells labelled

In retrospect, the stepwise procedure on the one hand caused a relatively long duration of the project, but on the other hand made it possible to plan further steps thoroughly and according to real needs which were economically and scientifically of benefit. Besides specific investigations, each step also allowed for the adoption / optimization of technologies and methodologies required for the project.

A stepwise procedure involving identifying, characterizing and evaluating the key features and their consequences for the programme is the essence of this approach. Examples include:

- The redox sensitivity of sediment samples from the uranium-bearing layers provoked improvements in sampling and sample handling methods;
- Observation of indications for microbial activity (e. g. framboidal pyrite) triggered microbial investigations including isotope methods.

The stepwise approach allowed for phases where results were evaluated and presented on international conferences. The presentation of specific results achieved during the first project steps raised the interest of partners and led to very close co-operation on specific topics with some of the partners.

This provided the opportunity to get in contact with international scientists, who showed interest in the Ruprechtov project, some of whom participated in the next phase contributing new ideas and new methods as well as experience and specific expertise on issues such as mineralogy, hydrogeology and uranium geochemistry.

2.4 Potential use of the outcome in performance assessment

From the outset the natural analogue project was started as a co-operation between the Czech Republic and Germany. The intention and objectives in initiating the project were to contribute to concrete issues of performance assessment for radioactive waste repositories in both countries, such as the barrier function of bentonite and the overburden. It should be noted that the repository concepts and strategy for safety demonstration under consideration have changed to a degree since then /STO 98/, /FIS 13/, /ÚJV 11/. This report refers to the situation at the starting point of the project in 1995.

2.4.1 Repository systems in Germany and the Czech Republic

At the time of project initiation the preferred option for the disposal of heat-generating radioactive waste in Germany was a deep geological repository in a rock salt formation. The preferred Czech concept still regarded the disposal of spent nuclear fuel and high-level radioactive waste in granitic formations. In both concepts argillaceous materials play an important role as an overburden or in the buffer.

2.4.1.1 Repository system with sedimentary overburden

The repository system for a radioactive waste repository consists of the repository including the infrastructure, the engineering barriers and the waste form within the host rock formation. A geological feature found in Germany is that sedimentary formations cover the potential host rocks (rock salt, clay, granite). In the northern part of Germany such formations (typically Tertiary and Quaternary) have a thickness of few hundred meters. In former safety strategies these overlying formations have been assumed as a geological barrier.

A large amount of information is available for the Gorleben area, which has been investigated as a potential repository site (salt dome). The key features of the overburden are briefly described here. The Tertiary and Quaternary sedimentary overburden of the salt dome and its neighbouring rim synclines form a system of aquifers and aquitards of up to a 430 m thickness /KLI 02/. The basis of the regional flow system is represented by the Tertiary Rupel Clay. The aquitard is a set of the Tertiary Hamburg Clay and the Quaternary Lauenburg Clay Complex, which is superposed by Weichselian and Saalian sediments representing the upper aquifer /KLI 02/. The specific hydraulic system can be roughly divided into a lower aquifer, an intercalated aquitard and an upper aquifer (Fig. 2.13). The lower aquifer consists mainly of Tertiary Lower Brown Coal Sands and Quaternary sands of the Elsterian meltwater channels. These sediments can be described as fine- to medium-grained arenaceous sands with a low silt and mica content. They are generally free of calcium carbonate and show lignite beds in the upper parts. The Elsterian meltwater sands show a sporadic content of brown coal and low contents of mica /ZIR 03/. The aquitard is represented by argillaceous and silty sediments with a certain content of mica and calcium carbonate /ZIR 03/. The most frequent clay minerals are kaolinite, illite and smectites /KLI 02/.

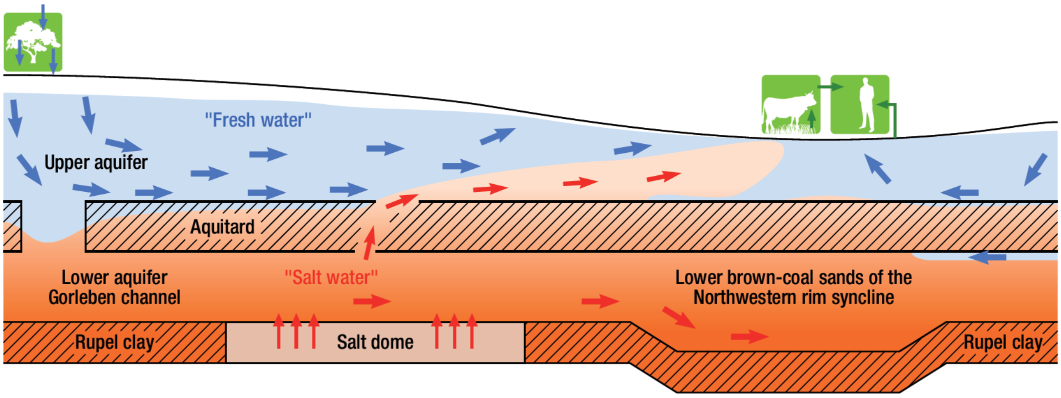

Fig. 2.13 Schematic aquifer subdivision in the overburden of the Gorleben salt dome (after /KLI 07/)

Due to the existence of lignitic material in the Elsterian Miocene sands, relatively high concentrations of dissolved humic and fulvic acids with concentrations up to 200 mg/L are observed in the aquifers of the Gorleben site /BUC 00a/.

2.4.1.2 Repository system with clay buffer and backfill

The Czech repository concept refers to the Swedish and Finish concept KBS-3 V and H /SKB 10/ and /ANT 08/. The most recent and currtently preferred method is to use supercontainers in horizontal deposition holes. Supercontainers consist of an outer perforated steel shell, bentonite pre-fabricated elements and a disposal canister (package, see Fig. 2.14). Open spaces between the supercontainers in deposition holes and access tunnels are filled by sealing and filling materials. Also concrete parts such as various injections and particularly concrete disposal holes plugs, individual shafts and galleries can be considered as part of the system. The natural barrier is the geological environment (host rock) and adjacent/overlying rock formations. The whole repository is located at a depth of app. 500 m (Fig. 2.14). Details of the technical design can be found in the Reference Projects /EGP 99/ and /ÚJV 11/. From the outset until the present, the crystalline host rocks (mainly granitoids) have been considered and six potential candidate sites in this environment initially pre-selected. Analogy is seen for the use of bentonite as a buffer and backfill material in this concept. Looking at the Ruprechtov site, the uranium accumulations are mainly located in the bottom part of the Tertiary sedimentary complex. The sedimentary complex also consists of partly argillized pyroclastic sediments that form bentonite sediment layers. The presence of bentonite in the system with anatural occurence of uranium can be then the major link to finding analogy with the Czech disposal concept.

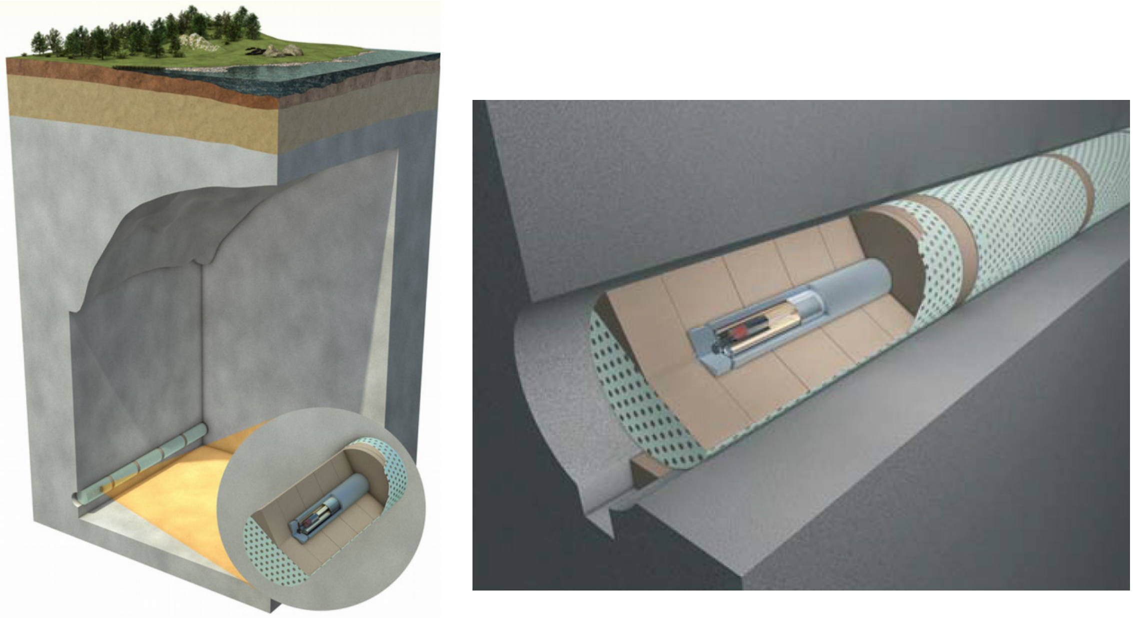

Fig. 2.14 The schematic concept of repository system (left) and deposition hole with supercontainers (right) in the Czech Republic (SÚRAO)

2.4.2 Relevant processes dealt within PA - input of Natural Analogues

The natural barrier role is a key aspect of any site and hence information on this may help to support decisions associated with the development of the repository programme /ALE 13/. The overburden was regarded as one important natural barrier for radionuclide migration in the repository system at the time of initiation of the Ruprechtov project /STO 98/. With respect to repository systems with sedimentary overburden, the major objective of this project is the investigation of radionuclide migration processes in Quaternary and Tertiary formations. In particular, the aim was to look for evidence which would allow conclusions to be drawn about key processes such as:

- Radionuclide sorption;
- Matrix diffusion;
- Dilution and dispersion;
- Radionuclide immobilization (precipitation or trapping);
- Colloid effects (including organics);
- Impact of microbes.

With the exception of matrix diffusion these processes are expected to affect potential radionuclide transport in the overburden of repository host rocks as schematically shown in Fig. 2.15. If radionuclides are released from the host formation, they will enter the adjacent sedimentary formation and be subject to transport and retardation processes. In performance assessment this migration of radionuclides is simulated by flow and transport codes for porous media, taking dispersion and dilution processes into consideration. The key retardation process for radionuclides in the sedimentary layers is sorption, which is usually treated by the K_d concept. A sound understanding of this process is necessary in order to defend the concept and data range used in the safety assessment. Furthermore, the occurrence of colloids (inorganic and organic) and microbes and correlated processes and their impact on radionuclide transport must be addressed in the Safety Case. Natural systems are convenient for learning about the occurrence, extent and complexity of these processes. Precipitation or co-precipitation processes might also play a role, when significant changes in the geochemical conditions occur along the transport pathway.

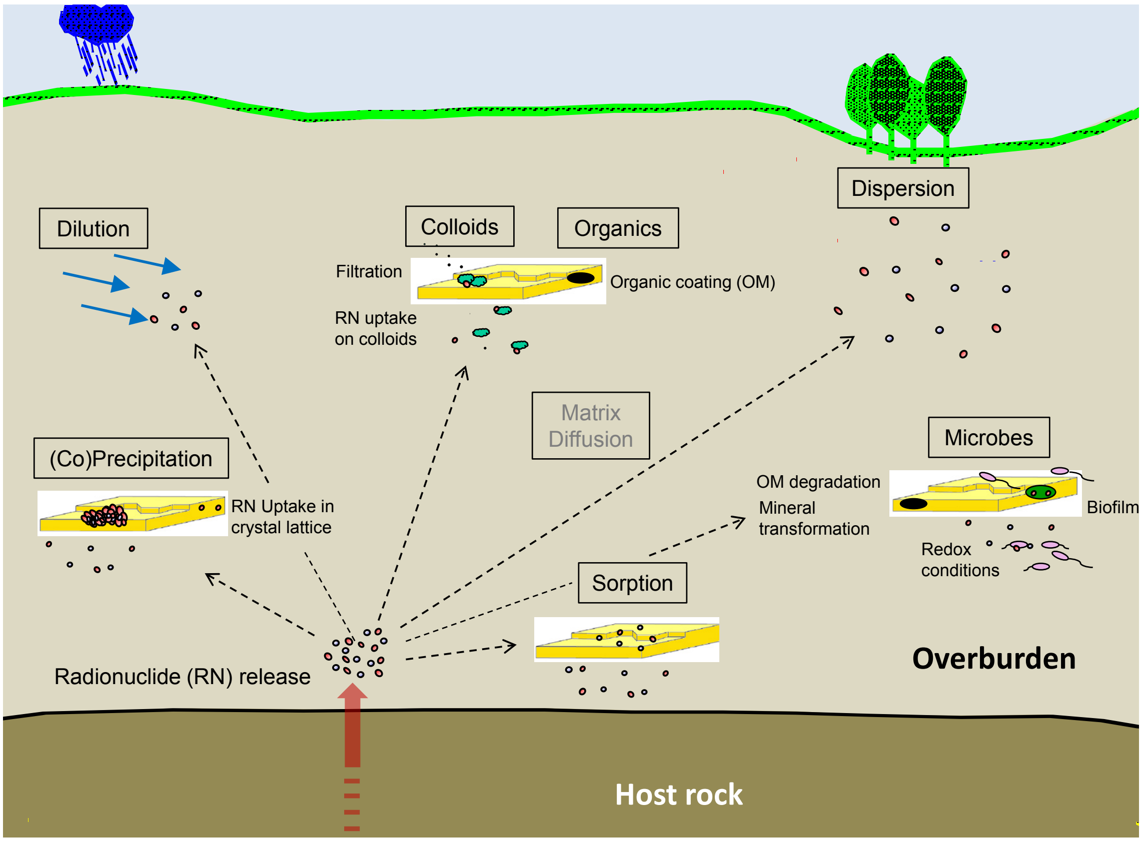

Fig. 2.15 Potential relevant processes with respect to radionuclide migration in the overburden of a geological repository

Sedimentary organic carbon (SOC) and high concentrations of dissolved organic carbon (DOC) are observed to occur in parts of the overburden in Northern Germany (see Chapter 2.4.1.1). Therefore it is of high interest to increase the knowledge of processes connected with the behaviour and transformation of organic matter in a natural system. This comprises the interrelation between SOC and DOC, potential mobilization processes of immobile organic matter and their impact on radionuclide mobility. The existence of organic matter is also a prerequisite for microbial activity. Microbes might be involved in organic matter degradation processes and the uptake of radionuclides but at the same time also in determining / changing geochemical conditions such as pH, redox or mineral phases and formation of biofilms, e. g. /MEA 11/. The investigation of these processes in a natural system will provide knowledge about whether these processes occur, the extent of their occurrence and interrelation or coupling between the different processes.

With respect to the repository system with sedimentary overburden, investigation of these processes and their potential impact on the mobility of uranium has been the major objective for the initiation of the Ruprechtov project. The existence of a Tertiary basin filled with argillaceous material (kaolinite, smectite, illite) with embedded sandy layers, the knowledge of uranium anomalies in the Tertiary layers in the surrounding of the Ruprechtov site (Hajek, cf. Annex A.1), and the frequent occurrence of lignitic material in the Tertiary sediments have supported the decision to select Ruprechtov as a natural analogue investigation site.

Another issue of performance assessment is the question of the long-term stability of the geological formations of interest. It is of particular concern whether sedimentary formations exposed to the surface are stable in the long term. In this respect, long-term stability not only relates to mechanical stability but also the stability of geochemical conditions. The natural system provides the opportunity to investigate this stability and the corresponding processes promoting or disturbing it. This is particularly interesting for systems which operate relatively near the surface.

With regard to a repository system in granite, an important performance assessment aspect is the barrier role and long-term stability of a bentonite buffer, which is usually emplaced around a waste container (see Chapter 2.4.1.2). The smectite-rich argillized Tertiary pyroclastic layers might be regarded as an analogue for the bentonite material. Therefore, processes in the “clay sediment - porewater - groundwater” system are relevant for the granite option. One of these processes, which can be studied at the Ruprechtov site, is the behaviour of U and Th in this system with special regard to speciation in porewater and groundwater, migration and interaction with clay sediment. The proof of the isolation function and long-term stability of the clay barrier is the main issue for safety demonstration. The origin and evolution of groundwater and porewater in the presence of clay sediments is also related to performance assessment issues. The geochemistry of groundwater and porewater will fundamentally influence the behaviour of radionuclides (in terms of mobility/immobility). Moreover, investigation of colloids can provide additional information about radionuclide migration pathways. Another aspect is the behaviour of U and Th in the case of disturbation of the reducing conditions. The possibility of kaolin mine opening above the uranium accumulations allows the study of the impact of oxygen on the stability of uranium in the clay environment. Oxidation/reduction processes play an important role in the geochemistry of the whole repository system.

3 Methods

In this chapter, key information is given on the methods which have been applied to the site characterization of the Ruprechtov site. The methods are divided into eight groups by their typical characteristics. Seven groups are technical investigation or analytical methods, whereas the eighth group describes the modelling tools. The subchapters highlight the major objectives and areas of application of each set of methods; they give some technical information and summarize the experiences obtained during the project. Details for each single method are listed in standardized tables in Annex A.2.

3.1 Drilling methods

The drilling of boreholes has been an essential prerequisite within the Ruprechtov analogue study. The most important reasons for this are as follows:

- Drilling provides rock material from the underground, allowing the description and investigation of its content and properties and thus the geological characterization of the site;
- The drill hole itself gives an opportunity to study certain rock properties in-situ by means of geophysical logging and, for example, hydrodynamic tests;
- Well filters enable the inflow of groundwater from a selected layer into the drill hole and thus sampling of groundwater using bailers or pumps as well as the in-situ determination of groundwater parameters using corresponding probes.

In general, all drill holes (see Tab. 3.1) within the framework of the Ruprechtov analogue study have been created using a truck-mounted drilling rig (Fig. 3.1) with a rotating core drill pipe. The essential feature of this drilling method consists of a rotating drill rod driven by a power rotary head. The deeper the hole becomes, the more time consuming the process is due to the so-called round trips (drill pipes have limited length of e. g. 9 m in case of the Russian ZIF-650M drilling machine, each of which must be removed and dismounted, if a drill core from the bottom of the drilling has to be recovered). For core drillings (as undertaken in the project) the core bit (crown) is mounted at the lower end of the drill pipe and cuts the core material from the rock, which is then slid into the pipe or barrel.

A drilling fluid[3] is used to facilitate the drilling operation, for many reasons (e. g. cooling the crown, transporting the cuttings to the surface), this circulates through the pipe downhole and through the annular space back to the surface. It is obvious that the use of such a fluid will also impact the drill core or cuttings during drilling operation as well as the native rock around the bore surface.

One technical target of the project has therefore been to optimize the drilling operation in such a way that the drill core with its redox-sensitive uranium content is affected geochemically as little as possible by the use of drilling fluid. On the other hand, experience at the Ruprechtov site has shown that drilling without any drilling fluid damages the drill core mechanically, so that particularly clayey samples are squeezed within the barrel and no structural analysis or assignment of e. g. mineralogical findings to defined layers is possible. In addition, the removal of the drill core from the pipe barrel is almost impossible if the use of drilling fluid is avoided. In such cases, the use of high water pressures was necessary to remove the core, which – in addition to mechanical damage – had now been affected chemically, too. Without being able to provide a specific quantification the recommendation from the project is not to avoid drilling fluid but to reduce it to a technically acceptable minimum amount. Chemical analyses across a drill core sample have proved that the impact of drilling fluid on the sample is restricted to few millimeters. During the preparation of samples for further investigation, this can be taken into account by discarding the outer millimeters of a drill core.

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[3] E. g. water

Fig. 3.1 Truck-mounted drilling rig (ZIF-650M) in operation at the Ruprechtov site

Tab. 3.1 Overview of all drilling campaigns within the Ruprechtov project

Drilling campaign	Date	Drillings	Aim
1 (a)	1996	NA1 NA2	Verification of U-accumulations Overview of stratigraphy, lithology, mineralogy and chemistry
1 (b)	1998	NA3	Sediment analyses
2	1999	NA4 NA5	Detailed sediment analyses Lining for use as monitoring well
3	2002	NA6 NA7 NA8 NA9	Underlying kaolin and granite Similar stratigraphy, alternate position U-source, outcropping granite Lining as monitoring well
4	2005	NA10 NA11 NA12 NA13 NA14 NA15	U-source, granite at alternate position U-anomaly at alternate position Checking differences between nearby NA4 and NA6 Similar stratigraphy at alternate position Detailed investigation of underlying kaolin / granite U-anomaly at alternate position Lining as monitoring well → groundwater flow pattern
5	2009/10	NAR1 NAR2 NAR3 NAR4	Influence of kaolin mining on groundwater level and oxygen contact Lining as monitoring well

Further details are discussed in Chapter 3.2 since drilling operations are connected with further measures used to obtain quality core samples.

In total, 19 drill holes have been drilled during the project, ranging between a few meters deep (at a location with shallow sediments) and several tens of meters (maximum app. 70 m at a location with thick sedimentary cover, thick kaolin and the aim of reaching the underlying granite).

3.2 Drill core and GW-sampling methods

Samples from local underground, either geological material or groundwater, are an essential basis for all scientific investigations. In this regard, the quality of a sample strongly affects the quality of the results. Therefore, it has been an essential task to take samples for geochemical and geotechnical investigations, transport and prepare them in an appropriate manner.

Drill cores

As already mentioned in Chapter 3.1, drill cores (at least the segments to be further investigated) should be taken in a manner such that the impact of oxygen (atmosphere) or external water used as a drilling fluid is reduced to a technically and practically unavoidable level. Drilling Campaign No. 1 had no such requirements, so the recovery and handling of drill cores happened as “normal” without any precautionary measures. Starting with Drilling Campaign No. 2, the requirements mentioned above, should be met. The first attempt was made by equipping the drill pipe with an inner plastic liner, i. e. the drill core was pushed directly into the liner instead of the drill pipe. After recovering a drill core section at the rig, the open front was immediately sealed using wax with low melting point. Theoretically, this procedure should have been successful. But from a practical point of view, there eare a number of shortcomings:

- In several cases, the liner was not designed adequately for the drilling forces and broke;
- The recovered cores were sealed “invisibly” in the liner; the direct addressing of the actual stratigraphic position, on-site planning of drilling operation or selection of sub-samples was impossible.

From the third campaign onwards, the following procedure (see Fig. 3.2) was proved and retained:

- Directly after recovery, the core was placed in a half-shell and scanned for gamma radiation to identify layers with a higher uranium-content;
- By cutting the surface of the core along a small strip, the main mineralogical, and petrographic properties and stratigraphic position could be determined;
- Thereafter, the half-shell containing the core to be protected was pushed into a plastic tube and the front was sealed using an appropriate cover;
- Before sealing it completely, the atmosphere (ambient air) in the void space of the tube was replaced by an inert gas (i. e. nitrogen).

It was proved that this procedure assures effective protection against the effect of air-borne oxygen for several months; if needed or wanted, nitrogen can be added again in the interim before analyzing the material.

Fig. 3.2 Drill core sampling and storage procedure (Drilling Campaigns No. 3 – 5)

The development of the sampling procedure across all of the phases of the Ruprechtov analogue study is displayed in Tab. 3.2. It must be mentioned that only the combination of optimized drilling and sampling procedures allows the requirements to become fulfilled.

Tab. 3.2 Development of drill-core sampling

Drilling campaign	Characteristics	Features	Further requirements
1	„Normal“ drilling with core tube „Normal“ storage and transport in conventional core boxes Preparation of bulk samples	Overall chemistry, mineralogy; verification of U-accumulation; rough correlations	Sampling and storage without oxygen contact (redox-sensitivity of minerals)
2	Drilling with core tube and inner-liner No drilling fluid Sealing of [m]-segments (end-faces) using wax with low melting point	Liner damage by tough clays; no description of core material; difficult to prepare sub-samples Effective exclusion of air contact	On-site description of cores; reliability of core recovery and easy handling
3	Drilling with „normal“ core tube No drilling fluid Direct core description Prompt sealing of cores in PVC-tubes (flushing of void spaces by inert-gas)	Prompt information on stratigraphy; easy to prepare sub-samples; effective exclusion of air contact Partially bad core quality, disruptures with impact of mud („Schmand“)	Improved quality of cores[4]
4, 5	Small amounts of drilling fluid (natural water) As in 3rd campaign	Prompt information on stratigraphy; easy to prepare sub-samples; effective exclusion of air contact; improved core quality (very low impact of drilling fluid)	No further requirements

Groundwater

Beginning with Drilling Campaign No. 2, all boreholes were lined with casing and filter sections at the appropriate depth of groundwater horizons to be investigated (Fig. 3.3).

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[4] See Chapter 3.1 for complementary optimization of drilling operation

Fig. 3.3 Installation of casing with filter sections in a borehole for its use as monitoring well

Tab. 3.3 Groundwater sampling and treatment in the field

Ion / element to be analysed	Sample bottle	Filtration	Sample treatment
Na, K, Mg, Ca, Al, Sr, Ba, B, Fe, Mn, SO_4^{2-}, Zn, Ni, Pb, Cd, Cr, Sb Co, Cu, Ti, V, As, Se, U	50 mL PE	Pressure filtration < 0.45 µm in the field	Addition of 0.5 mL HNO_3 (65 %) p.a.
Si	125 mL PFA	Filtration < 0.02 µm in lab	Bottle brimful; fast and cooled transportation to lab
NH_4^+, NO_3^-, PO_4^-	250 mL glass	No filtration	Bottle brimful; stabilization with 1 drop $CHCl_3$; fast and cooled transportation to lab
Cl^-	500 mL PE	No filtration	Bottle brimful; fast and cooled transportation to lab
Iodine	500 mL PE	Pressure filtration < 0.1 µm in the field	Fast and cooled transportation to lab
CO_2, HCO_3^-	4 x 100 mL PE	No filtration	Bottle brimful; fast and cooled transportation to lab
TC, TIC, TOC	3 x 10 mL glass	No filtration	Sterile and air-tight seal; fast and cooled transportation to lab
DOC	30 mL screw top jar	Pressure filtration < 0.45 µm in the field	Addition of 1 mL H_3PO_4 (50 %)

All groundwater samples were pumped to the surface using slim commercial 12 V submersible pumps (NA4, NA5: bladder pump). All the wells were pre-pumped before the groundwater sampling campaigns (recommended 2 – 3 volumes of the well). The determination of on-site parameters and filling the sample bottles was conducted at constant electrical conductivity of groundwater. Very different treatment of the samples in the field was necessary for the subsequent laboratory analyses, and this followed the details given in Tab. 3.3. Pressure filtration was performed under a nitrogen atmosphere in order to avoid intense contact with oxygen Experience during the project showed that filtration in the field (where required) is decisive for the quality of results; otherwise interactions of water and suspended particles may occur during transport and storage. Special features needed for paticular analyses not listed in the table are directly mentioned in the related method-table in Annex A.2.

Soil water

In case of surface-near horizons without free groundwater-level, the use of so-called suction-cups was successfully applied in the low-permeable clay sediments. In contrast to soil samples, from which soil water (or water phase) can be extracted, suction-cups represent a non-destructive method which enables repeated sampling at the same location (Fig. 3.4). By applying a negative pressure, soil water is collected in a bottle. This procedure can last a long time (from hours to days).

Fig. 3.4 Soil water sampling using suction-cups - figure shows sampling bottles above-ground; the suction cups themselves were installed at various depths (app. 30 – 90 cm)

Mainly the bulk chemistry of the water can be analyzed using this sampling method. The duration of sampling and environmental impacts (e. g. temperature, sunlight) can alter the sample, affecting, for example parameters such as pH- or Eh-value. Furthermore, this method is restricted to soil formations which allow the tight installation and application of a vacuum.

3.3 Methods for characterizing geological parameters

Geological inspection of drill cores

The first approach for obtaining actual geological information from the site to be investigated was an inspection of the freshly collected drill cores directly in the field. One must be aware that there is always a conflict of interest between complete and immediate sealing of the core to prevent any impact of the atmosphere on the one hand (due to the content of redox-sensible elements), and the need to identifiy the geologigal formation that has been drilled in order to plan further drilling and prepare appropriate sampling on the other hand. For the needs of the project, it proved useful to display the actual core section briefly either in a standard core-box or the half-shell prepared for sampling, to cut off the part of the core contaminated during the drilling on one side (very few centimeter) and to describe the main macroscopic features of the material (Fig. 3.5). Interesting core sections for further investigations can be sealed immediately after this (see Chapter 3.2 for details). Geological addressing of the core is more accurate if the responsible geologist is experienced in the regional geology. In case of the current project, helpful support was provided by specialists from Geologický ústav AV ČR, v. v. i. (Institute of Geology, Academy of Sciences of the Czech Republic) and a local mining geologist from Sedlecký kaolin a.s.

Fig. 3.5 On-site inspection and description of drill cores by geologists

On-site gamma-scanning

For the purposes of the project it was essential to identify geological horizons with enhanced radioactivity directly after core recovery. This could be undertaken satisfactorily using a portable gamma ray spectrometer (i. e. GRS-500 by EDA instruments) directly on the drill cores (Fig. 3.6). The default setting (with no specific detection adjustments) always gave reasonably good information and allowed the reliable distinction of uranium-bearing strata. In practice, the gamma ray spectrometer was applied every app. 20 cm, resulting in five readings per meter of drill core. At a background value of roughly 200 cps (counts per second), even slight increases in the range of 30 – 50 cps have been clearly differentiated from the background. More distinct uranium enrichments could be identified by increased gamma radiation in the range of several 100 up to a few 1,000 cps.

Fig. 3.6 Identifying uranium-bearing horizons using a portable gamma ray spectrometer, applied to the drill cores

Permeability and pore space analysis

Rock permeability as one of the important hydrogeological parameters was studied on several different scales. On the small scale, Hg-porosimetry was used, which provides detailed information about pore size distribution for selected samples (resolution nm to µm, Method No. A.40). The results supported the lab scale measurements of permeability (hydraulic conductivity - K) and porosity (resolution cm). From these measurements the collected data can be assigned to the hydraulic conductivity of specified layer/sample (Method No. A.41). The large scale was covered by hydrodynamical measurement in-situ (wells) regarding the space of wells filtration horizons (resolution m).

3.4 In-situ measurements

In-situ measurements are an integral part of research on a natural rock formation and provide primary data and information about its properties and the surrounding environment. Among a wide variety of such methods available, only a limited number chosen for use in the Ruprechtov study, with particular focus on the identification and validation of geological, hydrogeological and hydrochemical conditions at the site.

One of these methods used at the Ruprechtov site was well logging, which provides a wide range of measurements of various physical characteristics of the formation to be investigated. As an in-situ method, well logging is able to provide data and information about “true” properties and conditions rather than e. g. a rock sample measured in the laboratory. The combination of several (geophysical) well logging methods is recorded as a drilling log, highly recommended to gather overall information of the site. The purposes of well logging at the Ruprechtov site were mainly to:

- Determine positions in the boreholes with elevated radioactivity (uranium accumulations);
- Identify zones with groundwater inflows into the well (after the filter sections were installed into these zones);
- Clarify the geological profiles (lithology);
- Verify the quality of filters and casings backfill.

Tab. 3.4 summarizes the geophysical logging methods described in the Annex (Method No. A.1) and the main outcomes for site investigations.

The hydrogeological characterization of the basin’s sedimentary rocks and the underlying granite was mainly based on hydrodynamic tests (Method No. A.4) performed on individual wells. Some basic knowledge was also gained from the evaluation of geophysical logging measurements in boreholes. In total 28 hydrodynamic tests were performed. Twenty-one tests investigated parameters in Tertiary sediments, and seven tests were conducted in fractured granite bedrock. Parallel to the hydrodynamic in-situ tests, laboratory tests were conducted with rock samples collected during the drilling campaigns. As expected, the in-situ values of hydraulic conductivity (for sedimentary rock samples) were in the range 1.10^{-7} to 1.10^{-6} m/s in comparison with the lab test values of 1.10^{-11} to 1.10^{-10} m/s. The main reason for the differences is the fact that laboratory tests are performed on small, low permeable clay samples. The water-bearing layers around the boreholes do not only consist of clay but also contain inclusions of more permeable lignite and sand.

Tab. 3.4 Geophysical well logging methods used at the Ruprechtov site

Logging method	Gathered data vs. depth	Interpretation - Ruprechtov use
Electrical resistivity (RAP)	Apparent electric resistivity of formation	Changes in resistivity reflect the lithology and water bearing horizons - main tool for identifying potential water inflows
Magnetic log (MS)	Magnetic susceptibility	Any ferro-magnetic minerals providing immediate quality indications - identifications of paleosiderite concretions ($FeCO_3$)
Gamma ray log (GR)	Natural gamma radiation	Universal application for quality and correlation - uranium accumulation identification and correlation with gamma log on drill cores
Gamma - gamma log (GGK)	Bulk density (uncollimation tool)	Based on density difference identification of layer thickness - clarify the geological profiles (lithology)
Gamma - gamma log (XGGDL)	Bulk density (collimation tool)	Based on density difference identification of layer thickness - clarify the geological profiles (lithology)
Neutron - neutron log (XNN)	Count rate of thermalized neutrons	Rock mass assessment and porosity indicator in known lithologies - verify the quality of filters and casings backfill
Caliper log (DIA)	Real diameter of the borehole	Measurement of borehole diameter allowing location of casing type, breakages, location of fractures / fissures and other openings
Temperature log (TM)	Temperature of borehole fluid	Differences in groundwater temperatures may indicate water inflows
Fluid - resistivity log (RM)	True electrical resistivity of fluid in the borehole	In comparison with temperature log it can be used for identification of groundwater sources - potential water inflows
Photometry log (FM)	Optical transparency of borehole fluid	Additional technique - almost no relevant data because of mud after drilling

Hydrodynamical parameters were used in hydrogeological modelling to obtain flow velocities and flow directions, which enable the creation of a hydrogeological model of the locality.

Also a monitoring network for monitoring the groundwater hydrological regime has been established in an area of about 1 km^2 in both main aquifers. All 25 wells were progressively included in this network, also covering older observation wells excavated for other purposes (kaolin exploration, monitoring of the mining impact). The hydraulic heads of groundwater and temperatures in the selected observation wells were measured using autonomous data loggers (Method No. A.2). The values from the data loggers were checked by manual measurements. The data were used for:

- Characterizing the hydrological regime and developing a model of the locality;
- Identifying the impact of mining activity on hydraulic head changes (before and after the mining activity).

An important aspect of the in-situ methods was focused on in-situ measurement of electrochemical parameters such as pH, Eh, temperature, conductivity and dissolved O_2. The measurements can be realized in several ways, but it is experience of the study, that the data reliability of electrochemical parameter measurement increases in a row: on-site measurement in groundwater sample, on-site measurement in flow-tight cell, in-situ measurement with multiparametric probe (Method No. A.3) in the borehole. The main aim was to obtain representative values for electrochemical parameters in-situ (mainly for redox potential and pH). On the basis of these representative values we were able to compute the uranium speciation (pH-Eh diagram) and deduce more geochemical information. The value of the redox potential should be checked against measurements of redox pairs present in the system (e. g. Fe^{2+}/Fe^{3+}, S^{2-}/SO_4^{2-}).

3.5 Chemically based analytical methods

Chemically based analytical techniques are a prerequisite for the characterization of a site. The characterization of the hydro-geochemical conditions builds the basis for a sound interpretation of the processes, occurring at a site today and in the geological past. The chemically based analytical methods applied in the Ruprechtov analogue project cover a wide range of different techniques. We can divide these methods into three sub-groups concerning their orientation and focus in the project:

- Analytical methods;
- Extraction and separation methods, and
- Sorption and speciation methods.

Analytical methods were used for the classical qualitative and quantitative analysis of elements of interest in liquid (groundwater, porewater and soilwater) and solid (rocks) samples. Beside the major ions and selected trace ions special attention was paid to analysing the concentration and speciation of Th and U. In particular mainly spectroscopic methods were used (Method No. A.22 and Method No. A.23). The comparison of the common detection limits for U and Th of different techniques applied in our laboratories is shown in Tab. 3.5. A significant role was played by the sampling schemes for groundwaters (see Tab. 3.3), which – before the schemes unification – led to slightly different results in the two organizations.

Tab. 3.5 Detection limits of different methods for U and Th (various sources)

Analytical method	Detection limits			
	U		Th	
	Liquid sample [mg/L]	Solid sample [mg/kg]	Liquid sample [mg/L]	Solid sample [mg/kg]
FAAS	100	10,000	-	-
ICP-OES	0.5	250	0.05	25
ICP-MS	0.000005	0.05	0.0001	0.05

For redox pairs of relevance such as Fe^{2+}/Fe^{3+} and SO_4^{2-}/S^{2-}, additional analyses in groundwater and porewater were performed to confirm the redox measurments and to identify redox pairs, which impact the Eh-values. For LIBD was used to analyse colloid concentrations (Method No. A.30). Attention was paid to the source and the origin of dissolved organic carbon in the Ruprechtov groundwaters (Method No. A.31). The role of organic matter was further investigated using a comprehensive chemical separation process (Method No. A.32) and additional identification and characterization of microbial processes (Method No. A.34).

An important aspect of the investigations was dedicated to separation and extraction techniques. The modified sequential extraction technique (Method No. A.25) was used for rock samples. Generally, this allows the progressive selective dissolution of rocks by chemical agents in order to study the distribution of elements among different fractions.

The following limitations should be taken into account during the evaluation of sequential extractions:

- Redistribution of elements among phases during the extraction;
- Non-selectivity of reagents for the individual steps;
- Incomplete extraction and precipitation of new solid phases during extractions.

Because the redox state of U in the mobilization/immobilization process is crucial, special techniques to determine U(IV) and U(VI) in sediments and groundwaters (Method No. A.26) were used. It was vital to avoid oxidation during this procedure. For rock samples, this was achieved by identifying U-rich accumulations and sub-sequent application of the U(IV)/U(VI) separation method immediately after drilling. For groundwater samples, firstly Ar-flooding of the borehole was conducted some minutes before sampling and then the whole procedure was performed under an Ar-atmosphere. To obtain an overall picture about U-distribution in the system, porewater was also extracted from argillaceous samples using a squeezing technique (Method No. A.24).

Uranium behaviour was further studied using sorption and speciation methods. Because the natural samples originally contain U, the batch sorption experiments had to be modified to obtain proper sorption isotherms (Method No. A.27 and Method No. A.29). Great effort was put into U-speciation in real groundwaters. First, the U-speciation was calculated using geochemical codes on the base of real data (groundwater analyses, long-term measurements of pH and Eh). Then it was attempted to confirm these calculations through analytical measurement using Time Resolved Laser Induced Fluorescence Spectroscopy (Method No. A.36). Unfortunately, we did not succeed with the natural groundwater samples, because of interferences with organic compounds. The influence of organic matter (mainly humic substances) on U-speciation in groundwater was also studied through complexation experiments (Method No. A.33).

3.6 Micro- to nanoscale analytical methods

The use of micro- and nanoscale methods for studying macroscopic minerals gives an insight into the characteristics and behaviour of these minerals. In combination with macroscopic methods they are a powerful tool to identify relevant minerals and to characterize the morphology, texture and valence state of elements in order to obtain a better understanding of processes, which have occurred in the geological medium. The methods applied in the Ruprechtov study and their objectives for application are summarized in Tab. 3.6. All methods were applied to solid samples.

The positions of uranium-rich samples in drill cores, which have been in the focus of the Ruprechtov study, were identified using field and lab γ-scan methods. Then, in order to apply the micro-scale methods it was very efficient to gain a first idea about the spatial distribution of uranium-bearing minerals on a centimeter to micrometer scale by autoradiography (Method No. A.9). A good experience from the Ruprechtov samples was to cut samples into two pieces, use one for autoradiography and apply the direct counterpart, with the mirrored autoradiographical information for analytical scanning electron microscopy (ASEM) or electron microprobe study.

Tab. 3.6 Micro-/nanoscale methods applied to Ruprectov samples and objectives of their application

Method	Objective of application
Autoradiography	Identification and spatial distribution of major concentrations of radioactive compounds
Micropetrography	Characterization of lignitic material (origin, morphology, degree of coalification)
XRD	Determination and quantification of modal mineralogy of sediment samples
Electron microprobe	Identification and quantification of U-bearing minerals. Documentation of mineral textures and structures
µ-XRF/XANES	Determination of 3D distribution and valence state of elements
ASEM	Identification and characterization of minerals, mineral alteration and alteration products
TEM	Search for and chemical characterization of nanometer-sized uranium minerals

Electron microprobe (Method No. A.12), ASEM (Method No. A.14) and µ-XRF/Xanes (Method No. A.13) work with typical spatial resolutions in the range of 1 – 3 microns. Both former methods can be applied well to characterize minerals by size and shape, the content of uranium and other relevant elements, the sample texture and the morphology of surfaces. This information can be and has been used to, for example distinguish between primary and secondary U-bearing minerals, identify mineral growth or weathering and estimate the uranium content of the sample.

With the confocal geometry of µ-XRF/-XANES it became possible to conduct 3D micro tomography of the sample. X-ray fluorescence (XRF) is suitable for the analysis of element distributions and depending on the excitation energy also derives information about the redox state of an element. The existence of tetravalent U in most of the samples could be confirmed for the Ruprechtov study and a correlation to As(V) was shown. For the redox state of uranium in mineral form, in addition, µ-Xanes (X-ray Absorption Near-Edge Structure) provided evidence for U(IV) in the samples with secondary U-enrichment. As additional information from µ-EXAFS (Extended X-ray Absorption Fine Structure), which analyses interatomic distances and the number and type of nearest neighbours, the secondary uranium compound in a uranium-rich sample was assessed to be a Ca-U phosphate compound, very likely ningyoite. In conclusion, µ-XRF/-XAFS provided useful information to support results from macroscopic methods such as U(IV))/U(VI) separation and esequential extraction. Furthermore, it provided insight into uranium enrichment processes, which had occurred in the past.

Transmission Electron Spectroscopy (TEM, Method No. A.15) allows mineral investigations on the nanoscale. In case of the Ruprechtov samples mass balancing showed that a significant amount of uranium is expected to occur in minerals with sizes below µm or amorphously distributed, i. e. not detectable by methods working on the microscale. For the Ruprechtov samples, uranium could be detected in Ti-oxide minerals of sub-micron size. However, the preparation of samples with electron transparent foils with standard dimensions of 15 x 10 x 0.15 µm needs great effort and makes it necessary to analyse a fair number of samples to obtain sound information on the sub-micron uranium phases. This method has been applied at a late stage of the Ruprechtov project and, therefore, has not given enough credit to gather more knowledge about the fine grained uranium phases.

Micropetrography (Method No. A.10) is a method commonly used in coal petrography. It is applicable to organic-rich rock samples and allows the characterization of plant remnants according to their origin, morphology and optical quality. In combination with a sedimentary study, the extent of coalification and the coalification conditions of lignitic material from Ruprechtov such as oxic/anoxic sedimentation environment were determined.

Sample preparation required different effort for the different methods. A high level of effort is needed to prepare very thin samples covered by transparent gold films for application in TEM (s. above). The preparation of suitable thin sections is also necessary for electron microprobe, which needs experience in the argillaceous material of the uranium-bearing clay/lignite-sand layers at Ruprechtov. Thin sections also need to be prepared for Micropetrography. Almost no sample treatment is required for µ-XRF/-XAFS, ASEM and autoradiography. The surface should be flat, but drying and the evacuation of samples is not necessary, since no vacuum is needed to conduct these methods. This is particularly the case with ASEM, which can work at different pressures, remarkable, since conventional SEM is usually conducted under a vacuum.

3.7 Isotope investigation methods

Environmental isotopes today routinely contribute to investigations of groundwater cycles (origin, age and circulation times) but also complement geochemistry and physical hydrogeology in natural systems. The investigation of isotopes in water, solutes and solids provide information about groundwater quality, geochemical processes and the evolution of the system, recharging processes, rock-water interaction, the origin of salinity and contaminant processes.

Isotope investigation methods aimed at different aspects were applied at the Ruprechtov site. Firstly, tritium, stable and carbon isotope methods were applied to determine the local hydraulic patterns of the site (Method No. A.16, Method No. A.17). Secondly, isotope signatures of carbon, sulfur (Method No. A.18) and helium (Method No. A.19) were investigated in order to identify and characterize the extent of geochemical and microbial processes, particularly those affecting the carbon cycle. K/Ar dating (Method No. A.20) was used to determine the age of the basaltic intrusions at the Ruprechtov site as a component of the geological evolution of the site. Finally isotopes of the uranium decay chain (Method No. A.21) were investigated to better characterize mobile and immobile uranium phases and derive information on the time scales of the deposition / mobilization process as well as long-term stability of the phases.

Tab. 3.7 Objectives for the use of isotope methods at Ruprechtov site

Method	Medium	Information
^{3}H	GW	Identification of young meteoric water
^{4}He	GW	Identification of input of endogenic gases
δ^{18}O, δ^{2}H	GW	Identification of groundwater origin and mixing
δ^{13}C	GW DIC	Carbon source and geochemical processes impacting carbon chemistry
δ^{13}C	GW DOC	Initial values and GW age
δ^{13}C	Siderite	Reference value for DIC input from SIC
^{14}C	GW DIC	GW age, mixing processes, carbon chemistry
^{14}C	GW DOC	Initial values and GW age
δ^{34}S	GW SO_4	Identification of microbial sulfate reduction process
^{40}K/^{40}Ar	Basalt	Age of basaltic intrusions
^{234}U, ^{238}U	GW	Traces of α-recoil processes → stability of immobile phases Qualitative information on water flow
^{234}U, ^{238}U, ^{230}Th	Sediment	Identification of uranium deposition and removal processes Identification of time scales and long-term stability

The key information obtained from each method is listed in Tab. 3.7. A detailed description of how each method contributed to the investigation of key scientific or safety-related aspects can be found in Chapter 4.

Radioactive isotopes are a suitable tool for dating natural fluids and solids. Fig. 3.7 shows typical dating ranges of respective isotope methods /EIC 13/, which are directly correlated to their half-lives. Sveral methods for groundwater dating are available, covering the whole range of days up to millions of years. Young waters and waters with ages up to 10 thousands of years are of relevance for the Ruprechtov project; therefore, mainly tritium and ^{14}C (in combination with δ^{13}C) were analysed in the water samples (see Chapter 4.2).

Furthermore, δ^{13}C and ^{14}C isotope signatures of inorganic and organic carbon components provide information about the origin of the carbon sources such as volcanic gases, dissolved carbonates, organic materials, etc. and transformation processes such as microbial degradation of organic materials. In addition, the δ^{34}S and δ^{18}O isotopes of sulfates, sulfide and oxides contribute to the identification of microbial processes. With the exception of δ^{18}O analysis in oxidic compounds all of these methods were applied (see Chapter 4.2).

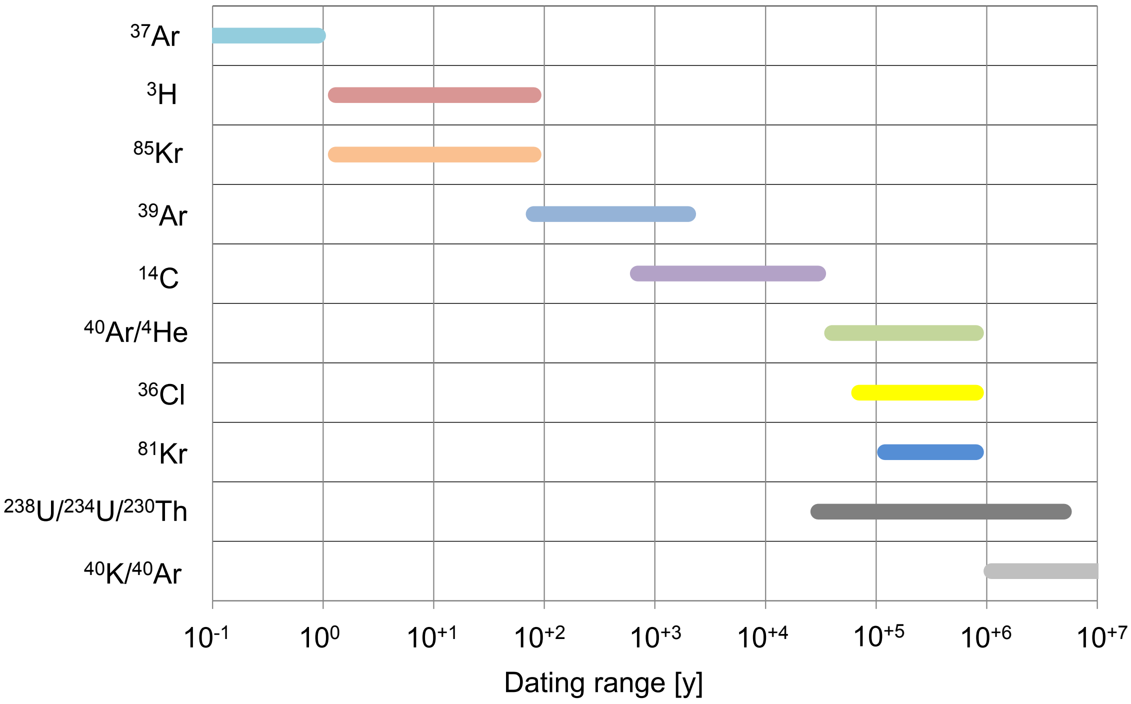

Fig. 3.7 Isotopes to be used for dating of groundwater, porewater and solid phases and their application range

Finally two isotope investigation methods for solid samples were applied to answer specific questions. Using K/Ar-dating the date of basaltic intrusions at Hajek, near the Ruprechtov site, could be determined to 15 million years, which is relevant information for the geological evolution of the area. The activities of the isotopes of the uranium decay chain in solid samples and leachates from sequential extraction and U(IV)/U(VI) separation were analysed (see Chapter 4.6).

The functioning of the methods, key features and references containing more detailed descriptions are given in Annex A.2. The major technical data and requirements are listed in Tab. 3.8.

Tab. 3.8 Sample requirements for and precision of isotope analysis in water and solid samples

Isotope	Method	Water or solid sample[1]	Precision	Detection limit
^{3}H	Scintill.	100 – 500 mL	±0.1 TU	0.02 TU
$^{18}O/^{16}O$, $^{2}H/^{1}H$	IRMS	30 mL	±0.1‰ $\delta^{18}O$, ±1‰ $\delta^{2}H$	
$^{13}C/^{12}C$	IRMS	1000 mL	±0.1‰	
^{14}C (DIC/DOC)	AMS or β	10 mg / 5g	±0.1 pmC	0.1 pmC
^{4}He	QMS	100 – 500 mL	±5%	
$^{36}Cl/Cl$	AMS	500 mL	±5%	
$^{37}Cl/^{35}Cl$	IRMS	100 mL	±0.1‰ $\delta^{37}Cl$	
$^{34}S/^{32}S$	IRMS	500 mL	±0.2‰ $\delta^{34}S$	
$^{234}U/^{238}U$	α/SF-MS			
$^{234}U/^{238}U/^{230}Th$	α/SF-MS			
$^{40}K/^{40}Ar$				

[1] depending on the concentration of the respective isotope

Several practical results were derived from the application of these methods, which are compiled in the respective tables in Annex A.2 and briefly summarized here. In general, it is important to avoid evaporation of the samples in order to avoid changing the isotope ratios. This is of particular importance for gas analysis, e. g. He-isotopes. Here specific sampling procedures need to be used.

With regard to carbon isotopes, the applied method delivered a good understanding of processes involved in carbonate geochemistry. However, the age could not be reliably determined due to the complex situation in the Ruprechtov groundwater. Here the application of an additional method, namely groundwater dating ^{39}Ar might have helped to better determine the data range of groundwater ages. A positive experience, which led to the further development of methods, is related to the uranium chain isotopes. Nearly all of the samples from Ruprechtov showed distinct $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ activity ratios, which strongly underpinned the long-term stability of the near-surface uranium enrichment, and in combination with other methods allowed the clear distinction between the U(IV) and U(VI) phases (see Chapter 4.6).

3.8 Modelling tools

The application of modelling tools is essential in order to interpret and further evaluate the results from the characterization methods and to understand the accompanying laboratory experiments. Three different groups of models have been applied in the Ruprechtov project: hydrogeological modelling, geochemical modelling and principal component analysis.

Hydrogeological models are generally applied to determine flow fields in geological media. This is an indispensable instrument for evaluating hydraulic field data such as hydraulic heads, permeabilities (or transmissivities) and knowledge about geological structures, and information about water recharge and discharge. Depending on the degree of salinity of the water, density-driven flow needs to be taken into consideration.

At the Ruprechtov site, the groundwaters in the Tertiary basin and in the underlying granite are characterized by a low ionic strength; therefore, density effects were not considered in the flow modelling. The major area of interest is the Tertiary basin. Although isotope data indicate some inflow from underlying granite in the area of known fractures, in general, the groundwater flow in the Tertiary is separated from the underlying flow regime in the granite by the kaolin layers and can therefore be modeled separately. Hydrogeological modelling was performed with MODFLOW using the graphical user interface Groundwater Vistas (Method No. A.42).

The application of the model is straightforward and the results well underpinned the interpretation from the stable isotope signatures that the groundwater flow direction is generally from south-west to north (north-east) and that preferred pathways occur in the northern and southern parts of the investigation area. A clear drawback of the model's application at the Ruprechtov site is the low-permeable rock featuring high heterogeneity and uneven distribution of permeability on the low spatial scale. Flow is expected to be strongly influenced by water bearing layers of increased permeability with sometimes very low thickness. Sandy layers of low thickness and brown coal inclusions are particularly responsible for increased flow. A much higher amount of data would have been necessary to reproduce the flow on this scale. One consequence of this is that transport modelling including the use of coupled codes was not performed.

Principal Component Analysis (PCA, Method No. A.43) is a multivariate analysis method used for the statistical evaluation of large data sets. The goal of this method is to reduce the number of variables without a significant loss of information. The technique is based on an orthogonal linear transformation which transforms the data to a new coordinate system representing the principal components (PC). The first PC covers the greatest data variability. The second and each subsequent PC is orthogonal (perpendicular to all foregoing PC´s) and describes the maximum of the remaining variability.

For the Rupredchtov project the method was applied to identify the most important factors controlling the groundwater geochemistry and to evaluate the large data sets of all elements derived from the sequential extraction of several sediment samples using the PAST and The Unscrambler® software. The method helped in identifying and illustrating the key geochemical processes of groundwater evolution and identified similarities in the elemental distributions in leachates from sequential extraction. One positive experience was the correlation of uranium with arsenic and phosphate in a number of samples being in good agreement with the results from SEM-EDX and micro-XAFS indicating the occurrence of uranium phosphate minerals and redox processes with the involvement of As (see Chapter 4.6).

By far the most prominent for the project was the application of geochemical speciation tools (Method No A.44). Geochemical programmes are based on the equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. Recently, they have evolved to model kinetic reactions and 1D (one-dimensional) transport.

Several codes are available for geochemical modelling. For the Ruprechtov project, PHREEQC /PAR 12/ and Geochemists Workbench /BET 13/ were preferentially applied. Both programmes are widely used and therefore well qualified. The quality of the results is directly correlated to the quality of the input data and the applied database. The programmes were used to determine the geochemical speciation of chemical elements, saturation indices of mineral phases and evolution of water chemistry along the reaction path including the reactions and isotope signatures involved. One crucial issue for the situation at Ruprechtov is the distribution of redox species, particularly of uranium. A critical parameter concerns the analysis of the redox conditions, which is covered by high uncertainty. In case of the study, the use of redox data measured in-situ, which clearly deviated from on-site and of course laboratory analysis, seemed to be most promising. Using the most recent database /GUI 03/, quite plausible results (see e. g. Chapters 4.3 and 4.6) have been obtained.

Inverse geochemical modelling, where net geochemical mass-balance reactions between an initial water and chemically evolved water along a hydrologic flow path are calculated, based on the geochemical composition of both waters, was applied to better understand the geochemical evolution, particularly the carbon chemistry and resulting isotope signatures. The PHREEQC and Netpath codes were used. The results gave a clear indication of the relevance of the involved processes. However, a quantitative evaluation including a better estimation of the groundwater ages was impeded by the high heterogeneity and uneven distribution of hydraulically acting features, petrography and mineralogy. Therefore, the evolution from a selected upstream to a selected downstream well is probably influenced by additional small scale mixing processes, which are difficult to quantify.

4 Application of methods to selected topics

This chapter describes how the different methods have been applied, in order to understand key aspects of the Ruprechtov site with relevance to the scientific and safety related issues discussed before. For all key aspects the output of each method as well as the interpretation and interplay of the different methods in comprehensively describing the key aspect is illustrated. Therefore standardized flow schemes were developed, which are linked to the descriptions of each method in Annex A.2 and easily allow finding details and experiences for the methods applied in the Ruprechtov project. Furthermore, this chapter briefly describes the major scientific results from the Ruprechtov programme, giving links to references with more detailed descriptions, where necessary.

4.1 Information from topics needed for system understanding

With respect to the questions which arise from PA (see Chapter 2.4.2) and the specific characteristics of the site, and in order to understand the complete system today and its evolution during the geological past, five major investigation topics were identified: (i) hydrogeological flow patterns, (ii) geochemistry, (iii) microbiology, (iv) interrelation of organic and inorganic carbon, and (v) uranium migration processes. All of these topics are to some extent correlated to each other. The interplay of these features and processes forms the basis for the understanding of the whole system.

Investigation of the hydraulic flow patterns is important for identifying whether hydraulic connections are occurring in the Tertiary sediment layers, or if pyroclastic clays represent a more or less tight, diffusion-dominated system. It is important to understand the current geochemical conditions, particularly the evolution of groundwater from the recharge area along the pathway through the Tertiary sediments. On the one hand, the geochemical conditions are impacted by microbial effects and the interaction processes of organic and inorganic carbon and on the other hand they also affect both of these. All three topics influence uranium migration / immobilization processes.

A large amount of information has been derived from investigations of drill cores and analyses of groundwater wells. A total of 16 boreholes were drilled and 15 wells lined in the study area in order to sample and characterize groundwater flow. Seven additional boreholes, which were drilled within the framework of kaolin exploration at the site, became available for this study. These additional boreholes are equipped with relatively long screens, which may lead to the mixing of water originating from different water-bearing horizons. The locations of the boreholes which have been drilled or which became available at the site and represent the basis for the descriptions in the next chapters are illustrated in Fig. 4.1 (excluding four new boreholes, NAR1 to NAR4).

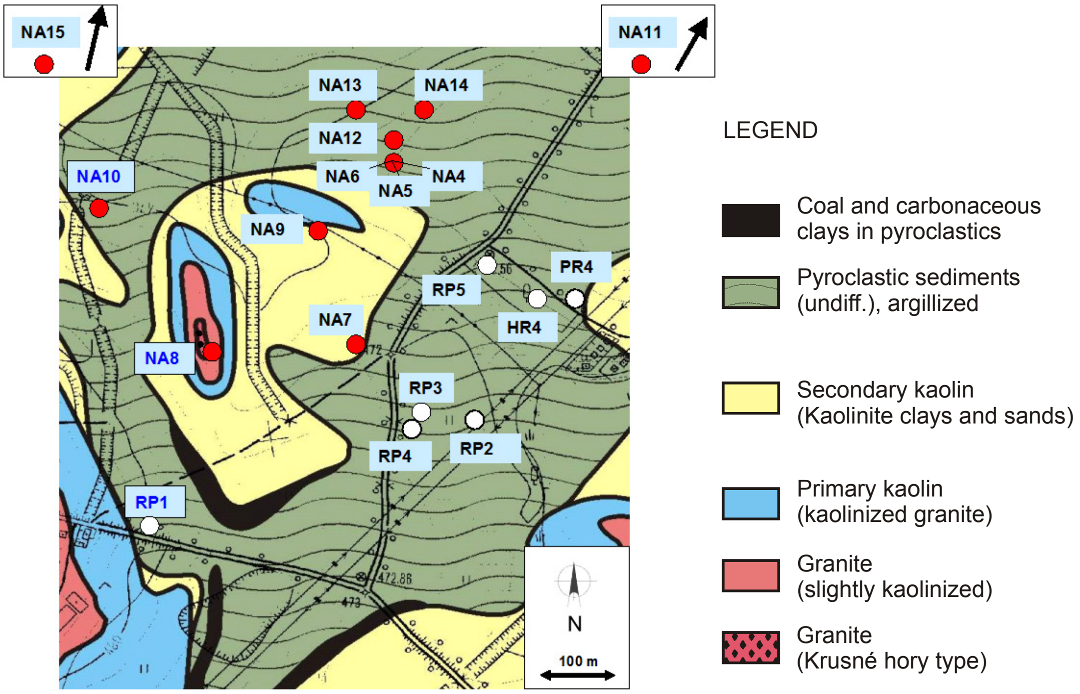

Fig. 4.1 The location of boreholes at the Ruprechtov site, shown on the background of the geological map

Dark (red) dots indicate research boreholes drilled in the framework of this study. White dots indicate boreholes which were drilled for other purposes and made available for this study. The figure is based on topographical map, which also shows, for example, roads and drainage channels.

4.2 Identification of (groundwater) flow patterns

One important topic for site understanding is the characterization of groundwater flow in the area. Based on existing knowledge it was expected that groundwater flow in the Tertiary basin is hydraulically separated from the deeper flow system in the underlying granite.

The methodological approach for the evaluation of the hydraulic situation in the Tertiary basin is shown in Fig. 4.2.

The evaluation applied comprised:

- The geochemistry of the groundwater in the different wells, namely pH, Eh, concentrations of major and trace ions and concentration of DIC and DOC;
- The isotope signatures in these waters, i. e. stable isotopes, carbon isotopes and He- isotopes;
- In-situ monitoring of hydraulic heads, as well as in-situ pH, and Eh conditions;
- Geophysical logging for each borehole, particularly indications of depth locations of water inflow;
- Hydrodynamic tests to characterize the hydraulic conductivity on the macro scale;
- Permeability measurements of sediment samples in the laboratory.

The flow scheme in Fig. 4.2 indicates how the required information is derived from the obtained data via interpretation and modelling.

Firstly, the relevant information concerns the structure of the hydrogeological units in the Tertiary basin. On-site determination of hydraulic conductivities (hydrodynamic tests), in agreement with observations from geophysical logging, revealed the existence of water-bearing layers with k_f-values of 10^{-5} m/s to 10^{-8} m/s but thicknesses of only about 1 to 2 m. These water-bearing layers occur mainly in the vicinity of clay/lignite-sand layers. Permeability measurements of selected drill cores showed that, in contrast, the pyroclastic argillaceous sediments and the underlying kaolin have a lower hydraulic conductivity, with typical k_f-values of 10^{-10} m/s to 10^{-11} m/s.

Secondly, tritium isotopes indicate the existence of young groundwaters. As expected, tritium is absent in the majority of the analysed boreholes, confirming the pre-bomb age of the groundwater. Some traces of ^3H were found in NA8, NA10, NA11, NA13, RP2, RP3 and HR4. The highest concentration of ^3H (9.7 TU), comparable with the current concentration of ^3H in local precipitation, was found in borehole PR-4. Borehole PR 4 was provided from the kaolin exploration and is not restricted to one deeper horizon. Therefore inflow of surface-near water is expected. This also occurs to some extent with RP2, RP3 and HR4, whereas NA8 and NA10 are located in the recharge area of the granite.

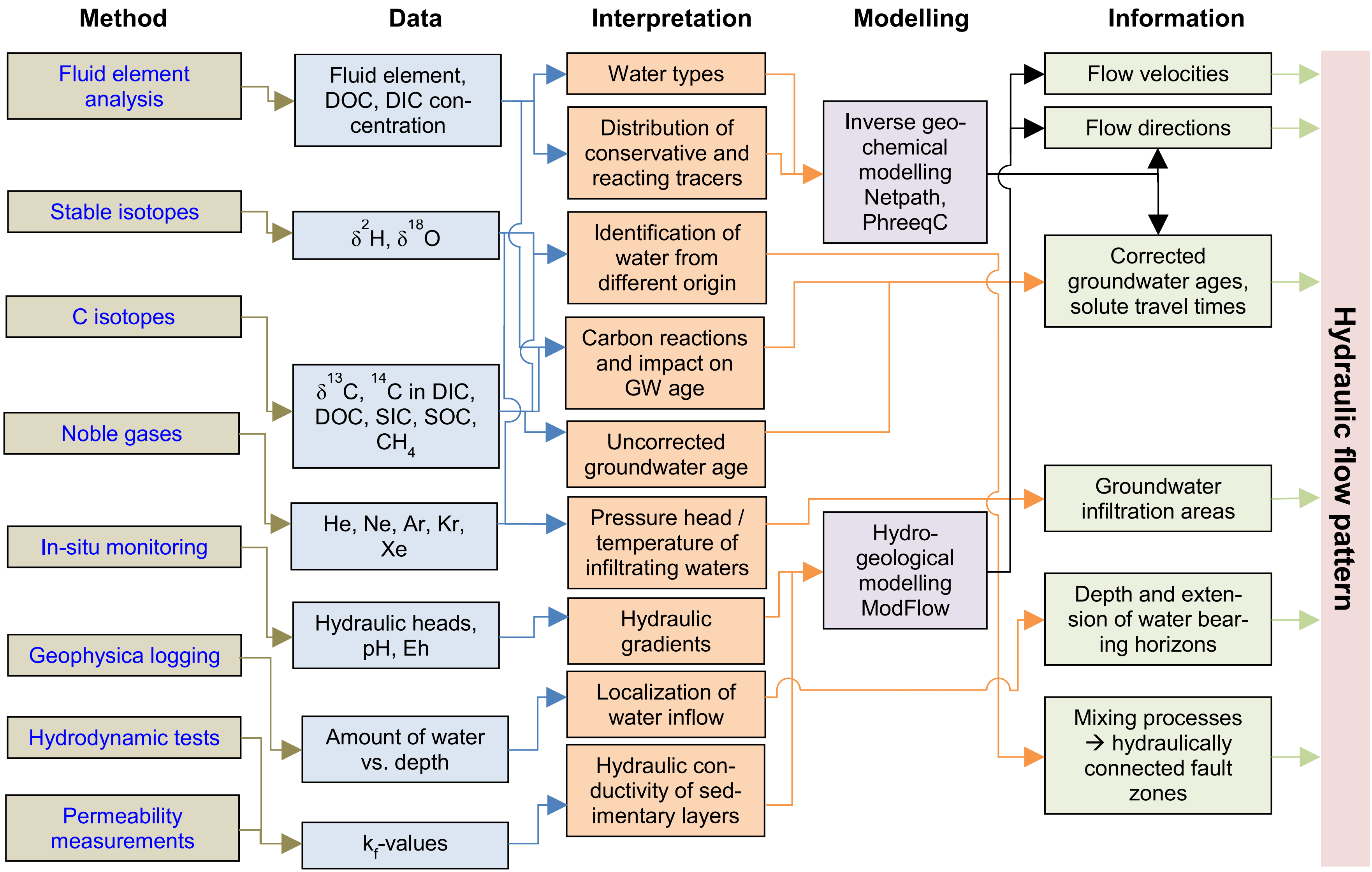

Fig. 4.2 Evaluation scheme with methods, data, interpretation, modelling for characterization of hydraulic flow pattern

Thirdly, deuterium and ^{18}O analyses provide information about water origin, flow paths and mixing processes. The deuterium and ^{18}O contents in the analysed wells are presented in Fig. 4.3. It is apparent that the stable isotope composition of the analysed water samples varies across a rather broad range: $\delta^{18}O$ changes from approximately -9.8 ‰ to -8.8 ‰. In general, the data points cluster around the world meteoric water line (WMWL). The range of δ^2H and $\delta^{18}O$ values in recent local infiltration waters have been determined on the basis of isotope analysis of representative water samples in the study area /NOS 02a/. This range is marked on Fig. 4.3 by the bold grey line. A number of data points reveal more negative δ^2H and $\delta^{18}O$ values when compared to local recent infiltration waters, suggesting the influence of the altitude and/or a climatic effect.

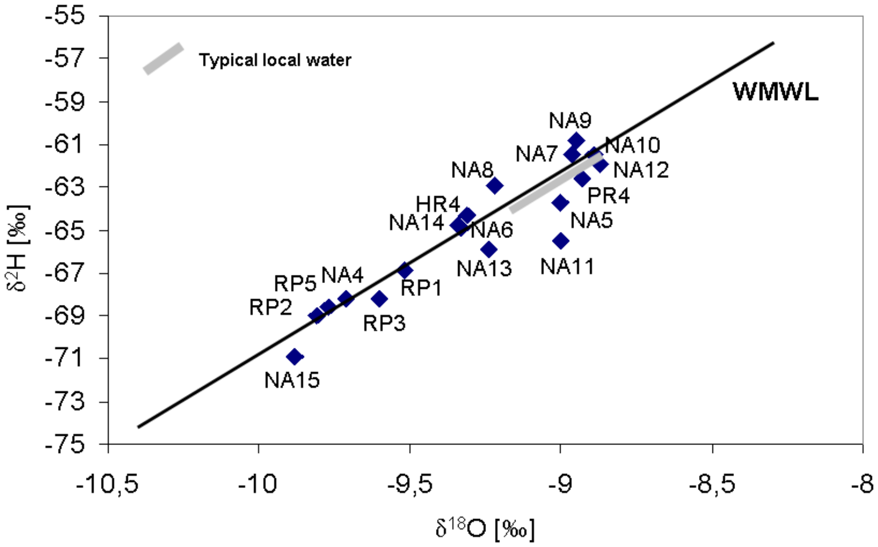

Fig. 4.3 Stable isotope composition of the analysed groundwater samples in the Ruprechtov aquifer system

The bold grey line denotes the isotope signature of local, recent infiltration waters

The spatial distribution of δ^2H and $\delta^{18}O$ values is shown in Fig. 4.4. In general, the analysed waters can be divided into two groups: isotopically heavier groundwater in the NW region of the study area (marked with a white box) and isotopically light groundwater in the SE region (marked with a grey box). The waters in the NW region can be further subdivided into a group with $\delta^{18}O$ values between -8.8 ‰ and -9.0 ‰ and a group with $\delta^{18}O$ values between -9.2 ‰ and -9.4 ‰.

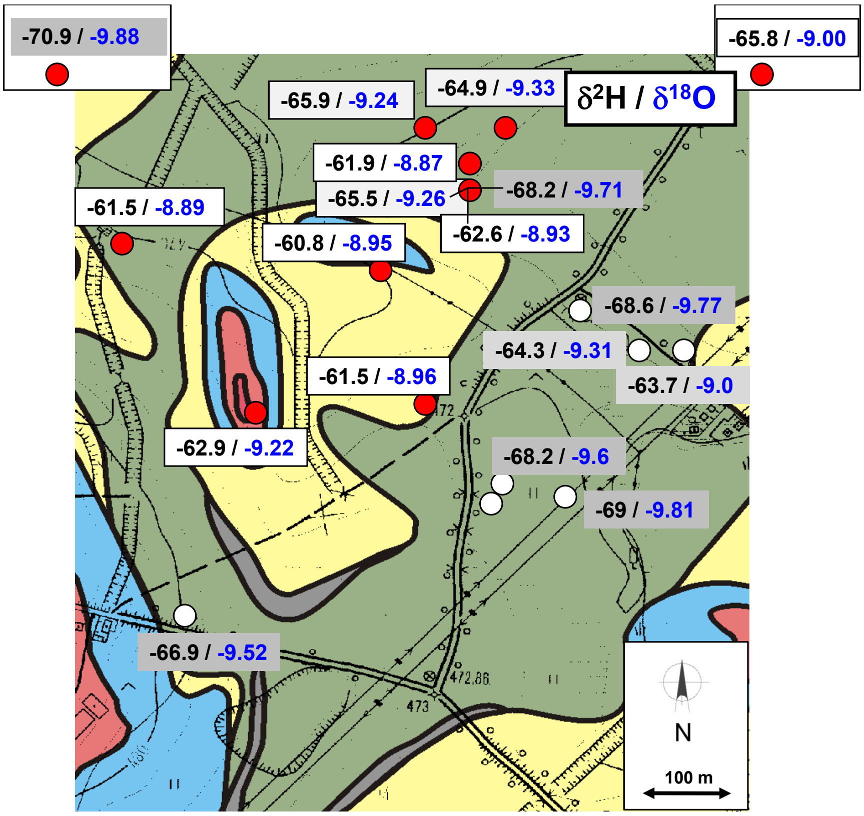

Fig. 4.4 Spatial distribution of δ^2H and δ^{18}O values in groundwater samples representing the Ruprechtov aquifer system

Additionally, from the distribution of hydraulic heads (measured in April 2004 and shown in Fig. 4.5) it can be derived that a hydraulic gradient extends from SW to NE. The boreholes sampling water from granite are marked in a white box; all other values are given in a light grey box. Three western wells (NA8, NA10 and RP1) represent groundwater from near-surface granite. They contain measurable amounts of ^{3}H but differ significantly in their stable isotope composition. Whereas NA10 and NA8 reflect signatures of recent local waters (cf. Fig. 4.3), water from RP1 is isotopically lighter. The most probable explanation for the differences in stable isotope composition among those wells is that the water from RP1 originates from an infiltration area which is elevated by about 200 to 300 m when compared to the other two wells.

Several boreholes in the south-eastern region of the study area (RP2, RP3, RP5) reveal similar stable isotope signatures to that of the RP1 borehole. This suggests a hydraulic connection between RP1 and the SE region of the study area. PR4 and HR4, located in the eastern part of the study area, are older drillings which are not well documented. The elevated δ^{18}O values measured in those wells might be caused by the admixture of surface water. This is very likely, particularly for PR4, where the filter horizon covers a depth interval from 5 m to 32 m. A strong indication for such an admixture of surface water is provided by the elevated ^{3}H content in those wells (9.7 TU and 1.2 TU in PR4 and HR4, respectively).

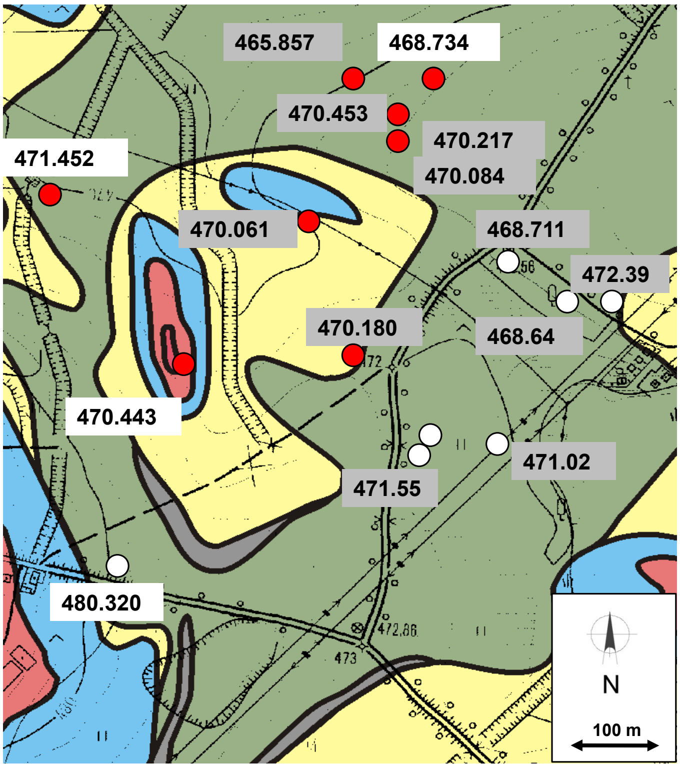

Fig. 4.5 Hydraulic heads in the Ruprechtov aquifer system based on measurements made in April 2004

Water samples originating from near-surface horizons (boreholes NA9, NA7 and NA5) reveal stable isotope ratios similar to NA10, indicating hydraulic connections to the infiltration area in the NW of the study area.

Boreholes located in the northern part of the study area reveal a relatively large range of δ^2H and δ^{18}O values. NA12 shows similar values to NA10, suggesting hydraulic connection to the western infiltration area. A cluster of three wells (NA4, NA5, NA6) shows isotopically depleted water in the deeper horizon (NA4 and NA6, screened from ca. 33 m to 37 m), suggesting an elevated recharge area, whereas NA5, screened between 19 m and 21 m, falls into the range of recent local infiltration (cf. Fig. 4.4). Other boreholes in this region (NA13 and NA14) seem to represent mixtures of isotopically depleted water and local infiltration water. NA13 shows some traces of ^{3}H, which is rather unexpected for the deep horizon sampled by this well.

The water in the deeper granite (NA14) may represent a mixture of water originating in the north-western infiltration area and water infiltrated in the south-western area. Additionally, there seems to be a hydraulic connection between the north-western infiltration area and the water-bearing horizons in the northern area of the Tertiary (NA12, NA13, NA6). Since those wells are located in a region of low kaolin thickness, where fault zones occur, local connections between water-bearing horizons in the Tertiary and underlying granite are likely. Therefore, the groundwater in this region might represent a mixture of underlying granite water and infiltration water from the north-western infiltration area. This is important to know, since inflow from deeper granite might have represented a transport pathway for uranium into the enriched zones in the Tertiary sediments. A correlation with the morphology and thickness of the kaolin layers site suggests that valley areas with a very low thickness of underlying kaolin might represent hydraulic connections between the Tertiary sediment layers and granite.

Information on hydraulic conductivity, water levels and knowledge about re- and discharge was fed into the hydrogeological model. The calculation results from flow modelling using MODFLOW are shown in Fig. 4.6 (left). The model results and the different lines of evidence discussed above provided the basis for the conceptual model of the groundwater flow pattern in the studied Ruprechtov aquifer system shown in Fig. 4.6 (right). The general direction of the groundwater flow is from SW to NE, with a local infiltration area in the outcrops of granite around NA8.

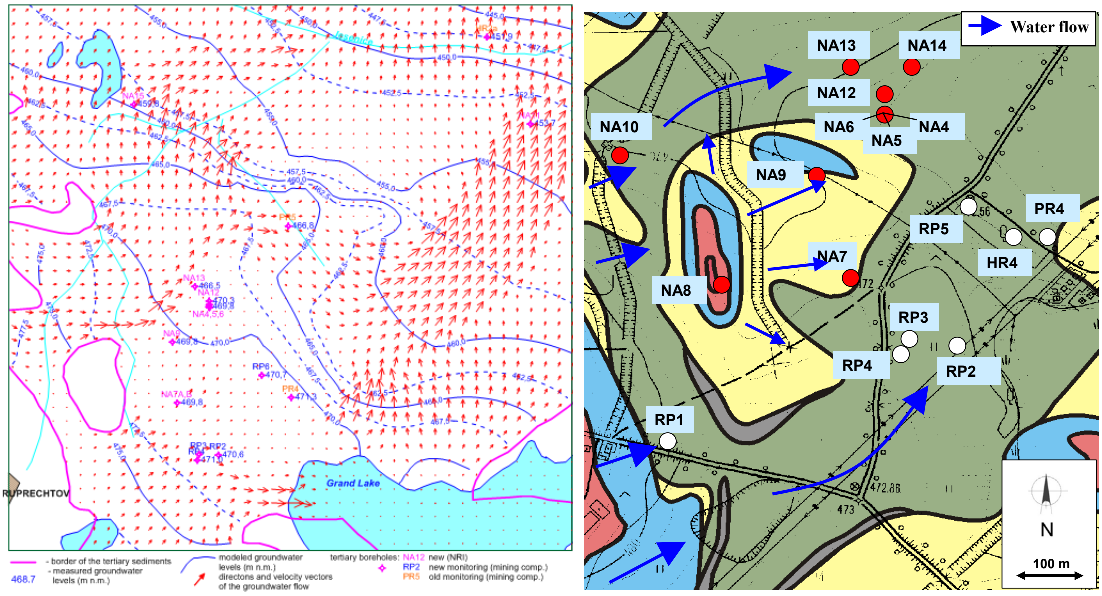

Fig. 4.6 Results from the flow modelling and conceptual model of groundwater flow pattern in the Tertiary basin of the studied Ruprechtov aquifer system

4.3 Geochemistry / geochemical milieu

The approach and methods used to characterize the geochemical conditions are illustrated in the evaluation scheme in Fig. 4.7. Of course there is overlap with the methods applied for hydraulic flow patterns. The evaluation scheme comprises:

- Basic chemical composition of the fluid derived from fluid element analysis using standard procedures;
- Signatures of carbon isotopes and He- isotopes in these waters, which particularly provide information about reactions within the carbon cycle;
- Laser induced breakdown detection (LIBD) for the determination of colloid concentrations and size distribution;
- Solid element analysis for element distribution in the solid phase;
- Geophysical logging together with drill core description for the characterization of petrography;
- Spectroscopical methods XRD, EPMA and ASEM to identify and characterize minerals by type, size, shape and content of elements (especially U);
- Sequential extraction to obtain information about the chemical form of key elements;
- Analyses of Fe(II) and Fe(III) to obtain supporting information about the redox environment of the samples.

The data set including major and trace ions as well as hydraulic data and isotope signatures in all of the Ruprechtov wells is compiled in Tab. 4.1 and Tab. 4.2. The hydrochemical conditions of the site are characterized by low-mineralized waters with ionic strengths in the range between 0.003 mol/L and 0.02 mol/L. The pH values vary across the range of 6.2 to 8 and the Eh-values from 435 mV to -280 mV. More oxidizing conditions with lower pH-values are found in the near-surface granite waters of the infiltration area. In the clay/lignite horizon more reducing conditions with Eh values as low as -280 mV predominate.

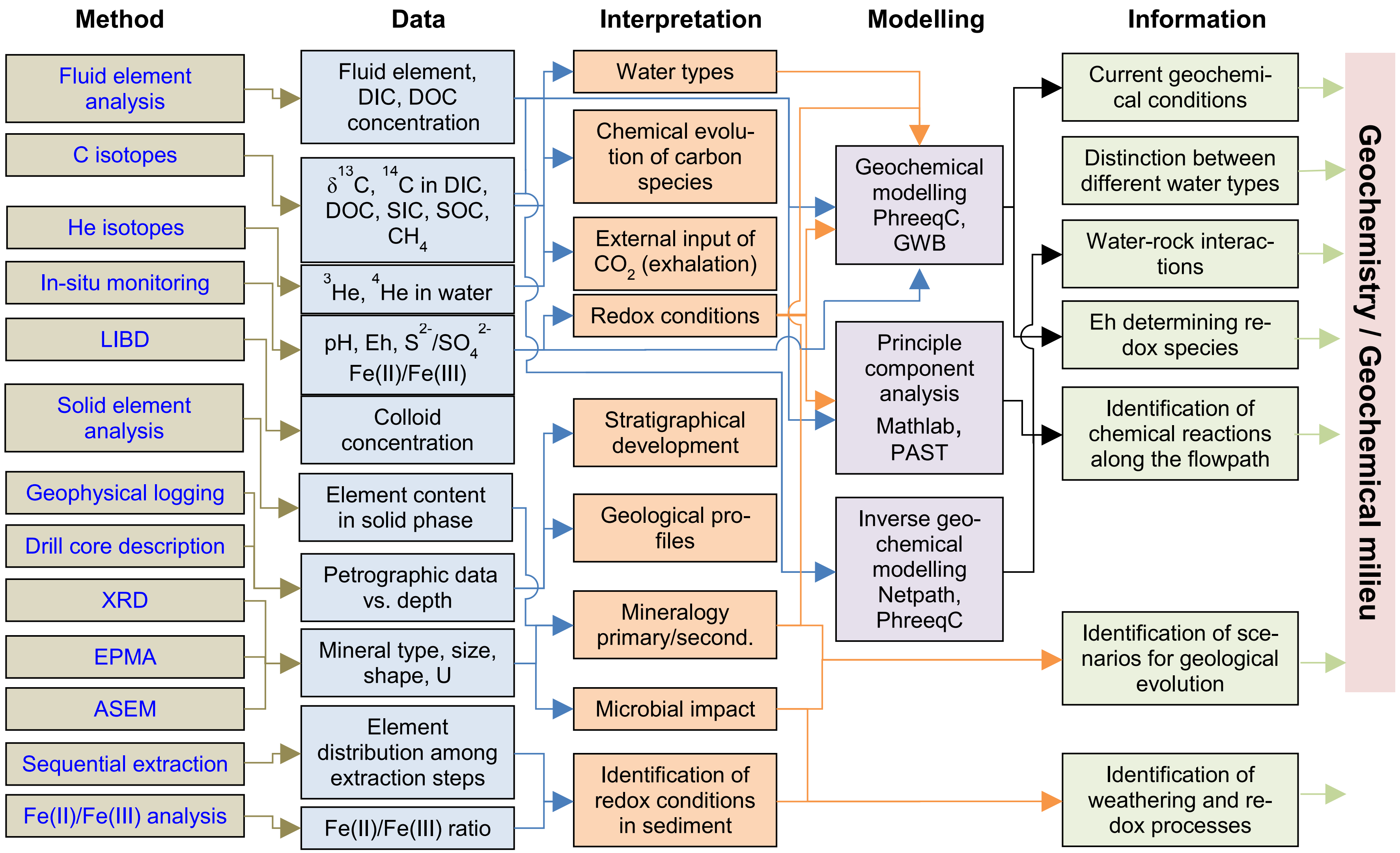

Fig. 4.7 Evaluation scheme with methods, data, interpretation, modelling for geochemistry / geochemical milieu

Tab. 4.1 Physical and chemical parameters of groundwater samples collected in the Ruprechtov aquifer system during the sampling campaign in May 2004

All concentrations are expressed in mg/L, Eh values are expressed in mV. (n.a.: not analysed)

	NA4	NA5	NA6	NA7	NA8	NA9	NA10	NA11	NA12	NA13	NA14	NA15	RP1	RP2	RP5
T[°C]	9.60	9.00	9.80	9.10	9.00	7.30	8.40	9.80	9.10	9.90	9.20	9.40	9.70	9.60	9.10
pH1	n.a.	n.a.	8.00$^{1)}$	8.00$^{1)}$	6.20$^{1)}$	7.19$^{1)}$	7.40	6.89	6.65	7.65	6.85	7.29	6.81$^{1)}$	7.72$^{1)}$	7.00$^{1)}$
pH2	6.78	7.05	7.80$^{1)}$	7.05$^{1)}$	6.45$^{1)}$	6.83$^{1)}$	6.95	7.04	6.68	7.41	7.00	7.09	6.75$^{1)}$	7.35$^{1)}$	6.89$^{1)}$
pH3	6.75	7.04	7.57	7.49	6.15	6.97	6.67	7.11	6.73	7.66	6.94	6.71	6.40	7.70	6.93
Eh1	n.a.	n.a.	-280$^{2)}$	-35$^{1)}$	48$^{1)}$	324$^{1)}$	240	-91	-160$^{2)}$	-252$^{2)}$	-59	58	149$^{1)}$	-3.8$^{1)}$	133$^{1)}$
Eh2	6	-10	-115$^{1)}$	-107$^{1)}$	143$^{1)}$	355$^{1)}$	485	65	15	25	120	245	363$^{1)}$	25$^{1)}$	160$^{1)}$
Al	0.20	0.26	0.22	0.33	0.10	0.15	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.14	0.21	0.25
Ca	51.00	68.90	48.00	86.85	26.24	28.03	40.40	65.60	44.70	54.60	48.70	31.60	31.00	47.10	43.70
Fe	1.87	0.99	0.73	0.13	1.32	0.91	0.37	5.45	2.27	0.83	0.10	0.31	0.34	2.89	1.16
K	13.10	12.30	12.05	6.50	1.40	2.70	8.40	18.90	9.70	16.50	14.60	10.80	2.90	10.30	11.20
Mg	23.60	29.35	18.60	17.90	4.00	5.30	8.40	28.90	19.80	21.70	20.80	12.50	8.80	23.80	21.40
Na	23.30	45.25	37.20	16.40	10.90	14.10	15.50	91.20	20.10	35.80	39.50	25.30	13.40	41.80	19.20
Si	10.30	7.80	7.40	4.40	15.05	18.70	13.00	7.70	15.90	8.00	12.60	11.60	16.80	3.30	9.90
Cl	3.90	8.80	3.60	6.60	4.30	0.60	5.90	10.40	4.30	10.10	13.60	4.00	20.70	26.40	5.54
SO_4	19.80	31.50	49.50	28.20	59.10	11.80	40.80	178.60	22.90	22.90	30.80	40.10	19.80	55.00	14.80
$PO_4^{2)}$	0.19	0.47	0.2	0.72	0.3	0.08	0.16	0.30	0.04	0.14	0.21	0.10	0.35	0.11	0.15
CO_2	40.71	43.60	6.70	9.60	31.70	8.60	24.50	40.60	63.00	10.50	32.80	13.80	44.40	1.00	20.50
NO_3	0.80	0.40	1.20	1.10	1.70	1.10	7.20	1.40	0.30	1.00	2.30	3.50	3.20	2.50	2.20
HCO_3	330.50	469.30	291.80	332.10	44.20	163.50	159.40	379.00	269.20	349.00	316.60	186.70	117.00	277.00	279.00
CH_4	0.634	0.097	0.072	0.007	n.a.	n.a.	0.003	0.011	0.028	0.04	0.022	0.004	n.a.	n.a.	n.a.

pH1: measured in situ; pH2: measured on site; pH3: measured in laboratory (T=20°C); Eh1: measured in situ, Eh2: measured on site

[1)] sampling campaign from May 2003

[2)] long-term value

Tab. 4.2 Depth of screened horizons, lithological units and environmental isotope data for boreholes in the Ruprechtov aquifer system sampled between 2003 and 2006

The table also shows DIC, DOC and SO_4^{2-} concentrations in the analysed groundwaters. (n.a.: not analysed)

Well No.	Screen horizon [m]	Lithology	k [m/s]	$\delta^{18}O$ [‰]	$\delta^{2}H$ [‰]	Tritium [TU]	^{14}C DIC [pmc]	^{14}C DOC [pmc]	$\delta^{13}C$ DIC [‰]	$\delta^{13}C$ DOC [‰]	$\delta^{34}S$ SO_4^{2-} [‰]	DIC [mg/L]	DOC [mg/L]	SO_4^{2-} [mg/L]
NA4	34.5-36.5	clay/lignite, U	1.52E-06	-9.78	-68.0	<0.5	3.2	40.0	-11.0	-26.6	24.63	74.2	4.22	19.8
NA5	19.3-21.3	U	5.47E-08	-8.98	-61.9	<0.5	5.3	n.a.	-10.9	-25	n.a.	90.8	n.a.	31.5
NA6	33.4-37.4	clay/lignite, U	5.62E-07	-9.27	-64.6	0.6	13.1	n.a.	-12.4	-26.8	23.5	60	3.27	49.5
NA7/1	15.5-19.5	kaolin	1.88E-07	-8.96	-61.5	<0.5	n.a.	n.a.	n.a.	n.a.	n.a.	61.7	3.88	28.2
NA7/2	10.5-11	clay/lignite, U	4.40E-05	-9.00	-61.1	<0.5	39.4	n.a.	-16.1	-27.3	20.4	60.8	n.a.	12.3
NA8	8.5-24	granite	2.00E-06	-9.22	-62.9	1.1	71.9	64.6	-21.9	-27.8	-8.5	14.5	3.01	59.1
NA9	4.4-10	kaolin	3.26E-06	-8.95	-60.8	<0.5	72.1	n.a.	-20.5	-27.1	n.a.	37.1	n.a.	11.8
NA10	19.5-27.5	granite	2.86E-08	-8.89	-61.5	1.6	54.6	n.a.	-16.2	-26.4	0.2	33.8	1.99	40.8
NA11	33.2-39	clay/lignite, U	6.50E-06	-9.00	-65.5	1.5	7.8	n.a.	-9.6	n.a.	n.a.	82.4	n.a.	178.6
NA12	36.5-39.3	clay/lignite, U	3.80E-07	-8.87	-61.9	<0.5	26.5	70.0	-16.0	-25.6	20.11	67	3.69	22.9
NA13	42.2-48	clay/lignite, U	2.30E-09	-9.24	-65.9	1.5	n.a.	44.3	n.a.	-27.2	n.a.	68.8	2.32	22.9
NA14	67.6-77.6	granite	2.75E-08	-9.33	-64.9	0.6	9.8	n.a.	-12.8	n.a.	16.43	69.1	n.a.	30.8
NA15	28.8-31.6	granite	1.19E-07	-9.88	-70.9	<0.5	11.8	n.a.	-13.7	n.a.	n.a.	39.4	n.a.	40.1
RP1	5-18	granite	3.37E-07	-9.52	-66.9	<0.5	21.0	n.a.	-16.8	n.a.	3.48	33.4	1.36	19.8
RP2	25-43	clay/lignite, U	2.78E-06	-9.81	-69.0	1.1	16.8	n.a.	-13.2	-26.6	n.a.	52.4	1.83	55.0
RP3	25-48	clay/lignite, U	2.25E-05	-9.60	-68.2	1.0	13.3	n.a.	-15.3	-26.6	n.a.	59.7	n.a.	24.6
RP5	30-58	clay/lignite, U	5.08E-08	-9.75	-68.4	<0.5	6.4	n.a.	-11.7	n.a.	n.a.	58.1	n.a.	14.8
HR4	46.5-95	granite	n.a.	-9.31	-64.3	1.2	29.9	n.a.	-14.5	-26.2	n.a.	n.a.	n.a.	n.a.
PR4	5-32	clay/lignite, U	n.a.	-9.00	-63.7	9.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Data are single values from measuring campaigns in 2003, 2004 and 2006, respectively. Exceptions are $\delta^{18}O$, $\delta^{2}H$ and ^{3}H data for wells NA4, NA5, NA6 and RP5 and ^{14}C values in DIC for wells NA4 and NA5, which are averages of 2 or 3 analyses, respectively.

The groundwater from nearly all of the boreholes of the clay/lignite horizon is of the Ca-HCO_3-type. The exceptionally high Na and SO_4 concentrations in NA11 are probably an artefact of contamination by drilling fluid. The waters from the infiltration area in granite (NA8, NA10 and RP1) as well as water from borehole NA12 with significantly lower alkalinity and Ca concentration are defined as Ca-SO_4-type water. All DOC values are in a range between 1 mg/L and 5 mg/L. CH_4 concentrations of over 0.01 mg/L (up to 0.7 mg/L) were detected in a number of boreholes from the clay/lignite horizon.

In order to identify the most important factors controlling the groundwater geochemistry, a principal component analysis (PCA) was performed using the PAST program /HAM 01/. The results of the PCA are illustrated in Fig. 4.8 and show that most information is covered by two components: Principal Component 1 (PC1) accounts for 80.6% and Principal Component 2 (PC2) accounts for 15.3 % of the variability in the data set. PC1 is well defined and has a highly positive loading for HCO_3, positive loadings for Ca, Na, and Mg and a highly negative loading for the redox potential, i. e. samples with low Eh are covered by this component. It represents a geochemically evolved reducing groundwater, similar to the water from the clay/lignite horizon, with increased concentrations of cations and high concentration of HCO_3^-. PC2 is not as well defined and has a positive loading for Si, highly negative value for HCO_3 and negative values for Na, and Mg. This component represents immature groundwater, probably dominated by the dissolution of silicates close to the recharge areas in the granitic formation.

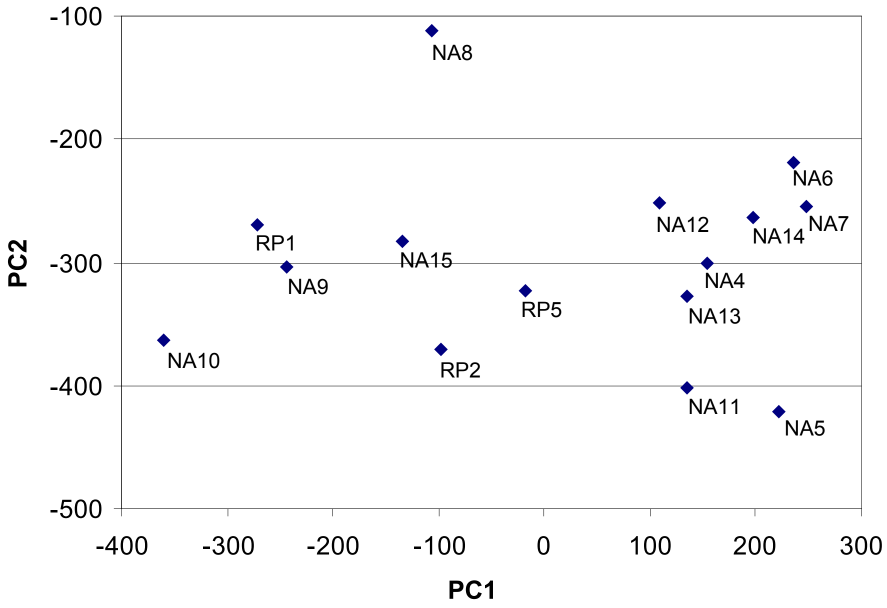

Fig. 4.8 Results of the Principal Component Analysis: plot of PC1 vs. PC2 (see discussion in the text)

The groundwater in most of the analysed wells reaches saturation with respect to carbonate minerals. Calculations using PHREEQC showed that only the groundwater samples from the boreholes NA8, RP1, NA12 and NA9 are undersaturated with respect to carbonate-bearing minerals: see Fig. 4.9 /NOS 09a/. These wells (particularly NA8, RP1, NA9) represent infiltration waters or kaolin waters from shallow horizons without contact with the clay/lignite horizon.

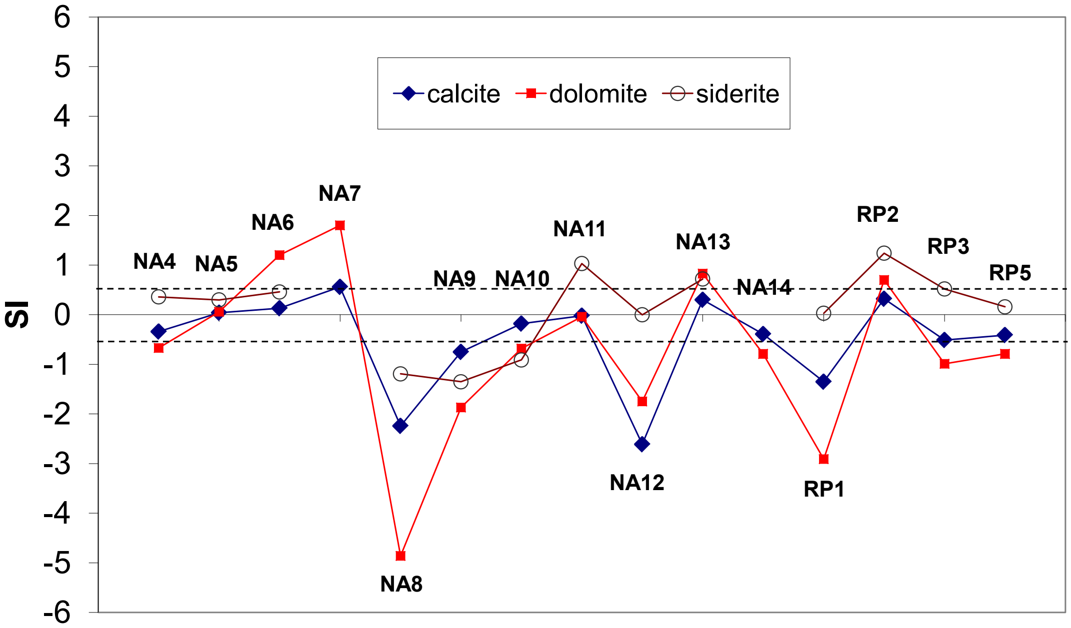

Fig. 4.9 Saturation indices (SI) for carbonate-bearing minerals in selected groundwater samples from the Ruprechtov site

The horizontal lines indicate SI-ranges where equilibrium is assumed.

In the clay/lignite horizon, the conditions are reducing, supported by the existence of the mineral phases pyrite and siderite occurring with contents of up to 2 % in sediment samples from this horizon. Eh values have been measured on site and in situ. The first method is more susceptible to disturbance by contact with the atmosphere, which is probably responsible for the higher Eh values observed in the on-site measurements. The in-situ probe measurements of Eh values in the clay/lignite horizon always showed an Eh decrease during the analyses. In order to find the stable values long-term measurements for three boreholes (NA6, NA12 and NA13) were performed. This measurement showed a stabilization of the Eh-value after few days. We decided to trust these values and used them for the following interpretation.

Redox conditions in natural systems could be controlled by different and heterogeneous redox couples. The clay/lignite layers are quite heterogeneous, typically containing quartz and clay minerals (smectite, illite, kaolinite) as major components, organic matter and to a lesser extent minerals such as anatase, pyrite and siderite /NOS 06/. Geochemical calculations using PHREEQC were performed in order to analyse the redox-controlling species in the system. Due to the occurrence of significant amounts of dissolved sulfide and sulfide minerals in the clay/lignite layers, the redox pairs SO_4^{2-}/HS^- and the heterogeneous redox pairs SO_4^{2-}/pyrite were included in the analysis. Many natural systems are dominated by redox pairs of iron. Therefore we also calculated the couple $Fe^{2+}/Fe(OH)_3$, considering a relatively fresh amorphous precipitate according to data from /LAN 97/. There is no indication of goethite or haematite occurring in the clay/lignite horizon. The results are shown in Fig. 4.10. The measured Eh values from the three boreholes are compared with the values calculated from these redox pairs.

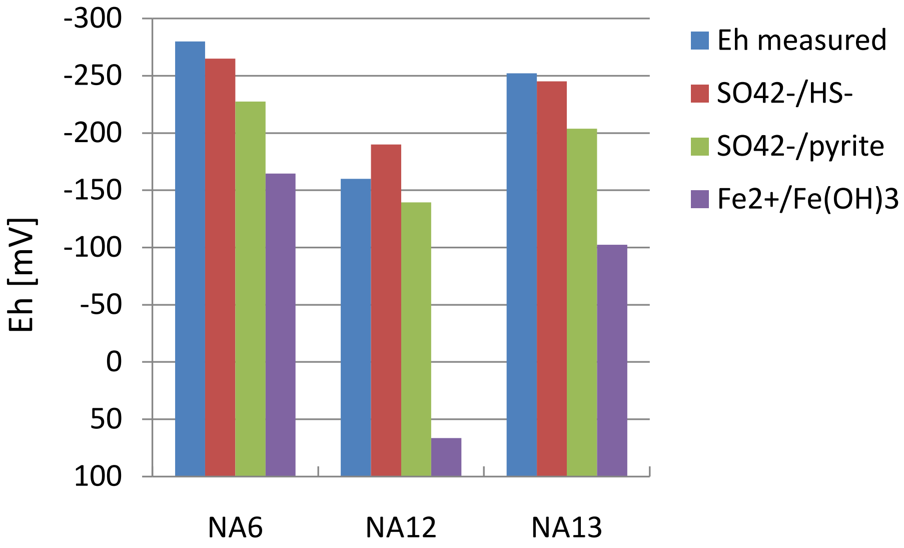

Fig. 4.10 Measured Eh values compared to potential redox pairs

A reasonably good agreement is found between the redox potential measured by the Pt electrode and the SO_4^{2-}/HS^- couple, whereas the redox pair $Fe^{2+}/Fe(OH)_3$ shows low agreement in particular for borehole NA12. As discussed in /NOS 09a/ (see also Chapter 4.4) there is strong evidence that microbial sulfate reduction and oxidation of organic matter occurs in the clay lignite horizon. In particular, the $\delta^{34}S$ values in the boreholes from the clay/lignite horizon are strongly increased with respect to the values in the infiltration waters (see Tab. 4.2 and Fig. 4.14). Furthermore, the existence of sulfate reducing bacteria has been shown and pyrite minerals in framboidal shape, typically formed by microbial processes, are frequently found in the clay/lignite layers /NOS 06/. The observed sulfide values in the clay/lignite waters are significant but not too high, lying in a range between 0.05 and 0.12 mg/L. Microbial catalysis efficiently accelerates the sulfate reduction, and operational redox potentials resulting from this kinetic process may closely approximate equilibrium values /STU 96/. This might explain the agreement of the measured and calculated values for the SO_4^{2-}/HS^- couple.

Besides the redox conditions, carbon chemistry plays an exceptional role at the Ruprechtov site, evidenced by the occurrence of organic-rich layers and relatively high CO_2 partial pressures in the clay/lignite horizons. The interrelation between organic matter and inorganic carbon is described in detail in Chapter 4.5. Here, only the major aspects affecting the geochemical conditions are discussed.

In order to better understand the geochemical evolution from the immature water at infiltration to the more mature waters in the clay/lignite horizon (see above), isotopes of C in the Ruprechtov aquifer system were analysed /NOS 09a/. This comprised $\delta^{13}C$ values and ^{14}C activities in both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) pools in groundwater as well as in sedimentary inorganic carbon (SIC) and sedimentary organic carbon (SOC). These measurements were then interpreted with the aid of simple models (open- and closed-system) using PHREEQC as well as inverse geochemical modelling performed with the aid of NETPATH /PLU 94/. Through this process, geochemical reactions and changes in isotope signatures along the flow path can be identified, as described in more detail in /NOS 09a/.

Modelling of chemical and C isotope data highlights that additional sources of C operate in the system, which explains the observed chemical and isotope evolution of the DIC reservoir. The most probable sources of this additional C include the biodegradation of dissolved and sedimentary organic C as well as the influx of endogenous CO_2. The former is clearly underpinned by an increase of $\delta^{34}S$ in dissolved SO_4^{2-} and an increase of biogenic DIC and phosphate with increasing DIC concentration along the potential flow path of the groundwater in the system. The latter is further supported by the observed $^3He/^4He$ ratio, which is increased against typical values in atmosphere. This indicates a low inflow of endogenous gases including mantle CO_2, which is much more active in other parts of the Ohre Graben /WIE 99/. In summary, the increased CO_2 partial pressures can be explained by input from the degradation of organic matter and to a lesser extent by mantle CO_2. Both the relatively low Eh values and the increased CO_2 partial pressures significantly affect the speciation of uranium as discussed in Chapter 4.6.

In order to check the impact of colloids on the mobility of uranium, groundwater from selected wells were analysed for their colloid content using Laser-induced Breakdown detection (LIBD). The waters from three wells (RP2, NA6 and NA7) are in direct contact with the clay/lignite-sand horizon. As shown in Fig. 4.11, rather low colloid concentrations of between 170 and 450 µg/L were observed in all of the waters, where most of the particles have sizes > 450 nm. These particles might not be mobile at low groundwater velocities.

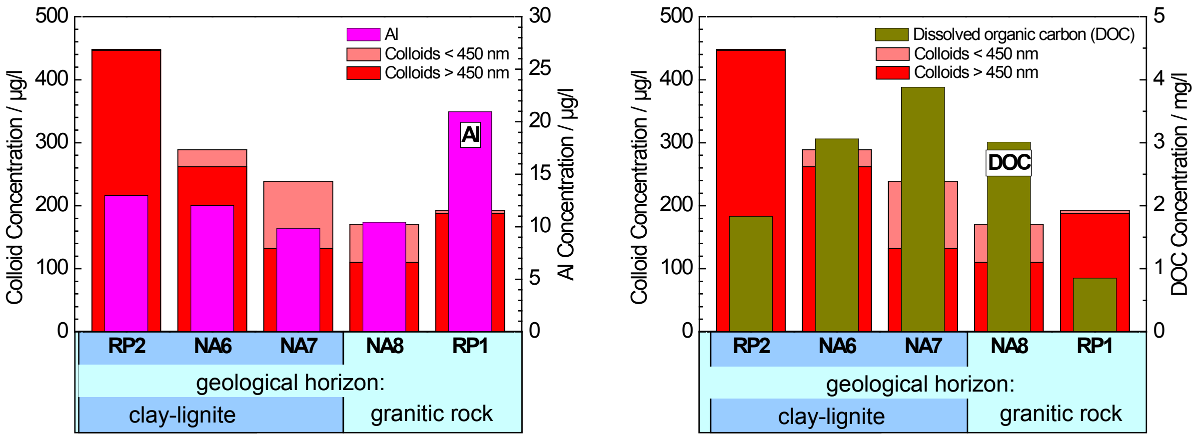

Fig. 4.11 Comparison of colloid concentration determined by LIBD (left) with the Al content of the groundwater (analysed by ICP-MS) and with the dissolved organic carbon concentration (right)

There is no clear correlation between colloid concentration and element concentrations. Furthermore, dependency of colloid concentrations on the geological situation of the sampling location is also not distinctive from these five samples. DOC measurements revealed rather low concentrations with no correlation with LIBD data on colloid concentrations. Different to the Gorleben aquifer, we are facing conditions at the Ruprechtov site where significant content of lignite-like solids is found in the sedimentary layers, however very low soluble organic species, and especially very low concentration of humic and fulvic acids, if at all, in the groundwater. Possible reasons for this are further discussed in Chapter 4.5.

4.4 Microbiology

From the outset, the role of microbes was considered to be significant in impacting the relevance (kinetics) of geochemical processes, because the environment was favourable for the occurrence of bacteria (organic-rich layers in Tertiary sediments). The scheme in Fig. 4.12 summarizes the methods used in these investigations.

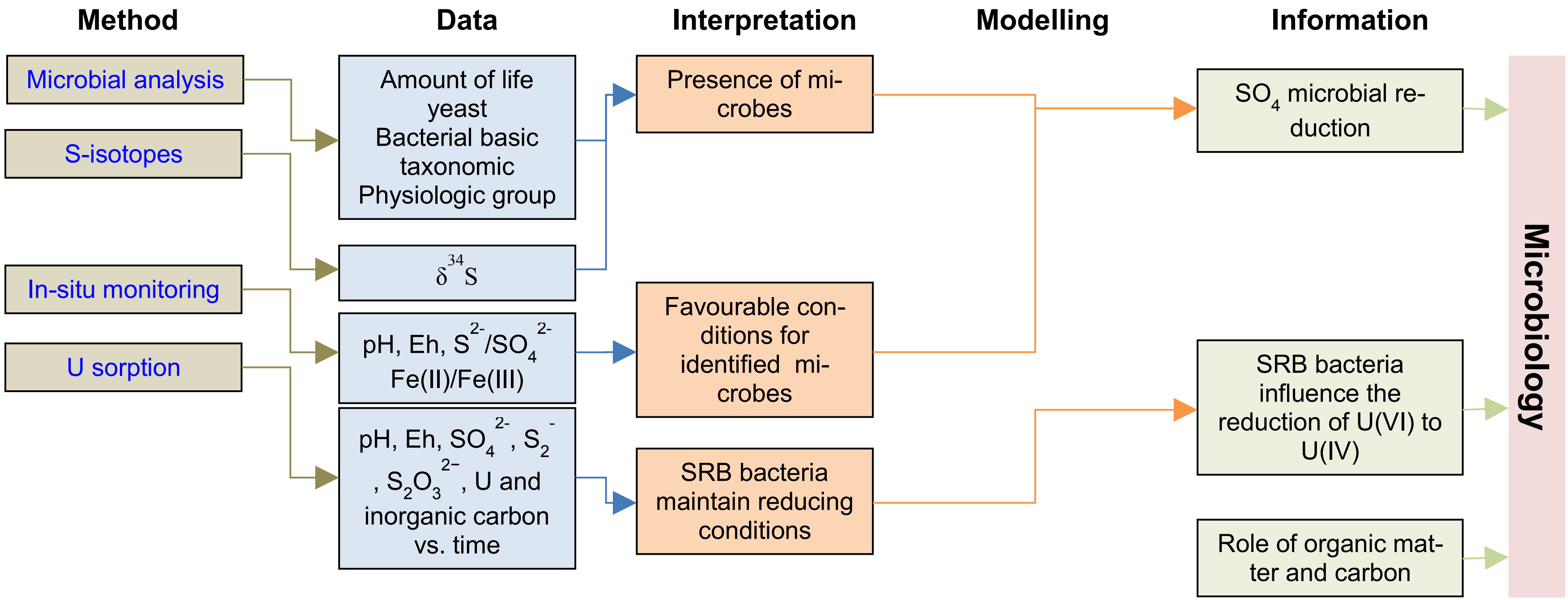

Fig. 4.12 Evaluation scheme with methods, data, interpretation and modelling for microbiology

Important consequences of microbial activity at the Ruprechtov site were expected in two respects:

- Impact on redox conditions
- Impact on the degradation of organic matter

Concerning the impact on redox conditions, emphasis was placed on the role of sulfate-reducing bacteria. This is due to the existence of a significant amount of sulfide minerals in the clay/lignite-sand horizon, in particular pyrite nodules. Frequently, pyrite nodules were found as an aggregation of small grains called framboidal pyrite (see Fig. 4.13), the origin of which can be connected with microbial activity /QAF 09/.

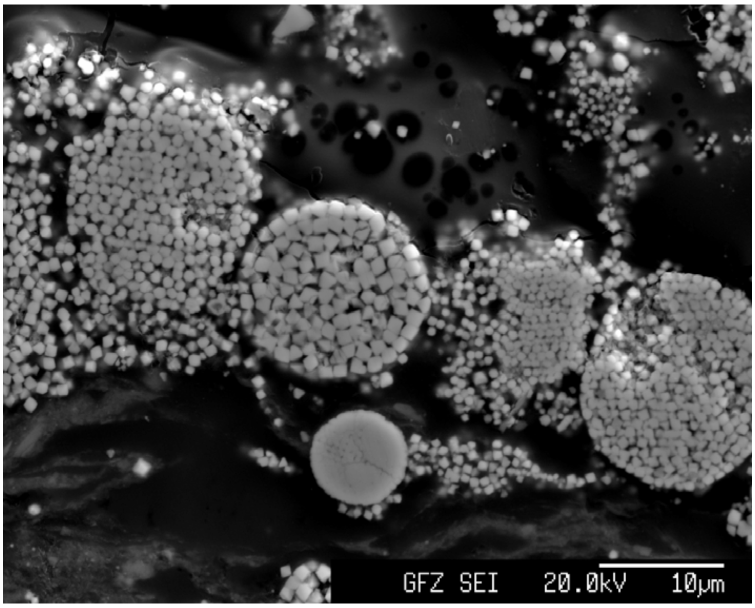

Fig. 4.13 Back-scattered electron mineral images from EPMA, intact and disintegrating grains of framboidal pyrite (NAR2, depth 28.82 – 28.86 m)

Indeed, autochthonous sulphate-reducing bacteria were detected in undisturbed samples derived under as far as possible sterile conditions /NOS 06/. The general characterization concerning the microbial activity of two groundwater samples is shown in Tab. 4.3.

Tab. 4.3 Characterization of bacteria in two groundwater samples from the clay/lignite horizon

	Borehole NA4	**Borehole NA5**
Total amount of G+ bacteria / mL	0.42×10^3	2.30×10^3
Total amount of G- bacteria / mL	1.13×10^3	9.00×10^3
Proportion of anaerobic bacteria	78 %	70 %
Proportion of aerobic bacteria	22 %	30 %

The microbial sulfate reduction is accompanied by isotope fractionation. The lighter isotope ^{32}S is preferentially metabolized by the microbes, leaving residual SO_4^{2-} in the solution enriched in ^{34}S, whereas $\delta^{34}S$ values in precipitated sulfides decrease. To identify the microbial activity at the Ruprechtov site, sulfur isotopes were analysed in dissolved sulfate sampled from different monitoring wells (Fig. 4.14). The wells in the infiltration area (dashed red line) are represented by low values of $\delta^{34}S$ in in dissolved sulfate compared with much higher values in groundwater wells from clay/lignite horizon (red solid circle). Substantial $\delta^{34}S$ enrichment of dissolved SO_4 in these boreholes is a strong indication that SO_4 reduction occurs in the clay/lignite layers /NOS 09a/.

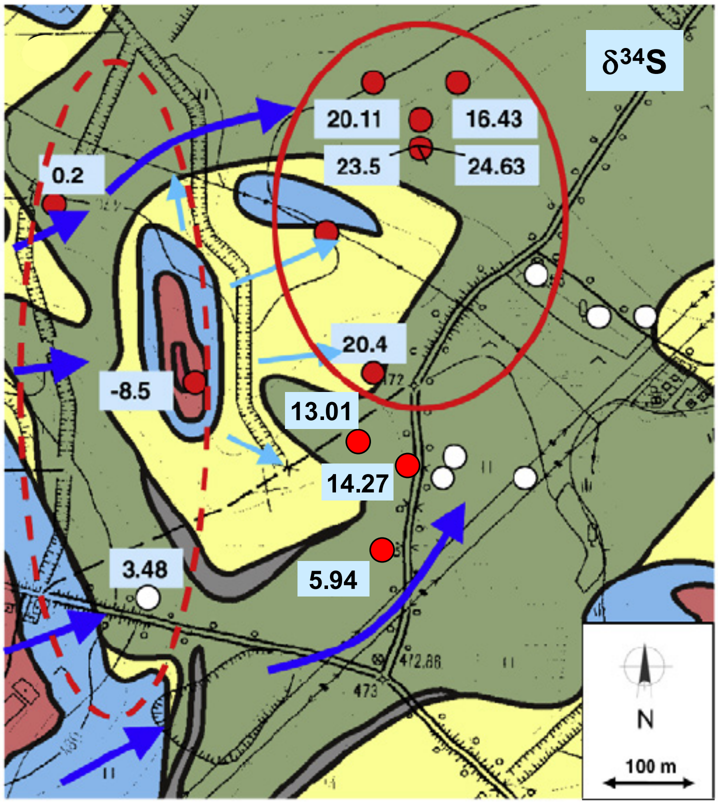

Fig. 4.14 Spatial distribution of $\delta^{34}S$ values in monitoring wells

Also the in-situ monitoring of the redox potential showed a highly reductive environment in the clay-lignite horizon (e. g. min. values of Eh -280 mV in NA6), which was also often accompanied by a typical hydrogen sulfide smell (e. g. conc. S^{2-}: 0.095 mg/L in NA6).

Experiments with the groundwater / sediment system from borehole NA4 showed that stimulation of growth of sulphate-reducing bacteria by sulfate, lactate and phosphate addition under initially oxidizing conditions caused a decrease of the Eh value from 400 mV to about -100 mV with a simultaneous decrease of the pH value from 7.8 to 5. Thereby the initial uranium concentration of $2 \cdot 10^{-6}$ mol/L dropped down to values about 10^{-8} mol/L. The composed sulfide is precipitated by the formation of iron sulfides. This showed the importance of the role of sulphate-reducing bacteria. Firstly, formation of sulfides can be of relevance in uranium retention processes, as shown in this study. Furthermore, they are able to maintain the reducing conditions, in a range, where uranium likely exist as U(IV). Finally they can contribute to the long-term stability of reducing environments by consuming oxygen in infiltrating groundwater /NOS 06/.

The impact of the second important role of bacteria in the degradation of organic matter and release of dissolved organic material such as humic and fulvic acids is further discussed in the next chapter. However, the conditions for the microbial degradation of sedimentary organic matter by SO_4 reduction in the clay/lignite layer are fulfilled. The SO_4 is available in all boreholes in a high enough concentration and the presence of SO_4-reducing bacteria has been confirmed.

4.5 Role of organic matter and carbon

If sedimentary organic matter (SOM) is present in a rock sequence, it can be important with respect to geochemical processes. SOM might very often act as a natural sorbent and it can usually have a strong impact on the environmental conditions. However, in the case of the Ruprechtov site, uranium enrichment was never found directly within organic-rich layers. The uranium-rich sequences were usually found located in sandy horizons with increased permeability in close proximity to the organic-rich layers. Interest was then focused on the natural processes that SOM can potentially undergo (see methods used in Fig. 4.15), especially degradation (mineralization) of SOM.

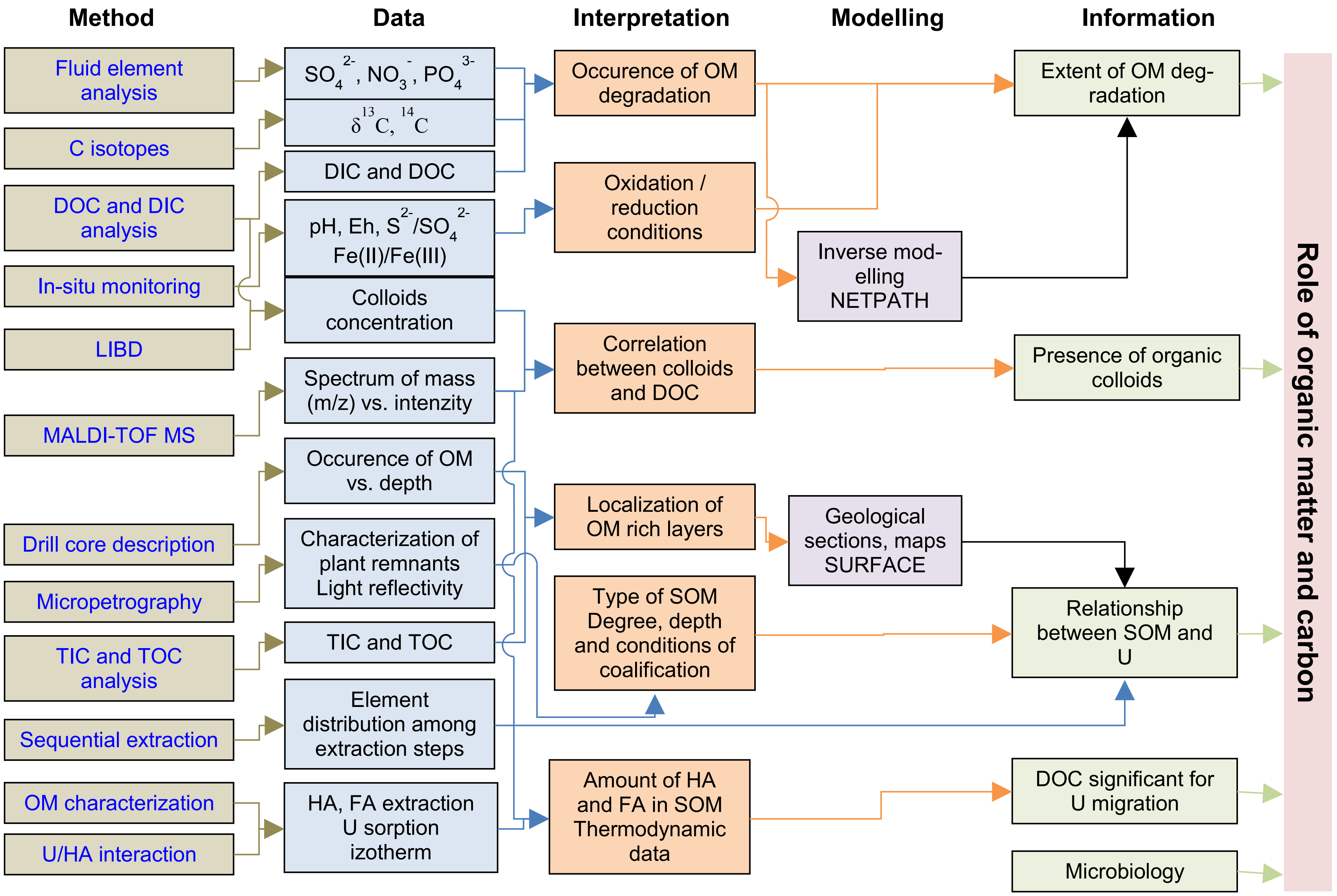

Fig. 4.15 Evaluation scheme with methods, data, interpretation and modelling for organic matter and carbon

The conceptual scheme of mineralization by the oxidation of sedimentary organic carbon and subsequent formation of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) is presented in Fig. 4.16. Electron acceptors such as SO_4^{2-} are reduced; the concentrations of these species decrease coupled with an increase in DOC.

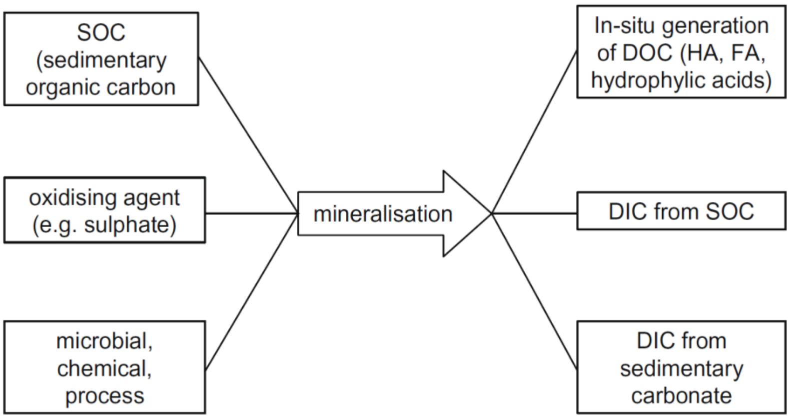

Fig. 4.16 Conceptual description of the mineralization of sedimentary organic carbon /BUC 00/

At the Ruprechtov site, the SOM is generally formed by individual coal seams and slightly dispersed organic matter at a low stage of coalification. The stages of coalification go up to lignite. The main components of detritic and xylodetritic coal samples and clay-lignite samples are mineral admixtures and huminite maceral groups. The organic matter probably originated from peat bogs with clastic sedimentation under changing redox conditions, which is underpinned by a $\delta^{13}C$ average value of -27 ‰. The total organic carbon (TOC) content varies between less than 1 up to a few tens of wt.%. The concentration of DOC in the groundwater is low, with values from 1 to 5 mg/L (of carbon), with only slightly elevated values in water from the clay/lignite horizon as compared to granite. These low concentrations contrast with the high content of SOM in the clay/lignite horizon (up to 40 wt.%). The explanation is likely a low availability of SOM for degradation, as was shown in laboratory experiments. Only a small fraction of sedimentary organic carbon (SOC) is extractable/releasable to the groundwater /CER 11/. An additional reason for low DOC content might be relatively strong sorption properties of clay material, which could fix humic substances on the sediment matrix /CER 09/.

The dissolved organic matter (DOM) characterization in groundwater from the clay/lignite horizon using MALDI-TOF MS indicated lower mass organic molecules having fulvic acid characteristics. The organic substances leached out artificially from SOM have the same mass / charge fingerprint as natural DOM in the groundwater from the

Ruprechtov site. Therefore, humic substances extracted from SOM in the laboratory can be considered as representative of mobile organic matter /HAV 09/, and were used to investigate the interaction with uranium (see below).

Carbon isotopes are measured in order to identify water ages, and/or to characterize water mixing processes as well as reactions within the carbon cycle. Radiocarbon activity ^{14}C and $\delta^{13}C$ values of DIC were determined for 16 boreholes (see Fig. 4.17). $\delta^{13}C$ values of the DOC pool were obtained for 15 wells while ^{14}C activity in DOC was determined for only 4 wells. The following are the most important reactions influencing ^{14}C and $\delta^{13}C$ ratios in DIC /NOS 06/:

- Dissolution of sedimentary inorganic carbon (SIC);
- Microbial degradation of SOC (see Fig. 4.16);
- Input of endogenic CO_2 from exhalation.

Each of these reactions is accompanied by a specific evolution of ^{14}C and $\delta^{13}C$ signatures in DIC. Therefore the analysis of the signatures in the DIC pool allows the derivation of information about the relevant reactions taking place.

The ^{14}C activities and $\delta^{13}C$ values of DIC cover a wide range of values, from 72.1 to 3.2 pmc and from -21.9 ‰ to -10.4 ‰, respectively. The ^{14}C activity found in the DOC pool ranges from ca. 40 to 70 pmc, while $\delta^{13}C$ DOC values vary only slightly, between ca.-25.0 ‰ and -27.8 ‰. Sedimentary inorganic C from the Tertiary formation is free of radiocarbon and its $\delta^{13}C$ values are expected to be around 0 ‰. This was confirmed by analysis of $\delta^{13}C$ in siderite from boreholes RP5 and NA5 showing values of 1.8 ‰ and 2.6 ‰, respectively. Dissolution of SIC leads to reduced activities of ^{14}C and a gradual increase of the $\delta^{13}C$ values of the DIC pool. The $\delta^{13}C$ value of the SOC pool is expected to be around -25 ‰ to -27 ‰. This is underpinned by the analysis of two samples from Tertiary SOC in core material from RP2 showing values of -26.6 ‰ and -24.9 ‰, respectively /NOS 06/. Although SOC in the Tertiary is obviously free of radiocarbon, the dissolved organic C originating in the soil zone may contain significant amounts of ^{14}C, depending on the age of organic matter from which the dissolved fractions (HA, FA, hydrophilic acids) were derived. The endogenous CO_2 is free of radiocarbon and, according to the literature, its $\delta^{13}C$ values vary from -6 ‰ to -3 ‰. In the Eger rift region, approximately 30 km SW of the study area, $\delta^{13}C$ values of endogenous CO_2 were found to be around -2.7 ‰ /NOS 09a/.

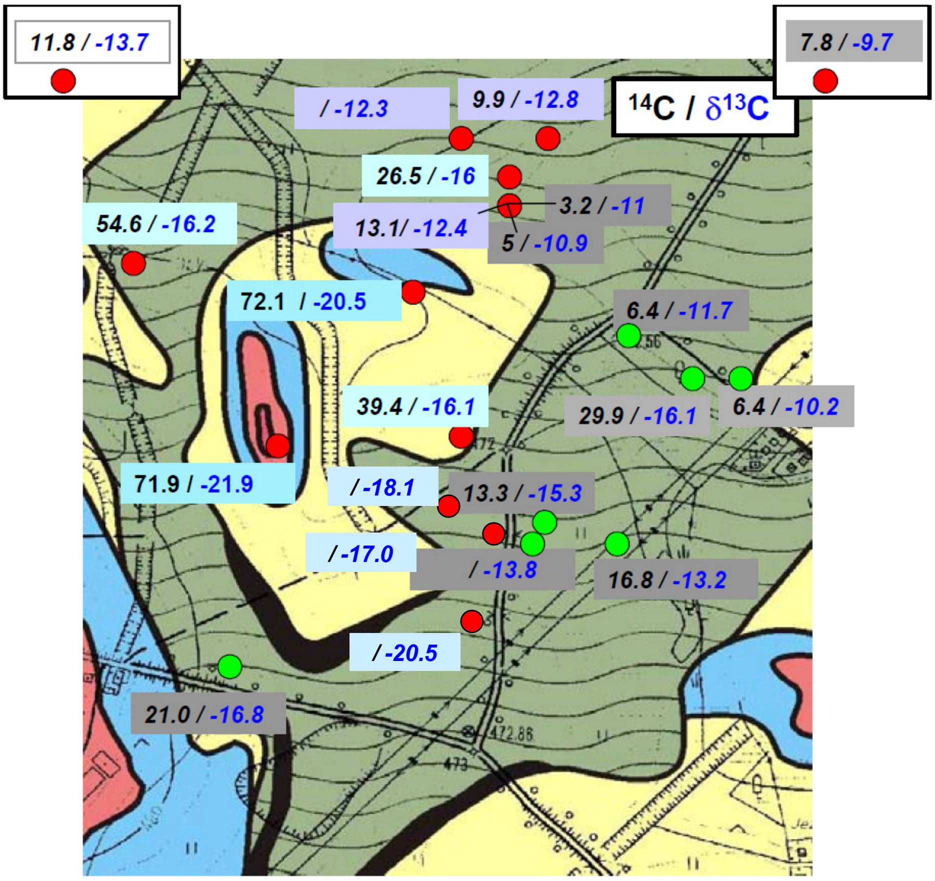

Fig. 4.17 Distribution of ^{14}C (of DIC in pmc) and δ^{13}C (of DIC in ‰) in different boreholes at the Ruprechtov site

Subsequent modelling of C isotope data with the aid of simple models (open- and closed-system) as well as inverse geochemical modelling performed with the aid of the NETPATH code highlighted the need for additional sources of C in the system to properly explain the observed chemical and isotopic evolution of the DIC reservoir. The most probable sources of this additional C include the biodegradation of dissolved and sedimentary organic C and the influx of endogenous CO_2 /NOS 09a/.

A further indication of the relevance of microbial SOC degradation in the clay/lignite horizon is derived from sulfur isotopic data. The mineralization (oxidation) of SOM is accompanied by the reduction of oxidizing agents (in the clay/lignite horizon preferably SO_4^{2-}); decrease of oxidizing agent concentrations with the progress of the oxidation process and thus with the increase in the DOC content according to the following equation:

$$2\,CH_2O + S^{(VI)}O_4^{2-} = H_2S^{(-II)} + 2\,HCO_3^- - 8e^- \qquad (4.1)$$

Microbial processes lead to the oxidation of SOM. SOM is then partly oxidized and released into the groundwater as DIC and DOC both with $\delta^{13}C$ values of around -27 ‰. The dissolution of SIC with $\delta^{13}C$-values of approximately 0 ‰ increases in $\delta^{13}C$ of DIC. The isotopic signature of DIC in different boreholes then leads to a value of $\delta^{13}C$ approx. -13.5 ‰ (equimolar mixing line, see /BUC 00/). The process has been clearly visible at the Ruprechtov site, resulting in two different patterns of carbon isotope signature development (Fig. 4.18).

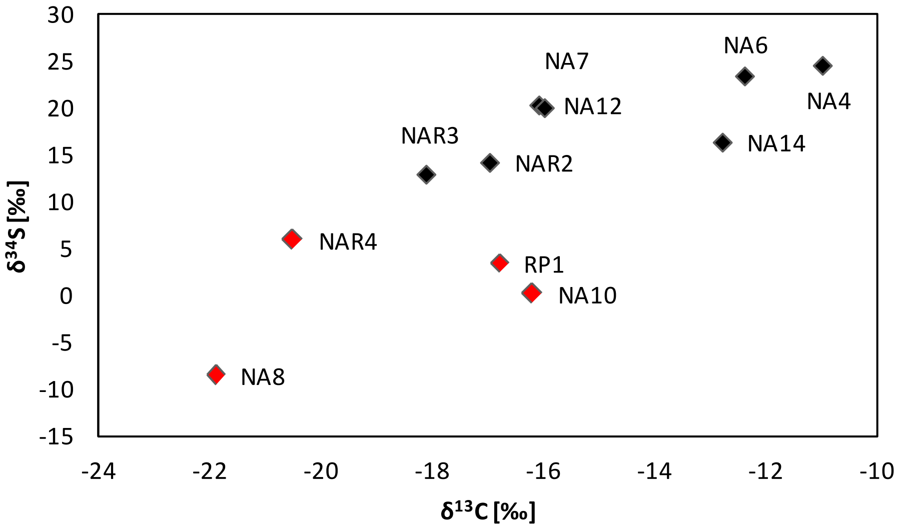

Fig. 4.18 Isotopic composition of Ruprechtov groundwater samples $\delta^{13}C$ (of DIC) versus $\delta^{34}S$ (of SO_4)

Some attention was also paid to the interaction of U(IV) with mobile organic matter, especially humic substances, which probably form the dominant part of DOC. One study focused on the influence of U(IV) sorption on sedimentary samples in the presence of humic acid in synthetic groundwater /ABD 01/. Two samples from clay/lignite-sand horizon were selected. Sorption experiments were performed with U(IV) under a nitrogen atmosphere, since long-term in situ Eh/pH measurements in this environment gave rise to $U(OH)_4$ as the major species in solution. The humic acid was previously extracted using the alkaline method. The results showed, that low concentrations of humic acid (5 – 10 mg/L C) do not affect the sorption of U(IV) on the sedimentary samples. Because the DOC concentrations in the groundwater are at the same level (up to 5 mg/L), we concluded that the impact of humic substances on uranium sorption is low. The second study aimed at the complexation of U(VI) with humic acids extracted from the site /CER 11/. The complexation was studied as a function of both humic acid and U(VI) concentration using the ion-exchange method, evaluated by the Charge Neutralization Model. In evaluating the experimental results, the model took into account different U species in given conditions. The results showed that the fraction of complexed uranium increases with increasing humic acid concentration, but no significant influence on the stability constant was observed. However, when the U(VI) concentration in the complexation process was studied, the stability constant decreased with the increasing concentration of U(VI). If uranyl carbonate complexes, which can play an important role in natural waters, were omitted for simplification reasons in the evaluation of experiments, the complexes of U(VI) with humic acid would be dominant at low concentrations of U(VI) (up to 10^{-6} M) and humic acid concentrations higher than 10 mg/L.

4.6 Uranium transport and uranium enrichment process(es)

For the determination and characterization of processes connected to uranium migration, i.e. transport, mobilization and immobilization processes, a couple of different microscopic and macroscopic methods have been applied, as illustrated in Fig. 4.19. The applied methods comprised: (i) characterization of groundwater conditions, (ii) in situ characterization of uranium-enriched sections in the drill core, (iii) analysis of uranium in the solid using microscopic methods such as EPMA, ASEM, µ-XRF/-XAFS and macroscopic methods (solid element analysis, sequential extraction, U(IV)/U(VI)-separation), and (iv) a set of experiments to analyse the impact of uranium sorption and interaction with organic colloids such as humic acids (HA). Several of these methods were applied to characterize the geochemical conditions in general, but also delivered specific information for the characterization of uranium occurrences and processes connected to them.

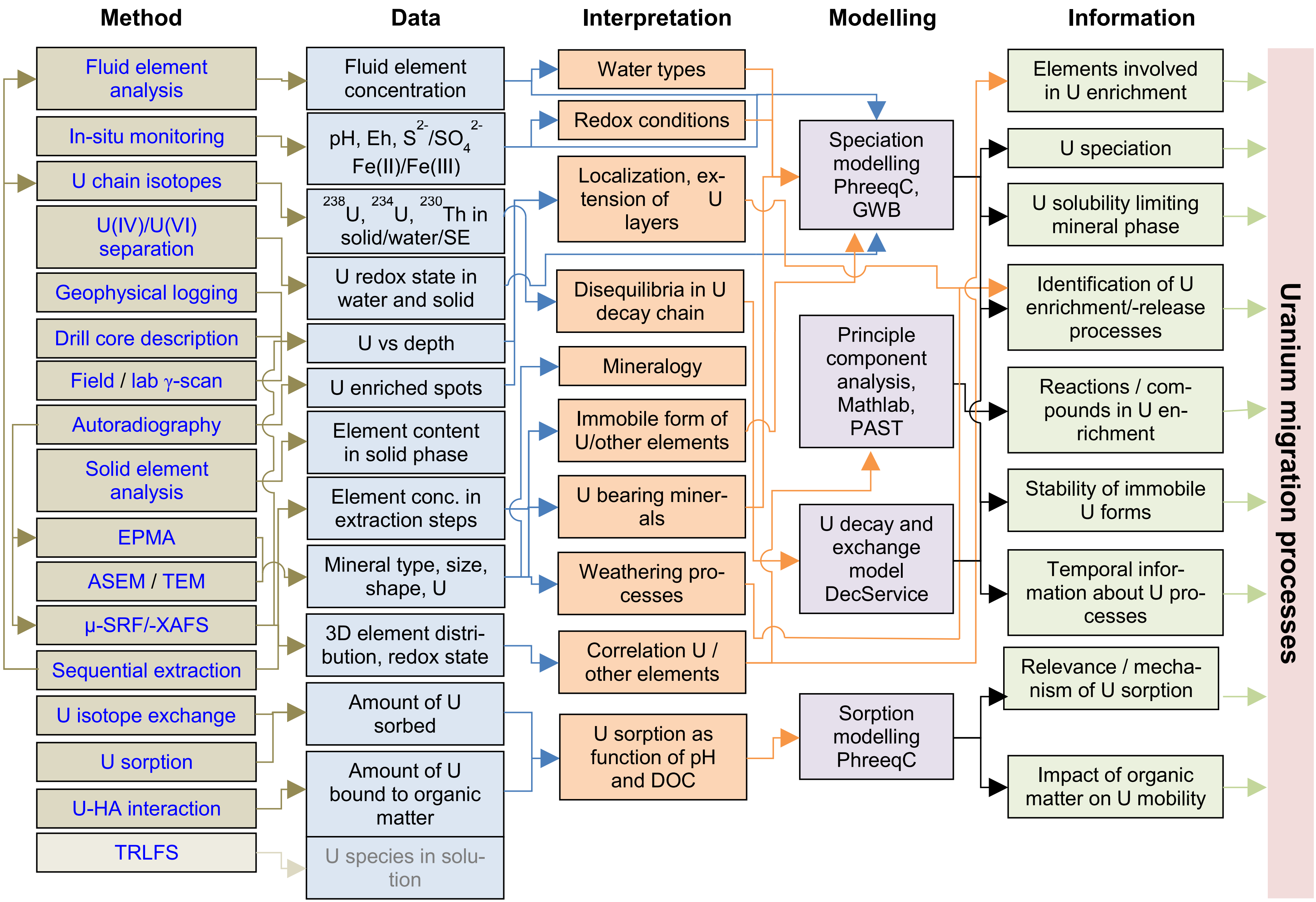

Fig. 4.19 Evaluation scheme with methods, data, interpretation and modelling for uranium migration processes

For groundwater conditions, emphasis was placed on uranium concentrations, U redox state speciation, and $^{234}U/^{238}U$ activity ratios as well as characteristics strongly influencing uranium mobility, i.e. Eh, pH and p_{CO2}, e.g. /LAN 78/. The geochemical conditions and therewith the latter values are already discussed in Chapter 4.3. Fig. 4.20 shows uranium concentrations of all groundwater wells at Ruprechtov /NOS 09b/. The boreholes from the infiltration area in granite, NA8, NA10 and RP1, are depicted on the right of the diagram. These values are in the range 1.8 to 12 µg/L. The uranium concentrations in the clay/lignite horizon are below 2.1 µg/L and with two exceptions below 1µg/L. As expected, the values in the more reducing clay/lignite horizon are lower than those in the more oxidizing granitic waters. Speciation calculations support the higher mobility of uranium in more oxidizing groundwater, as shown in the Eh/pH diagram for typical conditions at the Ruprechtov site in Fig. 4.21; for details see /NOS 09b/. The data for the more oxidizing granite groundwater from the infiltration area are dominated by uranyl-carbonato complexes, whereas the groundwaters from the clay/lignite horizon are at the boundary of the stability fields for the tetravalent aqueous $U(OH)_4$ complex and the hexavalent complexes $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$.

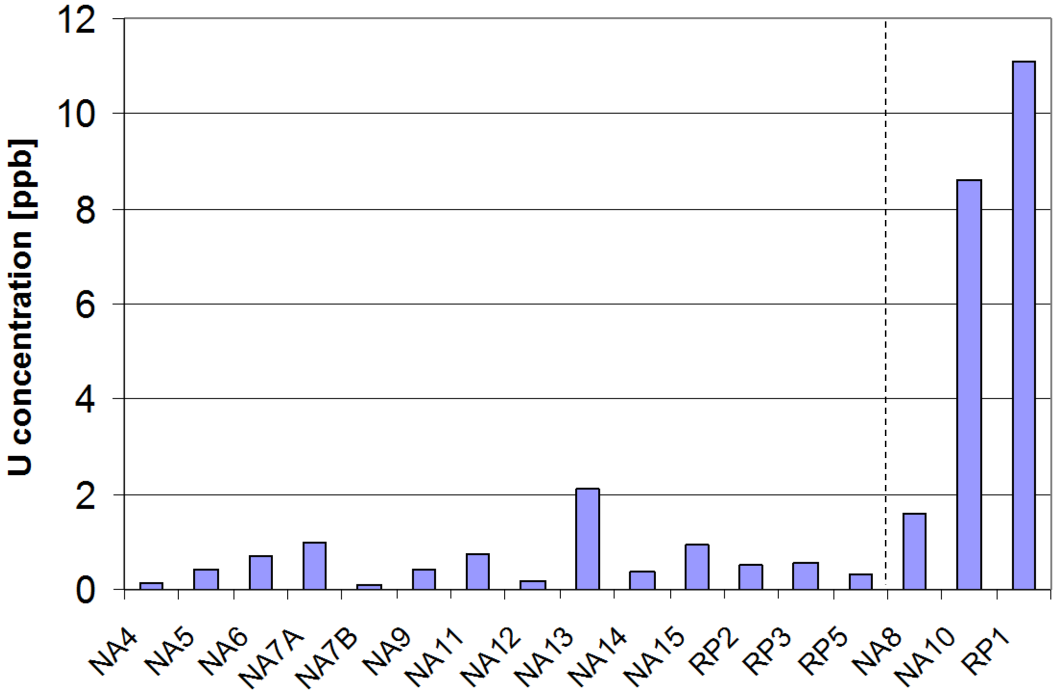

Fig. 4.20 Uranium concentrations in the groundwater in the Ruprechtov wells. Boreholes from the infiltration area in granite: NA8, NA10, RP1

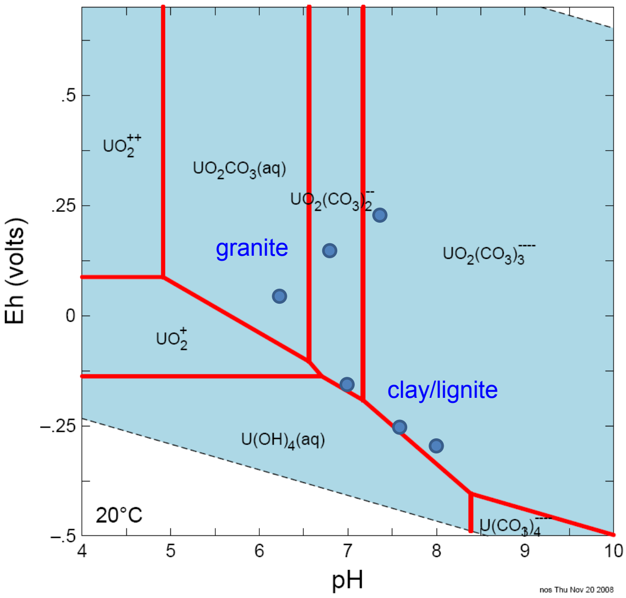

Fig. 4.21 pH/Eh diagram for Ruprechtov groundwater; U concentration 10^{-3} mg/L, CO_2 activity = 10^{-3}

The expected U(IV) fractions in solution were calculated for all three clay/lignite groundwaters. To verify the oxidation state of uranium in the groundwater, a method for separating U(IV) and U(VI) in solution was applied (see Method No. A.26) at drill core NA6. The first campaign found total U concentration of 0.55 µg/L with U(IV)-fractions of 15.2 % and 22.2 % respectively and the second campaign a total U concentration of 0.91 µg/L and a U(IV) fraction of 16.6 %.

Because of the high CO_2 partial pressure (from microbial SOC degradation and probably CO_2 exhalation; cf. /NOS 09a/), in this system, part of the dissolved uranium can be stabilized as U(VI) by carbonato complexes even for quite reducing conditions. The calculated fraction of U(IV) in groundwater NA6 at pH 8 assuming equilibrium is shown in Fig. 4.22. For these calculations, the impact of the trivalent carbonate complexes of uranyl with alkaline earth elements on U speciation was tested using the Ruprechtov conditions. The most important Ca-HCO_3 type waters at the Ruprechtov site are the calcium complexes. The reactions

$$UO_2^{2+} + Ca^{2+} + 3\ CO_3^{2-} = CaUO_2(CO_3)_3^{2-} \qquad (4.2)$$

$$UO_2^{2+} + 2\ Ca^{2+} + 3\ CO_3^{2-} = Ca_2UO_2(CO_3)_3(aq) \qquad (4.3)$$

with log K values of -26.93 and -30.79 for reactions (2) and (3) /BER 01/ were included in the database. The strong complexation of uranyl in neutral/alkaline conditions leads to further stabilization of U(VI), explaining the relatively low U(IV) fractions measured in the clay/lignite groundwater NA6 by U(IV)/U(VI) separation.

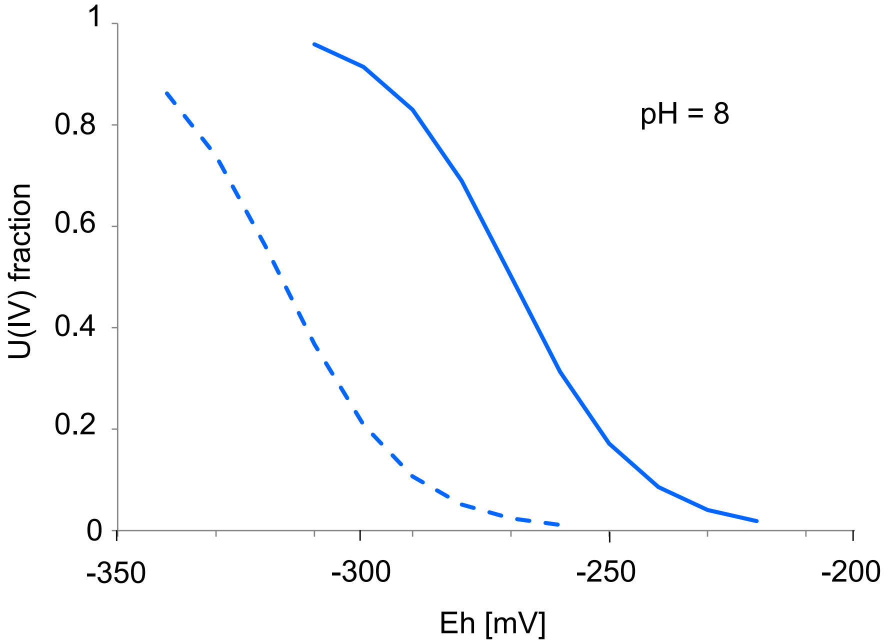

Fig. 4.22 Fraction of U(IV) in dependence of Eh-value at pH 8, for conditions of NA6 groundwater for calculations without (bold line) and with consideration of $(Me^{2+})_nUO_2(CO_3)^{-(4-2n)}$ complexes (dotted line)

The calculation of saturation indices is an appropriate method for understanding which uranium phases control the uranium solubility in the natural system. In many reducing groundwater systems, uraninites or pitchblendes with stoichiometry of UO_{2+x} are found to be the phases controlling the dissolved uranium concentration. Two secondary uranium(IV) phases have been observed in the uranium-enriched sediments at the Ruprechtov site: UO_2 and ningyoite ($CaU(PO_4)_2 \cdot 1\text{-}2H_2O$). Since no stoichiometric determination of the UO_2 phase was performed, the saturation indices of different U(IV) mineral phases were taken into account. Thermodynamic data for ningyoite are not available in the NEA TDB and have been taken from recommendations in /LAN 97/.

The results of the calculation are shown in Fig. 4.23. The groundwaters from the clay/lignite horizon are strongly oversaturated with respect to the crystalline uraninite and coffinite indicated by saturation indices (SI) in the range between 5 and 7. The mixed valence uranium oxides $UO_{2.25}$ and $UO_{2.33}$ are also oversaturated (SI between 2.5 and 4). The mixed valence oxide $UO_{2,66}$ is always undersaturated with SI values below -0.8. No saturation of U(VI) minerals was indicated. Assuming an uncertainty range of ±0.6 (shadowed area in Fig. 4.23) for the saturation index, resulting from uncertainties in the thermodynamic data, the results indicated that the uranium concentration in the groundwater is controlled by amorphous UO_2. The SI values for ningyoite are also close to saturation in groundwaters NA6 and NA13, but not in NA12. So, there is generally good agreement with the observed mineralizations in the clay/lignite horizon. Metastable amorphous UO_2 has also been shown in other studies to be likely the uranium controlling mineral phase, e.g. /IWA 04/. These results also indicated that no significant U-release can be expected under the geochemical conditions in the clay/lignite horizon, in agreement with the very low $^{234}U/^{238}U$ activity ratios observed in the uranium(IV) mineral phases as indicators for their long-term stability; see below and /NOS 08/.

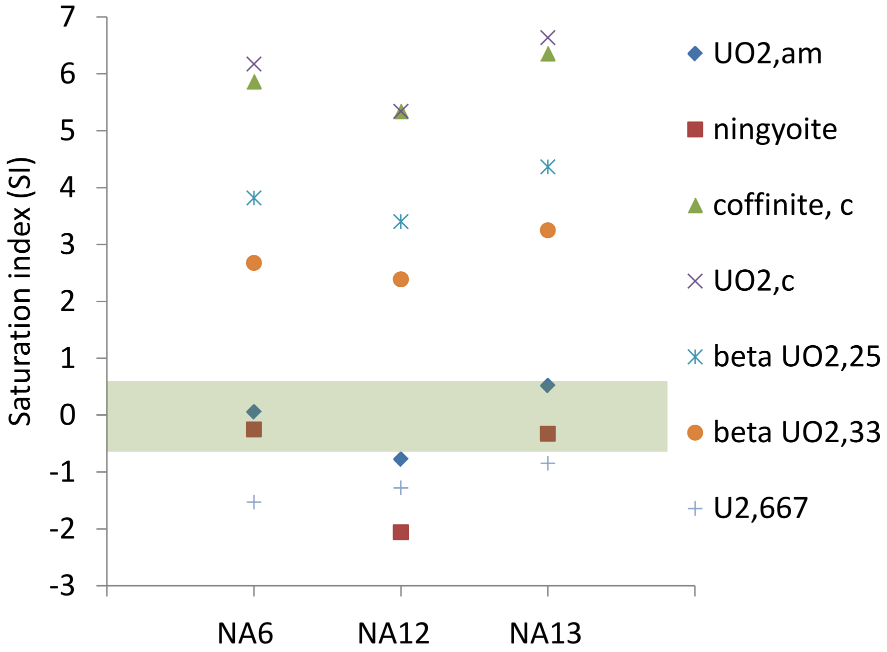

Fig. 4.23 Saturation indices of various U(IV) minerals calculated for groundwaters NA6, NA12 and NA13

With respect to the prevailing processes and corresponding time scales in the geological past, analysis of isotopes in the uranium decay chain in solid and water samples and microscale spectroscopic methods have delivered valuable information. Not only time scales but also information about the nature of groundwater flow can be derived from decay series analysis. In any naturally occurring uranium-containing material that has remained fully undisturbed for several millions of years, a state of secular radioactive equilibrium between the parent and the daughter nuclides in the radioactive decay chain will have been established, i.e. all radionuclides of a respective decay chain show the same activity. However, natural systems are seldom closed and small mass flow due to diffusion or advection occurs wherever water is in contact with the material. Under water-rock interaction, geochemical processes such as chemical weathering, erosion, precipitation of minerals from aqueous solutions and adsorption may cause fractionation between mobile and immobile elements, resulting in a state of disequilibrium between parent and daughter nuclides, i.e. the parent-daughter activity ratio deviates from unity. Therefore, uranium disequilibrium series analysis allows the judgement of whether uranium has been mobile in the geological past or not.

The analysis and interpretation of uranium disequilibrium series in sediments and $^{234}U/^{238}U$ isotope ratios in groundwater is well documented, e.g. /OSM 76/, /OSM 92/, /IVA 92/, and has been applied in several natural analogue studies (e.g. /MIL 00/ and references therein). When they identify the mobility and/or immobility of uranium, such investigations at potential repository sites also yield information about past groundwater flow. For example, radiochemical studies in Boom Clay showed that in general the uranium decay chain is in a state of secular equilibrium, indicating no significant mobility of uranium /DEC 04/. It also indicates that no advective water flow has occurred during the last million years in the Boom Clay, since not even more mobile ^{234}U, formed by α-recoil and subsequent processes, has been released from the bulk uranium. In a similar way, analysis of the Tono uranium deposit showed that some migration of uranium has occurred along faults and fractures, but the largest motion of uranium has been through the rock matrix over a distance of less than one metre during the past million years /NOH 92/. These results are often also used as strong arguments for the long-term stability of geochemical conditions at the site, which increase confidence in the predictions of the future evolution of the site /NEA 08/.

At the Ruprechtov site, uranium disequilibrium series analyses were used to obtain information on the long-term stability of the immobile uranium phases described above /NOS 08/. The activities of ^{238}U, ^{234}U and ^{230}Th were analysed in the bulk samples from several boreholes from the uranium-enriched clay/lignite horizon. The results were plotted in a Thiel's diagram /THI 83/, where one can study features of uranium mobility in respective samples and, consequently, evaluate the dynamics of the system (Fig. 4.24). The diagram shows segments which outline data with different uranium behaviours. The segments are determined by (i) the $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ equilibrium lines (i.e., activity ratios are unity), and (ii) the line obtained when a tangent is drawn on the closed system chain decay curves evolving towards radioactive equilibrium ($^{230}Th/^{238}U = 1$ and $^{234}U/^{238}U = 1$) after the sudden accumulation and removal of uranium at time zero. Data points plotted above the $^{234}U/^{238}U$ equilibrium line represent samples where bulk U has been affected, either by accumulating or removing U from the system. The segments S1 and S2 represent U series disequilibria, which cannot be created by closed system chain decay, outlining samples where episodic and/or continuous uranium movement may have occurred, i.e. an open system.

Nearly all of the data for the Ruprechtov samples are plotted in the U-addition area, indicating a sink for uranium. A high fraction of data points are accumulated in segment S1, which represents samples from which ^{234}U has been or is being selectively removed by the groundwater. Selective ^{234}U release here means that bulk uranium is not affected in the respective conditions, i.e. being geochemically stable. The release of ^{234}U from the system confirms water flow in or near the clay/lignite horizon. The ages of uranium phases in the respective samples are beyond the U series method. Thus, at least a significant fraction of the uranium in the clay/lignite horizon is more than one million years old, i.e. if any geological process affected the site, the clay/lignite horizon has remained geochemically undisturbed. Furthermore, because a number of data points are plotted in the bulk uranium addition area, some uranium accumulation may still be in progress.

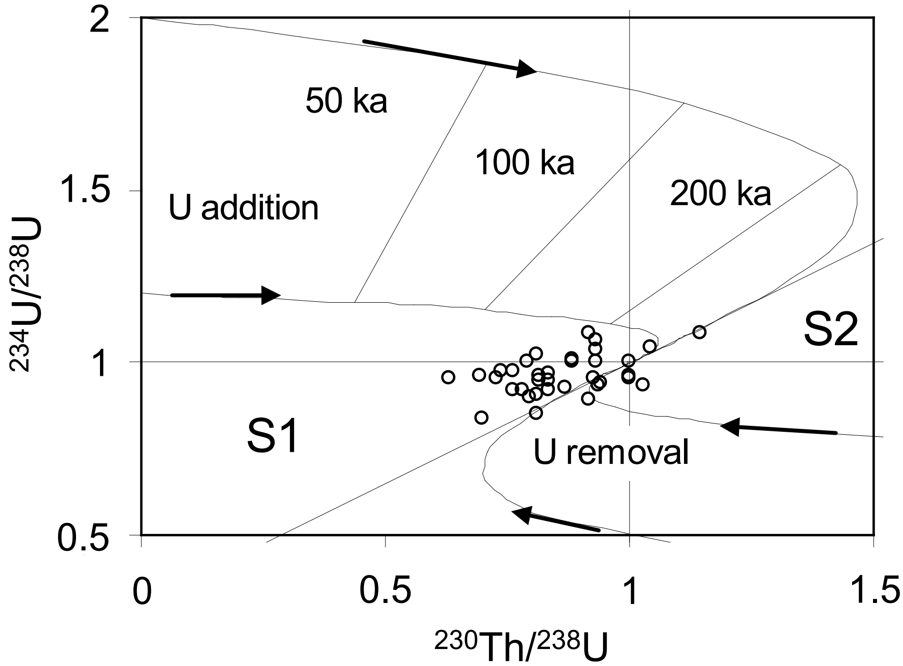

Fig. 4.24 $^{230}Th/^{238}U$ and $^{234}U/^{238}U$-activity ratios of bulk samples from the clay/lignite horizon plotted in a Thiel's diagram /NOS 08/

In order to better characterize the different uranium forms, the geochemical distribution and redox state of uranium were studied using sophisticated chemical separation methods. U(IV)/U(VI)-separation /ERV 96/ and sequential extraction (SE), coupled with analysis of the $^{234}U/^{238}U$ activity ratio, denoted as AR, in each phase, identified that the major part of uranium occurs in the tetravalent state, in agreement with the results from spectroscopic methods (see above). An important observation was that the tetravalent uranium form exhibits an AR below one in nearly all samples, with values generally in the range between 0.2 and 0.8 /NOS 08/. AR values significantly below unity are caused by the preferential release of ^{234}U, which is facilitated by the preceding ^{234}Th α-recoil process contributing to ^{234}U being created in the hexavalent state (see, e. g., /SUK 06/ and references therein). In order to attain low AR values of approximately 0.2 for the U(IV) phase, it must have been stable for a sufficiently long time to allow ^{238}U to decay to ^{234}U and form $^{234}U(VI)$, i. e. no significant release of bulk uranium must have occurred during the last million years. This is in agreement with the hypothesis that the major uranium input into the clay/lignite horizon occurred during the Tertiary, more than 10 million years ago as described in /NOS 06/. In conclusion, no evidence for significant uranium release from the clay lignite horizon in the geological past has been found.

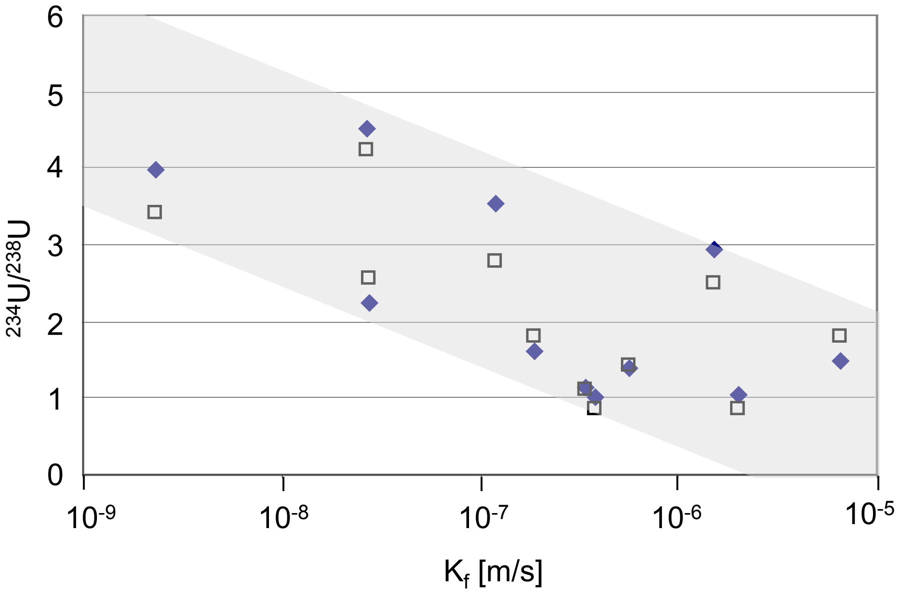

Fig. 4.25 $^{234}U/^{238}U$ activity ratios in groundwater from granite and clay lignite horizon versus hydraulic conductivity measured in these wells by α-spectrometry (open squares) and ICP-MS (filled)

The low ARs in the U(IV) phase observed in this study correlate with the AR values >1 (between 1.5 to 4) in the pore and groundwater from the clay/lignite horizon; see Fig.

4.25 /NOS 08/. This is expected, because in anoxic sediment conditions, bulk U release is strongly suppressed and the release of $^{234}U(VI)$ formed by decay is favoured. This is in agreement with results from the Finnish study sites, where the $^{234}U/^{238}U$ release ratio has been suggested as an indicator for redox conditions /SUK 06/. There, very high $^{234}U/^{238}U$ release ratios (down to 6.5) have been observed in strongly reducing groundwaters, whereas values around 1 occur in oxidizing groundwater. Furthermore, a trend in the Ruprechtov waters is visible (see grey shadowed area in Fig. 4.25), showing an increase of the $^{234}U/^{238}U$ ratio with decreasing hydraulic conductivity. This supports the preservation of the disequilibrium values in more stagnant water in water low-conducting areas.

Spectroscopical methods were applied in order to better understand the details of uranium accumulation. The key results described in detail in /NOS 06/ and /NOS 08/ can be summarized as follows:

- Existence of detritic uranium-bearing minerals in the clay/lignite layers was shown using electron microprobe and ASEM;
- The uranium content was calculated to be too low to explain the high uranium content in these layers;
- ASEM/EDX analysis identified UO_2 and ningyoite as secondary minerals occurring in the clay/lignite layers;
- Missing lead content analysed by electron microprobe confirmed the secondary nature of UO_2 minerals in the clay/lignite layers;
- Mass balancing of secondary minerals and their U content still indicated that additional uranium was expected;
- The assumption that additional uranium occurs in crystals or amorphous phases with sub-µm sizes was investigated in selected samples with TEM. The occurrence of uranium in small TiO_2 crystals was shown, but not in the amounts expected.

Part of the work at Ruprechtov was dedicated to the identification of reaction mechanisms leading to the observed uranium immobilization. For the characterization of such processes on a microscopic scale, both confocal µ-XRF and µ-XANES analyses were applied, which identified the uranium as U(IV). These results were in good agreement with the results from chemical separation and other spectroscopic methods such as ASEM, which also identified U(IV) /DEN 05/. As demonstrated in Fig. 4.26 (left), the shape and intensities show the average valence state of the sampled volume to be U(IV). None of the three curves show the multiple scattering feature 10 – 15 eV above the white line (WL) characteristic of U(VI), nor do they show a significant decrease in WL intensity which would be expected for U(VI) as be seen in the schoepite spectrum.

Using µ-XANES and µ-XRF, it was also shown that As exists in two oxidation states, As(0) and As(V). The analysis of a number of tomographic cross-sections of elemental distributions recorded over different sample areas shows a strong positive correlation between U and As(V). Through further development of the method, using the new planar compound refractive lens (CRL) array at the Fluoro-Topo-Beamline at the ANKA synchrotron facility of the Forschungszentrum Karlsruhe, a higher spatial resolution (focus beam spot size of 2 x 5 µm2 (V x H)) was achieved. The high resolution made it possible for the first time to discern an As-rich boundary layer surrounding Fe(II)-nodules, see Fig. 4.26, right /DEN 07/. This suggests that an arsenopyrite mineral coating of framboidal pyrite nodules is present in the sediment. Uranium occurs in the direct vicinity of the As-rich layers. In conclusion on these results, a driving mechanism for uranium enrichment as secondary U(IV) minerals in the sediment was suggested. Mobile, groundwater-dissolved U(VI) was reduced in the arsenopyrite layers to less-soluble U(IV), which formed U(IV) mineral phases. As(0) was then oxidized to As(V) and the uranium remained associated with it.

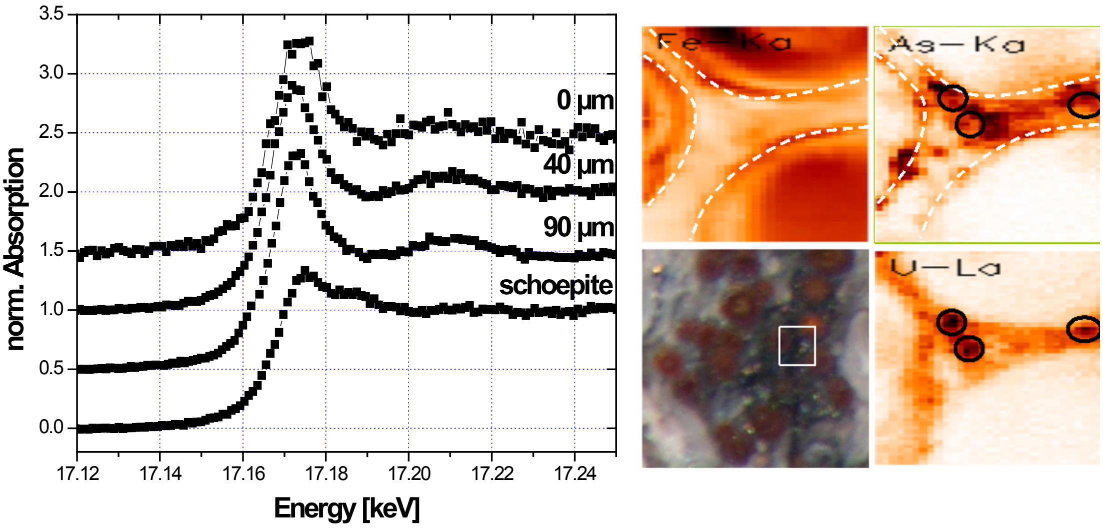

Fig. 4.26 Results from µ-XANES (left) and µ-XRD (right) of a sample from borehole NA4 /DEN 05/, /DEN 07/

The results from these microscopic methods were supported by cluster analysis performed on the results from sequential extractions, which also indicated that uranium occurs in the tetravalent state, since the major part of the uranium is extracted in the respective steps for (reduced) U(IV) forms and the residual fraction /HAV 06/. A strong correlation of U with As and P was found, using cluster analyses performed to identify possible correlations between elements, supporting the mechanism postulated above and the existence of uranium phosphate mineral ningyoite identified by ASEM.

5 New results from national and international R&D

5.1 Development of regional stratigraphy

The modern lithostratigraphy of the Sokolov Basin Tertiary sediments has been presented by /PES 10/, whose concept is based on observation in the central part of the Sokolov Basin conducted during the geological exploration and subsequent mining of brown coal. The distinct character of the Hroznětín section of the basin in terms of development is mentioned sporadically in /PES 10/. The new lithostratigraphic concept influences the positioning of certain uranium-bearing layers. The division of the sediments into three formations is identical to the premise of previous concepts; the sediments are divided (from bottom to top) into:

- Staré Sedlo Formation;
- Nové Sedlo Formation;
- Sokolov Formation;
- Cypris Formation.

With regard specifically to the Hroznětín section of the Sokolov Basin, there is no evidence of the presence of the Sokolov and Cypris Formations. A basic characterization of individual members of the Tertiary sediments in the Hroznětín section is shown in Tab. 5.1.

The Staré Sedlo Formation sediments are the oldest Tertiary sediments in the basin and lie unconformably on granite or metamorphosed complexes. The formation is not developed continuously throughout the Sokolov Basin area; rather it is present principally in the central part of the basin, where a maximum thickness of 42 m has been observed. The rocks which make up the formation consist of sand, sandstone, gravel and conglomerate, often with lenses and intercalations of sandy and silty kaolinitic clay. The predominant part of the sediments was deposited before the end of the Eocene. The absence of volcanic material is typical of these sediments.

Intensive tectonic and volcanic activity typifies the sedimentation of the youngest **Nové Sedlo Formation**, the maximum thickness of which is 85 m; the lower and upper boundaries are disconformable. The age of the sediments is predominantly Oligocene, with only the uppermost part being of Miocene age.

Tab. 5.1 Karlovy Vary - Eibenstock composite pluton, Staré Sedlo and Nové Sedlo Formations – brief description (modified after /PES 10/)

Age		Formation/Member		Description
Miocene **Oligocene**	egerian	**Nové Sedlo Formation**	Chodov Member	Lower and upper boundaries are concordant. Volcanoclastic rocks, predominantly tuff and aglomerates with effusives and lava flows. Strong argilization to montmorillonitic or kaolinitic clay. Thickness increases from W to E (max. 80 m)
	rupelian		Josef Member	The thickness of this unit in its central part is 20 m, of which 16m is made up of coal. It is missing in the north-eastern (Hroznětín) part of the basin.
			Davidov Member	Unassorted gravely and sandy kaolinitic clay to clayey gravel. Of greater areal extent than the Staré Sedlo Formation, thickness 2 m – 60 m. Disconformity at the base.
Eocene	Eocene / Oligocene	**Staré Sedlo Formation**		Uneven development particularly in the central part of the basin, maximum observable thickness 42 m. Rocks typically consist of sand, gravel, sandstone, conglomerate with layers and lenses of sandy to silty kaolinite clay. Two cycles, of which the uppermost is more fine-grained and more extended. Good assortment and high maturity of sediments. Unconformity at the base.
Carboniferous		**Karlovy Vary - Eibenstock Composite Massif**		Karlovy Vary - Eibenstock composite pluton. The older intrusive complex consists of Nejdek Granite (porphyritic biotite granite to monzogranite), the younger intrusive complex is made up of Eibenstock (Karlovy Vary) porphyritic coarse-grained granite /KLO 10/.

According to the afore-mentioned new lithostratigraphic concept, this (Sedlo) formation is divided into the following three members (from bottom to top):

- Davidov Member;
- Josef Member;
- Chodov Member.

The **Davidov Member** lies partly on the Stare Sedlo Formation (mainly in the central part of the basin) on kaolinized granite and on metamorphosed complexes and is made up predominantly of unsorted sand, gravel and kaolinitic clay and often of clayey sand and gravel; the thickness varies from 2 m to 60 m. This unit contains the oldest traces of volcanic activity, namely from the Doupovské Hory volcanic complex. The sediments are predominantly of proluvial origin. The intensive tectonic movements which occurred during the sedimentation of this member are illustrated by the thick fossil taluses found in the Odeř uranium mine.

The main differences between the Staré Sedlo Formation and the Davidov Member sediments are outlined in Tab. 2.5.

The boundary of the **Josef Member**, which is of Oligocene age and the Davidov Member is conformable, but considerably heterochronous. The maximum thickness of the Josef Member sediments in the central part of the Sokolov Basin amounts to 20 m. The coal seam, in which thin layers of argillized tuff and tuffite are present, reaches 16 m. The Josef Member is not developed in the north-eastern part of the Sokolov Basin (Hroznětín section).

The **Chodov Member** represents the uppermost member of the Nové Sedlo Formation. Its boundary with the Davidov and Chodov Members is conformable and slightly heterochronous. The Chodov member is made up of a complex of volcanoclastic material, predominantly tuff, agglomerates and tuffites; lava flows are rare. The rocks have been argillized into the form of kaolinite, montmorillonite and siderite clay. Thin layers of organic-rich clay were sedimented during the course of volcanic activity interruption; the Doupovske Hory volcanic complex constituted the main source of volcanic material, in addition to which several dozen small volcanic centres existed within the basin and its surrounding area. The maximum known thickness of the Chodov Member is 80 m; the thickness of the sediments increases in a west to east direction.

The Chodov Member sediments are the youngest Tertiary sediments in the Hroznětín section of the Sokolov Basin.

The lithology of the Stare Sedlo Formation and the Davidov Member provide only limited potential for distinguishing the rocks which make up these units on the basis of core description; only the presence of volcanic material has been confirmed. The main differences between the Stare Sedlo Formation and the Davidov Member sediments are outlined in Tab. 5.2.

Tab. 5.2 The main differences between the sediments of the Staré Sedlo Formation and those of the Davidov Member of the Nové Sedlo Formation (modified after /PES 10/)

Parameter	Stare Sedlo Formation	Davidov Member
Age	Eocene/Oligocene	Oligocene
Lithology	Sand, gravel, sandstone, conglomerate with layers and of sandy to silty kaolinite clay	Unassorted clayey gravel to gravelly and sandy kaolinitic clay, locally traces of bentonite
Origin	Fluviatile	Proluvial to fluvial (short transport)
Bedding	Distinct, diagonal or trough type	Not, or less, distinct
Roundness of clasts	Well-rounded	Subangular to angular
Degree of sorting	Good	Low
Lithification	High	Low
Composition of sediments	Monomictic to oligomictic	Petromictic
Textural maturity	Good	Low

The definition of the Davidov Member in some cases impacts the position of uranium-bearing layers in the Tertiary sediments of the Hroznětín section of the basin. The sequence of sediments (sand and gravel with kaolin admixture, coal fragments and a volcanic material admixture) over the Odeř deposits, described by uranium exploration geologists as “deluvium” /OBR 71/, is most probably of the Davidov Member, sedimented under specific conditions in the proximity of the active Krušné Hory Fault. This sequence contains uranium-rich layers, which were mined in the second half of the 20th century.

Samples D2 (34.85 m) and D5 (38.50 m) from the NA5 borehole core contain coal fragments, kaolinite and montmorillonite in addition to nyngyoite, zippeite, uraninite and uranium-bearing leucoxene. Sample D5 was described by Viktor Dobiáš /HER 00/ as montmorillonite claystone. Moreover, in this case, it is reasonable to state the presence of a uranium-rich layer in the Davidov Member sediments; uranium-rich layers were also found in the same position in boreholes NA3 and NA14.

Determining the stratigraphic position of the lowermost uranium-bearing layer over the Hájek North deposit remains problematic. This layer (with an average thickness of 1.46 m) with a higher uranium content in the Hroznětín section of the basin is made up of sand, sandstone, quartzite and fragments of coal and has been affected by intensive epigenetic pyritization. The presence of volcanic material is not mentioned in the layer description. The stratigraphic position of this layer remains unclear.

With the exception of the lowermost uranium-bearing layer over the Hájek North deposit, all of the uranium-rich layers in the Tertiary sediments of the Hroznětín section of the Sokolov Basin are concentrated in the Nové Sedlo Formation, i. e. in sediments deposited at the time of Doupovské Hory volcanic centre activity.

5.2 Findings from comparable analogue studies

A comparison of analogue studies on uranium deposits shows that the conditions at the Japanese Tono Mine features certain genetic similarities to the uranium enrichments at Ruprechtov and the surrounding region. The investigation of some aspects of the Ruprechtov study on the behaviour of uranium in natural sedimentary systems in the overburden of potential host formations, might have also been possible at the Tono site. Both studies give to some extent smilar evidence for key processes affecting geochemistry and therewith uranium immobilization processes in sedimentary, lignite-bearing formations.

The Tono-deposit in Gifu Prefecture, central Japan, is attributed to the sandstone type. Within a Tertiary-Quaternary basin, a series of up to 600 m thick sediments covers late cretaceous granites. Uranium is bound to lignitic, fluviatile rocks in the lower horizons of the Toki formation (see Fig. 5.1) at the Tertiary basis, which is overlaid by the Hongo, Akeyo and Oidawara formations. As a result of erosive processes of ancient rivers uranium has preferentially accumulated in so-called paleochannels, filled with arkoses, sandstones and conglomerates, app. 100 m below the surface /SHI 97/.

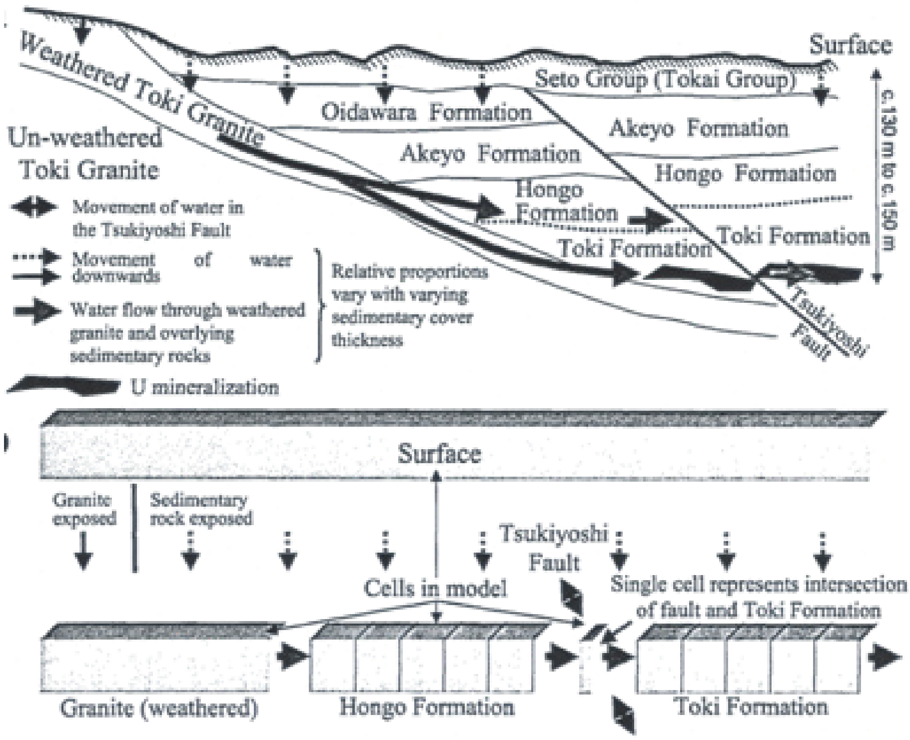

Fig. 5.1 Geological cross-section of the Tono site indicating water flow and uranium enrichment processes and a simulation model for U transport and retardation at the Tono site /MET 04/

The Tono natural analogue project was aimed at characterizing geological, hydrological and geochemical processes that have effectively immobilized U within the Tono uranium deposit for more than 10 million years. This is a similar time scale for uranium immobilization as that for the uranium deposit at the Ruprechtov site.

The basement granitic rocks contain more than 6 g/t U and are the source of the secondary Tono uranium deposit similar to the situation at the Ruprechtov site. Moreover, several of the key processes involved in uranium immobilization in the Tertiary sedimentary formation at Tono site, have also been observed at the Ruprechtov site. The occurrence of pyrites indicates strongly reducing conditions in the sediments deeper than app. 60 m below ground level. It has been shown that some pyrite had precipitated through microbial sulfate reduction during the diagenesis of the lacustrine formation /SHI 99/. The investigations at the Tono site further suggest that microbial sulfate reduction involving organic matter, followed by pyrite precipitation, are the dominant redox reactions in the deeper parts of the sedimentary rock /IWA 04/. The dissolved sulfate is surmised to have originated from the dissolution of sulfate and sulfide minerals that precipitated in a sub-marine environment during and/or after sedimentation of the marine formation, in the upper part of the sedimentary rocks. Such redox processes in the water-mineral-microbe system are inferred to have continued from the time when the marine formation underwent uplift above sea-level (5 – 0.7 Ma) because sulfate-reducing bacteria can use sulfate ions dissolved in fresh water that infiltrates from the marine formation and organic matter located in the deeper sedimentary rocks. The long-term geochemical conditions since the present geological structure formed are summarized in Fig. 5.2. The past *Eh* conditions can be estimated by assuming equilibrium of the redox reaction between sulfate and sulfide. They may be reasonably bounded by redox potentials corresponding to the HS-/SO_4^{2-} or pyrite/goethite couples. The calculated Eh-values range from -250 to -410 mV for the groundwaters of pH 8 – 10, /IWA 04/.

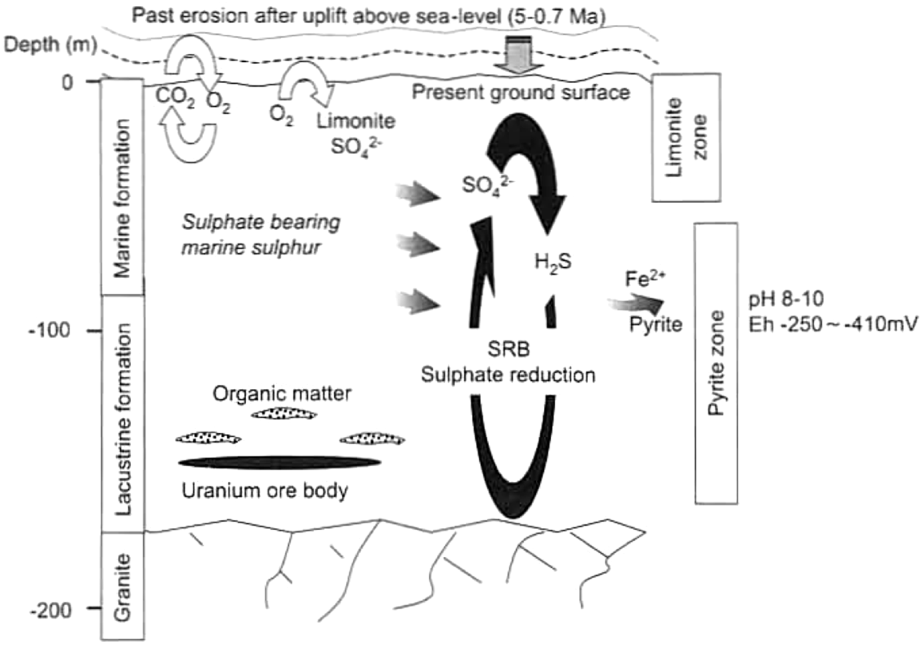

Fig. 5.2 Geochemical model for long-term pH-Eh conditions around the U ore body at the Tono site /IWA 06/

As described in Chapters 4.3 to 4.6 similar processes act and have acted in the past in the clay lignite layer at the Ruprechtov site causing reducing geochemical conditions with pH values of around 8 and Eh values in the range of -250 to -280 mV.

In accordance with the study at the Ruprechtov site, the uranium-series disequilibria on samples from the Tono sandstone showed that reducing condtions in the matrix of the sedimentary rocks have been maintained for the last million years /NOH 92/. While some migration of uranium along faults and fractures is observed, the largest motion of uranium has been through the rock matrix over a distance of less than 1 m during the past one million years. Both sites, Tono and Ruprechtov, therewith constitute examples of a long-term geochemically stable environment in sedimentary formations.

Another important result from the Tono uranium deposit is the evidence that uranium concentrations are determined by amorphous uraninite. In /ART 06/ it is stated that more evidence from analogue studies is needed to support this hypothesis. The thermodynamic calculations based on the uranium concentrations and pH/Eh conditions in the clay/lignite layers suggest that amorphous uraninite is also the solubility determining mineral phase at the Ruprechtov site (cf. Chapter 4.6). These results support the commonly made assumption in safety assessments that maximum U concentrations in groundwater will be limited by the equilibrium solubility of UO_2(am). Therefore, evidence from more than one study helps to establish confidence in methods used in such assessments to estimate the long-term concentration ranges of uranium in groundwater.

In a scientific work by /MET 04/, all data from the Tono-deposit (including results of intensive field and lab investigations) have been used to develop an uranium migration- resp. retardation model for the site that is able to consider long-term system changes and data uncertainties. A reference scenario has been developed on the basis of a system analysis, which includes all knowledge about the evolution of the deposit and its current state (see Fig. 5.1).

The essential deposit-forming events were uranium mobilization in the upper parts of the Toki granite under oxidising conditions and uranium transport by groundwater into the overlying sedimentary rocks. Reducing conditions in these sediments provoked secondary U enrichment. Involving sensitive parameters and different uncertainties model variants, a stable model has been developed, which is applicable to other occurrences of this type of U deposit.

The basis for such a model has also been provided by the investigations at the Ruprechtov site with their geological, petrographical, hydrogeological and geochemical characteristics. The development and application of such a model is strongly recommended for future site-specific investigations.

6 System understanding

The evaluation of the selected key topics described in Chapter 4 provided the basis for reaching a comprehensive system understanding of the Ruprechtov site. It comprises the current situation, the geological development and the key processes, which are occurring or occurred during the geological past at the Ruprechtov site. In addition, new knowledge from other research became available and was incorporated into the synthesis of the system.

6.1 Geological evolution

Study of the evolution of the Ruprechtov area over all geological ages has not been a target of the project. Nevertheless, the results gained from the entire investigation give the opportunity to highlight some aspects of the site's geological development. A final evaluation is neither wanted nor possible, however, future studies can build on the knowledge illustrated here.

The initially developed, relatively simple model of uranium mobilization was based on some information from the literature and on the results of the first few drillings at the site which were initially restricted to a very small area where, at this time at least, a measurable uranium accumulation in the sediments could be expected (cf. Chapter 2.3). In general, this simplified model involved a) the dissolution of uranium under oxidizing conditions from its source, the surrounding granite, b) its transport via groundwater in permeable sediments and/or surface water, and c) its precipitation/sorption on lignite intercalations under reducing conditions representing a so-called roll-front deposit /NOS 02/, /NOS 06/.

A central role within the geological sequence found at the Ruprechtov site is played by kaolinized granite which is encountered between the underlying/surrounding granite (U-source) and the overlying sediments with its U-deposits. Here, the process of kaolinization, i. e. the alteration of granite into kaolin, also determines the overall scenario for uranium mobilization, transport and immobilization. Besides the classical explanations, more recent studies, including the actual Natural Analogue Study at Ruprechtov, offer the possibility of placing two different explanations for kaolin genesis side by side. These two explanations are referred to as variant X and variant Y, without implying an order or assessment. Very briefly, under variant X kaolinization took place on granite which had been exposed to the land surface and at a time where the granite, resp. the kaolinized granite had not yet been covered by volcanic ashes. The essential basis of variant Y is that kaolinization occurred after the sedimentation of volcanic ashes, covering the granite. The attempt to decide between variant X and variant Y by determining the age of kaolin using K/Ar-dating of illites present in the kaolin unfortunately failed, since the illite content was too low to permit dating.

6.1.1 Variant X

According to extensive and long-lasting investigations associated with kaolin mining, the Karlovy Vary area kaolinization proceeded during the Cretaceous and Paleogene, at least partly before the Cenomanian /KUZ 83/. Therefore, primary kaolinite-bearing deposits were formed through the alteration or kaolinization of feldspar-rich rocks such as granite, gneiss, syenite, arkose, and feldspar-rich volcanic ash by either weathering or hydrothermal processes. During the kaolinization process, kaolinite was formed by the hydrolysis of anhydrous aluminium silicates and about 25 % by weight of the granite was lost, mainly in the form of potassium, sodium, magnesium, calcium and silica /HAR 96/. The process of kaolin weathering due to variant X is schematically shown in Fig. 6.1. The original landscape is characterized by granitic hills and troughs. Surface weathering of granite leading to formation of kaolin occurs in a warm and humid climate. In such a climate it is very likely that small ponds or swamps will occur in trough-areas, at least temporarily. These water-bearing units represent good conditions for granite weathering and the formation of kaolin. The elevated areas of the granite are not exposed to standing water bodies and therefore should be less weathered. Even if there is weathering in the elevated areas, it is very likely that the weathered material is mechanically transported down the slopes into the trough areas. Therefore, the highest kaolin thickness is expected to be found in the troughs of the former granitic surface and the lowest kaolin thickness in the former granitic hill areas.

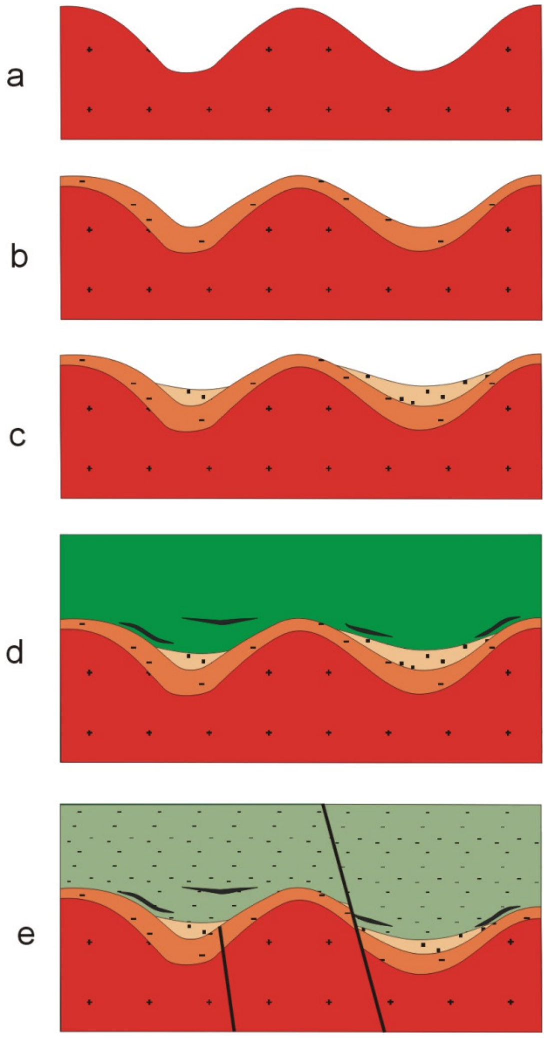

Fig. 6.1 Variant X: Schematical representation of its relevant phases during geological evolution at the Ruprechtov site

a, b) weathering of surface-exposed granite (red) to primary kaolin (orange) in warm humid climate c) redistribution and rewashing of primary kaolin to secondary kaolin (beige, dotted) d) sedimentation of pyroclastics / tuff (green) and deposition of organic matter (black layers) e) alteration of tuff (bentonization - light green, dashed)

Variant X fits very well with the sedimentological record of individual boreholes and also with the observation of the open kaolin deposits /BOS 04/. In boreholes, the basal sediment of Tertiary age built by the Davidov Member of Nové Sedlo Formation or by the Staré Sedlo Formation (in the broader region) lies mostly on the primary kaolin. Both sediments are of similar composition and contain sand to gravel with a cement of kaolinitic sandy and silty clay or layers of kaolinitic clay (see Tab. 5.2). In the area of study, this basal sediment contains traces of montmorillonite, thus its sedimentation proceeded before or during the beginning of volcanic activity of the Doupovské Hory volcanic centre. The overlying Tertiary sediments consist predominantly of argilitized volcanic material (recently bentonite) with lenses and thin layers of coal or organic-rich clay. The organic rich sediments could be interpreted as the sediments of ponds and swamps existing during the interruption of the Doupovské Hory volcanic centre volcanic activity. Layers of organic-rich sediments of both a large areal extent and very limited lenses such as the sediments of small isolated ponds are clearly visible in the borehole records. To the west of the Ruprechtov area, the impact of the mentioned volcanic activity decreases rapidly. In this part of the Sokolov Basin, coal seams of economic importance were deposited at this time. The deposition of organic matter took place in a swamp-lake environment /BOS 04/. Irregular floods stratified a fine-grained sediments and flood facies which interrupted the continuous accumulation of organic matter. Very frequent pyrite nodules and grains indicate a significantly reducing environment of sedimentation and very early diagenesis (syndiagenesis) of sediments. In addition, micropetrography analysis of coaly samples confirmed the simultaneous deposition of organic and mineral material in an aquatic environment with periodic floods. The high sulfur content in the pyrites and organic matter confirm that the sedimentation environment had rather anoxic character /SYK 04/.

During the accumulation of U in the sediment, the changes from strongly oxidizing conditions (flowing water in streams) to reducing conditions (swamps, peat bogs) also took place alongside sorption on organic matter and clay minerals. This process also supports the presence of kaolinized rock residues of Karlovy Vary pluton (kaolinized feldspars) and U detritial minerals from granitoids in almost all mineralized positions. The accumulation process of U deposits in the sedimentary environment is a significant indicator of the syngenetic model of U origin in the Hroznětín basin.

6.1.2 Variant Y

Five main phases of variant Y, a - e, are depicted in Fig. 6.2. The major difference from variant X is that the process of kaolin weathering occurred after the deposition of volcanic ashes covering the underlying granites. The original landscape, characterized by granitic hills and troughs (see above), was covered by volcanic ashes after the main volcanic activity during the Lower Oligocene to Miocene. Certainly, a large amount of mantle CO_2 was released by the volcanic activity and probably trapped alongside oxygen in the deposited volcanic ashes. It is very likely that CO_2 additionally poured out from fault zones. These processes caused CO_2-rich oxidising waters, which were able to strongly alter the underlying granite.

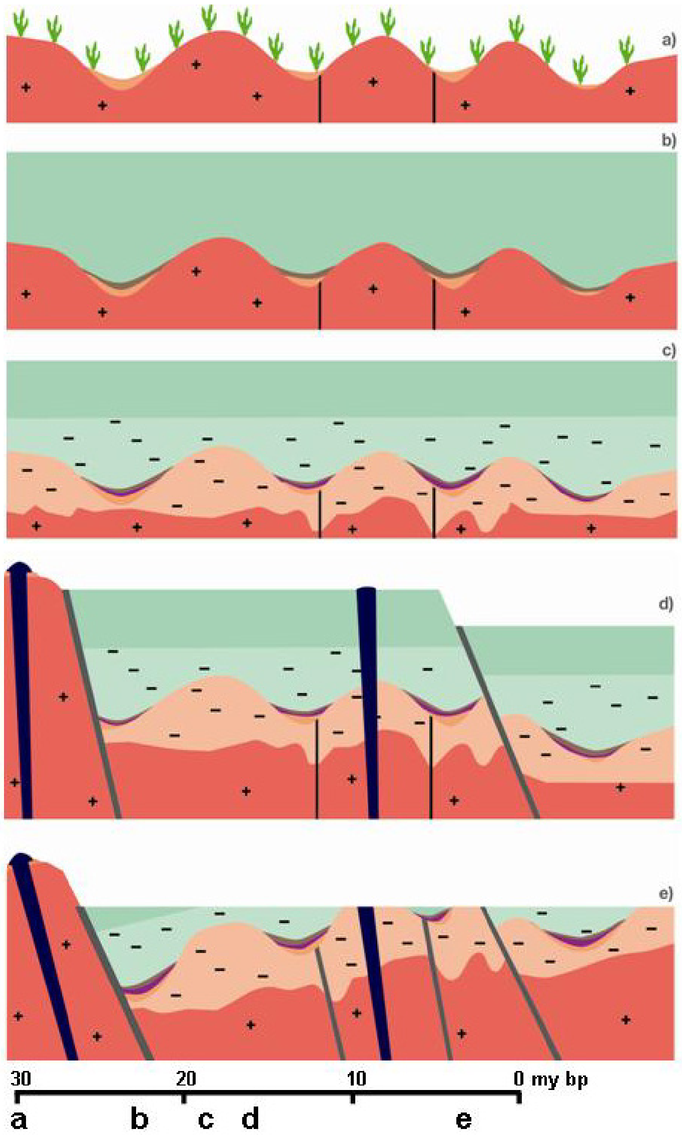

Fig. 6.2 Variant Y: Schematical representation of its relevant phases during geological evolution of the Sokolov basin

a) Pre-Oligocene (> 30 m years): influx of detritic material (orange) through physical weathering of the granite present at the surface (red) b) Lower Oligocene - Miocene (30 – 16 m years): deposition of organic material (brown) in trough areas; after that, main phase of volcanic activity with wide-area sedimentation of pyroclastics / tuff (green) c) Lower Oligocene - Miocene (30 – 16 m years): alteration of granite (kaolinisation - light red, dashed) and tuff (bentonisation - light green, dashed) d) Miocene (16 – 15 m years): rift formation, combined with fault zones (grey) and basalt intrusions (dark blue) e) Pliocene - Quaternary (< 5 m years): further evolution of the Ohre rift and partial erosion of the pyroclastic sediments

Alteration of the underlying granite mainly occurred through the reaction of feldspars with CO_2-rich water and the formation of kaolinite according to the generalized formula:

$$2\,KAlSi_3O_8 + 2\,CO_2 + 7\,H_2O = Al_2Si_2O_5(OH)_4 + 4\,SiO_2 \cdot n\,H_2O + 2\,K^+ + 2\,HCO_3^- \qquad (6.1)$$

Through this reaction, kaolin is formed in the place of granites and is widespread with variable thickness. The special characteristic of variant Y is that stronger kaolinization occurred in elevated granites, leading to a greater thickness of kaolin in these areas.

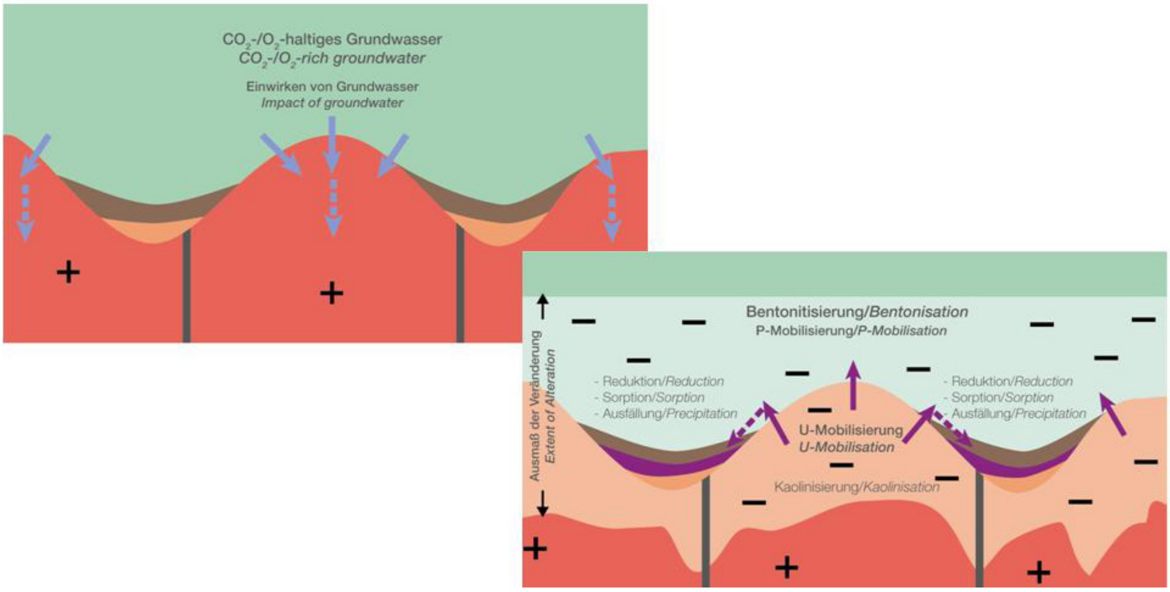

Fig. 6.3 Schematical representation of the alteration processes in granite (kaolinisation) and tuff (bentonization) through the impact of CO_2- and O_2-rich groundwaters in phase “c” of the geological evolution

The previous wide area sedimentation of pyroclastic sediment has led to the condition where the thickness of kaolin is largest where the granite previously showed morphological elevations. Uranium (magenta) is accumulated in those former valleys in which lignite or lignitic clay has also accumulated

In this variant, it is in phase "c" (Fig. 6.3) that the major uranium accumulation occurs: Following the sedimentation of the pyroclastics, weathering of the underlying granite mainly took place as a result of the reaction of feldspars with CO_2-rich groundwaters and the formation of kaolin. CO_2-rich groundwaters furthermore initiated the mobilization of the uranium from accessory minerals through the formation of soluble UO_2-carbonate complexes. Within the kaolin, the uranium was mainly transported through diffusion. At the boundary layer between the kaolin and the overlying pyroclastic sediment, advective transport was also possible over short distances in a local horizon with increased hydraulic conductivity. The main immobilization processes that could be considered were uranium reduction in/close to lignite-rich sediments – combined with the formation of secondary uranium(IV) minerals such as uraninite, ningyoite and uranium co-precipitation within $FeAsS_2$ phase.

There are arguments for both variants. In /NOS 06/ it was argued that the resulting distribution of kaolin thickness in variant Y is expected to be highest in the elevated areas and lowest in the trough areas of the former granitic surface. For variant X the results would be vice versa, i. e. the kaolin thickness should be increased in valley areas and low or nearly non-existent in elevated zones (cf. Fig. 6.2). The kaolin thickness observed today at Ruprechtov is shown in relation to the depth of the interface pyroclastic sediments / kaolin in Fig. 6.4. A clear correlation between both parameters is visible from this map: High kaolin thickness is found in elevated areas of the interface between pyroclastic sediments / kaolin and low kaolin thickness in depressions as expected for variant Y. A second argument for the main kaolinization process occurring after being covered with volcanic ash is the strong slope of the kaolin hills, which might not have been stable without a stabilizing cover (see discussion in /NOS 06/).

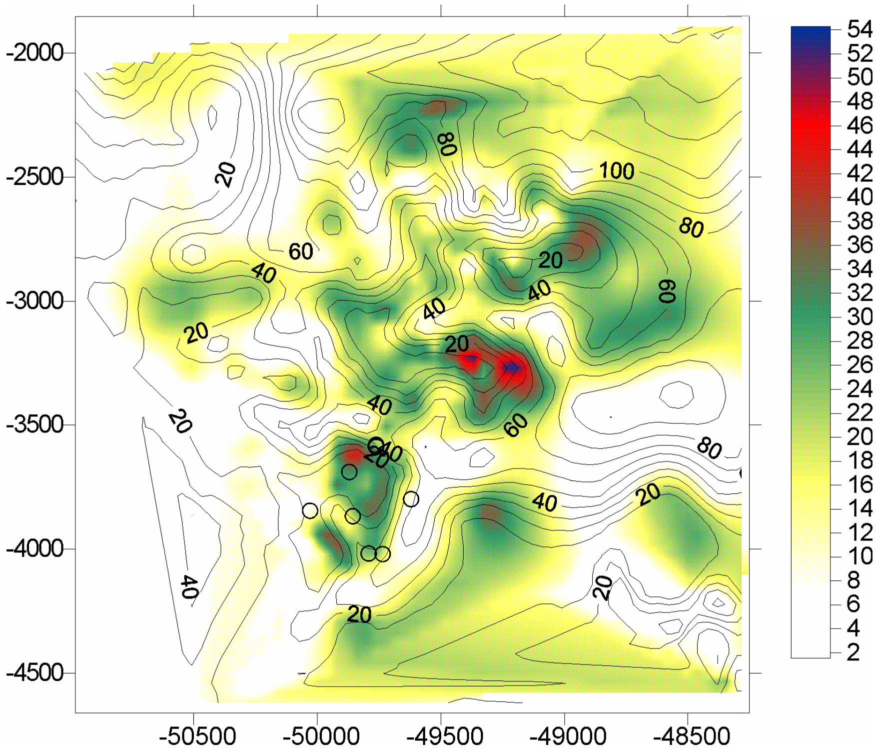

Fig. 6.4 Correlation of depth of interface pyroclastic sediments / kaolin (isolines [m below ground]) with kaolin thickness (colour-scale [m])

However, it is questioned, whether processes occurring after covering with volcanic ash could have caused weathering depths of several tens of meters. Such deep weathering is more likely to have occurred during long periods of hot and humid climates. This is, for example, discussed in /STO 78/.

The strongest argument supporting variant X is the existence of rewashed "secondary kaolin" under the layers containing pyroclastic material. Both primary and partly secondary kaolin are covered by the Staré Sedlo Formation and Nové Sedlo Formation with sediments containing volcanic material. Then, primary kaolin has been partly rewashed and sedimented in surface waters (lakes, rivers, ponds) as "secondary kaolin". After sedimentation, the kaolin was covered by younger sediments.

Without intending to state a final decision, actual studies supported by the recent drilling programmes spread over wider areas and involving more detailed laboratory tests have shown that the bedding conditions are governed by strong morphology at the Tertiary base and that the uranium accumulations found in the lignite-clay/sand horizon cannot have been formed by one single process, but by several different causes:

- Syn-sedimentary influx of detritic uranium minerals;
- Spatially limited mobilization of uranium from the surrounding granite during the kaolinization of the latter, diffusion and retardation (reduction, sorption, precipitation) in the zone within the lignite-clay/sand horizon;
- Influx from the underlying granite in zones of low kaolin thickness and/or via fault zones and retardation (reduction, sorption, precipitation) in the zone of the lignite-clay/sand horizon.

6.2 Key processes and interrelations

The strongly reducing conditions in lignite-rich horizons could be verified by means of pH-Eh measurements in the corresponding groundwaters. The Eh-values of the groundwaters in clay sediments lie clearly below those of granitic waters. According to this, U can be supposed to exist in immobile U(IV) which could be also declared by low U groundwater concentration (see below).

Geochemical calculations have confirmed that U(IV) is the preferential oxidation state in the clay/lignite layers. These calculations also indicated that the redox conditions in the clay/lignite horizon are controlled by the SO_4^{2-}/S^{2-} couple. The uranium concentrations in the clay/lignite layer observed today are determined by amorphous UO_2 and ningyoite. Although U(IV) is the dominating redox state for uranium in the solid phase, geochemical calculations and U speciation analysis have showed that U(VI) can occur in solution to a significant extent. For the typical Ca-HCO_3 type waters with relatively high CO_2 partial pressures, U(VI) might be stabilized by ternary Uranyl-Ca-Carbonato complexes. Nevertheless, the expected uranium concentrations are extremely low. The very thin lignite-clay/sand horizon can therefore act as a highly effective transport barrier for uranium. There are no indications whatsoever of a renewed release of uranium from the accumulation horizons.

Further information on the processes involved in uranium immobilization have been obtained from geochemical and isotope analyses. At the Ruprechtov site, the involvement of microbes in the uranium immobilization was shown to be quite important in an indirect way. In the geological past, pyrites have been formed by microbial sulfate reduction, still traceable in the typical framboidal shape of the pyrites in the clay/lignite layer. The reduction of sulfates to sulfides was shown in batch experiments with indigenous microbes and sediments extracted from drill cores. This microbial sulfate reduction is still active today, as demonstrated by the increase of ^{34}S values in dissolved sulfates from the infiltration area compared to the clay lignite layers /NOS 09a/. The microbial sulfate reduction seems to contribute to maintaining the reducing conditions and therewith to the long-term immobility of uranium /NOS 09b/. Microbial sulfate reduction involving organic matter and subsequent pyrite formation have also been identified as dominant buffering reactions at the Tono site which have maintained slightly alkaline and strongly reducing conditions at least during the past several 100,000 years /ART 06/.

The integration of all of the results showed that organic matter did not play such an important role through direct interaction with uranium. According to the results from the Sedimentary Organic Carbon (SOC) characterization it seems that the low concentration of dissolved organic matter in the Ruprechtov system has mainly been caused by the low availability of organic matter to the processes of degradation. Only a very small fraction of the SOC is accessible to the groundwater. An additional reason could be the strong sorption properties of the clay, which fix humic acids on the sediment matrix and therewith further reduce the mobile concentration. These results from sorption experiments are described in Chapter 4.5. In addition, sorption experiments with U(IV) in the presence of humic acids on material from clay lignite horizon, demonstrate well that HA concentrations below 5 mg/L do not impact sorption values of uranium and therewith do not contribute to the mobilization of uranium.

However, sedimentary organic carbon (SOC) has contributed and still contributes to maintaining reducing conditions in the clay/lignite layers. This is supported by the finding that the highest accumulations of uranium were located slightly below the zones, which are highly enriched in organic matter. It can be concluded that SOC within the sedimentary layers was (and to some extent still is) microbially degraded. Dissolved organic carbon (DOC) is released through this process, providing protons to additionally dissolve sedimentary inorganic carbon (SIC). Moreover SO_4^{2-} is reduced leading (and having led in the geological past) to the formation of iron sulfides, especially pyrite. Reducing conditions, being maintained amongst others by sulphate-reducing bacteria, caused the reduction of As, which sorbed onto pyrite surfaces, forming thin layers of arsenopyrite. U(VI), originally being released from the outcropping/underlying granite, was reduced to U(IV) on the arsenopyrite surfaces. UO_2 and uranium phosphates were formed by the reaction of U(IV) with phosphates PO_4^{3-}, released by microbial SOC degradation.

The Ruprechtov site is a good example to demonstrate that Tertiary argillaceous sediments can exert a strong barrier function for uranium, when specific prerequisites are fulfilled. Major uranium transport has occurred only over distances of about tens to a maximum of some 100 m during the Tertiary. Uranium was transported as U(VI) and was reduced in a lignite rich clay horizon. It was immobilized by forming uraninite, and phosphate-bearing minerals such as ningyoite. There is no evidence of uranium mobilization during the last million years. But there is indication that during the last several 100,000 years still further uranium enrichment occurred in this lignite-rich clay horizon. This is probably due to transport from the underlying granite through zones of low kaolin thickness and/or fault zones. The uranium concentrations in the groundwater of the uranium-rich clay/lignite-sand horizon are low, in the range of 11 μg/mL although this horizon is only 25 to 65 m below the surface.

6.3 Abstraction to the Safety Case

In order to draw up a Safety Case, geological evidence is needed for the long-term stability of host rocks or overlying geological formations, which are regarded as an additional barrier. Therefore, information which is available to characterize the barrier function and the long-term stability of such formations is important. The Ruprechtov natural analogue provides evidence that uranium is and has been effectively immobilized in a sedimentary layer of a formation, which has been exposed to surface erosion in the geological past. All of the results indicate that uranium was efficiently immobilized in a reducing environment (controlled by the SO_4^{2-}/S^{2-} couple) over millions of years and no significant release of immobilized uranium occurred within that time, although the uranium-bearing horizon is in direct vicinity of water flowing layers. Even though a portion of the dissolved uranium exists in the U(VI) state, probably stabilized by carbonate complexes, the uranium concentrations in solution have remained quite low, with values typically below 1 µg/L in the uranium-enriched horizon. The key processes involved in uranium immobilization have been identified.

The observation of the strong impact of microbial processes contributing directly and indirectly to the uranium immobilization is one further important result from the Ruprechtov study with respect to making a Safety Case. This shows the importance of addressing the role of microbes in the Safety Case. In the case of Ruprechtov, microbes have a “positive” effect, contributing to the long-term geochemical stability of the sedimentary layers and therewith to the long-term immobilization of uranium.

Several analytical methods for the characterization of dissolved and solid phase uranium have been applied and further developed including uranium series disequilibrium measurements and U(IV)/U(VI) separation using $^{234}U/^{238}U$ isotope analysis. Innovative microscopic methods have been used in combination with macroscopic methods contributing to the identification of key processes at the Ruprechtov site. These new methods are particularly important for yielding information about the (hydro)geological past of a potential repository site, which is important in increasing confidence in the predictions of the site’s future evolution. This in turn is one prerequisite for building a Safety Case. Geochemical calculations indicate that at both sites amorphous UO_2 controls the uranium concentration in solution, with a higher soluble form suggested to occur in fractures at the Forsmark site. A further important result for the Safety Case is the evidence from a natural system that the trivalent carbonate complexes of U(VI) with alkaline earth elements – thus far only determined in lab experiments – should be considered in the thermodynamic description of the uranium speciation.

Although the Ruprechtov site turned out to be rather complex with regard to its hydrogeology and geological evolution, the mechanisms for the immobilization of uranium have been identified. By the application of a set of different microscopic and macroscopic analytical methods distinct immobile uranium phases have been characterized and their long-term stability shown. The results further indicate that DOC does not contribute to themobilization of uranium, because of the relatively low DOC concentration in the clay/lignite layer. DOC is formed by microbial degradation of SOC in the clay/lignite layers, but only a very small fraction of the SOC seems to be accessible.

In general it has been shown that sedimentary layers can provide a strong barrier function for uranium, when specific prerequisites are fulfilled. Under the strongly reducing conditions in the clay/lignite layers at the Ruprechtov site, there are no indications for significant uranium release during the last million years. The low uranium concentrations in the groundwater of app. 10^{-9} mol/L are mainly determined by amorphous UO_2. A similar observation is derived from the Tono analogue study. The results support the commonly made assumption in safety assessments that maximum U concentrations in groundwater will be limited by the equilibrium solubility of UO_2(am) and therewith provide confidence in the methods used to estimate the long-term concentration ranges of uranium in groundwater.

Due to the analogy between argilitized tuffs and a bentonite buffer, the strong buffering and long-term stability of the uranium enrichment can also be transferred to the demonstration of the safety function of the bentonite buffer as an engineered barrier. Moreover, this barrier function of clay sediments was preserved even at a few meters distance from the operating kaolin mine. Because of the low permeability of the clay, the reducing conditions and therewith the stability / immobility of uranium have been maintained.

7 Lessons learnt / experiences gained

Compared to other countries, the topic of natural analogues was less pronounced in the German and Czech repository R&D programme. Up until the mid-1990s, only few small-scale projects had been initiated and performed. In 1995, this changed somewhat, when the Ruprechtov project – a longer-lasting, larger and large-scale in-situ project – started to investigate the Ruprechtov site. This was initiated as part of the early co-operation between GRS and ÚJV. In 1998, the Natural Analogue project was incorporated into the Czech national DGR (deep geological repository) programme. Follow-up projects on both sides initiated intensive investigations and research at the site. Some of the activities were included in the 6th Euratom IP Project Fundamentals processes of radionuclide migration (FUNMIG). Later, the projects focused on specific issues such as the role of organic matter or redox processes. In retrospect, the Ruprechtov study has provided a great deal of experiences, knowledge, know-how and skills, which have been described in detail in this report and concern:

- The use of knowledge from natural analogue studies for selecting sites with geological potential for the investigation of radionuclide retention / isolation by natural systems;
- The development of a general strategy for field investigation;
- The application of drilling, sampling and site characterization methods and their optimization during the work progress;
- The application and further development of laboratory methods and experiments;
- A better understanding of natural processes;
- Abstraction to the Safety Case;
- International co-operation and project management.

The Ruprechtov project has demonstrated that understanding the evolution of a geological site (past and future) and evaluating the long-term behaviour of a deep repository require a broad and well-founded knowledge of the geological conditions (regional and local) including all geo-historical processes. This makes up the scientific basis for site investigation and the interpretation of genetic-mineralogical, geochemical, hydrological and other important geo-parameters. The overall geological knowledge together with the findings from the investigations provide the information needed for a first, model-like assessment of the long-term performance of geological barriers as part of repository systems.

The outcome of this project has confirmed the association of specific uranium-bearing minerals with different genetic types of uranium accumulation and different stages of the genetic evolution of the geological system. In addition, the interpretation of the findings from petrographic, mineralogical and microscopic studies have given distinct indications not only for uranium migration but also for uranium accumulation and sorption processes in argillaceous formations under the present environmental / climatic conditions. In general it was proved that argillaceous sediments, even close to surface, can contribute essentially to the retention of uranium for long (geological) periods of time. Specifically, in the case of the Ruprechtov site, lignite-bearing sediments are the source for a microbial milieu which provides long-term reducing conditions and the efficient immobilization of uranium.

The performance and the success of a research project of this kind depend significantly on the availability of professional experience in the issues concerned and scientific knowledge. This has been demonstrated to some extent by the literature survey performed on relevant publications and reports covering subjects such as the use of natural analogues in radioactive waste disposal research, the formation of natural uranium deposits under different geological conditions and the basics of the national and regional geology. The analysis and the evaluation of around four hundred documents made it possible to view the investigation results in the context of the actual state-of-the-art in uranium mineralogy and geochemistry. All of this provided the information required for defining more clearly the scientific goals over the course of the project and, respectively, for outlining the overall investigation results.

One major advantage from the beginning was in a broader sense the easy accessibility of the site, which should be a prerequisite, because the need for discussion / negotiation / explanation with local responsible persons is inescapable. On the other hand, the high quality kaolin at low depth, which meant that it was easy to mine, led at the outset of the project to different interests being held by the kaolin mining company because of economic planning. However, through the negotiation of clear arrangements and good relations between the scientists and the mining company, both sides were able to perform their work as intended. In a few cases, these arrangements limited the selection of a borehole location and also led to the abandonment of a few boreholes, but the relevant information was always communicated in advance. The interdependency with the kaolin mining company also had positive aspects, e. g. groundwater wells constructed by the kaolin mining company were made available for use in the study and vice versa, hydraulic and geochemical information from the Ruprechtov study was also integrated in the environmental impact assessment of the kaolin mining company.

A further argument for the decision to choose this location was the limited extension of the Tertiary basin suggesting a system with limited complexity in its geological evolution. During the detailed investigations this assumption turned out to be unjustified, since the results clearly showed that uranium enrichment happened through many different processes over different time scales. Indeed, this posed an additional challenge but did not constrain the investigations.

Furthermore, the objective to investigate uranium retention in the sandy argillaceous inclusions / layers in the Tertiary basin was achieved, because the uranium enrichment turned out to be very stable and no traces of either a uranium plume or uranium immobilzation could be found in any of the investigations. This characterizes the location to be a strong analogue for a long-term stable geochemical environment being the cause of the high stability of the immobile uranium. However this fact did not allow the study and modelling of the migration of uranium on a pathway through the sedimentary environment, which had also been one of the initial ideas.

An additional aspect of choosing the site / location was the objective to study organic material, particularly sedimentary organic material as a source of organic colloids such as humics or fulvics, which might act as a carrier for radionuclides. This would have been of interest for the German scientists, because high concentrations up to 200 mg C/L of humic colloids have been observed in the overburden of the Gorleben site, considered in the past for hosting a HLW repository. The investigations at the Ruprechtov site showed a very low availability of sedimentary organic matter for degradation and consequently only low concentrations of dissolved organic carbon (humic colloids) in the groundwater, limiting its value as an analogue for the specific situation at Gorleben. Nevertheless, valuable contributions have been made to an increase in knowledge on the interrelation / interaction of organic and inorganic carbon. Moreover, it indicates and gives some confirmation, as observed in several other natural analogue studies, that the impact of colloids on a potential radionuclide transport in many natural systems is limited.

The whole study was performed stepwise, which is necessary for such an analogue site investigation. This investigation strategy is a key prerequisite for maintaining flexibility. The stepwise procedure caused the relatively long duration of the project, which, however, is also revealed by experiences from other analogue site investigations of this kind; around 15 years were necessary to yield full site understanding. On the other hand, this approach made it possible to plan further steps thoroughly and according to the real needs and requirements, which was economically and scientifically of benefit. Besides specific investigations, each step also allowed the adoption or modification of technology, e. g. drilling technique or the kind of instrumentation and the use of analytical equipment. Moreover it allowed, for example, the identification of key features of the groundwater and sediments, which needed to be carefully accounted for in the following steps of the project. These findings then led to a change / optimization of (i) sampling, (ii) sample handling and (iii) experimental procedures. This concerns, for example, the redox sensitivity or high heterogeneity on low spatial scale of sediment samples from the uranium-bearing layers. The former aspect provoked an improved sampling method, providing rapid isolation of drill core material from the ambient atmosphere directly after drilling as well as the application of experimental procedures under anaerobic conditions.

This redox sensitivity of the drill core material led to the decision to perform some of the analysis directly on-site instead of later on in the laboratory. One example is the uranium(IV) / uranium(VI) separation, which is, of course, very sensitive to oxidation by atmospheric oxygen. Therefore, a mobile glove box was applied to perform U(IV)/U(VI) separation under Ar atmosphere on selected samples directly after drilling. As expected, the results showed an extremely low fraction of the oxidized form U(VI). On the other hand, a drawback of this decision was that no information about the absolute U-content in the sample was available directly after drilling. Unfortunately, the selected core was one in which the uranium enrichment was rather low, leading to low U signals. This is a consequence of the high heterogeneity (also in uranium content) on a relatively small spatial scale.

For each of the methods applied during the Ruprechtov study, specific positive and less positive experiences were gained, which are described in the “method tables” in Annex A.2.

Some specific drawbacks should also be mentioned. The low-permeable system at the site with low water supply in some of the boreholes represented a special challenge for groundwater sampling and in-situ measurements. It was not possible to completely change the well volume in some of the groundwater wells, because the inflow was too slow. In such a case, just to “optimize” the system, borehole pumping was performed several days before a sampling campaign. The problem of confidence in the results of Eh measurement has been discussed several times. We observed that we never reached Eh-values as low as those measured with our in-situ probe in the borehole. Moreover, each pumping in the near-surface boreholes could be recognized by an increase in the in-situ Eh-value. Several hours up to a few days were needed to receive a stable and reproducible signal which was used for interpretation and modelling.

The study also showed that the methods adapted have been restricted in some aspects, so that not all questions could be answered completely. One example concerns the identification of low size U-bearing minerals (diameter below 1 µm). From mass balancing it is obvious that part of uranium will be enriched in the submicron phases. Therefore, within the last stage of the project, we applied transmission electron microscopy (TEM), which actually allows detection down to a nanometer scale. However, this effort failed, particularly due to the difficulty of selecting the correct samples on that small spatial scale. No uranium phase could be identified. Such an investigation should have been started earlier and more effort should have been dedicated to it.

Uranium speciation in solution was investigated using U(IV)/U(VI) separation. This method was optimized during the project but also requires a great deal of effort and logistics. We succeeded in measuring U(IV) and U(VI) fractions in three boreholes, which agreed well with modelling results. However, to underpin these results more analyses using a larger network of boreholes correlated with in-situ and chemical parameters would be necessary.

Some development work was also dedicated to the Time Resolved Laser Fluorescence Spectroscopy (TRLFS), with the final aim of identifying U(VI) species. A particular aim was to prove the existence of ternary uranyl carbonato complexes in a typical groundwater from Ruprechtov. We have been successful in identifying four uranyl species, including $Ca_2UO_2(CO_3)_3$, in synthetical Ruprechtov water and determining their lifetimes. However, the step to directly measure a sample taken from a Ruprechtov well with relatively low uranium concentration is still a challenge and was not performed within the project.

With respect to the Safety Case, evidence has been achieved through several different observations that a sedimentary formation may act as a strong long-term barrier for uranium migration. Similar to the findings from the Tono study, microbial sulfate reduction involving organic matter degradation is inferred to be the dominant buffering reactions that has maintained the strongly reducing conditions in the sedimentary uranium deposit over time frames of hundreds of thousands up to million years and efficiently immobilized uranium. The results support the assumptions that under these conditions maximum U concentrations are determined by amorphous uraninite, which is a frequent assumption in safety assessments and herewith underpinned by analogue information.

To perform the project in the way in which it was done was only possible because of co-operation with international experts and working teams. Such a study requires not only knowledge and expertise in different disciplines such as geology, mineralogy, hydrology, hydrogeochemistry and microbiology to establish a broader view on the topic, but also specific technical experience such as application and evaluation of isotope methods or use of specific modern and state-of-the-art micro-/nano analytics. A particularly important aspect of this co-operation was method-development and testing. This comprised, for example, colloid sampling under undisturbed conditions, first applied to natural samples and further development of µ-XRF and µ-XANES as well as the application of modern isotope analyses such as the study of $\delta^{34}S$ signatures to identify relevant processes in the field.

All of these methods are important for the investigation of a potential repository site including laboratory and field experiments.

During the duration of the project relevant documentations, in the form of publications, conference proceedings, reports (including internal company reports), diploma and PhD theses have been created and included into the database. A complete list of these investigations is compiled subsequently.

List of project publications

Journals

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A Annex: Background information

A.1 In-depth information about uranium deposits in the Czech Republic related to the selection of the Ruprechtov site as a Natural Analogue

A.1.1 Uranium mining and utilization before 1945

Practically, all the important developments in the early history of uranium mining and utilization were connected with the Krušné Hory Mountains on the border of the Czech Republic and Germany:

1727	Franz Ernst Brückmann (a German doctor from Braunschweig) identified pitchblende (uraninite) at the Jáchymov silver mines (the term pitchblende had been used by silver ore miners in the Krušné Hory mountains since at least the 15th century);
1789	Martin Heinrich Klaproth (a German chemist) discovered uranium in pitchblende from the Johangeorgenstadt deposit;
1843	the first reference to the use of pitchblende from Jáchymov for the production of dyes for glass and ceramics;
1862	Adolf Patera introduces new technology for the industrial production of uranium dyes for china and glass at a Jáchymov chemical factory;
1898	Marie Curie-Sklodowska discovered radium and polonium in uraninite from the Jáchymov deposit.

Prior to the First World War, Jáchymov with its mines was the world leader in terms of radium production; in 1913 radium extraction in Jáchymov reached 2.12 g. In 1927, the Jáchymov factory produced 21.1 t of uranium dyes and 2.0 g of radium. In 1929, the production of dyes was 23.3 t and that of radium 3.5 g. The production of dyes ceased in 1939. The data are summarized in Tab. A.1.

Tab. A.1 Uranium production from the Jáchymov deposit before 1945 /POK 94/

Years	U production [t]
1853 - 1913	150
1914 - 1938	275
1939 - 1944	44

A.1.2 Uranium mining after 1945

The Soviet Army occupied the State mines in Jáchymov on 11th September 1945. In November of the same year an agreement between the Soviet and the Czech Governments on the extension of uranium ore mining and its export to the Soviet Union was signed. From this date up to 1961 the exploration and mining of uranium remained under the strict supervision of Soviet specialists /PLU 98/.

The post-war acceleration in the exploration and mining of uranium deposits in the Czech Republic was remarkable: whereas no uranium production is reported in 1946, in 1951 approximately 500 t of U (metal) was produced, in 1952 nearly 1,000 t and in 1954 1,500 t. The development of the production of U in the period 1946 – 2013 is shown in Fig. A.1. Annual production reached a maximum in 1960 at more than 3,000 t. Since 2000, uranium has been mined at the Rožná mine only and production has gradually decreased from 500 t U in 2000 to some 200 t U in 2013.

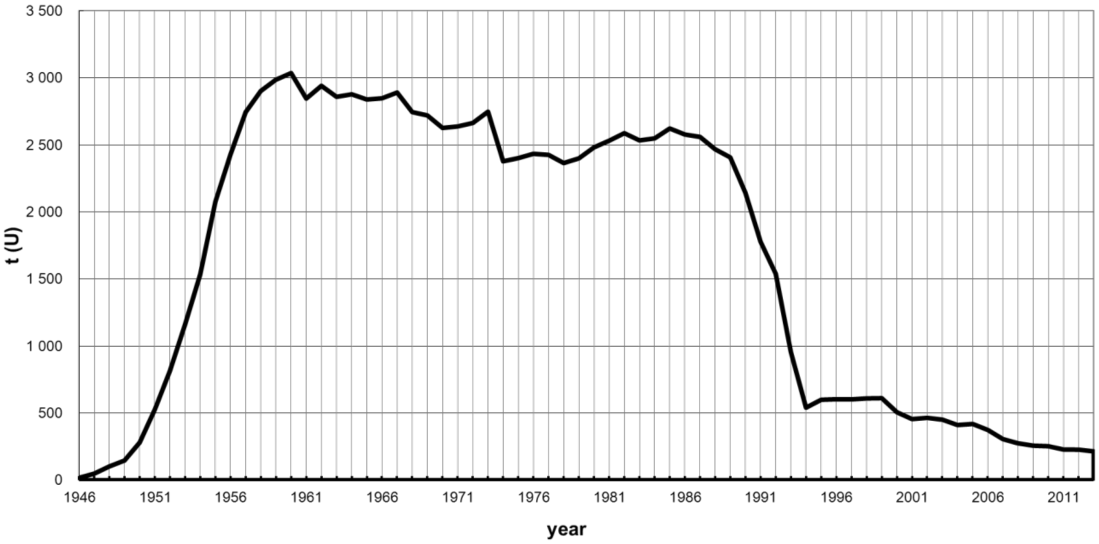


Fig. A.1 Uranium production in the Czech Republic in the period 1946 – 2013 /KAF 03/

In the period 1946 – 2000 a total of 164 deposits and uranium mineralization occurrences were explored of which 86 deposits and occurrences were mined. More than 10,000 t of U was mined from just 4 deposits, 1,000 – 10,000 t from 8 deposits and 50 – 1000 t of uranium from 20 deposits. 54 occurrences yielded between 0.1 and 50 t U, Location of deposits on which more than 1,000 t of uranium were mined is visible from Fig. A.2.

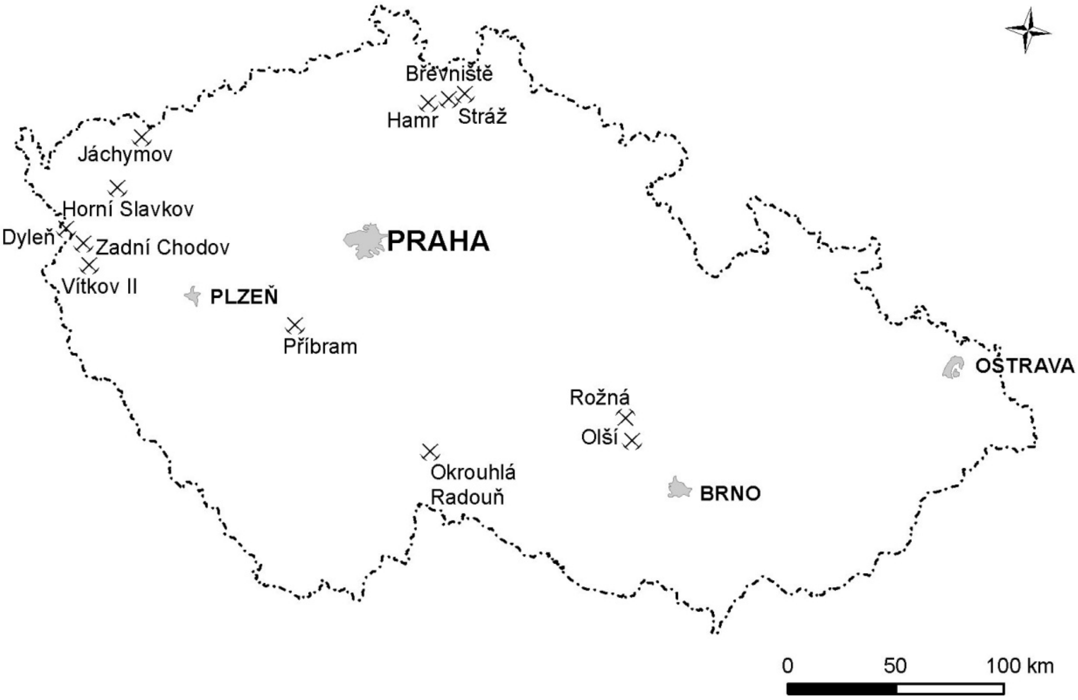


Fig. A.2 Geographical position uranium deposits with production more than 1,000 t U in the Czech Republic (after /KAF 03/)

Uranium deposits consist of two main genetic types /IAEA 09/, which produced more than 99 % of the total production in the Czech Republic: the vein type (granite related) and sandstone deposits. Coal and lignite deposits (other types after /IAEA 09/ were of a low importance. Uranium production from these deposit type was less than 1 % of total Czech Republic production. A comparison of the production of these types is provided in Tab. A.2.

Tab. A.3 provides basic data on Czech uranium deposits with a production of over 1,000 t of metal.The deposits shown in the table in bold are described below. The major part of the information is taken from /KAF 03/.

Tab. A.2 Uranium production in the period 1946 – 2000 by type of deposit /KAF 03/

Type	U production [t]	%
Vein type (granite related)	77,169	72.1
Sandstone deposits	29,014	27.1
Uraniferous coal and lignite		
Permo-Carboniferous	608	0.5
Tertiary	289	0.3
Total	107,080	100.0

Tab. A.3 Basic data on Czech uranium deposits with a production of over 1,000 t of uranium /KAF 03/

Deposit	Type	Start of exploration	Operation	U production [t]
Příbram	Vein type	1947	1950 - 1991	50,200
Rožná	Vein type	1954	1957 - today	17,241
Stráž	Sandstone	1965	1967 - 1996	14,674
Hamr	Sandstone	1962	1973 - 1993	13,264
Jáchymov	Vein type	1945	1945 - 1964	7,950
Zadní Chodov	Vein type	1952	1952 - 1992	4,151
Vítkov II	Vein type	1960	1961 - 1991	3,973
Olší	Vein type	1954	1959 - 1989	2,922
Horní Slavkov	Vein type	1946	1948 - 1962	2,668
Okrouhlá Radouň	Vein type	1962	1972 - 1990	1,340
Břevniště	Sandstone	1966	1982 - 1990	1,108
Dyleň	Vein type	1964	1965 - 1991	1,100

Příbram

The Příbram uranium ore field is situated in Central Bohemia around 60 km SW of Prague (see Fig. A.2). It is the largest vein-type uranium deposit in the Czech Republic and one of the largest in the world.

Nearly all the veins which bear uranium mineralization (96 %) occur in the metamorphosed sediments of the Dobříš Group of Upper Proterozoic age close to the contact with the Central Bohemian Pluton of Variscan origin. The ore field consists of 20 vein clusters which form a strip some 24 km long and 1 – 2 km wide elongated in the SW-

NE direction. The maximum lenght of veins was 2,700 m, their extreme thicknes up to 20 m.

Some 2,500 veins were opened for mining purposes; uranium mineralization was discovered in 1,601 veins. More than 100 t of uranium were mined from just 88 veins. In addition, 35 veins contain polymetallic mineralization (principally Pb, Zn and Ag) and 19 veins contain silver mineralization. 87 % of the uranium-bearing veins were positioned in the N-S to NW-SE direction.

The principal uranium mineral consisted of uraninite and the content of uranium antraxolite was higher in the deeper part of the deposit. The content of coffinite made up only a small percentage of uranium mineral bulk.

The development of the veins was very complex; however, four main stages have been distinguished:

- Siderite with polymetals and quartz;
- Calcite;
- Calcite, uraninite;
- Ccalcite, sulfide, uranium antraxolite, coffinite, fine silver and arsenide.

The age of uranium mineralization has been estimated at 265 Ma.

During the exploration and mining phases 25 km of shafts, 300 km of chimneys and 2,188 km of various types of horizontal galleries were constructed. The deposit was mined to a depth of 1,800 m.

In addition to 50,200 t of uranium some 300,000 t of polymetallic ore with a content of 6,195 t Pb, 2,417 t Zn and 28.9 t of Ag were mined.

Rožná

The deposit is situated in Central Moravia some 40 km NE of the city of Brno (see Fig. A.2). Ore-bearing structures developed in Moldanubian rocks and terminate on the boundary with the Moravosilezian Complex. Mineralization is fixed mainly to fine-grained biotite gneiss and less often to amphibolite, pyroxenite and erlane.

The largest part of the mineralization is bound by tectonic zones in the NNW-SSE direction and a steep dip to the W which are filled with crushed graphitic and chloritized rocks. The mineralized zones are partly brecciated, mineralization is of diffuse boundaries and the length of individual zones reaches 15 km with a maximum thickness of 10 m.

Uranium-bearing veins developed only rarely in structures lying in a NW-SE direction; this type of mineralization is of minor importance.

The most common uranium-bearing minerals consist of uraninite and coffinite; brannerite and a number of other uranium-bearing minerals have also been recorded. In addition, sphalerite, galenite, chalkopyrite and selenide are also present. The age of uranium mineralization has been estimated at 250 – 270 Ma and that of the rejuvenated mineralization of coffinite at 150 – 180 Ma.

During the exploration and mining stages 6.7 km of shafts, 92 km of chimneys and 493 km of various types of horizontal gallery were constructed. Mineralization developed to a depth of 1,200 m.

A total of 17,240 t of uranium was mined during the period 1957 to 2000. From 2000 to present some 400 t of U has been produced annually. Currently, Rožná mine is the only uranium deposit still operated in Europe.

Stráž

The deposit is located in the North Bohemia region around 90 km N of Prague (Fig. A.2) and is the largest stratiform deposit bound to the Czech Cretaceous basin sediments. Some 27 % of total Czech uranium production was mined from deposits of this type.

A large paleo-depression in the eastern part of the deposit created the conditions for the build-up of a very thick layer of Cenomanian age sediments and, subsequently, to the estimation of a large volume of reserves.

Ore bodies developed partly in fresh-water Cenomanian sandstone, and mainly in the sandstone and siltstone of the lowermost part of the Cenomanian sediments of marine origin. The bodies are horizontal to subhorizontal and have a bedding, tabular or lenticular shape. The thicknesses of individual bodies vary from several decimetres to 8 meters; roll structures are common. Disseminated, organodetritic and diffuse structures are also present.

Uranium mineralization as part of the cement is made up predominantly of uraninite and uranium blacks. Baddeleyite, ningyoite and phosphate are less common.

The ore-bearing sediments lie at depths of between 130 m and 270 m. Uranium was extracted using the underground acid leaching technique. In total 7,684 boreholes were sunk. Leaching ended in 1995 and currently a huge remedial environmental recovery programme is underway. A total of 14,674 t of uranium was obtained from this deposit.

Jáchymov

The deposit is situated in North West Bohemia some 30 km N of the city of Karlovy Vary. From the point of view of the history of mining it is a deposit of world importance (town physician Georgius Agricola - the father of mineralogy). The mining of the deposit, which lies in metamorphosed rocks of the Jáchymov Group of Lower Paleozoic age at the intersection of the Jáchymov deep fault (NW-SE direction) and the Krušné Hory fault (ENE-WSW), commenced in the beginning of 16th century by the silver mining. The most common rocks consist of slate, phylite, amphibolite and quartzite – locally with carbonate intercalations. Variscan granitoids of the Karlovy Vary - Eibenstock composite pluton occur SW of the deposit and underlie it. This deposit provides a typical example of a uranium-rich variant of a five-element ore deposit (Ag, Co, Ni, As, Bi) (similar to the Eldorado mine at Port Radium, Canada).

Veins in the E-W direction (the “morning veins” of medieval miners) are stable in terms of direction but weakly mineralized and with rare uranium mineralization. The main accumulation of uranium and young sulfide mineralization occurs in the so-called “midnight veins” (NW-SE to NE-SW directions). Some 970 veins were explored of which 370 were subsequently mined for uranium mineralization.

The vein mineralization is complex; however, six different stages can be distinguished:

- Old quartz with galenite, sphalerite and pyrite;
- Quartz with calcite, ankerite and fluorite;
- Carbonate and uraninite with coffinite;

- Carbonate arsenide with rare Ag and Bi;
- Sulfide arsenide with rare Ag and As;
- Young sulfide with calcite, galenite and sphalerite.

In total, 278 minerals have been discovered in Jáchymov veins of which 70 contain uranium.

In the period 1946 – 1964 some 9.6 km of shafts, 179 km of chimneys and 814 km of galleries were constructed during the exploration and exploitation stages and a total of 7,950 t of uranium was mined.

Zadní Chodov

The deposit is situated in West Bohemia around 60 km W of the city of Plzeň in the Moldanubicum of the Český Les near its contact with the Bor granite pluton of Variscan age in the proximity of the West Bohemian deep fault.

Migmatitized biotitic and cordierite biotitic gneiss with intercalations of amphibolite and quartzite characterise the surroundings of the ore bodies; sills of granite and diorite are common.

Uranium mineralization is bound to dislocation zones with strong hydrothermal alteration. The direction of the zones is N-E with a steep dip to the east. The length of the ore-bearing bodies is 20 – 350 m with a thickness of few decimeters up to 6.2 m. The prevailing forms of mineralization consist of disperse or brecciate forms and nests.

Uranium mineralization was found to be made up of coffinite, brannerite, uraninite and uranium blacks with a small amount of pyrite, chalkopyrite and galenite. The age of the brannerite was set at 140 – 165 Ma (the regeneration of Variscan mineralization).

A.1.3 Uranium mineralization in the Hroznětín section of the Sokolov Basin

The Hroznětín section of the Sokolov Basin, recently totally separated by denudation from the main part of the basin in the west is the only part of the Bohemian Massif where uranium mineralization bound to Tertiary sediments was present in a minable amount. All uranium deposits and occurences in Tertiary sediments belong to the other deposit types according to /IAEA 09/, namely to uraniferous coal and lignite deposits. This type is characterized by the elevated uranium content in lignite/coal and in clay and sandstone immediately adjacent to lignite.

Historically, 10 indications of uranium mineralization were explored in the Hroznětín section of the basin while an additional 4 indications were explored in isolated relics of Tertiary sediments outside the Hroznětín section.

Five small deposits were subsequently mined in the Hroznětín section of the basin as the result of geological exploration; their geographical position is shown in Fig. 2.9 and the relevant basic technical data is presented in Tab. A.4.

Tab. A.4 Technical data on deposits in the Hroznětín section of the Sokolov Basin

Deposit	Exploration/mining	Opening	U production [t]
Hájek South*)	1965 - 1978	Open pit	241.4
Hájek North	1976 - 1978	Underground leaching	?
Ruprechtov I	1964 - 1969	3 open pits	53.3
Ruprechtov III	1964 - 1969	Open pit, shaft	
Odeř	1963 - 1966	Open pit, shaft	61.1

*) 0.85 mio. m^3 of basalt for crushed stone, 0.25 mio. m^3 of raw kaolin and an unknown amount of bentonite were also obtained.

The economic importance of these accumulations was found to be very low, indeed a mere 356 t U was mined in the basin, i. e. approximately 0.3 % of the total uranium production of the Czech Republic.

The extreme horizontal and vertical variability both in terms of the thickness of the uranium - bearing layer and uranium content led to a large discrepancy between estimated reserves and the actual amount of ore mined; in some cases this led to the premature termination of mining activities /KLE 71/.

The **Hájek South** deposit located near the recent southern limit of the Hroznětín section (Fig. A.3) makes up the most important deposit in the area. The uranium mined from this deposit represented nearly 68 % of the uranium production of all the Tertiary sediment deposits. The deposit is situated in a trough, running in the NNW-SSE direction, which highly probably is of tectonic origin and was formed during the denudation of the granite surface and the deposition of basal Tertiary sediments. Uranium geologists have interpreted the basal Tertiary sediments deposited on the deeply-kaolinized surface of Karlovy Vary - Eibenstock granite as those of the Staré Sedlo Formation /KLO 94/; the sediments are made up of sandstone, predominantly coarse grained, and quartzite. In the upper part of the sequence, which has an average thickness of 3 – 4 m, an admixture of tuff is evident. The presence of volcanogenic material indicates the Davidov Member of the Nové Sedlo Formation /PES 10/.

The sedimentation of the Chodov Member of the Nové Sedlo Formation begins with a sequence of grey tuff with an organic admixture as well as with thin layers of organic-rich clay and thin seams of coal with a total thickness of up to 9 m; four uranium-bearing layers are also present in this sequence the thickness of which varies from 1 – 2 m. The predominant part of uranium mineralization is bound to coal seams and organic-rich clay. Mineralization in the volcanoclastic rocks is less common.

The dip of the sequence containing the Uranium-bearing layers is 10° – 20° to the north with a maximum depth of 85 m in the Hájek South deposit; uranium mineralization is present in finely dispersed form and the uranium minerals uraninite and coffinite have been discovered. In addition, uranium blacks are also present. The most common form of uranium mineralization consists of the sorption of uranium into organic material, pyrite, apatite and iron oxides and hydroxides. The average uranium content of the ore historically extracted from the Hájek South deposit was 0.088 %; all the estimated economic reserves of the deposit have been mined. Kaolin, basalt for crushed stone production and bentonite were mined at the same quarry.

The uranium-bearing horizon is covered by a layer of ash tuff with biotite. The rock is predominantly argilitized and could be used as low-grade bentonite. The minimum thickness of this sequence is 20 m in the southern part of the deposit increasing in a northerly direction.

Two flows of pyroxene olivine basalt in the Hájek South deposit provide examples of the sporadic presence of effusive rocks in the Hroznětín section of basin.

For the **Hájek North** deposit located in the middle part of the Hroznětín section (Fig. A.3) the lithology of the Tertiary sediments and their stratigraphy is very similar to that of the Hájek South deposit. Three uranium-bearing layers were discovered in this deposit; the lowermost layer lies in sediments of the Staré Sedlo Formation (according to interpretation of uranium geologists) and consists of a wavy sheet varying in thickness from 0.15 – 2.77 m with a size of approximately 400 m by 130 m and a depth between 88.7 m and 105.7 m beneath the recent surface. In contrast to the Odeř deposit and boreholes NA3, NA5 and NA14, there is no information in reports available which would allow a decision as to whether the uranium-bearing sediments belong to the Staré Sedlo Formation or the Davidov Member of the Nové Sedlo Formation.

The upper two layers are situated in the lower part of the Nové Sedlo Formation. Their thicknesses fluctuate between 0.7 m and 0.9 m. The uranium-bearing layers, at a depth of 48 – 67 m, are made up of tuff with an organic admixture and abundant thin layers of organic-rich clay and coal seams.

The form of uranium mineralization is very similar to that of the Hájek South deposit; the average uranium content of the ore was calculated at 0.154 %. The experimental underground leaching of the lowermost layer commenced in 1976, for which a total of 43 boreholes were sunk. Despite the positive results of experimental leaching, work at the site ceased due to the refusal to grant a mining licence. The volume of the uranium obtained is not available.

At the **Ruprechtov I** deposit situated in the proximity of the SW corner of the Hroznětín section /KLE 71/ uranium mineralization was bound to the basal part of the Nové Sedlo formation which is made up of tuff, partly argilitized, with abundant intercalations of organic-rich clay and a thin coal seam. The type of mineralization is not described in the afore-mentioned report, but it is not unreasonable to assume that it is the same as that of the Hájek South deposit.

The deposit was mined by means of three open pits, with a maximum depth of 13 m, located on either side of the Karlovy Vary - Hroznětín road near to the turning to the village of Ruprechtov. A pond situated near the road is a remnant of the Ruprechtov 1 open pit.

There was a very large difference between the estimated reserves and the results of mining at this deposit; indeed, according to /KLE 71/ no minable reserves were discovered at the Ruprechtov III open pit.

The **Ruprechtov III** deposit located some 700 m NW of the village of Ruprechtov consists of an accumulation of uranium in the form of uranium blacks in fractured limonitized zones of granite /KLE 71/. The upper part of the accumulation was mined using the open pit method; however, for the extraction of the main part of the reserves a shaft 81.5 m deep was sunk and a crosscut bored beneath the expected reserves. During the construction phase only a small amount of low quality ore was discovered; subsequently, a small part of the reserves was mined over a three-month period whereupon the shaft was closed.

The **Odeř deposit**, situated between the villages of Ruprechtov and Odeř, was exceptional in terms of the uranium deposits in the Hroznětín section of the basin due to its tectonic position, the presence of mineralization in a thick coal seam and the presence of uranium mineralization in a Quaternary peat bed.

The deposit was found to be bound to a deep depression of NNW-SSE direction in kaolinized granite. The depression is tectonically predisposed and its NNW rim consists of the Krušné Hory Fault; the area of the depression is approximately 1 km^2. The development of this depression was different to that of the rest of the basin. Movements along the Krušné Hory Fault led to a drop in the bottom of the depression and, consequently, very thick Tertiary sediments. The dip of the bottom of the depression is up to 60^o to the NW. The maximum thickness of the Tertiary filling is 290 m /OBR 71/.

Tertiary sedimentation commences with talus (diluvium according to uranium geologists) which is made up of boulders and blocks of granite, followed by sand and gravel to sandstone and a conglomerate with kaolin cement. Fragments of coal and volcanic material are also present. This sequence of Tertiary sediments might be interpreted as being of the Davidov Member /PES 10/. The sequence continues with sapropelite sedimentation and a coal seam with an average thickness of 13.5 m. The total area of the coal seam is 250 m x 400 m and it has a maximum thickness of 50 m. The seam is older than the Josef Member and younger than the coal seams of Sokolov Formation; thus it belongs to a group made up of intermediate seams which are known from the basal part of the Chodov Member. The seam is covered with clay with tuff intercalations.

The peat bed of Quaternary age developed only in the central part of the depression and has a maximum thickness of 4.5 m.

Four uranium-bearing layers were discovered during the exploration stage: one layer in Davidov Member sediments, two layers in a coal seam (one near the bottom, the other in the upper part) and a further layer in peat.

Uranium extraction began in 1963 in the form of a quarry and a 102.4 m deep shaft with crosscuts at 70.1 m and 95.1 m below the surface. The mine was abandoned in 1966, when the coal seam caught fire; a total of 61 t of uranium has been extracted.

A.2 Description of applied methods (cf. Chapter 3)

This Annex contains short standardized descriptions of the most relevant methods, which have been applied in the framework of the Ruprechtov Natural Analogue study. The respective tables all have the same structure and include key information about the functioning of a method, its application and technical details. Furthermore, the tables contain graphs summarizing key results, sketches of the apparatus, and also specific experiences obtained during the project.

Since the descriptions are limited to two pages, important references and review paper are mentioned if available. There, the reader will find more detailed information.

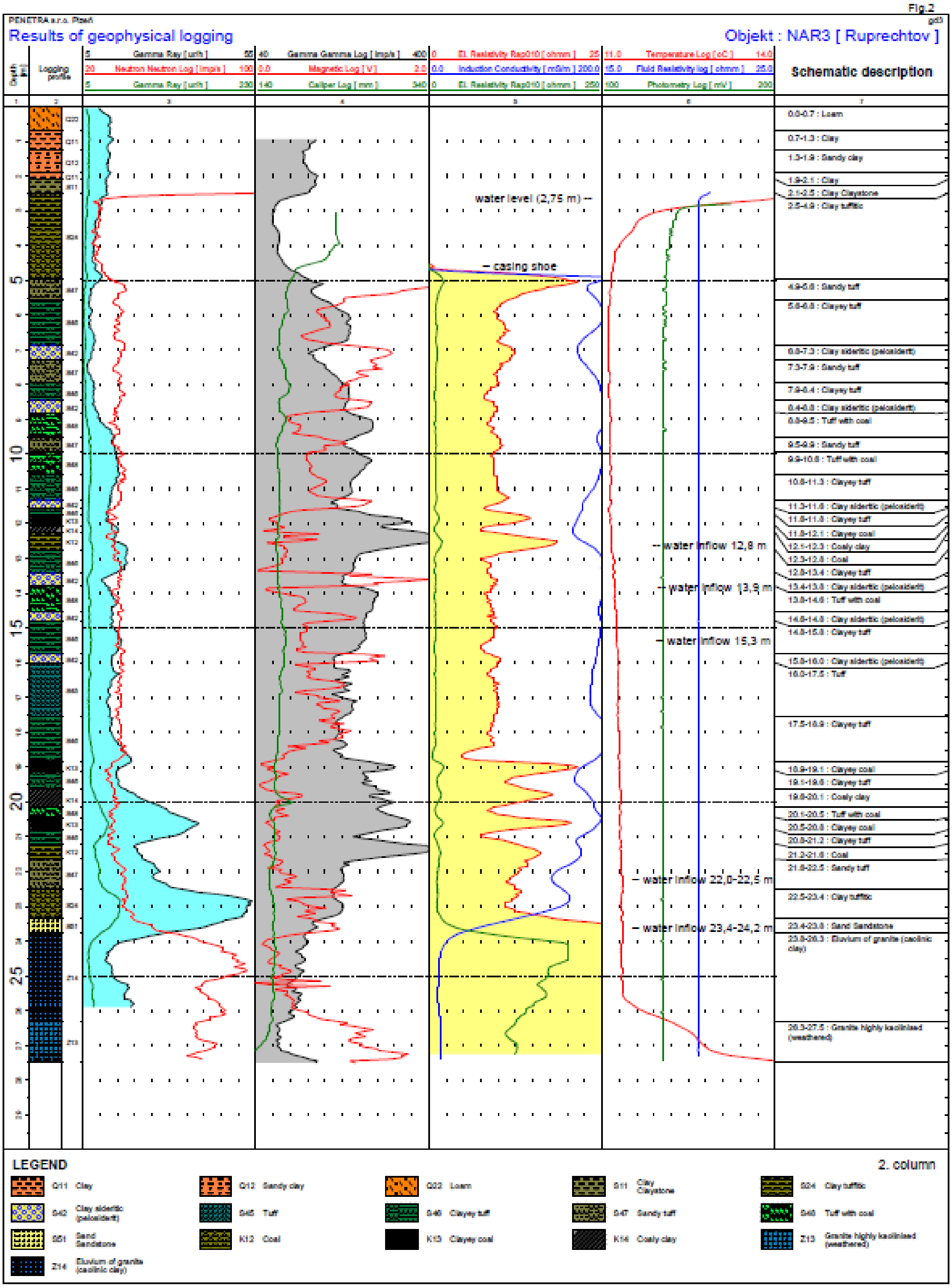
Method No. A.1: Well logging (T. Brasser, R. Červinka)

Name of method ***Application in the Ruprechtov project***	Well logging (also: geophysical well logging) Application of different logging tools in new drilled boreholes for getting in-situ and continuous, real depth related information about e. g. stratification, rock parameters, hydraulic properties, lining quality.
Device(s) / method(s) used / applied	Well logging was performed by PENETRA s.r.o., Plzeň„ using a logging unit from "Mineral Logging Systems, Inc. (MLS), USA", which was installed in an all-terrain vehicle.
Brief description of the functioning	A cable with various sensors is lowered and raised in the borehole while the readings are recorded continuously. Usually the following logs are performed and recorded: Apparent electrical resistivity of formation (RAP); apparent electrical conductivity of formation (IK); magnetic susceptibitity (MS); natural gamma radiation (GR); bulk density - gamma-gamma log (XGGDL); count rate of thermalized neutrons - neutron-neutron log (XNN); real diameter of the borehole - caliper log (DIA); temperature of borehole fluid (TM); true electrical resistivity of fluid in the borehole (RM); optical transparency of borehole fluid (FM).
State-of-the-Art and new developments	Yes, well logging is standard procedure for drilling campaigns.
Output of the method	See separate page, following this form.
Objective(s) for application in the Ruprechtov project	- Hints for final liner design (e. g. position of aquifers) - True depth of stratigraphic units - Site specific rock parameters and hydraulic properties
Practical procedure and experiences in the field	Logging is performed after completion of the drilling and cleaning of the borehole.
Applicability	Well logging can be applied to nearly all boreholes.
Limits of application	- A minimum depth of borehole is required to avoid impact of surrounding environment (depending on the length of the particular sensor) - A maximum depth might be given either by equipment available or by allowables with respect to the sensor - Borehole diameter must exceed logging-tool diameter
Uncertainties / accuracy (devices, methods, evaluation procedure)	Accuracy is specific for single sensors and therefore can't become generalized.
Method specific to defined boundary conditions	Partly yes; in case of instable borehole wall (e. g. in plastic clay formation), well logging might be restricted to methods applicable within a casing; in general, well logging is applicable to all geological media.
Experiences (pos. / neg., what to avoid)	Standard procedure also in the Ruprechtov analogue study; no specific experiences.
Effort, comments	Duration depends on depth of borehole and methods to be applied; for the Ruprechtov analogue study it has usually been in the range of few hours.

Links, references, other sources of information	- The manufacturer of MLS no longer exists - Operating company : PENETRA, s.r.o., Na Roudné 438/29, 30100 Plzeň, Severní Předměstí, +420 352 684 424 - For general information about well logging, see: http://en.wikipedia.org/wiki/Well_logging
Picture of the device	 *Borehole (well) logging tool (left), control and data recording unit (right)*

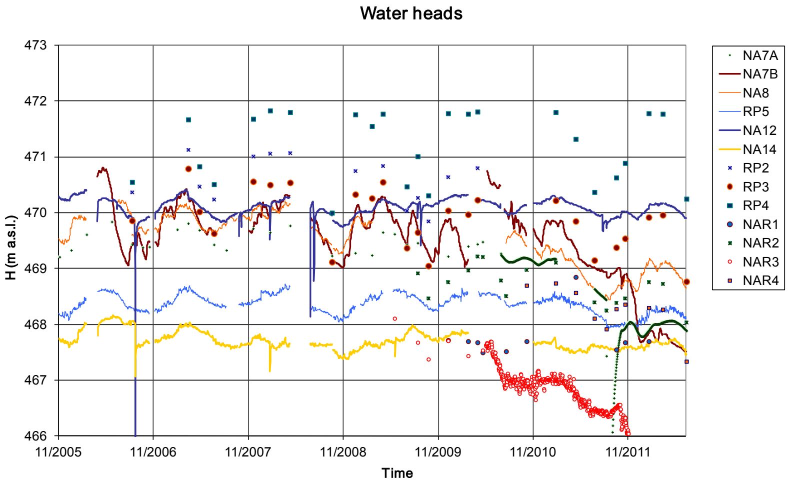
Well logging: Output of the method (example from NAR3-drilling)

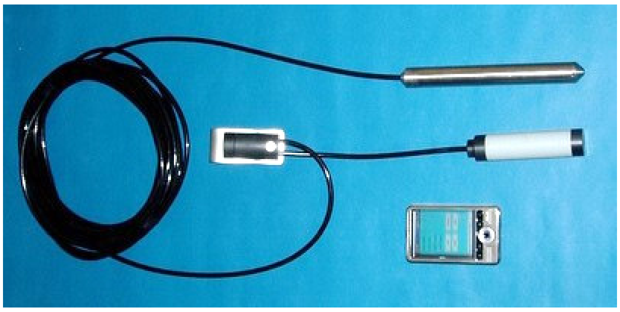
Fig.2



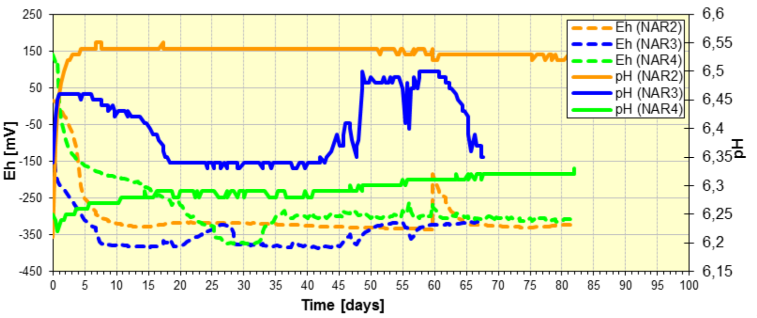
Typical output from well-logging: results from different sensors are plotted continuously against depth; in addition, e. g. the left column already represents interpretation of data (as geological profile)

Method No. A.2: In-situ monitoring 1 (R. Červinka)

Name of method ***Application in the Ruprechtov project***	In-situ monitoring - hydraulic heads Monitoring of hydraulic heads and temperatures in monitoring wells
Device(s) / method(s) used / applied	Autonomous data-logger LGR 2 HT (Geomon s.r.o., Czech Republic).
Brief description of the functioning	The datalogger operates on the principle of hydrostatic pressure measurement with automatic compensation of atmospheric pressure changes. The data of groundwater levels (and temperatures) are periodically stored in internal memory (up to 32,000 values) and can be transferred to computer via Bluetooth interface.
State-of-the-Art and new developments	Yes, datalogger are state of the art; comparable devices are available on the market (from multiple manufacturers).
Output of the method	 *Development of groundwater levels at Ruprechtov site (Tertiary aquifer and underlying granitic aquifer) from 2005-2011*
Objective(s) for application in the Ruprechtov project	Input for - Development of a hydrogeological model of the locality - Tracing influence of open pit mining development
Practical procedure and experiences in the field	- Installation of datalogger in the well, primal correction of depth by manual measurement of groundwater level - Periodical collecting of data (1x per 2.5 months) using smartphone, changing the 9V-battery 1x per 6 months, check of hydraulic heads by manual measurement
Applicability	Applicable to well diameter >5 cm.
Limits of application	- Length of cable and sensor have to be adapted to water level depths - Operating time limited by battery capacity
Uncertainties / accuracy (devices, methods, evaluation procedure)	- Hydrostatic pressure sensor o Range 40, 100, 200, 400, 800 kPa o Resolution 0.025 % o Linearity 0.1 % - Temperature sensor o Range 0 – 100°C o Resolution 0.025 % o Linearity 0.5 %

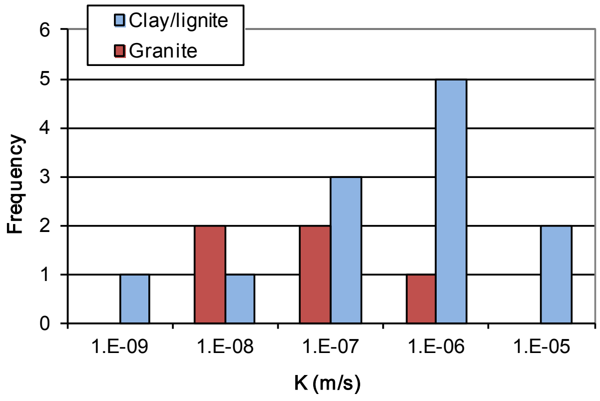
Method specific to defined boundary conditions	Equipment can be used under almost all relevant conditions; applicable to water in all geological media.
Experiences (pos. / neg., what to avoid)	System working without any problems for more than 15 years.
Effort, comments	Cost of device (LGR 2 HT) approx. 800 €, depending mainly on length of cable, i. e. on depth of groundwater level in respective borehole
Links, references, other sources of information	Manufacturer homepage for LGR 2 HT (Geomon s.r.o., Czech Republic): http://www.geomon.cz/, 10.01.2014
Picture of the device	 *Photograph of autonomous datalogger LGR 2 HT (Geomon s.r.o.)*

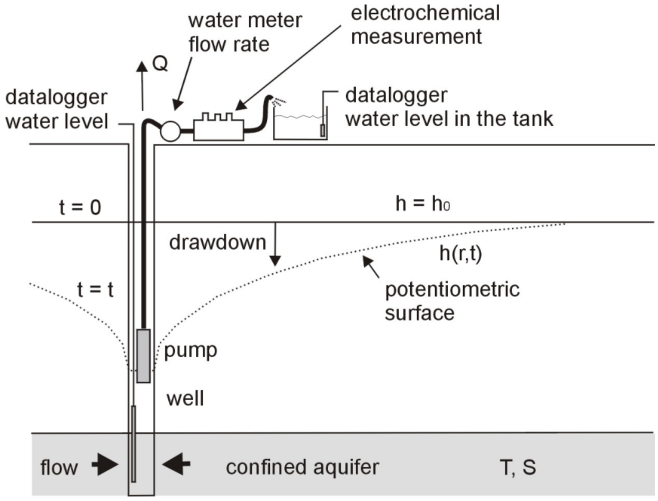
Method No. A.3: In-situ monitoring 2 (T. Brasser)

Name of method	Multi-parameter sonde for investigation of in-situ groundwater conditions
Application in the Ruprechtov project	Long-term monitoring and in-situ determination of pH- and redox-value, temperature, electric conductivity and oxygen-content in groundwater as well as water head above probe (in boreholes).
Device(s) / method(s) used / applied	HYDROLAB MS5, HACH Hydromet, 5600 Lindbergh Drive, Loveland, CO 80538 (in Germany distributed by OTT Messtechnik GmbH & Co. KG, Ludwigstr. 16, 87437 Kempten).
Brief description of the functioning	The MS5 is a portable instrument used for long-term monitoring or profiling applications; it has four configurable ports that can include a combination of the following sensors: ammonia, chloride, chlorophyll a, rhodamine WT, conductivity, depth, dissolved oxygen (LDO), nitrate, redox-value (ORP), pH, temperature, total dissolved gas, turbidity, and blue-green algae.
State-of-the-Art and new developments	Yes; comparable devices on the market from multiple manufacturers (e. g. WTW - now a brand of Xylem Water Solutions Deutschland GmbH; SEBA Hydrometrie GmbH & Co. KG).
Output of the method	 *Record of pH and ORP (Eh) values in different boreholes with MS5*
Objective(s) of application in the Ruprechtov project	Above all, determination of “real” (in-situ) pH- and redox conditions in groundwater, corresponding with U-rich layers in order to calculate the correct uranium species.
Practical procedure in the field	- Calibration of sensors acc. to manual - Setting of measurement parameters (e. g. selection of parameters, period, clock rate), check of battery quality - Setting the probe to the required depth, check of its operation - After defined measurement period reading out of stored records
Applicability	Operating temperature -5°C to +50°C; maximum depth 225 m; borehole diameter 2” minimum; memory 120,000 measurements.
Limits of application	- See ‘Applicability’ - Expected or confirmed values outside respective ranges - Time series restricted by battery life-time
Uncertainties / accuracy (devices, methods, evaluation procedure)	- Temperature-sensor: -5 to 50°C ± 0.10°C, resolution 0.01°C - pH-sensor: 0 to 14 units ± 0.2 units, resolution 0.01 units - ORP-sensor: -999 to 999 mV ± 20 mV, resolution 1 mV - LDO-sensor: 0 to 30 mg/L ± 0.01 mg/L, resolution 0.01 mg/L [for 0 to 8 mg/L]; ± 0.02 mg/L, resolution 0.1 mg/L [> 8 mg/L] - Conductivity sensor: 0 to 100 mS/cm ± 1 % of reading, resolution 0.0001 units - Water head sensor: 0 to 10 m ± 0.01 m, resolution 0.001 m; 0 to 25 m ± 0.05 m, resolution 0.01 m

Method specific to defined boundary conditions	No; except points mentioned in box 'Applicability', "Limits of application" and "Uncertainties / accuracy"; applicable to all geological media.
Experiences (pos. / neg., what to avoid)	- On-site readability of data (when connected to laptop) is strongly dependent on screen quality; this might also cause problems with setting of measurement parameters in the field - Depending on site conditions, disturbing the natural groundwater conditions by e. g sampling or just lowering the probe might last for long time (Ruprechtov site: weeks); correct measurement values can only be obtained after this time - Avoid contact of sensors with LNAPL and DNAPL liquids - Probe used before MS5 (Multi-Sensor-Modul MSM by UIT-Dresden has shown strong drift in pH- and Eh-measurements and has therefore been less suitable)
Effort, comments	- Except calibration and settings, no specific preparation is needed - Reading of data records just needs connection to computer - Time series may need several weeks in order to obtain correct values
Links, references, other sources of information	- Manufacturer homepage: http://www.hachhydromet.com/web/ott_hach.nsf/id/pa_home_e.html - Description and user manual: /HAC 11/, /HAC 06/ - Operating procedures are also described in /SWA 10/
Picture of the device	 *HYDROLAB MS5 - sonde (photograph by HACH)*

Method No. A.4: Hydrodynamic tests (R. Červinka, T. Brasser, D. Trpkošová)

Name of method	Hydrodynamic tests
Application in the Ruprechtov project	On-site measurement and evaluation of hydrodynamical parameters such as transmisivity (T) and hydraulic conductivity (K) in the filtration horizons of the wells.
Device(s) / method(s) used / applied	Standard hydrodynamic tests (pumping test, recovery test and slug test) with measurement of groundwater electrochemical values in output /ČSN 85/ - Pumps Grundfos SQE 2-55 and MP-1 (GRUNDFOS Holding A/S, Denmark), bladder pump JAK-40 - Datalogger LGR-2 (Geomon s.r.o., Czech Republic) - Electrochemical values (temperature, pH, ORP, O_2, conductivity) in special flow cell with GMH 3530 (GHM Messtechnik GmbH, Germany) Data evaluation by software AquiferTest /WAT 00/ and methods of /THE 35/ and /COO 46/.
Brief description of the functioning	Pumping test: water is pumped from a well at constant discharge and the change of water level inside the pumping well is measured. Test is finished, when a constant water level is reached. Data are in three different forms: time vs. water level, time vs. discharge and discharge vs. water level. Slug (or bail) test: a slug is inserted into a well (or removed from a well) and the change of water level inside the well is measured. Data are in one form: time vs. water level. The measurements of electrochemical values during the pumping enable to compare data with other measurements (with in-situ probe, individual sampling etc.).
State-of-the-Art and new developments	Yes; standard hydrological measurement and evaluation.
Output of the method	 *Histogram of hydraulic conductivity (K) in the monitoring wells at Ruprechtov site from both granite and clay/lignite horizons*
Objective(s) for application in the Ruprechtov project	Acquiring of hydrodynamical parameters for creating a hydrogeological model of the site; so also other values (e. g. flow velocities, flow directions) can be derived.
Practical procedure and experiences in the field	Before the hydrodynamic tests all wells were cleaned by airlift. For each well the hydrodynamic test is slightly different and individual.
Applicability	$K > 1 \times 10^{-9}$ m/s
Limits of application	See 'Method specific to defined boundary conditions'.

Uncertainties / accuracy (devices, methods, evaluation procedure)	Water level in a well with datalogger LGR-2 - 0 to 20 m, resolution 0.005 m, interval 1 and 10 min Flow rate - Water meter Helix Qn = 1.5 m^3/h, resolution ± 0.002 L/s, interval 10 min - Water level in tank with datalogger LGR-2, 0 to 1 m, resolution 0.001 m, interval 10 min, resolution ± 0.002 L/s GMH 3530 - Temperature sensor (national semiconductor LM-35 CZ): 0 to 100°C ± 0.5°C, resolution 0.025°C - pH sensor (ok 104): 0 to 14 units, resolution 0.01 units - ORP sensor (Ag/AgCl): -1999 to 2000 mV, resolution 1 mV - O_2 sensor: 0 to 30 mg/L, resolution 0.1 mg/L, water flow > 0.3 m/s - Conductivity sensor (4 Pt electrodes EC 34): 0 to 200 µS/cm, resolution 0.1 units, 0 to 2000 µS/cm, resolution 1 units, 0 to 20 mS/cm, resolution 0.01 units, 0 to 200 mS/cm, resolution 0.1 units
Method specific to defined boundary conditions	For very low permeable media (e. g. fractured hard rock, $K < 1 \times 10^{-9}$ m/s) the measurement technique and evaluation have to be adapted to water pressure tests / injection tests.
Experiences (pos. / neg., what to avoid)	The flow cell for measurement of electrochemical values should be protected against sunlight (to avoid cell heating).
Effort, comments	- Pumping test duration depends mainly on intensity of groundwater inflow into the well (starts on hours to tens of hours) - Data evaluation with special hydrological software - Costs depend on test duration and well location
Links, references, other sources of information	- All hydrodynamic tests were performed by Geomon s.r.o.: http://www.geomon.cz (26.02.2014) - Grundfos SQE 2-55 and MP-1 (GRUNDFOS Holding A/S, Denmark): http://www.grundfos.com (26.02.2014) - Autonomous dataloggers LGR 2 (Geomon s.r.o., Czech Republic): http://www.geomon.cz (26.02.2014) - GMH 3530 (GHM Messtechnik GmbH Standort Greisinger, Germany): https://greisinger.de/files/upload/de/produkte/bda/GMH3530_d.pdf (26.02.2014)
Picture of the device	 *Sketch draw of a hydrodynamic test*

Method No. A.5: Drilling technology (T. Brasser)

Name of method	Drilling technology
Application in the Ruprechtov project	Sinking of boreholes for recovery of drill cores, application of well logging, implementation of pumping tests, discharge of groundwater samples and in-situ measurements.
Device(s) / method(s) used / applied	Truck-mounted (TATRA 815) drilling rig (mostly ZIF-650M). Technology of core drilling using carbide core drill bits or DIA drill bits in granite parts. Drilling diameters range from 137 to 220 mm, but mostly ϕ 137/156 mm crown simple drill bit was used. The granite part of borehole NA6 was drilled with system WIRE-LINE.
Brief description of the functioning	The essential feature of the core drilling method consists of a rotating drill rod which is driven by a power rotary head. For core drillings (as done in the project) at the lower end of the drill pipe the core bit (crown) is mounted which cuts the core material from the rock in place and which is then slid into the pipe or barrel.
State-of-the-Art and new developments	Yes; the system of drilling with a drilling rig is in use since more than 100 yrs.
Output of the method	- Drill cores for geological description and scientific investigation - Borehole for in-situ measurements (e. g. well logging, pumping test) - Borehole for lining as groundwater monitoring well
Objective(s) for application in the Ruprechtov project	- Analyses of U-enriched sediments and surrounding rocks - Determination of rock-properties - Investigation of groundwater chemistry
Practical procedure and experiences in the field	Drilling rig has to be placed at the specified position in the field and operated according to the purpose of the drilling; provision of supplies and disposal must be ensured.
Applicability	No specific statement.
Limits of application	- The location must be accessible to the drilling rig - The geological strata underground must ensure certain stability of bore surface
Uncertainties / accuracy (devices, methods, evaluation procedure)	Quality of drill core and stability of drill hole are strongly dependent on geological formation.
Method specific to defined boundary conditions	No; in general, drillings are possible in all geological formations; depending on rock properties, mainly the core bit has to be adopted.
Experiences (pos. / neg., what to avoid)	No specific experiences.
Effort, comments	- Drilling is an essential tool for getting material and information from geological underground without any alternatives - Costs are strongly dependent on depth and width of the borehole, also well treatment, lining, equipment etc.; therefore they can't become generalized
Links, references, other sources of information	- Drilling company: http://www.geoindustry.cz/ - For general information: http://en.wikipedia.org/wiki/Drilling_rig#Hydraulic_rotary_drilling

Picture of the device	 *Photograph of drilling rig on TATRA 815 truck during operation at Ruprechtov site*

Method No. A.6: Drill core sampling (T. Brasser)

Name of method ***Application in the Ruprechtov project***	Drill core sampling Recovery and storage of redox-sensitive drill core material for scientific investigations and analyses.
Device(s) / method(s) used / applied	Insertion and sealing of the drill core concerned into commercially available PVC (sewer) pipe.
Brief description of the functioning	After short inspection of just obtained drill core (e. g. stratigraphic classification, gamma-scan) and decision on their suitability for corresponding analyses, the respective drill core will be handled and sealed as explained elsewhere (see Chapter 3.2).
State-of-the-Art and new developments	Yes; appropriate procedure that has proven effective in the project.
Output of the method	 *Drill core sealed in PVC (sewer) pipe, replacing the ambient atmosphere in the pipe by nitrogen*
Objective(s) for application in the Ruprechtov project	Investigation of redox-senitive elements, resp. phases (e. g. U, Fe) needs handling of core material avoiding any impact of oxygen (air, atmosphere).
Practical procedure and experiences in the field	Placing of drill core in a plastic half-shell for easier on-site inspections, thereafter pushing the half-shell with core into a PVC (sewer) pipe, sealing of front sides by appropriate tight cover, and replacing atmosphere in the void space of the tube by an inert gas (e. g. N_2).
Applicability	Applicable to all kinds of drill cores.
Limits of application	No limits known; might not be practicable with large-diameter cores.
Uncertainties / accuracy (devices, methods, evaluation procedure)	No information required or possible.
Method specific to defined boundary conditions	No, applicable to all kinds of drill cores.
Experiences (pos. / neg., what to avoid)	Matching diameter of PVC-tube reduces void space in the tube after inserting the drill core, and volume of inert gas needed.
Effort, comments	Easy, cheap and effective procedure.
Links, references, other sources of information	Pipes available at plumbing suppliers or building-centers, no special link or reference necessary.

Picture of the device	 *Air-tight sealed drill core for transport and storage of redox-sensitive material*

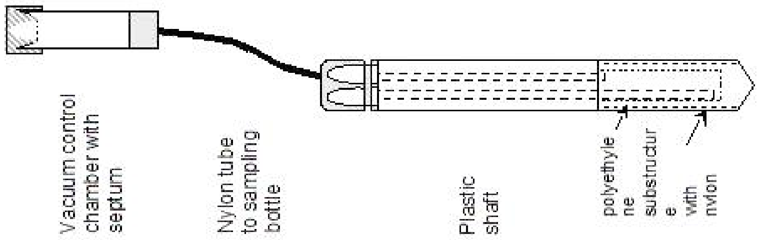
Method No. A.7: Groundwater sampling (T. Brasser)

Name of method	Groundwater sampling
Application in the Ruprechtov project	Discharge of groundwater samples for chemical and isotope analyses.
Device(s) / method(s) used / applied	Method to take groundwater samples is represented mainly by a combination of commercially submersible pump, hose line uphole and an appropriate set of screw cap tubes, resp. bottles (ranging from app. 10 mL up to 60 L) for transport to and storage in the lab.
Brief description of the functioning	Pump is installed or temporarily lowered down to the groundwater horizon to be sampled within the casing of a borehole. Filter tubes at relevant depths of the casing allow for groundwater inflow into the lined borehole and pumping the water uphole.
State-of-the-Art and new developments	Yes, method is widely used.
Output of the method	Groundwater samples for chemical and isotope analyses.
Objective(s) for application in the Ruprechtov project	Mainly chemical analyses; groundwater sampling for specific issues is described at the corresponding points of this annex.
Practical procedure and experiences in the field	Beside operation of the pump and filling the bottles, treatment must partly be carried out in the field (or pre-arranged in the lab, where possible); filtration is a special need for certain kinds of analysis see Tab. 3.3 for details).
Applicability	In principle, applicable to all lined boreholes with water table.
Limits of application	- Low hydraulic conductivity of the horizon to be sampled may yield in non-sufficient inflow of groundwater into the borehole - The pump performance must be in compliance with the water column to be pumped
Uncertainties / accuracy (devices, methods, evaluation procedure)	One has to be aware, that pumping in the described way from a certain depth is linked with inevitable changes of temperature and pressure; therefore it is to be reckoned with changes in speciation and/or precipitation.
Method specific to defined boundary conditions	No; applicable to boreholes in all geological media (see also “Limits of application”).
Experiences (pos. / neg., what to avoid)	- Pressure filtration was needed, since suspended particles did clog the filters fast and made a hand filtration almost impossible (self-constructed device by ÙJV, assembled from app. 1 m PVC tube, adapted filter-unit and pressurization adapter for nitrogen from pressure cylinder) - Sufficient energy supply must be kept ready (e. g. by 12 V car batteries) - In case of high water column, several pumps can be cascaded - Already filled bottles should be stored in cool, dark place and transported to the lab in short term
Effort, comments	- Easy, cheap and effective procedure - At higher requirements (e. g. continuous operation, pump capacity), special stainless steel pumps are available (e. g. Grundfos MP 1), connected with a price factor of up to app. 100
Links, references, other sources of information	No special manufacturer to be listed; standard product for garden and camping, available in shops or building-centers.

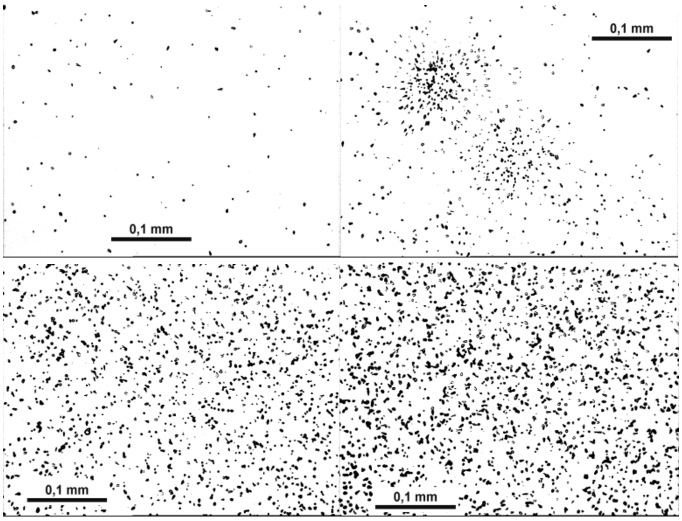
Picture of the device	 *Commercial 12 V submersible pumps as used in the project (scale: 10 cm-range) (photographs by manufacturers)*

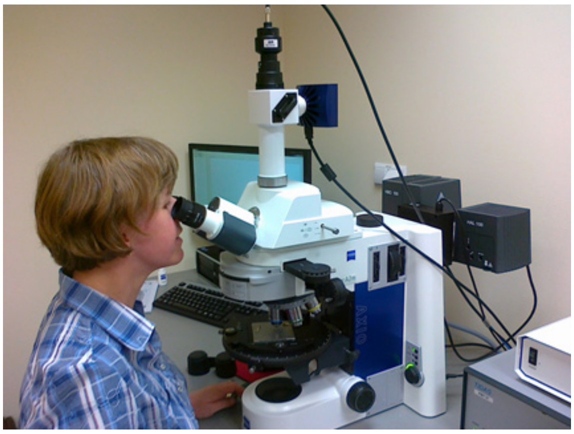
Method No. A.8: Soil water sampling (T. Brasser)

Name of method ***Application in the Ruprechtov project***	Soil water sampling Extraction of soil solution for the investigation of all kinds of inorganic solutes.
Device(s) / method(s) used / applied	Plastic suction cup, produced and distributed by ecoTech Umwelt-Meßsysteme GmbH, Bonn, Germany.
Brief description of the functioning	For taking soil water, a vacuum inside the suction cup is generated by a hand pump. The penetrating soil water is collected in the cup or additional bottle and then removed for analysis.
State-of-the-Art and new developments	Yes; established method in soil science. The suction cup used was developed especially for solutes with high sorption coefficients which cannot be extracted by any other suction cup materials with such a high yield. Its porous part is a sandwich construction consisting of a nylon membrane filter and a porous polyethylene substructure. The wide pores of the cover shield (500 µm) allow intensive contact to the soil texture. This is needed for hydraulic continuity and an accurate extraction of soil solution.
Output of the method	 *Soil water samples, obtained with suction cups*
Objective(s) for application in the Ruprechtov project	Investigation of hydro-geochemial conditions in near-surface strata.
Practical procedure and experiences in the field	Suction cup is installed in a hand drilled predrilling of app. same diameter; if needed, the cup must be slurried to ensure close contact to the soil; the preset vacuum needs to be checked.
Applicability	Soil, unconsolidated sediment.
Limits of application	Close contact between suction cup and soil resp. sediment is needed so that the vacuum is effective.
Uncertainties / accuracy (devices, methods, evaluation procedure)	No information required or possible.
Method specific to defined boundary conditions	See ‘Limits of application’.
Experiences (pos. / neg., what to avoid)	- Protection of aboveground parts is not provided by the manufacturer but required - Long time needed for sampling (hours up to days) may result in chemical changes of the soil water and/or precipitation

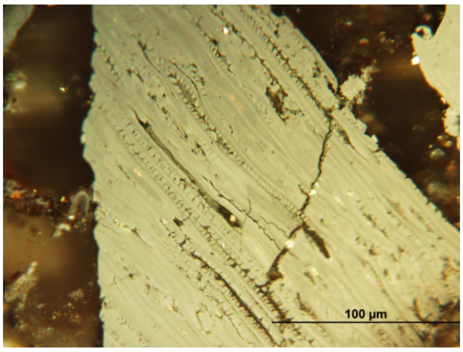
Effort, comments	- Easy to handle - Low costs - Time needed depending on soil properties (hours - days)
Links, references, other sources of information	- Manufacturer homepage: http://www.ecotech-bonn.de/en - Operational manual /ECO 00/
Picture of the device	 *Sketch draw of a suction cup (diameter app. 20 mm, length in scale)*

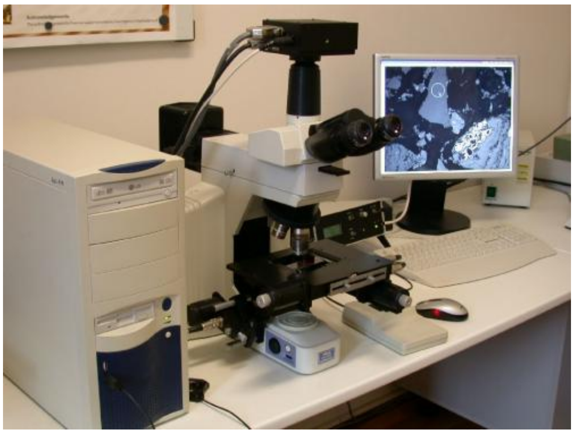
Method No. A.9: Autoradiography (J. Janeczek)

Name of method ***Application in the Ruprechtov project***	Micro-autoradiography Spatial distribution of alpha-emitters in rock samples; estimates of the amount of alpha-emitters (sources of radioactivity).
Device(s) / method(s) used / applied	Nuclear emulsion C-39, polarizing microscope M3500M James Swift equipped with Panasonic WV-CP410 camera, image analysis computer software Multiscan 8.0.
Brief description of the functioning	A flat polished surface of a rock sample is attached to the plate covered by nuclear emulsion and is left in a complete darkness for several months (at least 3 months). Afterwards, the plate is washed in 6N NaOH solution at 60°C for 8 hours to reveal alpha tracks. The alpha tracks are then observed under the polarizing microscope and micro-photographed. The obtained digital images are subsequently analyzed by using the Multiscan 8.0 image analysis software. The density of alpha tracks is estimated from the degree of the darkness of the image.
State-of-the-Art and new developments	Yes; Micro-autoradiography is a classic method to detect sources of alpha-tracks, i. e. radioactive minerals and their spatial distribution. However, usually it is used qualitatively to visualize the distribution of radioactive minerals. The application of the computerized image analysis to the Ruprechtov samples enabled quantitative estimates of the amount of radioactive minerals.
Output of the method	 *Results of micro-autoradiography of sample NA6-36 from Ruprechtov. Each image shows different part of the sample with various concentrations of alpha-emitters (radioactive minerals). The number of alpha-tracks (black dots and streaks) has been calculated using the image analysis. The upper right image shows two distinct sources of alpha emission (mineral grains). The lower right image shows uniform high-density distribution of alpha-tracks resulting from concentration of numerous tiny grains of radioactive minerals*
Objective(s) for application in the Ruprechtov project	The method pinpoints major concentrations of radioactive minerals and enables to visualize their spatial distribution. It is useful in distinguishing between primary (e. g. detrital) concentrations of radioactive minerals (e. g. in relation to sedimentary textures) from secondary radioactive minerals (i. e. those that formed as a result of alteration of the primary minerals and migration and subsequent precipitation of released radionuclides).

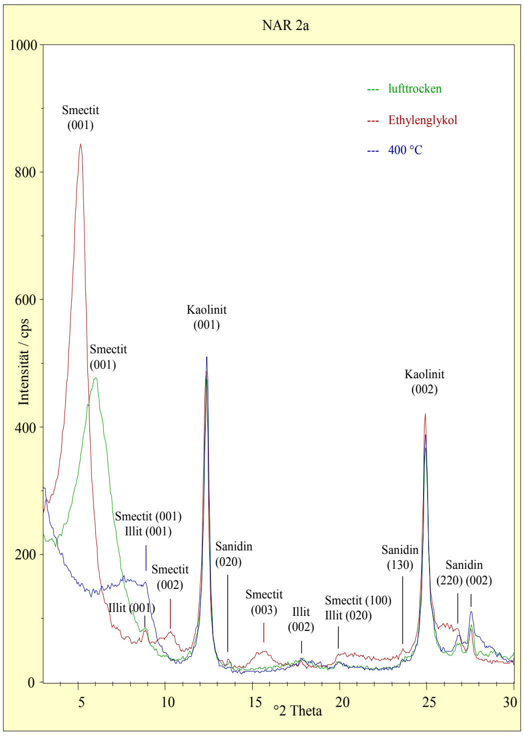
Practical procedure and experiences in the field	Standard rock sampling.
Applicability	Method applicable to rock samples containing radioactive minerals even in minor quantities.
Limits of application	Definitely time consuming method; it requires several months to obtain good quality images; however, today digital autoradiography is available due to advances in detection techniques that accelerate the process of imaging and shorten the analysis to hours.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Qualitative and simple method useful for detecting the sources of alpha tracks and their spatial distribution in the sample. It is highly sensitive to even trace concentrations of radionuclides under the condition of the properly chosen time of exposure. Calibration autoradiographic images by using reference samples with known contents of radionuclides may turn this method into quantitative determination of specific sample activity. Uncertaintity may arise from overlapping alpha-tracks leading to the overestimation of the iactivity of the radiation source.
Method specific to defined boundary conditions	Applicable to rocks with radioactive minerals.
Experiences (pos. / neg., what to avoid)	The time of exposure of nuclear emulsion to alpha-radiation is crucial. Too short exposure may result in underestimating the amount of alpha-track emitters. Experience in using the method is prerequisite; otherwise, trial and error approach is necessary. Modern detection techniques are recommended instead of classic nuclear emulsion to accelerate the analysis and to avoid a chemical development of images. Basis for other microscopic methods (µ-XRD, SEM, TEM, …).
Effort, comments	- Sample preparation: cutting the sample and polishing to obtain flat surface - Duration of the measurement(s) at least 3 months (with modern techniques: hours to days) - Data evaluation: approximately one hour - Costs (device / procedure / analysis): total 50 € per sample
Links, references, other sources of information	The Polish manufacturer of nuclear emulsion C-39 (CELOR, Warsaw) finished production of nuclear emulsion-covered plates.
Picture of the device	 *Polarizing microscope used for autoradiograph image analysis*

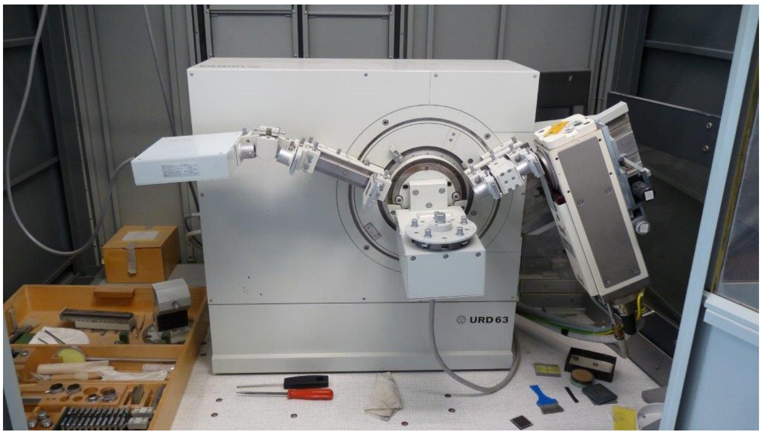
Method No. A.10: Micropetrography (R. Červinka)

Name of method ***Application in the Ruprechtov project***	Micropetrography Characterization of sedimentary organic matter (SOM) by methods from coal micropetrography; characterization of plant remnants according to their origin, morphology and optical qualities dependent at degree of coalification.
Device(s) / method(s) used / applied	Light reflectances are measured using the image analysis system LUCIA and Nikon microscope with immersion lens with a magnification 100x, /ČSN 10/ Microlithotype compositions are determined using fluorescence analysis, photometric device Opton-Zeiss with magnification 45x, /ČSN 75/, /ICC 01/.
Brief description of the functioning	Measurements of light reflectances, use of fluorescence analysis.
State-of-the-Art and new developments	Standard method used in coal petrography.
Output of the method	 *Microphotography of Ulminite in a sample from borehole NA12*
Objective(s) for application in the Ruprechtov project	- Characterization of plant remnants according to their origin, morphology and optical qualities and according to degree of coalification (according to light reflectivity) - Derivation of depth and conditions of coalification.
Practical procedure and experiences in the field	From organic rich parts of borecores the thin sections are prepared; the thin sections can be prepared also from powder glued with resin.
Applicability	Mainly for all organic rich sediments.
Limits of application	Minimum content (not specified) of organic material in the rock sample.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Specifications can be found in Czech technical standards /ČSN 10/ and /ČSN 75/ as well as in /ICC 01/.
Method specific to defined boundary conditions	See "Limits of application".
Experiences (pos. / neg., what to avoid)	Method suitable for determination of depth and coalification conditions (oxic/anoxic sedimentation environment) in combination with sedimentary study.
Effort, comments	- Sample preparation as a thin section - Institute of Rock Structure and Mechanics of the ASCR, v. v. i., CZ (Ing. Ivana Sýkorová, DrSc.), preparation of thin sections 12 €/sample, degree of coalification 30 €/sample, microlithotype compositions 30 €/sample, maceral composition 35 €/sample

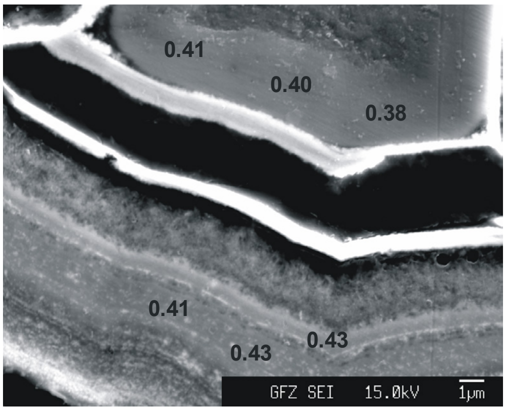
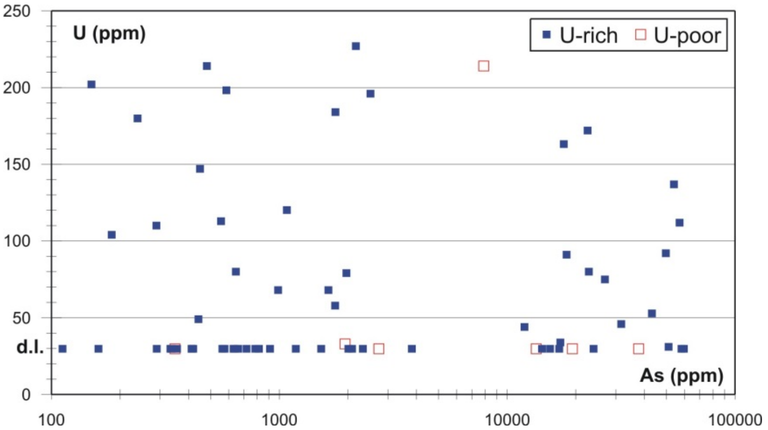
Links, references, other sources of information	International Committee for Coal and Organic Petrology http://www.iccop.org/, 11.06.2014.
Picture of the device	 *System LUCIA, Laboratory Imaging co., optical microscope NIKON (Institute of Rock Structure and Mechanics of the ASCR, v. v. i.)*

Method No. A.11: XRD (H.-J. Förster)

Name of method ***Application in the Ruprechtov project***	X-ray powder diffraction (XRD) Determination of rock modal mineralogical composition.
Device(s) / method(s)used / applied	X-ray diffractometer URD 63 (Präzisionsmechanik Freiberg, build 1985, updated 1996 and 2002) and (for special applications) XRD 3000 TT (SEIFERT, Hamburg, 1996) at Landeslabor Berlin-Brandenburg (LBB), Kleinmachnow.
Brief description of the functioning	X-ray Powder Diffraction is a method in which a beam of X-rays is directed at a fine powder of randomly oriented grains of crystalline substances. The X-rays are scattered in directions that depend on the crystal structure of the sample and the resulting X-ray diffraction pattern can uniquely identify the material.
State-of-the-Art and new developments	Although newer diffractometers with advanced software solutions are available from several manufacturer (PANanalytical, Bruker, Siemens), these older diffractometers are electronically and with respect to software packages up to date.
Output of the method	 *X-ray diffractogram (clay fraction < 2µm) of a lignite sample from borehole NAR2a*
Objective(s)for application in the Ruprechtov project	- Determination and quantification of modal mineralogy of U-rich and U-poor lignite samples - Determination and quantification of minerals constituting the clay fraction of lignite samples
Practical procedure and experiencesin the field	Stationary device in lab (not movable).

Applicability	- Principally applicable to all geological media including fluids and organic material. LBB has specialized on anorganic material, with special emphasis on the clay fraction - Quantitative analysis of bulk-rock modal composition requires 1 g of material powdered to a grain size < 32 µm - Quantitative analysis of the clay fraction requires 50 g of powdered material, from which the <2 µm-fraction will be separated
Limits of application	- Solid material must be crystalline. The total amount of amorphous substances could only be quantified as deficit to 100 % - LBB has no personal experience in the study of organic material
Uncertainties / accuracy (devices, methods, evaluation procedure)	- The relative error is ≤ 5 %, the detection limit amounts to ≤ 1-2 wt% - At LBB, the XRD results are routinely cross-checked via the element concentrations of the studied material obtained by X-ray fluorescence spectrometry (XRF) and CNS (carbon, nitrogen, sulfur) analytics; this procedure improves the quality of the output data
Method specific to defined boundary conditions	No (except amorphous minerals and unavailability of sufficient study material).
Experiences (pos. / neg., what to avoid)	XRD is particularly useful for the discrimination and quantification of clay minerals within sedimentary samples as those studied within the Ruprechtov project. U-minerals, if present, could not be identified since they occur at concentrations below detection limit.
Effort, comments	- Sample preparation may take several days until the required grain-size fractions are available for analysis. The measurements theirselves including evaluation of data take approximately 3-5 hours per sample - At LBB, full quantitative analysis including sample preparation and analysis of the clay-mineral fraction is ~ 300 € per sample. XRF plus CNS amount to ~ 150 €
Links, references, other sources of information	- General Principles of XRD /WAS 11/ - Detailed description of methodology applied at LBB /LUC 00/
Picture of the device	 *X-ray diffractometer URD 63*

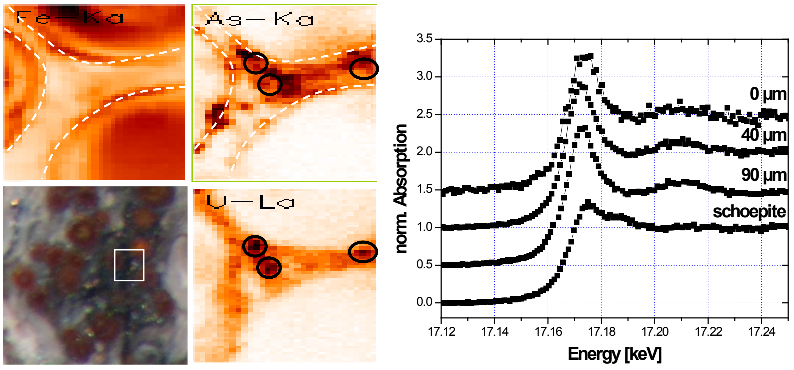
Method No. A.12: EPMA (H.-J. Förster)

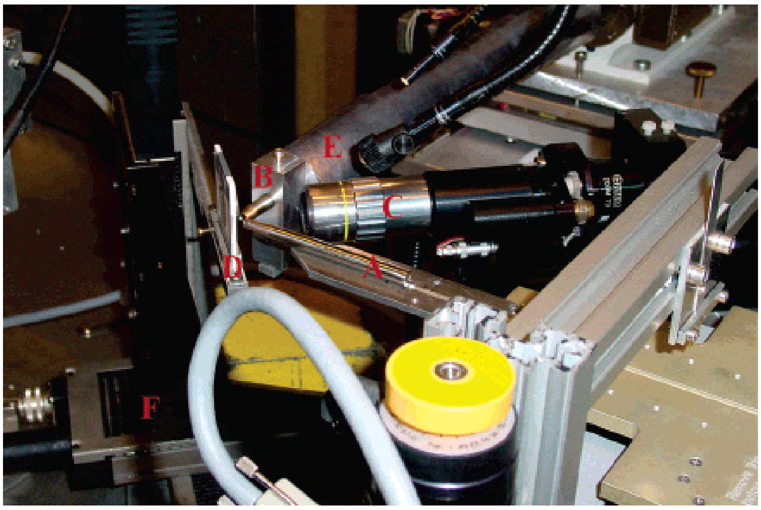
Name of method ***Application in the Ruprechtov project***	Field-Emission Electron-probe Microanalysis (FE-EPMA) Identification and quantitative analysis of U-bearing minerals.
Device(s) / method(s)used / applied	JEOL JXA-8500-F Field Emission Electron Probe Microanalyzer.
Brief description of the functioning	The electron microprobe technique employs an electron beam accelerated to a selected voltage of 3-20 kV, and focused on the surface of the sample. The electron beam is typically operated at probe currents of 5 to 50 nA and the beam spot size can vary from 0.04 to 20 µm. The volume excited by the electron beam varies in the range of about 0.03 to 4.5 cubic microns. The target (sample) generates characteristic X-rays, whose intensities are measured with wavelength or energy-dispersive spectrometers. Detection limits are typically between 20 and 400 ppm. The 8500-F has a thermal field-emission cathode to achieve ultra micro-area analysis.
State-of-the-Art and new developments	Yes.
Output of the method	 *Uranium concentration (UO_2 in wt%) of brookite intergrown with pyrite (bright)*  *Scatter plot of U versus As in pyrite from U-poor and U-rich lignite samples*

Objective(s)for application in the Ruprechtov project	- Identification and quantitative analyses of primary radioactive minerals in fresh granite (monazite, xenotime, uraninite) - Identification and quantitative analyses of secondary U-bearing minerals in altered granite and lignite (uraninite, brookite, anatase, pyrite) - Documentation of mineral textures and structures using secondary-electron (SE) and backscattered-electron (BSE) images
Practical procedure and experiences in the field	Stationary (not movable) device.
Applicability	To any solid anorganic material that is vacuum- and electron-beam stable.
Limits of application	- Quantitative analysis employing characteristic X-rays and reference standards can be made of all elements except H, He & Li - Samples are thin sections, thick sections or grain mounts that must be polished in order to generate plane surfaces.
Uncertainties / accuracy (devices, methods, evaluation procedure)	- The analytical uncertainties or normally on the order of <1 % for major elements, 1 – 5 % for minor elements, and > 5 % for trace elements - Special care must be devoted to the analysis of minerals that easily decompose under the electron beam and, thus, experience surface damage. Problematic are water-bearing species, certain carbonates, sulfates etc.
Method specific to defined boundary conditions	- Medium must be solid - An air-conditioned lab is required
Experiences (pos. / neg., what to avoid)	Method has greatly improved the knowledge about U-concentrations down to the lower ppm-level in primary and secondary minerals of grain sizes down to a few micrometers.
Effort, comments	- Sample preparation involves the cutting of rock samples and manufacturing of polished study material (takes at least several days) - Single-spot quantitative analyses take between 2 and 30 minutes depending on the number of elements to be analyzed and their concentrations - Generation of X-ray elemental distribution maps requires several hours - Between about 100 and 300 € per hour
Links, references, other sources of information	Manufacturer homepage: http://www.jeol.co.jp/en/products/detail/JXA-8530F.html
Picture of the device	 *JEOL JXA-8500-F workplace*

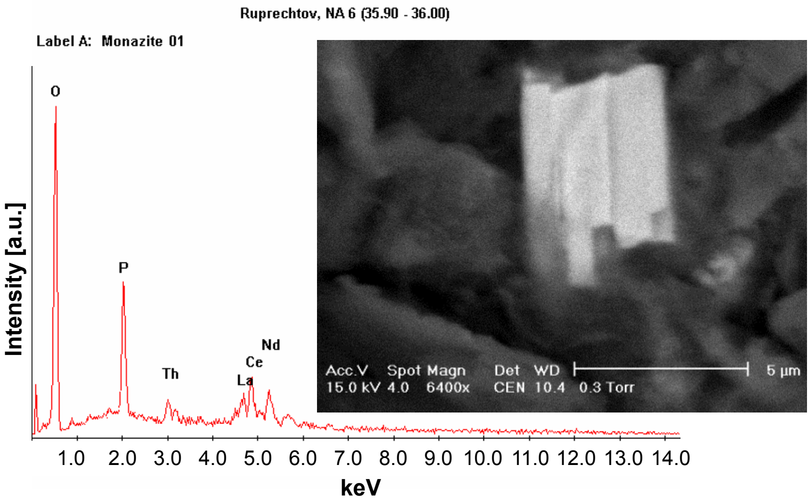
Method No. A.13: µ-XRF/µ-XAFS (M. Denecke, U. Noseck)

Name of method ***Application in the Ruprechtov project***	µ-XRF / µ-XAFS Spatially resolved µ-characterization of uranium and correlated elements in rock samples.
Device(s) / method(s) used / applied	Using focussed synchroton radiation, micro x-ray fluorescence (µ-XRF), micro extended X-ray Absorption Fine Structure (µ-EXAFS) and micro X-ray Absorption Near Edge Structure (µ-XANES) spectroscopy is applied. Measurements are performed in confocal geometry for obtained added depth resolution. Selected samples are then prepared as thin sections and investigated by combined scanning µ-XRF/µ-XRD, in order to identify element – mineral phase correlations. Measurements performed at HASYLAB, ESRF and ANKA.
Brief description of the functioning	µ-XRF: Element analysis by emission of secondary fluorescence after irradiation with focused x-ray radiation. Different focusing schemes are applied to attain different 2D spatial resolution in scanning mode. A polycapillary half-lens is used as collimating, primary focusing optic in experiments at HASYLAB, providing a beamspot of around 10-15 µm. At ANKA, a planar compound refractive lens array is used, providing a 2-4 µm beam. Comparable 2D resolution is obtained using focusing KB-mirrors at the ESRF. By a confocal geometry, resolution in the third (depth) dimension of around 10-15 µm is reached. µ-XAFS: Measuring changes in the absorption coefficient µ(E) as a function of the incident radiation x-ray energy. In the µ-XANES energy regime, near the selected element ionization energy, absorption of an x-ray photon leads to excitation of core electrons through the photoelectric effect, with the formation of many body excited states characterized by a core hole in a selected atomic core level, which are a function of the element valence and coordination environment. XANES spectra are interpreted through comparison to reference spectra („fingerprint“) or to theoretical calculations. In the higher energy µ-EXAFS, excited photoelectrons are scattered on nearest neighboring atoms. These backscattered electron waves interfere with outgoing photoelectrons, thereby producing signature interference EXAFS patterns, the frequency and intensity of which being dependent on the distance between the ionized atom and backscattering atoms and their number.
State-of-the-Art and new developments	The synchrotron techniques used are innovative and state-of-the-art. At the time, the confocal method was newly developed and our work represents the first time for its successful application to investigation of a natural sample and first µ-EXAFS ever measured in confocal geometry. The use of the LIGA fabricated planar compound refractive lens array for beam optics in the setup was also a world first. In the interim, the confocal technique has been adopted by most synchrotron laboratories.

Output of the method	Using confocal µ-XRF allows imaging of 3D element distributions; by imaging at selected energies as chemical (redox) contrast, element redox states can be mapped. We successfully did this for As(0) and As(V) distributions. By focusing the beam on hot spots identified in the element distributions and varying the incident energy, µ-XANES and µ-EXAFS are obtained, yielding valence and coordination geometry (interatomic distances, number and type of nearest neighbors) information, respectively. From µ-XRD data, 2D maps of mineral phases can be extracted. Comparing these to the element distributions reveal element associations with mineral phases.  *Left: 120 x 120 µm^2 image (2 x 4 µm^2 VxH steps) -60 µm from surface, showing that U is correlated with As on pyrite surfaces. Right: U L3 í-XANES recorded at various positions of the bore core section, at different depths below the surface indicated, and compared to U(IV) and U(VI) reference sample*
Objective(s) of application in the Ruprechtov project	Determination of 3D distribution of U and other relevant elements (As, Fe), and elemental correlations. Determination of U valence state and mineral phase, in order to assist identification of predominant immobilization mechanism on a molecular scale.
Practical procedure and experiences in the field	It is helpful to identify the localization of the element to be investigated, before analysis. Here, U hot spots were identified by autoradiography in advance.
Applicability	The method is applicable to solid materials. Spatial resolution is variable, about 2 µm at the time. Today sub-micron work is possible.
Limits of application	Technique requires access to a synchrotron, which is possible but requires long lead times of at least 6 months due to facility access procedures.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Close spectral energies of U Lα (13.6 keV) fluorescence with Rb Kα (13.4 keV) can lead to relatively large uncertainties in fits to their MCA fluorescence signals. We used an excitation energy above the U L2 edge (20.9 keV), so as to include the Lβ emission line and thereby improve the fit certainty considerably. Due to the near impossibility of correcting for self absorption of overlaying layers in confocal data, we did not quantify the element distributions. The measurments remain qualitative (relative amounts).
Method specific to defined boundary conditions	Method is restricted to elements with excitation energies below the incident radiation (around 20 keV) and without vacuum does not include light elements below Si.
Experiences (pos. / neg., what to avoid)	In situ characterization is possible; no sample preparation necessary other than cutting a bore core section. Drying and evacuation of samples is not necessary. Mixtures can be investigated without separation.

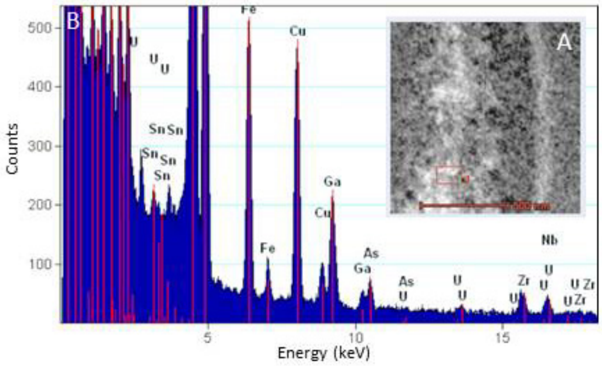
Effort, comments	- Synchroton radiation is needed to perform the method. - Simple sample preparation (cf. above)
Links, references, other sources of information	Relevant publications: /DEN 05/, /DEN 07/, /JAN 04/
Picture of the device	 *Schematic representation of the confocal setup (top, left); the sampling volume defined by the primary polycapillary (PC1) half-lens focus (full-width at half-maximum, fwhm) and the secondary polycapillary (PC2) half-lens (top, right); and a photograph of the experimental setup used (bottom). (A) PC1 half-lens; (B) PC2 half-lens; (C) microscope; (D) sample mounted on a slide frame; (E) detector head with lead shielding; (F) sample positioners /DEN 05/*

Method No. A.14: ASEM (J. Janeczek)

Name of method ***Application in the Ruprechtov project***	Analytical Scanning Electron Microscopy (ASEM) Identification and characterization of minerals in clay samples.
Device(s) / method(s) used / applied	Samples were examined by environmental scanning electron microscopy coupled with energy dispersive spectroscopy (ESEM-EDS) using a Philips XL30 ESEM instrument with EDAX Sapphire analyzer (accelerating voltage 15 kV, low-vacuum mode, H_2O pressure 40 Pa, uncoated samples).
Brief description of the functioning	REE- and Actinide-bearing mineral grains are identified using backscattered electrons (BSE) images at magnification 200 x. Contrast in BSE images comes primarily from point to point differences in the average atomic number of the sample. High atomic number nuclei backscatter more electrons and create bright areas in the image, so BSE images provided important information on particular mineral distribution. Grains selected on the basis of the BSE imagery are, qualitatively analyzed by EDS to determine elemental composition.
State-of-the-Art and new developments	The ASEM method applied for the Ruprechtov samples is conventional and commonly used. However, unlike in most SEMs, the variable-pressure SEM used in the Ruprechtov study requires almost no sample preparation prior to the analysis (no carbon-coating). Hydrated geological specimens that are either moist or wet can directly be observed without preliminary drying. In our instrument, the interior of the chamber is filled with water vapor at a pressure range of 10-100 Pa. In this type of microscope specimens may be examined using secondary and backscattered electrons and analyzed by X-ray microanalysis in their natural state, because the environment around the specimen no longer has to be at high vacuum.
Output of the method	 *BSE image and EDS spectrum of Th-bearing monazite in kaolinite from Ruprechtov drill core NA6. BSE image of monazite (bright angular grain) reveals that it is a detrital grain with no signs of chemical alteration; EDS spectrum is typical of monazite with Ce>Nd>La; a distinct peak of Th is noticeable; Detrital monazite turned out to be the major source of radioactivity in samples from Ruprechtov*

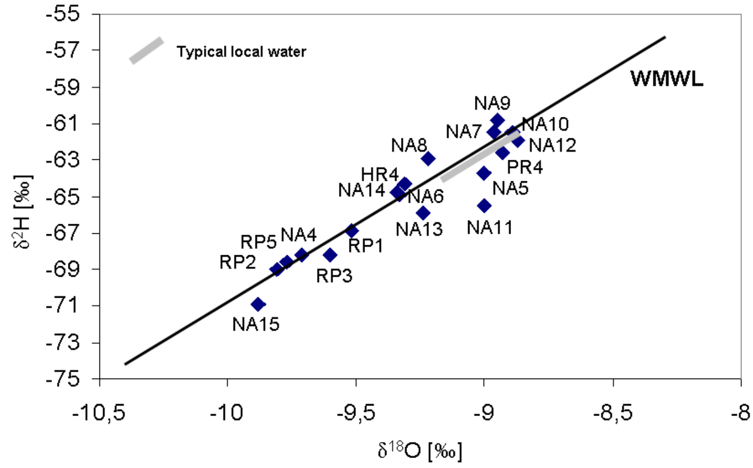
Objective(s) for application in the Ruprechtov project	Identification of minerals based on their X-ray energy spectra particularly useful for micron-sized grains; textural analysis of samples; spatial distribution of actinide-bearing minerals; detection of mineral alteration and products of this alteration.
Practical procedure and experiences in the field	Standard rock sampling; preferably flat surface of a sample to be analyzed; otherwise no special treatment is necessary. The scanning electron microscope is a stationary equipment.
Applicability	Environmental ASEM is applicable to all rock and mineral samples.
Limits of application	The resolution is 5.5 nm for BSE detector, therefore only grains > 2 µm can be observed in BSE images at magnification 200 x. Magnification limited in practice up to 50,000 x for non-metallic samples. For most elements the limit of detection by EDS is 0.2 wt.%.
Uncertainties / accuracy (devices, methods, evaluation procedure)	EDS qualitative and semi-quantitative analyses are reliable only for grains > 5 µm, because the volume of a grain has to be larger than the volume of interaction between X-rays and bulk sample.
Method specific to defined boundary conditions	Applicable to solid samples.
Experiences (pos. / neg., what to avoid)	Advantages include high spatial resolution, large depth of field and wide magnification range (12 to 50 000x) enabling observation of relatively large area and almost no sample preparation unless special requirements are needed; no negative experience, but see “Limits of application”.
Effort, comments	- Sample preparation: 15 minutes per sample - Duration of the measurement(s): depending on the mineralogical complexity of samples; on average it took 4 hours per sample - Data evaluation: 30 minutes per sample - Costs (device / procedure / analysis): 40 (20/-/20) € per sample
Links, references, other sources of information	Manufacturer homepage: - http://www.fei.com/ (as successor of Philips for scanning electron microscope) - http://www.edax.com/ (for energy dispersive detector, EDS)
Picture of the device	 *Working place for Analytical Scanning Electron Microscopy (ASEM)*

Method No. A.15: TEM (H.-J. Förster)

Name of method ***Application in the Ruprechtov project***	High Resolution Transmission Electron Microscopy (HRTEM) Search and chemical characterization of nanometer-sized Uranium minerals.
Device(s) / method(s)used / applied	FEI Tecnai F20 X-Twin transmission electron microscope (TEM) operated at 200 keV, with a field emission gun as electron source. The TEM is equipped with a Gatan Imaging Filter (GIF) Tridiem™, a high-angle annular dark-field detector (HAADF) and an EDAX X-ray analyzer with ultra-thin window. Electron transparent foils for TEM were prepared applying the focused ion beam technique (FIB). This technique allows site-specific sample preparation of TEM foils usually with the dimensions 15 x 10 x 0.15 µm. Ga-ions accelerated at 30 keV are used to sputter material from the target. The TEM is operated at Deutsches GeoForschungsZentrum GFZ, Potsdam.
Brief description of the functioning	Basic principle of TEM is similar to its optical counterpart, the optical microscope. The major difference is that in TEM, a focused beam of electrons instead of light is used to "image" and achieve information about the structure and composition of the specimen. An electron source usually named as the “Gun” produces a stream of electrons which is accelerated towards the specimen using a positive electrical potential. This stream is then focused using metal apertures and magnetic lenses called “condenser lenses” into a thin, focused, monochromatic beam. HRTEM is an instrument for high-magnification studies of nanomaterials. High resolution makes it perfect for imaging materials on the atomic scale. A main advantage of a TEM over other microscopes is that it can simultaneously give information in real space (in the imaging mode) and reciprocal space (in the diffraction mode).
State-of-the-Art and new developments	Titan TEMs offer a higher spatial resolution (~ 0.5 x) than the Tecnai-type TEM operated at GFZ (~ 1.7 x).
Output of the method	 *(A) High-angle angular dark-field (HAADF) image of a fine intergrowth of pyrite (bright) and Ti oxide (dark) in a lignite sample from Ruprechtov.(B) EDX spectrum of the area marked by a red rectangle in Image A indicating that pyrite contains detectable amounts of As, while Ti oxide has substituted measurable concentrations of U, Zr, Sn, and Nb*
Objective(s)for application in the Ruprechtov project	- Search for discrete U-minerals precipitated on the surface or within secondary pyrite and Ti-oxid in lignite - Clarification whether slightly increased U concentrations measured by FE-EPMA are related to discrete minerals or U substituted in the mineral lattices

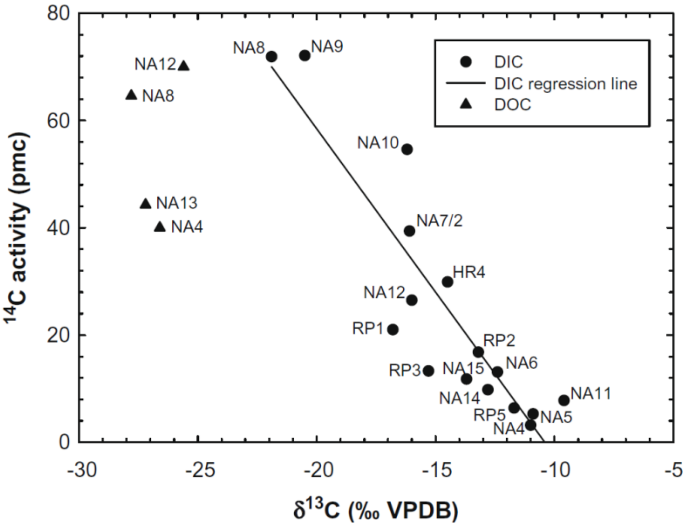
Practical procedure and experiences in the field	No field procedure, stationary (not movable) device in Lab.
Applicability	The FEI Tecnai™ TEMs are designed to offer an universal imaging and analysis solution for life sciences, materials sciences, geological sciences, nanotechnology, and the semiconductor and data storage industries.
Limits of application	Almost none.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Quantitative mineral data are normally aquired by standard-free EDX analysis, the precision and accuracy of which is poorer and the elemental detection limits are higher (~ 0.1 – 0.2 g/kg) relative to WDS analysis performed, for instance, by FE-EPMA.
Method specific to defined boundary conditions	No (except that an air-conditioned lab is required).
Experiences (pos. / neg., what to avoid)	Since discrete U-minerals may occur in grain sizes of lowermost nanometer level, this method was assumed to be one of few that is capable to prove them; nevertheless method has not given proper credit during the Ruprechtov project; it is strongly recommended to apply it more widely in future projects.
Effort, comments	- Sample preparation and study of each foil requires about the same time (several hours) - The costs for analysis have to be negotiated and are highly variable depending on what are the wishes of the client
Links, references, other sources of information	- Manufacturer homepage: http://www.fei.com/products/tem/tecnai/ - General principles of HRTEM /WIL 96/, /GIA 05/ - Detailed description of the instrumentation and methodology applied at GFZ, see /WIR 04/, /WIR 09/
Picture of the device	 *HRTEM workplace at GFZ*

Method No. A.16: **Stable isotopes (U. Noseck, M. Dulinski)**

Name of method ***Application in the Ruprechtov project***	Stable isotopes Analysis of stable isotopes (^2H, ^{18}O) in groundwater.
Device(s) / method(s) used / applied	1. ^2H: Zn reduction method /COL 82/ 2. ^{18}O: CO_2-equilibration method /EPS 53/ 3. Final analysis by dual inlet mass spectrometer
Brief description of the functioning	Zn reduction for ^2H: 10 mg of water is reduced with 0.3 g Zn metal in a sealed tube at 520°C to prepare hydrogen for isotopic analysis. After reaction the tube is attached directly to the isotope ratio mass spectrometer (IRMS) without further processing. CO_2-equilibration for ^{18}O: Equilibration of app. 12 mL (N.T.P.) CO_2 gas with 2 g of water in a thermostated bath at 28°C for 4 hours with shaking and then analysis of about 2 mL aliquot of the gas in a mass spectrometer.
State-of-the-Art and new developments	The method (1, 2, 3) applied at Ruprechtov is conventional and still commonly used. For selected samples the advanced laser spectroscopic method was applied using H_2O_{liquid}-H_2O_{vapor} equilibration laser spectroscopy, which is available since few years providing a fast way to obtain accurate high resolution ^2H and ^{18}O profiles from saturated and unsaturated geologic media. The precision and accuracy of the new method is comparable or better than conventional IRMS based methods. Only small samples are needed, can be conducted with dual hydrogen and oxygen isotope assays on single small core samples. Consumable and instrumentation costs are low /WAS 08/.
Output of the method	Content of ^2H and ^{18}O in water given as deviation from a standard, exemplarily shown for ^{18}O $$\delta^{18}O = \left[\frac{\left({^{18}O}/{^{16}O} \right)_{sample}}{\left({^{18}O}/{^{16}O} \right)_{standard}} - 1 \right] \cdot 1000$$ Standard: VSMOW (Vienna standard mean ocean water). Data are usually plotted as δ^2H vs $\delta^{18}O$ (see below).  *Stable isotope composition of the analysed groundwater samples in the Ruprechtov aquifer system. Bold grey line denotes isotope signature of local, recent infiltration waters*
Objective(s) for application in the Ruprechtov project	Identification of water infiltration area(s), water flow direction of the groundwater and hydraulic connections between Tertiary and underlying granite aquifer.

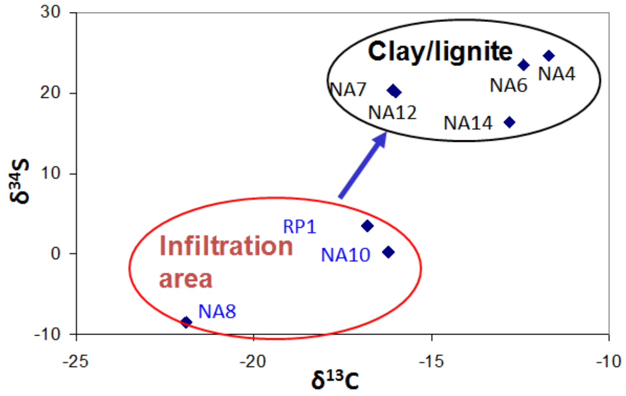
Practical procedure and experiences in the field	Standard groundwater sampling in 100 mL bottles. No special treatment needed.
Applicability	The method is applicable to all waters if an amount of 30 mL is available. With the improved laser method less water is needed and samples with (pore) water content >5 % can be analyzed.
Limits of application	- Direct measurement of water molecules, therefore no limitation by concentration, geochemical conditions or physical state of water - The only limitation is given by the needed amount of water (see above)
Uncertainties / accuracy (devices, methods, evaluation procedure)	- The analytical uncertainties for the conventional method (one standard deviation) are 0.1 ‰ for $\delta^{18}O$ and 1.0 ‰ for $\delta^{2}H$ - For the laser method the accuracy is higher with analytical uncertainties of 0.05 ‰ for $\delta^{18}O$ and 0.25 ‰ for $\delta^{2}H$
Method specific to defined boundary conditions	No; can be applied to all geological media. For media with very low water content, it is recommended to use the improved H_2O_{liquid}-H_2O_{vapor} equilibration laser spectroscopy method (see state of the art).
Experiences (pos. / neg., what to avoid)	It worked well to freeze the samples in order to avoid evaporation, which might falsify the results.
Effort, comments	- Duration of the sample preparation and measurement in laboratory is about 12 hours (set of 16 samples and 4 laboratory standards) for ^{18}O and 4 hours for ^{2}H (set of 5 samples and 1 laboratory standard) - Data are derived from mass spectrometer by standard procedures - In order to interpret the results with respect to the local modern infiltration water it is recommended to analyze a significant number of local surface waters, if no information is available. At Ruprechtov site 16 surface samples were analyzed /NOS 02/ - Costs: 60 € per sample to be analyzed at AGH Cracow (in year 2005) Laser method
Links, references, other sources of information	- IAEA water resources programme providing expert support to enable top quality isotopic measurements in MS laboratories around the globe and support for Data Management to help ensure QA/QC. http://www-naweb.iaea.org/napc/ih/index.html - Articles about method description for ^{2}H /COL 82/ and ^{18}O /EPS 53/ - Further development of the stable isotope analysis: /WAS 08/ - Review articles / books: /ROZ 93/, /CLA 97/
Picture of the device	 *The Los Gatos Research (LGR) Liquid Water Isotope Analyzer (LWIA-24d)* *Los Gatos Research, Inc. www.lgrinc.com*

Method No. A.17: C isotopes (U. Noseck, M. Dulinski)

Name of method ***Application in the Ruprechtov project***	Carbon isotopes Analyses of ^{13}C and ^{14}C content in SIC, DIC and DOC
Device(s) / method(s) used / applied	^{13}C: Degassing and analysis with dual inlet MS /MCC 50/ ^{14}C: Benzene synthesis with Liquid Scintillation /EIC 81/
Brief description of the functioning	^{13}C: The analyses of $\delta^{13}C$ in DIC followed the methodology of McCrea /MCC 50/. Barium carbonate precipitated in the field is decomposed in laboratory using 6 M HCl. Reaction vessel is blowed continuously with helium. Liberated CO_2 is separated from helium stream cryogenically, purified and then, analyzed using a Finnigan Delta S mass spectrometer. ^{14}C: The radiocarbon content is determined using benzene synthesis followed by liquid scintillation counting. 8 mL of benzene and 12 mL of Ultima-Gold scintillator (Packard & Co.) is mixed together in polyethylene vials and ^{14}C is measured by liquid scintillation counting (Quantulus, Canberra-Packard). About 5 g of carbon is needed for this procedure.
State-of-the-Art and new developments	The methods applied at Ruprechtov are conventional and still used. However, many laboratories today use Accelerator Mass Spectrometry (AMS) for ^{14}C and ^{13}C analysis with the same or better accuracy. This reduces particularly for ^{14}C the DIC amount needed from 5 g DIC to 1 mg and therewith the water sample amount from 60 L to 20 mL, minimizing also the potential for contamination by atmospheric CO_2. This method was applied for ^{14}C for few selected samples.
Output of the method	Content of ^{13}C in water is given as deviation from a standard, exemplarily shown for ^{18}O $$\delta^{13}C = \left[\frac{\left({}^{13}C / {}^{12}C \right)_{sample}}{\left({}^{13}C / {}^{12}C \right)_{s\tan dard}} - 1 \right] \cdot 1000$$ Standard: VPDB (Vienna Pee Dee Belemnite). Content of ^{14}C is given in percent modern carbon.  *Radiocarbon activity [pmc] versus $\delta^{13}C$ values of DIC and DOC pool in the sampled boreholes of the Ruprechtov aquifer system. Isotope signatures provided the understanding of the carbonate chemistry including the relevance of different C sources*

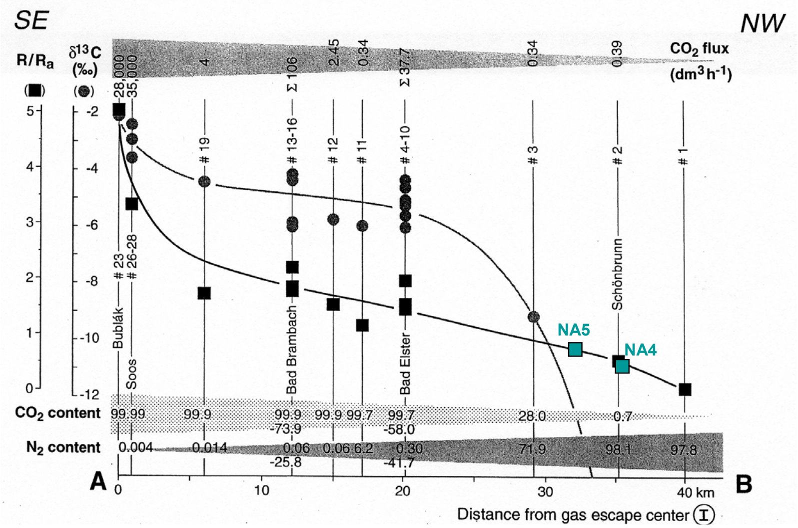
Objective(s) for application in the Ruprechtov project	Isotopes of C were determined to obtain additional information on the time scales of groundwater flow and to characterize water mixing processes as well as chemical reactions within the C system.
Practical procedure and experiences in the field	- ^{13}C: Groundwater sampling in 1 L bottles and in-situ filtration with 0.45 µm membrane filter. Sampling bottles are initially filled with argon to avoid CO$_2$ dissolution from atmosphere.For ^{13}C also release of a fraction from BaCO$_3$ was applied - ^{14}C: 60 L of groundwater are sampled in large canisters and spiked with BaCl$_2$ to precipitate DIC as BaCO$_3$
Applicability	The ^{14}C dating method is applicable to groundwater ages of 1,000 to 30,000 years. A specific amount of DIC is needed, requiring usually 50-60 L water samples
Limits of application	- The use of ^{14}C for groundwater dating is not always straightforward and could be complex. In many natural systems during evolution of the groundwater carbon isotope signature is changed by several processes (SIC dissolution or precipitation, input of DIC from organic matter). Such processes can be evaluated by ^{13}C values (signature for the carbon source). Thus it is essential to always measure ^{14}C together with ^{13}C - An alternative is the use ^{14}C in dissolved organic carbon (DOC) for GW dating. This approach was also applied at Ruprechtov
Uncertainties / accuracy (devices, methods, evaluation procedure)	The analytical uncertainty (1 standard deviation) is in the order of 0.2 ‰ for δ^{13}C. The ^{14}C concentration is reported in per cent modern carbon (pmc) and the quoted analytical uncertainty is in the order of 1.0 pmc and 0.3 pmc, for radiocarbon content in DIC and DOC, respectively.
Method specific to defined boundary conditions	Can be applied to all geological media, but see comment above.
Experiences (pos. / neg., what to avoid)	The applied method delivered a good understanding of processes involved in carbonate geochemistry. However due to the complex situation at Ruprechtov groundwater could not be reliably determined. ^{14}C in DOC failed due to artefacts from a nearby pile.
Effort, comments	- CO$_2$ extraction from BaCO$_3$ precipitate and its purification takes app. 4 – 5 hours, measurement of ^{13}C needs 15 – 20 minutes; Benzene synthesis requires 6 hours and ^{14}C counting by scintillation lasts about 1,000 min - Costs: 280 € per sample at AGH Cracow (in year 2005)
Links, references, other sources of information	- Publications from Ruprechtov /NOS 09a/ - IAEA instructions for isotope analysis (water resources program): http://www-naweb.iaea.org/napc/ih/IHS_video_overview.html - Articles / Review method description for ^{13}C, ^{14}C /CLA 97/ - Further development AMS /DEL 98/
Picture of the device	 *Groundwater sampling for ^{14}C with 60 L canisters in the field*

Method No. A.18: S isotopes (U. Noseck)

Name of method ***Application in the Ruprechtov project***	Sulfur isotopes Analyses of ^{34}S in sulfate dissolved in groundwater.
Device(s) / method(s) used / applied	1. Combustion 2. Analysis by mass spectrometery
Brief description of the functioning	The analyses of $\delta^{34}S$ in SO_4 follows the methodology of /COL 78/. SO_2 gas is released by combustion with excess Cu_2O and silica, at 1125°C. Liberated gases are then analysed with an isotope ratio mass spectrometer VG Isotech SIRA II. For preparation of the analysis sulfate is precipitated from solution as $BaSO_4$. (see “Experiences”).
State-of-the-Art and new developments	The method applied at Ruprechtov is conventional and still used. A recent advance is the development of continuous-flow techniques that use a combination of an elemental analyzer and gas chromatograph for online combustion and purification of gases that are then carried in a He stream directly into the ion source of a mass spectrometer, which allows for the mass production of data from small samples. This is particularly interesting for S minerals. Continuous-flow systems can measure the sulfur isotopic ratios of sulfide samples in the microgram range, compared to the milligram range for conventional techniques /GIE 94/. Sample gases are prepared by on-line peripheral devices such as elemental analyzers that are capable of processing 50 to 100 samples per day in a highly automated fashion. Furthermore, most sulfur isotope measurements can be made without mineral purification, if bulk sulfur data are all that is desired.
Output of the method	Content of ^{34}S in water is given as deviation from a standard: $\delta^{34}S = \left[\frac{\left({}^{34}S / {}^{32}S \right)_{sample}}{\left({}^{34}S / {}^{32}S \right)_{s\tan dard}} - 1 \right] \cdot 1000$ Reference for sulfur isotopes is Vienna Canyon Diablo Troilite (VCDT) with $\delta^{34}S$ = 0.0‰ by definition. Remark: Currently defined relative to a silver sulfide reference material (IAEA-S-1) with an assigned value of −0.3‰ because the supply of VCDT material has been exhausted  *An increase of ^{34}S content in dissolved sulfate compared to the infiltration area indicates that microbial reduction occurred in the clay/lignite horizon*

Objective(s) for application in the Ruprechtov project	Isotopes of ^{34}S in dissolved sulfate were determined to obtain the information, whether microbial sulfate reduction is (was) active at the site.
Practical procedure and experiences in the field	At least 500 mL of groundwater is used for the determination. No specific requirements for sampling are needed.
Applicability	The amount of sample required varies among laboratories, but typically 5 to 20 mg sulfate are needed corresponding to some hundreds of mL.
Limits of application	A specific amount of sulfur is needed for the analysis (see above). Therefore the corresponding amount of typically several hundred mL has to be available.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The analytical uncertainty (one standard deviation) is in the order of 0.3 ‰.
Method specific to defined boundary conditions	No, but see comment above.
Experiences (pos. / neg., what to avoid)	Groundwater need to be filtered in laboratory through 0.45 μm membrane filter. In order to increase concentration of sulfate samples were concentrated by evaporation and acidified by a few drops of conc. HNO_3. 1 mol/L of barium chloride free of carbonates was added. The solution is centrifuged (9,000 rpm/15 min) and the precipitate $BaSO_4$ was three times washed with deionized water.
Effort, comments	- Duration of the sample preparation and measurement in laboratory is about 1 hour - Costs: 65 € per sample at Czech Geological Survey, Prague (in year 2011)
Links, references, other sources of information	Publications from Ruprechtov /NOS 09a/ IAEA instructions for isotope analysis (water resources program): http://www-naweb.iaea.org/napc/ih/IHS_video_overview.html Articles / Review about method description for ^{34}S /CLA 97/, /KRO 91/, /ROB 06/
Picture of the device	 *Continuous-flow isotope ratio mass spectrometer. Wayne State University. College of liberal Arts & Sciences. http://clasweb.clas.wayne.edu/geology/IRISGeochemistryLaboratory*

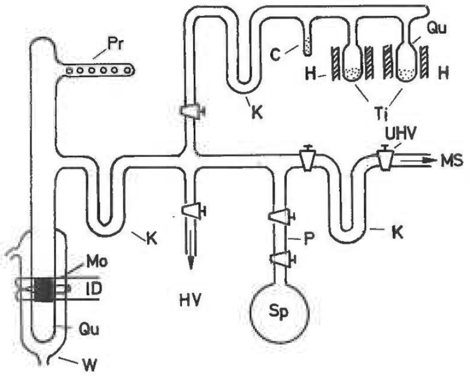
Method No. A.19: He isotopes (A. Rübel, U. Noseck)

Name of method ***Application in the Ruprechtov project***	Helium isotopes and noble gas temperature He-Isotope analysis and determination of noble gas temperature in groundwater.
Device(s) / method(s) used / applied	On-line vacuum extraction of noble gases from water and mass-spectrometric measurement of He, Ne, Ar, Kr, Xe isotopes.
Brief description of the functioning	A water sample of 20 to 40 mL is degassed into a vacuum at the sample preparation system. The extracted gases are separated from the water vapour, frozen on a 3K cold trap and subsequently released one after each other from the cold trap by stepwise increasing the temperature. The noble gases gases are measured on a MAP 215-50 mass spectrometer /CAS 00/.
State-of-the-Art and new developments	The method is still applied at various laboratories worldwide and widely used in hydrogeology and geochemistry /BUR 13/.
Output of the method	The results for noble gas concentrations are given in [ccSTP/g] denoting the dissolved amount of a noble gas in cubic-centimetres of gas at standard pressure per gram of sample water. The radiogenic fraction of ^{4}He produced in the subsurface is divided by an accumulation rate to determine groundwater ages. Noble gas ratios, esp. the ^{3}He/^{4}He ratio, are often not given as absolute ratios, but as multiple of the atmospheric air ratio. The noble gas temperature is given in [°C] which denotes the calculated mean ground temperature at the time of groundwater recharge. The temperature is not a direct output of the measurement, but is calculated reverse from a least square fit of the measured concentrations and the temperature dependent solubility of the noble gases Ne, Kr and Xe. The use of ^{3}He/^{4}He rations helped to identify subsurface gas sources (see figure and /NOS 06/):  *δ^{13}C and R/Ra-values in groundwaters in the Ohre rift area /WEI 99/*
Objective(s) of application in the Ruprechtov project	Determination of ^{4}He-ground-water ages in addition to ^{14}C ages and noble gas temperatures in comparison to stable oxygen and hydrogen isotope signatures.
Practical procedure and experiences in the field	Water samples of 20 – 40 mL are sealed in copper tubes of about 50 – 100 cm length which are sealed at both ends with stainless steel clamps. The sample container comprising sample holder, copper-tubing and clamps are dedicated constructions which are not available on the market and therefore have to be provided by the noble gas laboratory.

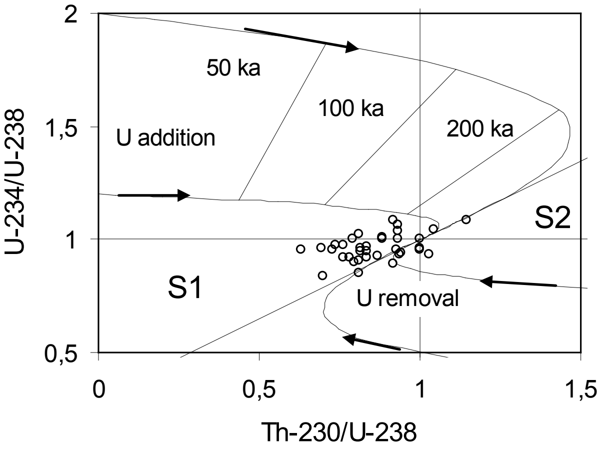
	Extreme care has to be taken during the sampling procedure to avoid degassing of the water e. g. due to pressure drop in the pump or the tubing and to avoid air bubbles in the samples since significant amounts of air would include more noble gas than the water sample.
Applicability	Noble gas temperatures in principle can be derived for all groundwater. ^{4}He-goundwater ages are especially suitable for older groundwater where the ^{14}C method is not applicable.
Limits of application	Helium can accumulate in the groundwater body from various sources, e. g. in-situ radiogenic production, mantle flow, crust flow. For complicate geological situations with accumulation from different sources and/or Helium loss to other geological formations, it can be found to be difficult to separate the different Helium fluxes to interpret the data. Calculating ^{4}He groundwater ages needs knowledge of the accumulation rate. For this, at least a number of samples along the groundwater flow path are usually necessary. Noble gas temperatures and ^{4}He ages have shown to give good results for confines aquifers /STU 92/, /STU 95/. For unconfined aquifers or complicate geologic situations, loss of noble gases to other geological formations or mixing of groundwater from different aquifers can result in misinterpretation of ^{4}He ages and noble gas temperatures.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The accuracy of the measurement is about 1 to 2 % of the absolute noble gas content and 0.5°C for the noble gas temperature. The overall accuracy of the procedure can be significantly higher depending on the quality of conditions during water sampling.
Method specific to defined boundary conditions	Method cannot be applied for aquifers with very low permeability, where only low pumping rates during water sampling can be established.
Experiences (pos. / neg., what to avoid)	No specific experiences.
Effort, comments	- Duration of sample preparation and measurement in laboratory is about 4 hours - Costs: 750 US$ per sample analyzed at Lamont-Doherty Earth Observatory, Columbia University (in year 2001)
Links, references, other sources of information	- IAEA instructions for isotope analysis (water resources program): http://www-naweb.iaea.org/napc/ih/IHS_video_overview.html - Sampling instructions of the noble gas laboratory at the Institute of environmental Physics, Heidelberg: http://www.iup.uni-heidelberg.de/institut/forschung/groups/aquasys/gp/methods/IUP_He_NG_sampling.pdf
Picture of the device	 *Copper tube for He sampling (source: /USG 14/)*

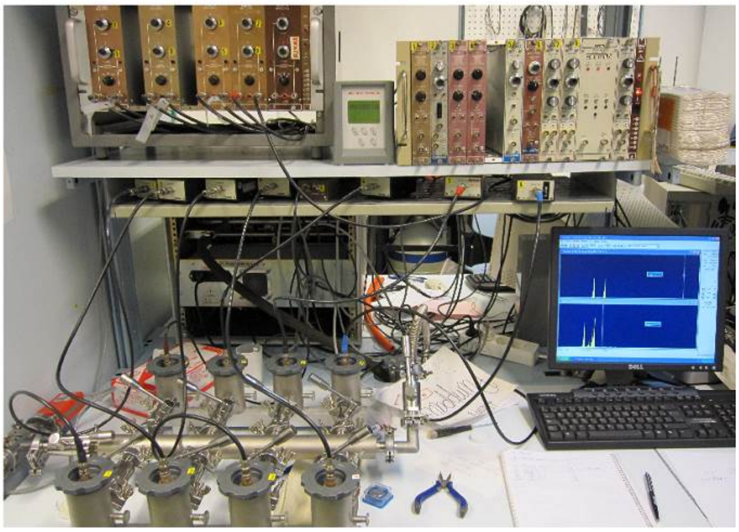
Method No. A.20: K/Ar isotopes (U. Noseck)

<table>
<tr><td><i>Name of method</i>
<i>Application in the Ruprechtov project</i></td><td>K/Ar-Isotopes
Dating of basaltic material by application of K/Ar-Isotope analysis in respective material.</td></tr>
<tr><td><i>Device(s) / method(s) used / applied</i></td><td>K-content: AES emission flame photometry
Ar-content: Mass spectrometer with isotope dilution method</td></tr>
<tr><td><i>Brief description of the functioning</i></td><td>Potassium content is determined by atom-emission flame spectrometry. Two aliquots of each sample are analysed.
Argon content is measured by a modified GD150 mass spectrometer, where the absolute Ar gas amount is determined by isotope dilution method. Therefore, a well-known amount of ^{38}Ar (determined via the international standard HD-B1 /HES 94/) is added to the sample gas and therewith $^{40}\text{Ar}_{rad}$ is measured. The sample is degassed at app. 1,300°C and finally 1,500°C to assure complete degassing of the sample. Purification of the sample gas was reached with Zr-, Cu/CuO-, Ti- and Zr-Al-SAES-getters. Mass discrimination of the spectrometer is determined with an Ar spike of atmospheric isotope composition. For age determination the IUGS constants of /STE 77/ are used.</td></tr>
<tr><td><i>State-of-the-Art and new developments</i></td><td>The method applied at Ruprechtov is conventional and commonly used.</td></tr>
<tr><td><i>Output of the method</i></td><td>
<i>Basalt sampling area at Hajek site</i>
<i>Results for K/Ar-dating, which was applied to three basalt samples from Hajek site</i>
<table>
<tr><th><i>Sample</i></th><th><i>K [%]</i></th><th>$^{40}\text{Ar}_{rad}$ <i>[nL/g]</i></th><th>$^{40}\text{Ar}_{rad}$ <i>[%]</i></th><th><i>age [Ma]</i></th></tr>
<tr><td><i>Basalt 1a</i></td><td><i>0.95</i></td><td><i>0.585</i></td><td><i>34</i></td><td><i>15.78</i></td></tr>
<tr><td><i>Basalt 1b</i></td><td><i>0.99</i></td><td><i>0.612</i></td><td><i>32</i></td><td><i>15.84</i></td></tr>
<tr><td><i>Basalt 2</i></td><td><i>1.38</i></td><td><i>0.824</i></td><td><i>57</i></td><td><i>15.30</i></td></tr>
</table></td></tr>
<tr><td><i>Objective(s) of application in the Ruprechtov project</i></td><td>Age determination of basaltic intrusions in the surrounding area.</td></tr>
<tr><td><i>Practical procedure and experiences in the field</i></td><td>No specific sampling needed.</td></tr>
<tr><td><i>Applicability</i></td><td>The method is applicable to tight rock material.
Usually the primordial isotopes ^{36}Ar and ^{38}Ar are also determined and used for correction of the primordial ^{40}Ar, which works well for ages > 1 million years. For younger ages today the ^{39}Ar-^{40}Ar-Method /REN 97/ is used, which is able to correct disturbances of K-Ar system without additional effort of mineral separation.</td></tr>
</table>

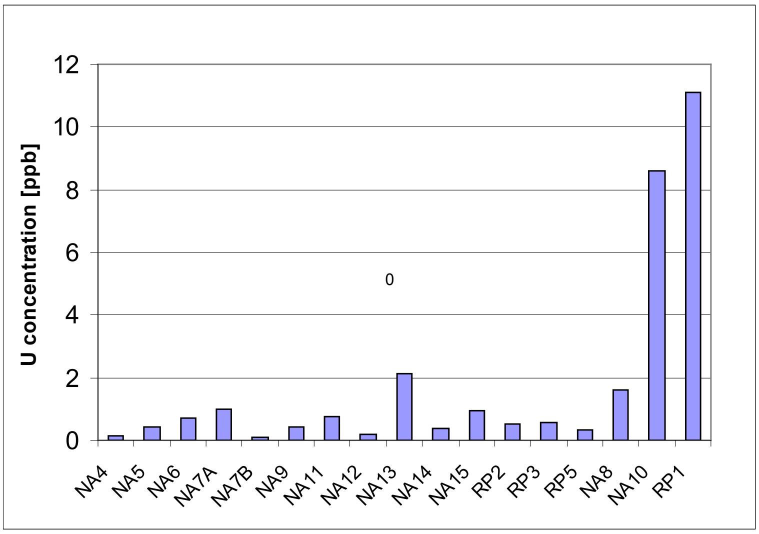
Limits of application	Prerequisite for application of the method is that the sample provides a closed system for K and Ar. Therefore the investigations on thin sections should be available to check the micro-porous structure, e. g. whether traces of alteration or fluid transport, which might impact the analysis, are visible.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Analytical precision in these measurements is better than ±1 % for K and ±3 % for Ar resulting in an analytical error of the determined age of app. ±3 %
Method specific to defined boundary conditions	Method is restricted to tight rock material. Age analysis of sedimentary materials like clays is not possible with this method.
Experiences (pos. / neg., what to avoid)	From the basaltic material pieces without visible surface alteration and preferably without secondary minerals are broken out. This material is ground, sieved and the grain fraction of 200-315 µm is selected for analysis. Since all three samples showed the same age, this was considered to be significant and indicated no disturbances of the sample.
Effort, comments	- Duration of the sample preparation and measurement in laboratory in total few weeks. - Costs: 350 € per sample (2005, “co-operation offer”) - Institute for Geosciences, University of Heidelberg http://www.geow.uni-heidelberg.de/
Links, references, other sources of information	Review article: /MCD 99/
Picture of the device	 *Digestion apparatus for the Ar dilution method /BEN 85/* (W: water cooling, Mo: molybdenum cup, Qu: quarz, ID: induction coil, Pr: sample, K: condensation trap, C: carbon finger, H: tube furnace, Sp: Spike flask, MS: mass spectrometer, HV: High vacuum pump)

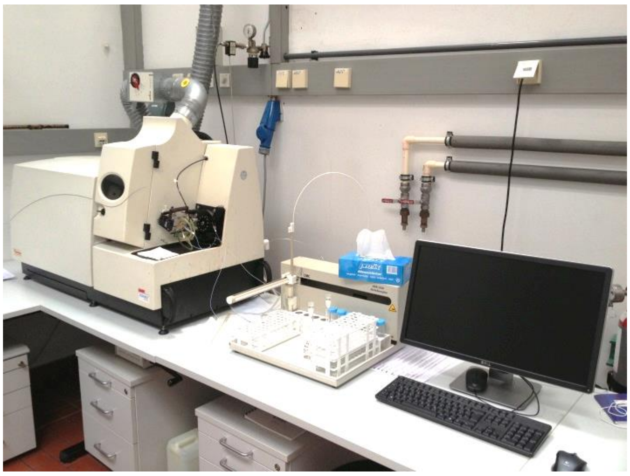
Method No. A.21: U chain isotopes (J. Suksi)

Name of method	Long-lived uranium decay chain isotopes
Application in the Ruprechtov project	Determination of uranium decay chain equilibrium state to date U movement and accumulation in Tertiary sediments.
Device(s) / method(s) used / applied	1. α-spectrometry 2. Wet chemical separation and ion exchange chromatography
Brief description of the functioning	Determination of uranium decay chain equilibrium state is done by comparing mobile ^{238}U and ^{234}U concentrations to immobile ^{230}Th concentration. Observed disequilibrium gives time-based information of U-accumulation and movement. Uranium decay chain isotopes are extracted from sample material in boiling concentrated HNO_3 and separated applying anion-exchange chromatography. Purified U- and Th-fractions are transferred on counting plates for α-counting to measure the concentrations.
State-of-the-Art and new developments	The techniques applied at Ruprechtov are conventional and still in routine use. High resolution sector field (HRSF) MS or multi collector (MC) ICPMS can be used to increase accuracy if required. High U concentrations in Ruprechtov samples allow easy and accurate disequilibrium determinations. Improvement in interpretation: Decservis-2 simulation program can be used to study the decay chain evolution that may have produced the activity ratios measured /AZZ 09/.
Output of the method	The method yields uranium decay chain isotope activity ratios which reveal the disequilibrium. Typically the data are presented in the form of a Thiel's diagram below /THI 83/ and interpreted according to the manner presented in /OSM 83/. The graph allows the evaluation of the geochemical nature and time scales of the processes responsible for the data obtained. From the data of U-enriched samples in the Tertiary sediments U immobilization is evident. 
Objective(s) of application in the Ruprechtov project	Identification and evaluation of uranium immobilization (and mobilization) processes in Tertiary sediments. Determination of temporal scales of mobilization / immobilization processes.
Practical procedure and experiences in the field	Lab-investigation at borehole samples.
Applicability	The method is applicable to samples where sufficient amount of U is available for the measurement. Generally, for α-spectrometry >1 μg and for HRSF/MC ICPMS >0.1 μg are needed to get statistically good result.
Limits of application	The only limitation is given by the amount of uranium (see above).

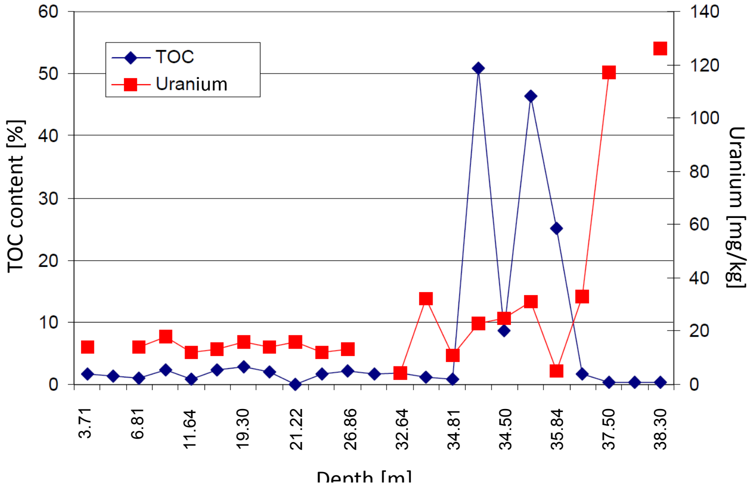
Uncertainties / accuracy (devices, methods, evaluation procedure)	Uncertainties are based mainly on α-counting statistic. In this work standard deviation (± 1σ) was around 4 % for $^{234}U/^{238}U$ and $^{230}Th/^{234,238}U$ activity ratios for 2 days measuring time. Usually for the $^{234}U/^{238}U$ activity ratio error bars well below 4 % were obtained.
Method specific to defined boundary conditions	The method can be applied to all geological media having enough U to get statistically good result (see Applicability). In general, Uranium decay chain techniques allow detection of U immobilization not older than 400,000 yrs. For longer timescales only qualitative statements are possible.
Experiences (pos. / neg., what to avoid)	Nearly all samples from Ruprechtov showed distinct $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ activity ratios, and clear differences between U(IV) and U(VI) phases. This enabled the combination of this method with separation techniques (see Chapter 4.6) and the investigation of sample alteration /HAV 11/. Analyses of several samples from different location are recommended as a basis for interpretation and identification of local differences.
Effort, comments	Duration of the sample preparation, analysis and measurement for U and Th isotopes is about 3 days depending on U concentration. More than one sample can be handled simultaneously. Data are derived from α-spectrometry by standard procedures. Most part of the costs consists of consumed time in analytical work and interpretation. Additional costs come from materials and chemicals. Consequently, the price per sample varies a lot an average being around 500 € for solid samples and 100 € for water samples.
Links, references, other sources of information	University Helsinki, Department of Radiochemistry: http://www.helsinki.fi/kemia/radiokemia/english/
Picture of the device	 *Eigth chambers system for α-spectrometry at University of Helsinki*

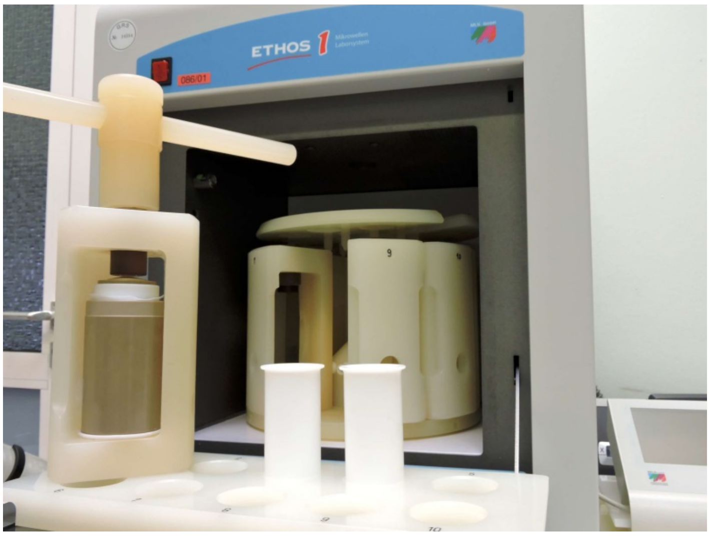
Method No. A.22: Fluid element analysis (U. Noseck)

Name of method ***Application in the Ruprechtov project***	Fluid element analysis Analysis of major and trace elements in groundwater.
Device(s) / method(s) used / applied	ICP-MS, ICP-OES, argentometric titration, ion chromatography, IR-spectroscopy, photometry.
Brief description of the functioning	Concentrations of trace elements are determined using an X-series ICP-MS with quartz-controlled 27 MHz ICP generator and high performance quadrupole mass analyzer. Concentration of silicon and major elements are determined with an IRIS Intrepid II XUV ICP-OES. Chloride is analysed by argentometric titration, alkalinity is determined by titration with HCl using the Gran plot to determine end-point, and SO_4^{2-} is quantified by ion chromatography. DIC is measured by conversion to CO_2 with H_3PO_4 followed by infrared detection with a TOC/TN 1200 analyser. For DOC analyses the sample is firstly acidified with H_3PO_4 to pH 2 in order to degas DIC. Then DOC is converted to CO_2 by combustion with O_2 and determined using infrared detection with the TOC/TN 1200 analyser. Phosphate and NO_3^- concentrations are determined by photometry.
State-of-the-Art and new developments	The methods applied are state of the art. New developments are especially in the field of ICP-MS. High resolution sector field (HRSF) ICP-MS provides an increased sensitivity and mass resolution compared to standard ICP-MS /MOL 04/.
Output of the method	Element concentrations in water samples.  *Uranium concentrations in groundwater samples from different wells at Ruprechtov site*
Objective(s) for application in the Ruprechtov project	Characterization of groundwater types from recharge area and evolution along the transport pathway in the Tertiary formations (major elements).
Practical procedure and experiences in the field	Analyses are performed in laboratory. Nevertheless an appropriate handling of groundwater samples in the field is prerequisite for reliable analysis data (see Chapter 3.2 and Method No. A.7).
Applicability	Methods are applicable to nearly all fluid samples.
Limits of application	A minimum amount of water is needed (25 mL per sample for ICP-OES, app. 5 mL for ICP-MS, and other methods mentioned above).

Uncertainties / accuracy (devices, methods, evaluation procedure)	The analytical uncertainties (one standard deviation) for ICP-OES are in the order of 2.5 % for major elements and <10 % for trace elements. For ICP-MS the analytical uncertainties are <10 % for the typical measuring range of 2-10 ppb. Uncertainties from sample preparation are included.
Method specific to defined boundary conditions	No; in many cases (ICP-MS and ICP-OES) the solutions need to be diluted to meet the specific detection range. Salinity of samples should be below ionic strength of 0.5 mol/L. High salinar samples need to be diluted appropriately.
Experiences (pos. / neg., what to avoid)	A careful and accurate sampling and sample handling is of high importance. Examples are DOC values, which have been too high because of the use of cellulose filters. Better results are obtained using filters wth Ag coating. For each analysis method usually three measurements per sample should be performed.
Effort, comments	Effort is dependent on the analytical method. For ICP-MS and ICP OES sample preparation procedure including calibration curve takes about one hour for one set of samples. Similarily for the other methods mentioned about 1 hour effort each is needed. Costs at GRS laboratory for a complete analysis are around 50 € per sample, depending on the number of parameters and the total amount of samples.
Links, references, other sources of information	- GRS publications: /NOS 06/, /NOS 09a/, NOS 09b/
Picture of the device	 *X-series ICP-MS, THERMO Corporation*

Method No. A.23: Solid element analysis (U. Noseck)

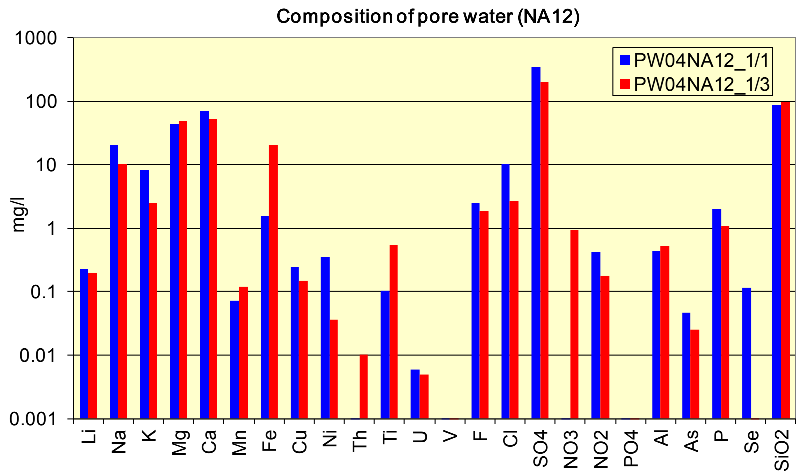
Name of method ***Application in the Ruprechtov project***	Solid element analysis Analysis of major and trace elements in solid sample material.
Device(s) / method(s) used / applied	1. Microwave digestion 2. Analytics as ICP-MS and ICP-OES, see Method No. A.22
Brief description of the functioning	For the microwave digestion firstly the material is grinded. Then 50 mg of the grinded sample is applied. It is exposed to a mixture of 7 mL conc. HNO_3, 5 mL of 30 % Hydrofluoric acid, 3 ml 35 % Hydrochloric acid and 3 mL 30 % H_2O_2 for app. one hour. During this time the sample is continuously exposed to microwave irradiation, the temperature and pressure incease up to 215°C, and app. 50 bar. After one hour digestion the sample is slowly evaporated and HF is released by repeated displacement with HCl. The residual is dissolved in 5 % HNO_3. Quantification of the dissolved elements in this solution is then carried out by ICP-MS and ICP-OES.
State-of-the-Art and new developments	This method represents the state of the art. The applied mixture of acids has to be adapted for the respective sample. In our case the mixture with HNO_3, HF, HCl and H_2O_2 worked well achieving a complete dissolution of the sample. Further, X-ray fluorescence represents an alternative, non-invasive method, but has not been used in our project.
Output of the method	The method is applied in order to determine the chemical composition of the sample. This is the basis for - Profiles of U, Th and other trace elements in the sediment - Semiquantitative evaluation of mineral phases content in a sample (using information from XRD, see Method No. A.11 and figure), - Investigation of correlations of elements, e. g. elements enriched together with uranium.  *Correlation of uranium with TOC content in borehole NA4*
Objective(s) for application in the Ruprechtov project	The objectives are listed above, i. e. characterize trace element profiles, determine the mineral composition of the sample and identify correlations of uranium with other heavy metals.
Practical procedure and experiences in the field	Digestion and analysis is performed in the laboratory. Since only 100 mg of sample (for repeat determination) is used, the sampling procedure should be carried out in a way assuring representativeness of the sample. No specific shielding is necessary.

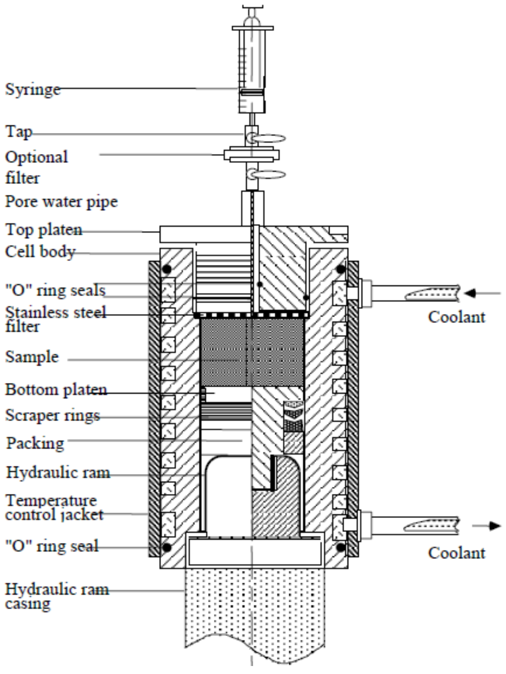
Applicability	The method is applicable to all kind of rocks. However, the applied mixture as well as the temperature - pressure conditions need to be adapted to each type of sample.
Limits of application	Si is not detectable using a digestion with hydrofluoric acid.
Experiences (pos. / neg., what to avoid)	Evaporation should be done in a controlled, careful and slowly way to avoid loss of material.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The analytical uncertainties for ICP-MS and ICP-OES are discussed in the description of Method No. A.22.
Method specific to defined boundary conditions	See "Applicability".
Effort, comments	About four hours per sample is needed for sample preparation, digestion and analytics with ICP-MS, ICP-OES.
Links, references, other sources of information	Relevant publications: e.g. /KIN 88/
Picture of the device	 *Microwave apparatus for digestion of solid material*

Method No. A.24: Porewater extraction (U. Noseck, R. Červinka)

Name of method	Porewater extraction
Application in the Ruprechtov project	Extraction and chemical analysis of porewater from argillaceous samples

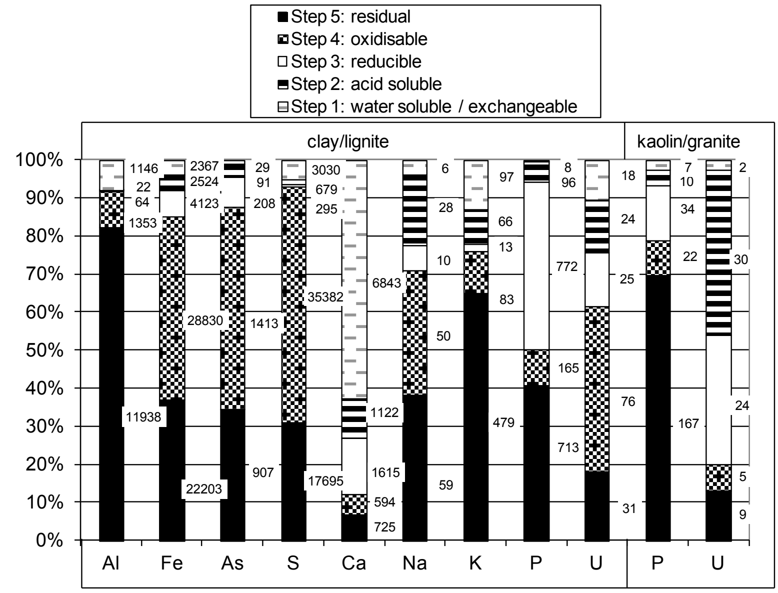
Device(s) / method(s) used / applied	Squeezing of samples as method for porewater extraction has beem performed in the following institutions:
	- Czech Technical University (CTU)
	  ○ Hydraulic press up to 400 kN, squeezing chamber, oxidizing conditions
	  ○ Determination of moisture content /ČSN 05/
	  ○ Chemical analysis by ICP-MS
	- British Geological Survey (BGS)

Brief description of the functioning	CTU - Technically same procedure as BGS, but under aerobic conditions BGS - A pump pressure of about 2 to 3 MPa is applied initially to remove most of the gas from the cell and allow the sample to 'bed in'. The system is left to stabilize at the ambient temperature of about 16°C. The syringe tap and labelled syringe of known weight (argon flushed syringe for the pseudo-anaerobic tests) are pushed into the top of the pore-water collection pipe - Applied stress is gradually increased throughout the extraction. The stepwise increase in stress during testing is dependent on the physical characteristics of the material tested and the volume of water required
State-of-the-Art and new developments	Yes, an overview of different methods can be found in /NEA 00/.
Output of the method	 *Composition of pore water from borehole NA12, depth 40.45 m (CTU, oxidizing conditions)*
Objective(s) for application in the Ruprechtov project	Chemical characterization of clay porewater in samples from argillaceous material.
Practical procedure and experiences in the field	- (CTU): Preserved core sample in N_2 atmosphere was adjusted into the chamber (ca 75 mm diameter and 100 mm height); during 9 days the pressure was gradually increased (23, 45 and 79 MPa), amount of squeezed water was measured - (BGS): All the undisturbed samples were prepared in the anaerobic chamber in an atmosphere of less than 100 ppm O_2.

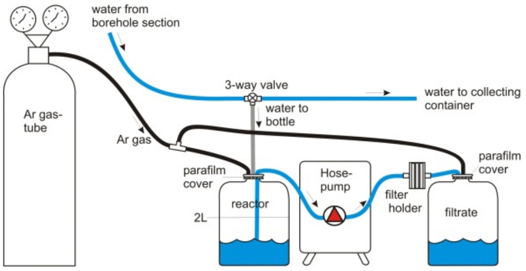
	The samples were cut to the required dimensions (less than 75 mm diameter and less than 100 mm height) with a 75 mm stainless steel cutting ring and a large knife; potentially contaminated or oxidised material within an approximate 10 mm annulus of the block was discarded; A separate sub-sample was also taken for moisture content determination
Applicability	Sample needs to provide plastic properties; method is not applicable to hard-rock samples.
Limits of application	The maximum stress is limited by the hydraulic press. A minimum content of water in the sample is needed.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Potential sources of error during porewater extraction are oxidation of sediments from atmospheric exposure, which can cause geochemical changes (confirmed by comparison of CTU and BGS results); chemical concentrations in porewater then do not accurately represent in-situ conditions.
Method specific to defined boundary conditions	See “Applicability”.
Experiences (pos. / neg., what to avoid)	BGS: The maximum stress applied was 60 MPa. Between three and six pore-water fractions (each of app. 5 g or more) were successfully collected from each sample. The total volume of porewater obtained per sample by mechanical squeezing varied between 1.68 mL and 21.44 mL.
Effort, comments	- Sample preparation to fit into the squeezing chamber - In order to obtain sufficient pore-water for chemical analysis of separate fractions, tests were carried out for between 1 and 334 hours
Links, references, other sources of information	- BGS porewater extraction: http://www.bgs.ac.uk/scienceFacilities/laboratories/engineering/squeezing.html - NEA status report on porewater extraction: http://www.oecd-nea.org/rwm/reports/2000/nea2530-porewater-extraction.pdf
Picture of the device	 *Schematic figure of the BGS squeezing cell /ENT 93/*

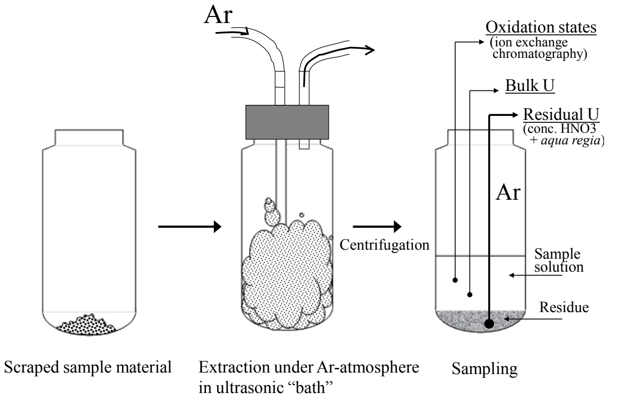
Method No. A.25: Sequential extraction (R. Červinka)

<table>
<tr><td><i>Name of method</i></td><td>Sequential extraction</td></tr>
<tr><td><i>Application in the Ruprechtov project</i></td><td>Distribution of U and other elements (Fe, Al, Ca, Na, K, P, As, S) among different fractions in clay sediments / granite bedrock.</td></tr>
<tr><td><i>Device(s) / method(s) used / applied</i></td><td>Five steps sequential extraction procedure (combination of /TES 76/, /PER 90/ and /BOR 94/ schemes) combined with wet chemical analytical method.</td></tr>
<tr><td><i>Brief description of the functioning</i></td><td>1 g of homogenized sample (dried under air conditions, grain size < 63 µm) is progressively contacted with reagents (agitating, shaking for specified time). Subsequently, in each step, the sample is centrifuged at 4,000 rpm (1717 × g) for 20 min and the supernatant is stored in a 50 mL volumetric flask. The solid phase is washed with 10 mL of deionized water and once again centrifuged at 4,000 rpm (1717 × g) for 10 min and used in next step. The supernatant is added into a 50 mL volumetric flask, acidified using 1 mL of concentrated HNO_3 (excluding the last fifth step) and refilled with deionized water up to a final volume of 50 mL. The content of uranium and other elements (P, S, As, Fe, Ca, Na, K, Al) in the leachate solutions is determined by ICP-OES or ICP-MS (see above). The results are corrected for blank samples of the individual reagents. For details of the five steps sequential extraction, see table :
<table>
<tr><th>step no.</th><th>Extractive reagent, pH, temp, time</th><th>Reagent/sample ratio (ml/g)</th><th>Desired fraction</th></tr>
<tr><td>1</td><td>1 $mol\cdot l^{-1}$ $MgCl_2$, pH 6, room temp., 1 h</td><td>30:1</td><td>water soluble / exchangeable</td></tr>
<tr><td>2</td><td>1 $mol\cdot l^{-1}$ CH_3COONH_4 in 25% CH_3COOH, pH 4.5, room temp., 5 h</td><td>30:1</td><td>acid soluble (aluminosilicates, carbonate complexes)</td></tr>
<tr><td>3</td><td>1 $mol\cdot l^{-1}$ $NH_2OH\cdot HCl$ in 25% CH_3COOH, pH 2, 12 h</td><td>30:1</td><td>reducible (Fe/Mn oxides)</td></tr>
<tr><td>4</td><td>0.02 $mol\cdot l^{-1}$ HNO_3 / 30% H_2O_2, 80 °C, 5 h</td><td>30:1</td><td>oxidisable (organic matter, sulfides)</td></tr>
<tr><td>5</td><td>conc. HNO_3, boiling</td><td>30:1</td><td>residual</td></tr>
</table></td></tr>
<tr><td><i>State-of-the-Art and new developments</i></td><td>Sequential extraction is widely used method for progressive selective dissolution of soils or rocks by chemical agents in order to study the distribution of elements among different fractions. Nowadays two procedures (almost standards) are used, Tessier's method /TES 79/ and so called BCR method /QUE 93/. For natural radionuclides the Tessier's method /TES 79/ or Schultz modification of Tessier method /SCH 98/ is used. For critical review of using the sequential extraction methods, see /BAC 08/.</td></tr>
</table>

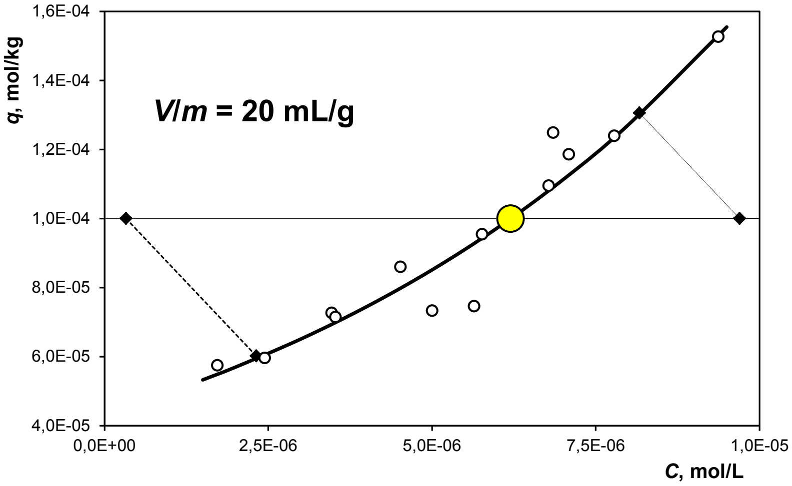
Output of the method	 *Average percentage fractionation of selected elements in individual steps of sequential extraction from both horizons (clay/lignite and kaolin/granite). Numbers on the right of the columns are average contents of the elements in mg/kg.*
Objective(s) for application in the Ruprechtov project	Identification of U and other elements distribution among different fractions in clay sediments / granite bedrock. Associations and correlations among elements, U mineralization.
Practical procedure and experiences in the field	The 4th step is very sensitive to organic matter content and the reaction with 30 % H_2O_2 can be turbulent (→ slow addition in small droplets, initiating of the reaction by heating). Samples containing oxygen-sensitive mineral phases (i. e. pyrite), should be preserved in special transportation boxes under inert atmosphere; also the first 3 steps of sequential extraction procedure should be done in anaerobic glove box or tent.
Applicability	The method is applicable to soils, sedimentary (especially clays) and hard rocks.
Limits of application	Redistribution of elements among phases during the extraction, non-selectivity of reagents for the individual steps, incomplete extraction and precipitation of new solid phases during extractions.
Uncertainties / accuracy (devices, methods, evaluation procedure)	In Ruprechtov study the best reproducibility for U was gathered with samples of U content > 100 mg/kg, because absolute concentrations of U in individual leachates were sufficient for good reproducible measurement.
Method specific to defined boundary conditions	Generally, the method itself is applicable to all geological media. But interpretation and in some cases also the selection of reagents differ for different geological media.
Experiences (pos. / neg., what to avoid)	For correct interpretation the combination of sequential extraction with other geochemical methods is needed (e. g. XRD, µ-XRF). For large data sets the Principal Component Analysis (PCA) is helpful.
Effort, comments	- Time consuming, five step procedure takes about 30 h for one sample - Costs are depending on rock type, reagents used, number of elements for analysis, etc.
Links, references, other sources of information	For further details see /NOS 08/.
Picture of the device	Standard laboratory equipment.

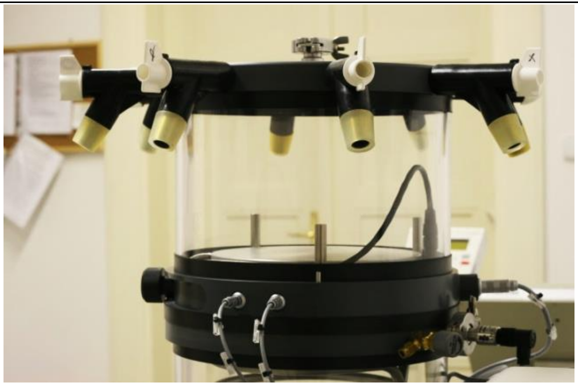
Method No. A.26: U(IV)/U(VI) separation (J. Suksi)

Name of method	U(IV)/U(VI) separation
Application in the Ruprechtov project	Analysis of U oxidation states in sediment samples and groundwater coupled with analysis of the ^{234}U/^{238}U activity ratio.
Device(s) / method(s) used / applied	1. α-spectrometry 2. Wet chemical separation
Brief description of the functioning	<u>Sediment:</u> U(IV)/U(VI) distribution is determined by applying a wet chemical method slightly modified from /ERV 96/. Uranium extraction from sample material is done in the 4 M HCl-0.03 M HF mixture under Ar atmosphere. U dissolution yield was 50 – 90 %. Insoluble U was considered U(IV). Extraction solution with U(IV) and U(VI) is fed into a Dowex 1x4 anion-exchange column where U(VI) is sorbed while U(IV) passes the column in the first 20 ml. Sorbed U(VI) was eluted with 20 mL of 0.1 M HCl. Separation is quantitative and no significant overlap of U(IV) and U(VI) fractions has been observed in the tracer experiments. U(IV) and U(VI) with their ^{234}U/^{238}U activity ratio were measured with α-spectrometry. <u>Groundwater:</u> U(IV) and U(VI) are separated from groundwater during sampling using a U(IV) specific co-precipitation technique (NdF_3-precipitation) which keeps U(VI) in solution /AND 83/. NdF_3 precipitate was filtered and the filter and filtrate water analysed for U. The U concentrations show how much occurs as U(IV) relative to U(VI).
State-of-the-Art and new developments	The methods applied at Ruprechtov are rarely used but have theoretically sound basis /AND 83/ and /ERV 96/. New developments have been done in controlling iron induced interferences during uranium extraction and using the ^{234}U/^{238}U ratio as a tracer in monitoring U(IV) and U(VI) separation. Significantly higher ^{234}U/^{238}U activity ratio in U(VI) fraction can be considered an evidence of a success of separation.
Output of the method	The method yields the U(IV)/U(VI) distribution in sediment and groundwater samples.
Objective(s) of application in the Ruprechtov project	Identifying the redox state of U compounds in sediment and groundwater and studying the option that the reduction of U(VI) to U(IV) controls U immobilization and accumulation in the sediment.
Practical procedure and experiences in the field	Solid sampling: No specific sampling was done, but see comment under "Experiences". Groundwater sampling (see figure below): The equipment consists of two plastic containers (HDPE), the reactor vessel where precipitation takes place and the container for collecting the filtrate. A Nucleopore polycarbonate filter (Θ 47 mm, 0.40 µm) placed in a plastic filter holder was used for filtration, and a peristaltic pump served to pump the solution through the filter. Pumping was done under Ar atmosphere. Groundwater collection, NdF_3-precipitation and filtration. A bypass was arranged to accommodate disposal of the water between each filling of the reactor vessel /SUK 07/.  *Equipment setup for field separation of U(IV) and U(VI) in GW*

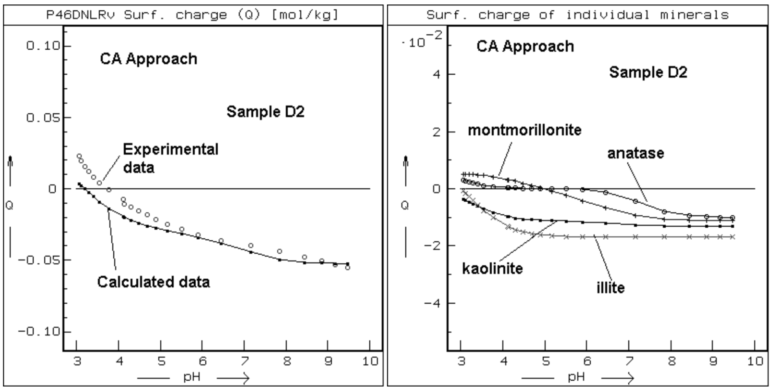
Applicability	The method is applicable if enough uranium is available for the measurement. In practice for α-spectrometry > 1 μg and for HR/MC ICPMS > 0.1 μg are needed to get statistically good result.
Limits of application	The limitation is given by the amount of uranium (see above).
Uncertainties / accuracy (devices, methods, evaluation procedure)	Analytical uncertainty is due to α-counting statistic. Main uncertainty is related to the material itself and particularly the iron in the material because possible post-sampling oxidation of the material increases Fe^{3+} which can disturb uranium redox-state during the extraction by oxidizing U(IV).
Method specific to defined boundary conditions	The method can be applied to all geological media. For solid samples higher amounts of redox-sensitive elements like iron (s. above) might perturb the measurement; for groundwater, undisturbed samples (without contact to the atmosphere) are needed.
Experiences (pos. / neg. what to avoid)	- Solid: In order to avoid oxidation of redox sensitive samples it is recommended to perform U(IV)/U(VI)-separation in the field directly after drilling and identification of U-rich areas by field γ-spectroscopy - Water: To avoid contact with oxygen (oxidation) Ar-flooding of the borehole some minutes before sampling was successful For filtration of groundwater and U(IV)/U(VI)-separation in the field pumps with enough (continuous, stable power and long-term electricity supply are preferable
Effort, comments	- Sample preparation, analysis and measurement for U isotopes take about 2 days depending on U concentration. Data are derived from α-spectrometry by standard procedures. Analysis of more than one sample is recommended to give statistically sound interpretation - Most part of the costs consists of consumed time in analytical work and interpretation. Additional costs come from materials and chemicals. Consequently, the price per sample varies a lot an average being around 500 € for solid samples and 100 € for water samples
Links, references, other sources of information	University of Helsinki, Department of Chemistry, Laboratory of Radiochemistry: http://www.helsinki.fi/kemia/radiokemia/english/
Picture of the device	 *Laboratory device for U(IV)/ U(VI) separation in the solid*

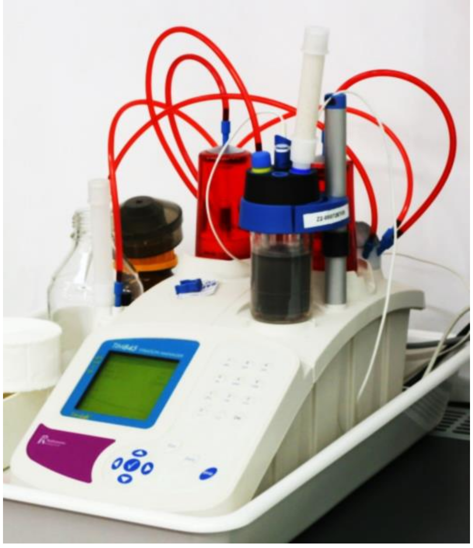
Method No. A.27: **U sorption (B. Drtinová, D. Vopálka)**

Name of method ***Application in the Ruprechtov project***	Uranium sorption Sorption behaviour of different rock types.
Device(s) / method(s) used / applied	- Standard sample pretreatment includes preservation in Ar-atmosphere, lyofilization, milling and sieving on standardized grain size - Batch sorption experiments in PE vials under oxic conditions at room temperature; U(VI) (for selected experiments spiked with ^{233}U) added in working solution - Determination of the uranium content by a set of methods (total: ICP MS, own modification of Kinetic Phosphorescence Analysis (KPA) method; 233U activity is determined by liquid scintillation counting) - Evaluation of experimental results by an interaction model that can be used in the subsequent transport modelling.
Brief description of the functioning	Investigation is performed by contacting rock samples with artificial formation water with defined U(VI) concentration Two approaches can be applied for evaluation of experiments: - Determination of the shape of the interaction isotherm that takes into account the determined amount of "exchangeable uranium". In the figure below the yellow point represents initial equilibrium conditions in the natural system and dashed lines the working lines for different initial uranium content in the modeled solutions  - Formulation of a sophisticated interaction model that will comprise uranium release/uptake on different sorption sites (of "layer" for ion exchange and "edge" for surface complexation). The characterization of the surface by acid/base titration (see method no. 10.28) is necessary for the construction of such type of model
State-of-the-Art and new developments	The first three methods mentioned under "Device/method" are conventional and still commonly used. The realization of the last method needs a specific approach to each type of rock material and anticipates the experience of a sophisticated software (e. g., UCODE + PHREEQC).
Output of the method	Formulation of the interaction model for each type of studied rock material that could be used in transport modelling.

Objective(s) for application in the Ruprechtov project	The formulation of interaction isotherms is the objective that should result from study of uranium content, sorption and isotopic exchange on different samples representing layers with higher content of uranium and neighbouring layers with practically no uranium content. Comparison of determined values of exchangeable uranium using ^{233}U on selected samples with the results of sequential leaching could help in discussion of uranium sorption and/or mineralization in studied rock materials.
Practical procedure and experiences in the field	Only lab experiments.
Applicability	Batch type sorption experiments are suited to studies of crushed materials. In comparison with the in many aspects more precise dynamic sorption experiments /REL 80/, /BER 88/ are batch experiments experimentally undemanding. The use of isotope ^{233}U not presented in the environment will help for the characterization of rock samples containing uranium and makes the analytics of the experiments faster.
Limits of application	The general drawback of static arrangement is the violation of natural hydrodynamic parameters due to crashing of the solid samples. The crucial limit is further the self leaching of uranium from some samples that contain pyrites. Of course, classic problems of micromethods, as sorption on the vessel walls can affect negatively the experiment /REL 80/, /BEN 94/.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The standard uncertainties of the experimental procedures and analytical methods used for characterizing rock materials are in the order of 10 %, but the uncertainty of parameters of models describing the interaction is greater due to the complexity of all equations that should be taken into account in the evaluation.
Method specific to defined boundary conditions	No; applicable to all rock types.
Experiences (pos. / neg., what to avoid)	Determination of uranium by KPA method and its modification is influenced by some matrix effects, therefore the application of the method of standard addition is recommended.
Effort, comments	Two steps are the most time and effort demanding: development of such modification of KPA method of uranium determination that will eliminate the matrix effect of the studied solutions and the formulation of an appropriate complex interaction model.
Links, references, other sources of information	Fundametal / Review reports: /REL 80/, /BER 88/, /NEA 12/
Picture of the device	 *A detail of the lyofilization apparatus LYOVAC GT2 used for the pretreatment of wet solid samples from Ruprechtov site*

Method No. A.28: Surface titration (K. Stamberg, B. Drtinova)

Name of method ***Application in the Ruprechtov project***	Characterization of surface by titration The aim of determination of titration curves and their subsequent evaluation via the surface-complexation model was to obtain data characterizing the sorption properties of the sediment samples respectively to their mineralogical composition.
Device(s) / method(s) used / applied	Automatic titrator 845 TIM with a combined electrode pHC2001-8 (Radiometer) was used. The sediments were pre-treated in order to remove carbonates and other impurities using the procedure described by /WAN 94/.
Brief description of the functioning	It is supposed that the protonation reactions and the ion-exchange reaction occur on the edge and layer sites, respectively /LUT 06/.
State-of-the-Art and new developments	The experimental method is conventional and its principal is commonly used. From the modelling point of view, there are two approaches at hand, namely, the so-called Generalized Composite approach (GC) and Component Additivity approach (CA). GC approach is generally used especially in a case of evaluation of titration curves /FIL 05/. CA approach is based on a weighted combination of models describing the surface reactions on individual solid phase components According to literature, this procedure was probably not used in a case of titration curves until now. Therefore, our application of CA approach can be regarded as a contribution to the characterization of solid phases having a different mineralogical composition.
Output of the method	The output of CA approach is demonstrated in graphical form in the figure (borehole NAR2, depth 29.86 m, sample D2); the corresponding output of GC approach can be found in /DRT 11/.  *Calculation of titration curve (left - total surface charge = f(pH), right - pH dependences of surface charges of individual minerals. CA approach includes non-electrostatic and ion-exchange models and data from RES^{3}T /HZDR 06/.* It is evident, that relatively good goodness-of-fit of experimental with the CA approach calculated data was obtained, especially if pH > 5
Objective(s) for application in the Ruprechtov project	The basic objective for application in the Ruprechtov project consists in the acquirement of parameters characterizing the surface sites of given sediments These values are important input data into codes by means of which the sorption/desorption of given contaminant by surface complexation models can be evaluated or simulated, over the course of migration process.

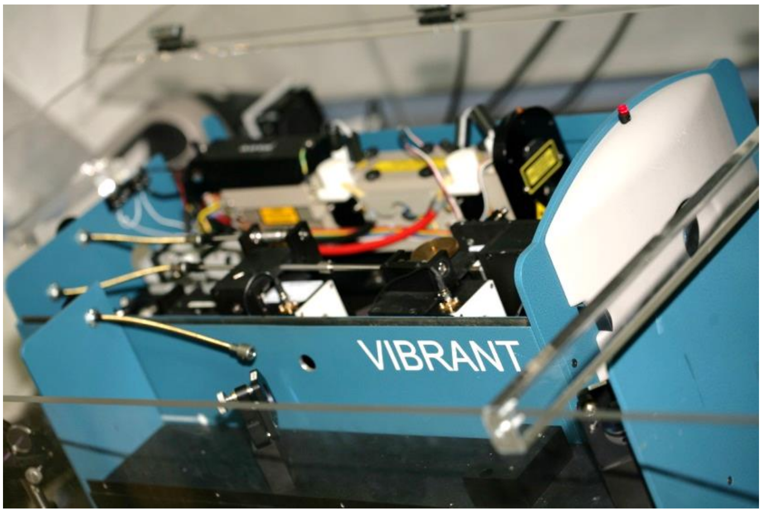
Practical procedure and experiences in the field	Only lab studies.
Applicability	In a case of GC approach, the applicability is restricted to sediments the mineralogical composition of which is constant. In a case of CA approach, the mineralogical composition of sediments can be to a certain extent different.
Limits of application	As for method itself: the reaction laboratory conditions have to be in agreement with the conditions in the bed of given sediment - especially, it holds for chemical composition of liquid phase and mineralogical composition of solid phase. As for personal experience: of course, the personal experience can play the important role, too. It holds not only for the laboratory experiments, but also for application of the corresponding codes.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The total standard uncertainties (deviations) of the determination of parameters mentioned above are in the order of 5 – 10 %.
Method specific to defined boundary conditions	Yes, the method is applicable to such geological media for which the mineralogical composition is convenient for all the conditions mentioned above.
Experiences (pos. / neg., what to avoid)	As for personal experience: of course, the personal experience can play the important role, too. It holds not only for the laboratory experiments, but also for application of the corresponding codes.
Effort, comments	The maximal effort was spend in the solution of CA approach method, especially if the values of parameters of individual minerals were found and selected.
Links, references, other sources of information	Fundamental / review reports: /LUE 06/, /WAN 94/, /LUE 12/.
Picture of the device	 *Automatic titrator TIM845*

Method No. A.29: U isotope exchange (D. Vopálka, B. Drtinová)

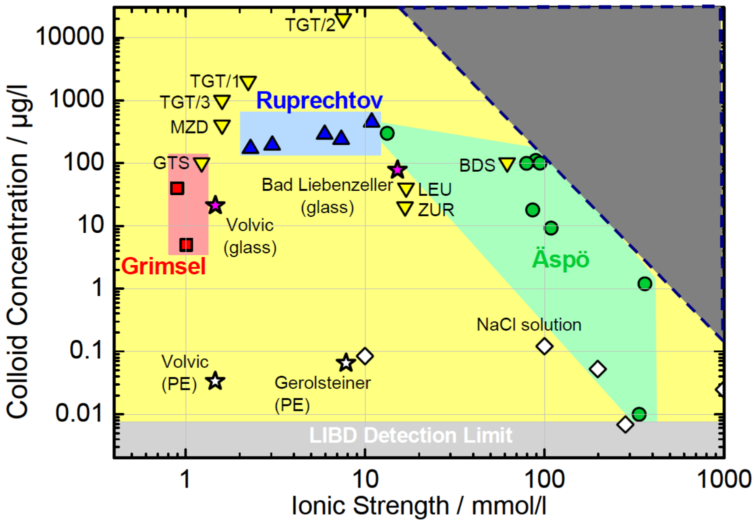
<table>
<tr><td><i>Name of method</i></td><td>Uranium isotope exchange</td></tr>
<tr><td><i>Application in the Ruprechtov project</i></td><td>Determination of exchangeable uranium by means of isotopic exchange (U_{nat} - ^{233}U).</td></tr>
<tr><td><i>Device(s) / method(s) used / applied</i></td><td>Standard sample pretreatment includes preservation in Ar atmosphere, lyofilization, milling and sieving on standardized grain size.
Batch sorption experiments in PE vials under oxic conditions at room temperature. U(VI) spiked by ^{333}U added in working solution.
Determination of uranium content by own modification of the KPA method, ^{233}U activity by liquid scintillation counting (Triathler, HIDEX, cocktail Rotiszint eko plus).</td></tr>
<tr><td><i>Brief description of the functioning</i></td><td>From the balance of uranium in the system, in which the natural uranium is initially present in both liquid and solid phases, and the liquid phase spiked by ^{233}U, the formula for the determination of “labile” /DAV 03/ and /VOP 06/ or exchangeable uranium q_0 is deduced

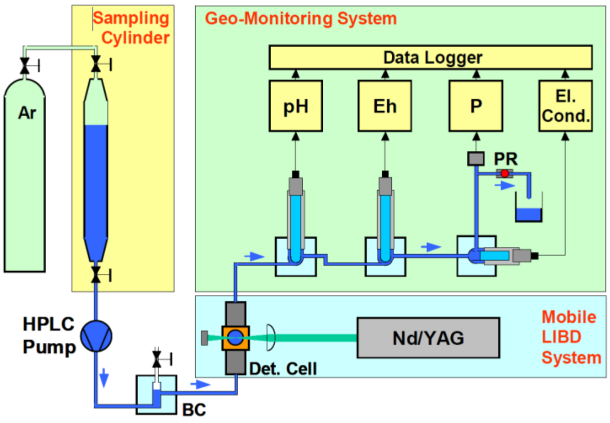
$$q_0 = \frac{C(V + K_d m) - C_0 V}{m} .$$

Here C_0 and C are initial and equilibrium concentrations of total uranium in the liquid phase (mg/L), m is mass of solid phase (kg), V volume of liquid phase (L) and K_d (L/kg) denotes equilibrium distribution coefficient determined from the balance of ^{233}U in the system.
Development of a modified KPA method for uranium determination on own TRLFS system, which consists of solid state tunable laser, pumped Q-switched Nd: YAG laser 1064 nm (with conversion possible by modules SHG (532 nm), THG (355 nm) OPO (410 – 2,400 nm), UV (355-410 nm) and FHG (256 nm), pulse length 2 – 12 ns and repetition rate 1-10 Hz, is performed. To reduce the influence of nonradiant processes such as quenching and thus to extend the lifetime of luminescence, a complexation agent Uraplex (pH 3) is added in a 1:1.5 ratio to the measured sample /CRO 97/. The sample is excited at 417 nm, where the fluorescence signal is strongest.</td></tr>
<tr><td><i>State-of-the-Art and new developments</i></td><td>The methods applied at Ruprechtov proceed from known principles. The realization of batch sorption method under oxic conditions needed a specific approach related to TRLFS system available. A broad study of the influence of the composition of water phase on the fluorescence signal of uranium was performed.</td></tr>
<tr><td><i>Output of the method</i></td><td>Example of comparison of exchangeable uranium determined by isotopic exchange with results of first two step of sequential leaching (seq. 1+2 = surface and U and U in carbonates), U-total represents the total content of uranium in the solid phase.
<table>
<tr><th rowspan="2">Borehole</th><th rowspan="2">depth [m]</th><th rowspan="2">water type /VOP 08/</th><th>q_0</th><th>seq. 1+2</th></tr>
<tr><th colspan="2">mg kg^{-1}</th></tr>
<tr><td>NA10</td><td>17.25</td><td>1</td><td>18</td><td>17.5</td></tr>
<tr><td>NA11</td><td>16.63</td><td>2</td><td>29</td><td>39</td></tr>
<tr><td>NA11</td><td>42.43</td><td>3</td><td>10</td><td>7.15</td></tr>
<tr><td>NA13</td><td>54.87</td><td>3</td><td>134</td><td>74</td></tr>
<tr><td>NA14</td><td>60.69</td><td>3</td><td>325</td><td>70.5</td></tr>
<tr><td>NA15</td><td>15.26</td><td>2</td><td>13.3</td><td>22.4</td></tr>
</table></td></tr>
</table>

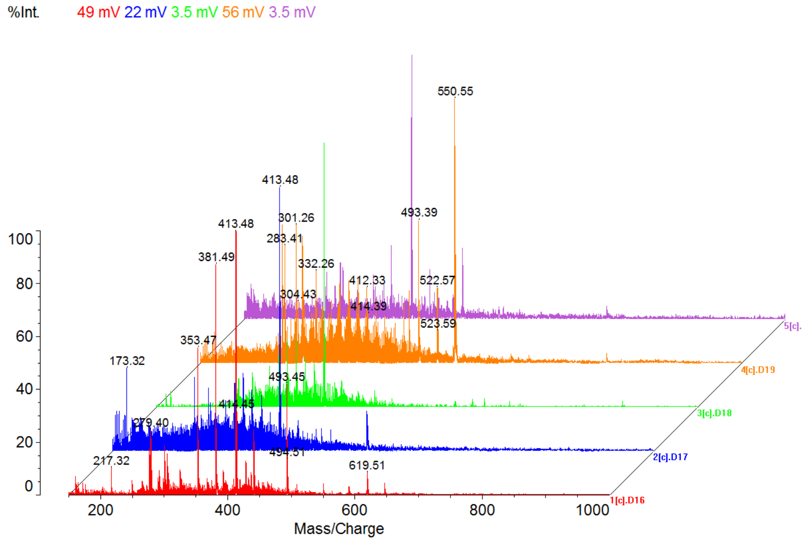
Objective(s) for application in the Ruprechtov project	Comparison of the amount of exchangeable uranium determined with ^{233}U with the results of sequential leaching could help in discussion of uranium sorption and/or mineralization in studied rock materials, as it gives complementary information about the form of uranium bound to the solid phase.
Practical procedure and experiences in the field	Only lab studies.
Applicability	The fast determination of total uranium /DEC 91/ and ^{233}U in one sample, which enabled to determine the amount of exchangeable uranium in solid samples, is comfortable and comparison of its results with standard method of sequential leaching is good.
Limits of application	The application of ^{233}U is without any problem, but the determination of total uranium could be influenced by the presence of anions influencing the fluorescence of measured uranium complex. Therefore the method of standard addition should be preferred.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The standard uncertainties of the experimental procedures and analytical methods used in the way of characterization rock materials are in the order of 10 %, but the uncertainty of parameters of models describing the interaction is greater due to the complexity of all equations that should be taken into account in the evaluation.
Method specific to defined boundary conditions	The method is applicable to rock samples originating from Ruprechtov site and other sites, in which the solid samples contain uranium.
Experiences (pos. / neg., what to avoid)	The parallel determination of both total uranium (KPA) and ^{233}U (radiometric) in one sample eliminates the influence of the inhomogeneity of solid phase, but the matrix effect is limiting in some cases.
Effort, comments	Development of a modified KPA method for uranium determination was time consumpting as the influence of some anions on the uranium fluorescence signal was not known from literature.
Links, references, other sources of information	Fundamental reports / reviews: /DAV 03/ Publications of CTU, Prague: /VOP 06/, /VOP 08/
Picture of the device	 *View of the TRLFS system in CTU laboratory, Prague*

Method No. A.30: LIBD (W. Hauser, U. Noseck)

Name of method	LIBD colloid analysis
Application in the Ruprechtov project	Measurement of colloid concentration in various groundwaters from Ruprechtov site.
Device(s) / method(s) used / applied	Laser-Induced Breakdown Detection (LIBD)
Brief description of the functioning	Colloid analysis is performed by the laser-induced breakdown detection (LIBD) in the laboratory using a closed flow-through cuvette without atmosphere contact The principle of LIBD is based on the generation of a dielectric breakdown in the focus region of a pulsed laser beam. As the threshold energy (irradiance) to induce a breakdown is lower for solids than for liquids or gas, the breakdown can be generated selectively in particles dispersed in solution at suitable pulse energy. Colloid concentrations are derived from the respective breakdown probability, represented by the number of breakdown events per number of laser shots, and the range of breakdown events within the laser beam axis determined by optical inspection of the laser focus area within the flow through cell. Colloid number concentrations (Pt/L) are given relative to a calibration with polystyrene reference colloids. Mass concentrations are calculated by assuming an average colloid density of 2.7 g/mL and spherical particle shape. A more detailed description of data evaluation is given in /HAU 02/.
State-of-the-Art and new developments	The applied method is state of the art. The in-situ apparatus was developed in the beginning of 2000 and applied at Ruprechtov in 2005. Of course, various other methods for colloid characterization, like Photon Correlation Spectroscopy (PCS) Flow Field Fractionation (FFF), MALDI-TOF (see Method No. A.31) or atomic force / electron microscopy are available. The major information derived for the Ruprechtov project was the colloid concentration.
Output of the method	Typical colloid concentrations are determined and have been compared with data from other sites.  *Comparison of colloid concentration in different types of natural groundwater, mineral water and synthetic NaCl-solution versus ionic strength (Data from Ruprechtov, Äspö tunnel; mineral water; NaCl solution, TGT: transit gas tunnel, MZD: Menzenschwand, GTS:Grimsel test site, BDS: Bad Säckingen, LEU: Leuggern, ZUR: Zurzach) from /DEG 96/, /SCH 10/*

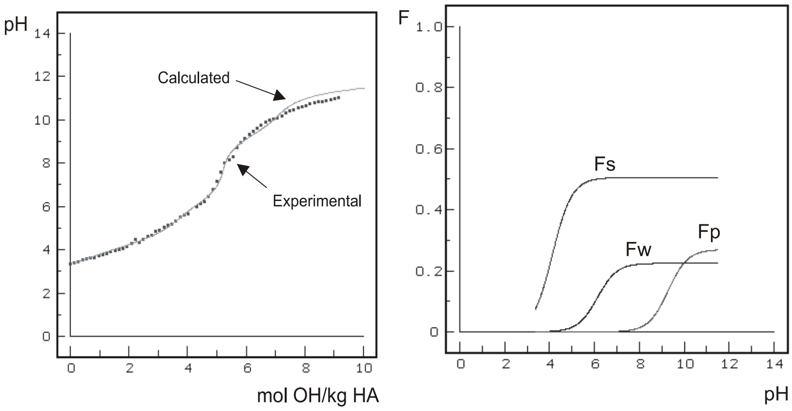
Objective(s) for application in the Ruprechtov project	Analyses of concentration, (type and size) of colloids in order to assess its impact on uranium. In the focus of interest were organic colloids, potentially released from sedimentary organic material.
Practical procedure and experiences in the field	For the borehole sampling steel cylinders with 3 L internal volume (outer diameter 76 mm, total height 800 mm) and a special inert coating are used. These cylinders were intensively cleaned and tested in the laboratory before use. Before transport to Ruprechtov the cylinders have been flushed with Argon gas and successively evacuated (pressure ~10^{-2} bar) to avoid a contact of the sampled groundwater with oxygen. The manually operated valves on top and on the bottom of the sampling cylinder are closed. The sampling cylinders are inserted into the respective borehole to the sampling depth. Then a remotely operated solenoid valve on top of the sampling cylinder is opened. This configuration allows a remote groundwater sampling in deep boreholes with as low disturbance as possible. Afterwards in laboratory each cylinder is connected with the high-pressure flow-through detection cell of the LIBD system for the detection of colloids, pH, Eh, electrical conductivity and for taking samples for chemical groundwater analysis. In order to avoid sampling of colloidal material, which becomes mobilised due to mechanical disturbance from insertion of the sample container into the borehole, samples should be taken an hour after sample container insertion
Applicability	The method is applicable to aerobic and anaerobic conditions down to concentrations of few ppt.
Limits of application	
Uncertainties / accuracy (devices, methods, evaluation procedure)	The LIBD sensitivity, as determined with the pure water dispersion of polystyrene reference particles for the smallest size available (19 nm), is attained down to few ppt at threshold energy of 1.4 mJ
Method specific to defined boundary conditions	The described method is applicable to water bearing systems. The system should be as undisturbed as possible.
Experiences (pos. / neg., what to avoid)	Samples taken with routine sampling procedure led to formation of iron oxide colloids formed by oxidation (contact with atmosphere) giving non-realistic values. The newly developed remote system allowed sampling groundwater under nearly undisturbed conditions.
Effort, comments	- Sampling in the field needs about two hours per borehole - Stable values in the lab were obtained after about 35 minutes
Links, references, other sources of information	Fundamental articles: /PLA 01/, /WAL 03/, /BUN 05/, /KIM 06/
Picture of the device	 *Mobile LIBD system*

Method No. A.31: MALDI-TOF (R. Červinka, J. Havel)

Name of method ***Application in the Ruprechtov project***	MALDI-TOF MS The Matrix Assisted Laser/Desorption Ionization - Time of Flight mass spectrometry (MALDI-TOF MS) was applied for organic substances characterization of Ruprechtov samples: groundwater, leachates and extracted natural humic substances from sedimentary organic matter.
Device(s) / method(s) used / applied	Mass spectra were measured using the AXIMA-CFR from Shimadzu (Kratos Analytical, Manchester, UK) mass spectrometer. For using this technique for organic substances characterization see /REM 95/.
Brief description of the functioning	Matrix-assisted laser desorption/ionization (MALDI) is a soft ionization technique used in mass spectrometry, allowing the analysis of biomolecules and large organic molecules. The sample is mixed together with a large quantity of matrix. The matrix absorbs the UV light from UV laser beam and converts it to heat energy. A small part of the matrix with the sample (upper part around 0.1 μm) heats rapidly and is vaporized. Charged ions of various sizes are generated and in electric field are guided to TOF MS. The time of ion flight differs according to the mass-to-charge ratio (m/z) value of the ion. In case of humic substances and also Ruprechtov samples, the spectra are measured in the laser desorption ionization (LDI) mode without using any matrix. All samples are dissolved in NaOH solution. 1 μL of solution is dropped to a sample plate, dried in an air stream at room temperature and inserted into the vacuum chamber of the instrument. After high vacuum is reached ($1{\cdot}10^{-5}$ Pa) the mass spectra are measured. The resulting spectra are always accumulated from at least 1000 shots /HAV 09/.
State-of-the-Art and new developments	Yes, but new instruments are available on the market (e.g. Shimadzu).
Output of the method	 *MALDI-TOF MS spectra of extracted humic substances from Ruprechtov sedimentary organic matter: red - humic acid HA-12/3 (borehole NA12), blue - humic acid HA-14 (borehole NA14), green - humic acid HA-14 different extraction technique (borehole NA14), orange - fulvic acid FA-12/3 (borehole NA12), purple - humic acid Leonardite (see IHSS)*

Objective(s) for application in the Ruprechtov project	To identify the source and the origin of dissolved organic carbon in Ruprechtov groundwaters; for further details see /HAV 09/.
Practical procedure and experiences in the field	Only sampling of groundwater was performed in the field, method itself is performed in laboratory.
Applicability	- The method was applied to the real groundwaters and also to its concentrates. The spectra were almost similar except the area of high m/z values. The dissolved organic carbon concentration was up to 4 mg/L for real groundwaters - The extracted humic substances were characterized by average molecular weight and by size distribution
Limits of application	Mainly for large organic molecules.
Uncertainties / accuracy (devices, methods, evaluation procedure)	See Shimadzu web-link (below)
Method specific to defined boundary conditions	No, but it is more relevant to organic rich rocks (e. g. sedimentary rocks)
Experiences (pos. / neg., what to avoid)	For spectra analysis and comparison the special software is needed from the supplier of measuring instrument.
Effort, comments	- No special preparation of samples (humic substances) - The purchase price of the equipment is very high
Links, references, other sources of information	- Measured by Masaryk Univerzity, Faculty of Science, Department of Chemistry, Brno - Shimadzu http://www.shimadzu.com/an/lifescience/maldi/index.html, 12.06.2014 - International Humic Substances Society (IHSS) http://www.humicsubstances.org/index.html, 09.06.2014
Picture of the device	 *AXIMA-CFR mass spectrometer (Kratos Analytical)*

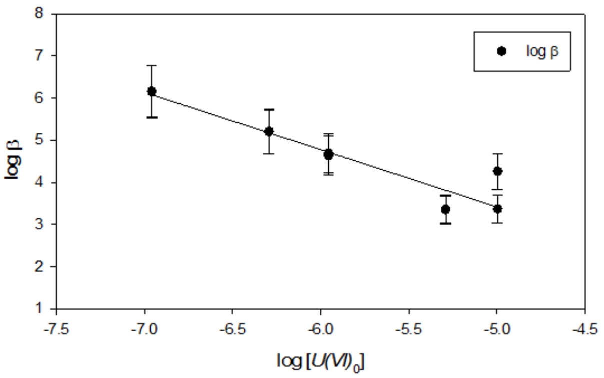
Method No. A.32: OM characterization (R. Červinka)

Name of method	Organic matter (OM) characterization
Application in the Ruprechtov project	Characterization of humic substances from sedimentary organic matter (SOM) at Ruprechtov site.
Device(s) / method(s) used / applied	Humic acid (HA) and fulvic acid (FA) extraction and main characterization - Alkaline extraction method /SWI 96/ and /MAL 91/ - Elemental composition: C, H, N, S, O - Fourier transform infrared spectroscopy (FTIR) - Exchange and loading capacity and protonation constants of HA /CER 11/
Brief description of the functioning	The alkaline extraction method is based on dissolution of HA in alkaline solutions and their precipitation in acidic solutions according to IHSS. FA are extracted with column XAD-8 resin. The characterization methods are standard procedures, except the exchange capacity and protonation constants determination. The total proton exchange capacity is determined by back titration of excess $Ba(OH)_2$ /STE 82/. The dissociation of two types of carboxylic and one phenolic functional groups is studied by the continuous potentiometric titration procedure and their protonation constants are found /FUK 95/, /STA 03/.
State-of-the-Art and new developments	To minimize the chemical modification of the humic substances the mild extractans can be used as $Na_4P_2O_7$ or HCOOH instead of NaOH. Mild extractants have lower yield of extraction. For the extraction of representative sedimentary organic matter the anaerobic conditions should be maintained during the extraction.
Output of the method	 *Titration curve of extracted HA-12/3 humic acid: experiment and fit - left. Relative abundance (F) of humic acid functional groups in dependence on pH. Fs - strong carboxylic groups, Fw - weak carboxylic groups and Fp - phenolic groups - right*
Objective(s) for application in the Ruprechtov project	Objectives were formulated on the base of previous results: - The colloids in groundwater are not organic origin - The contents of dissolved organic carbon (DOC) in groundwaters are low - The molecular patterns (mass/charge) of organic compound in groundwaters are similar to HA extracted from organic rich sediments (MALDI-TOF) First, the extraction and characterization of HA was accomplished with further study of a complexation between the U(VI) and HA /CER 11/ (see also Method No. A.33)

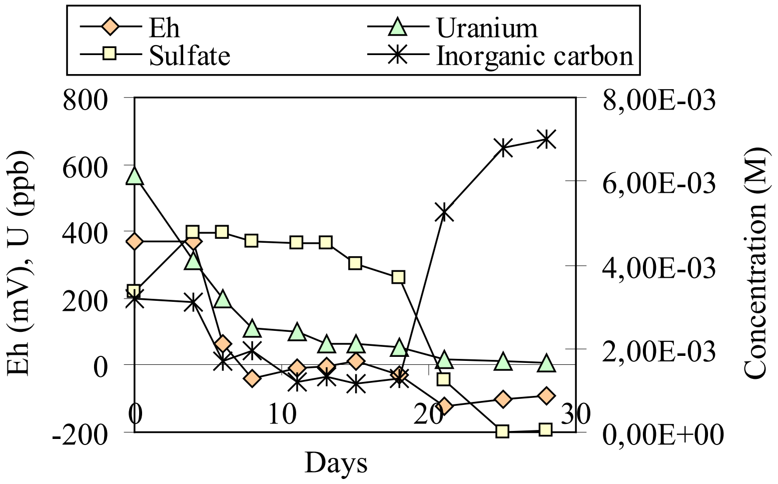
Practical procedure and experiences in the field	Only laboratory measurement and procedures.
Applicability	In principle, the titration curve of the given humic acid can be obtained using the classical volumetric procedure (titration with NaOH in inert atmosphere). There is the question, namely, which type of model is the best one - in literature can be found different models based on the number and properties of individual functional groups, and on the purpose of its application (it is the main viewpoint).
Limits of application	The limits can exist as a result of the composition and purity of given HA, and therefore, it is necessary to draw the attention to this problem. At first, the purification of HA has to be accomplished.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The uncertainties of resulting protonation constant values depend above all on the analytical method used, but also on the number of experimental points and so on. As a rule, the standard deviation amounts to 5 – 10 %. Evaluation procedures are based on the application of given model, corresponding code and numerical methods.
Method specific to defined boundary conditions	Mainly for sedimentary and organic rich samples.
Experiences (pos. / neg., what to avoid)	- The final step in extraction procedure - freeze drying - is helpful - The standard of HA or FA is highly recommended for experiments, available e. g. at IHSS
Effort, comments	- The extraction is time consuming - Costs: Elemental composition: C, H, N, S, O 20 € / sample, Lyophilization 60 € / 500 mL-sample
Links, references, other sources of information	International Humic Substances Society (IHSS) http://www.humicsubstances.org/index.html, 09.06.2014
Picture of the device	 *Eluates (0.1 M NaOH) with fulvic acids, the solution colour depends on FA concentration*

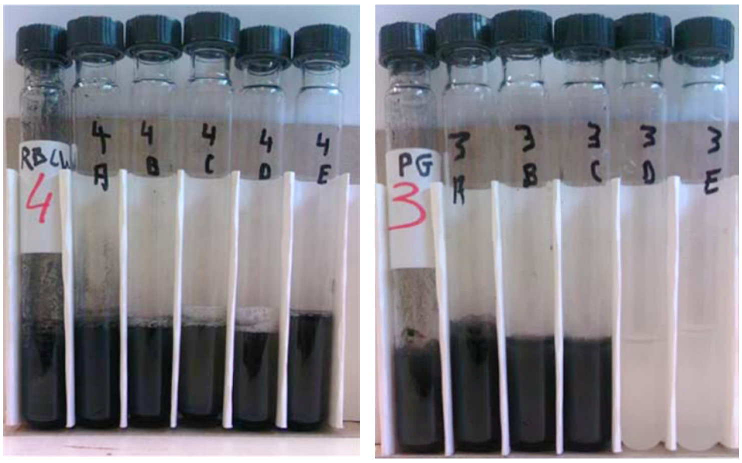
Method No. A.33: U/HA interaction (R. Červinka, K. Štamberg)

Name of method ***Application in the Ruprechtov project***	Interaction between uranium and humic acid Complexation between U(VI) and humic acid (HA) extracted from Ruprechtov sedimentary organic matter (SOM) and determination of complex thermodynamic constant.
Device(s) / method(s) used / applied	Complexation of U(VI) with HA - Cation exchange technique, e. g. /CZE 94/, /STA 03/ - Liquid scintillation counting with Triathler multilabel counter - Evaluation by charge neutralization model (CNM) /CZE 94/, /KIM 96/ and /CER 11/
Brief description of the functioning	The cation exchange method is performed with a strongly acidic cation exchange resin, where only cationic forms of U(VI) are exchanged by the resin. After equilibration, U-HA complexes, non adsorbed cationic forms of U and anionic ligands of HA remain in solution. The distribution of cationic forms of U between the solution and the cation exchange resin is measured in the presence and absence of HA. The stability constant is calculated from the balance shift in the system U(VI) - cation exchange resin - HA to the system U(VI) - cation exchange resin. Liquid scintillation counting is a standard method for measurement of alfa and beta emitters. The charge neutralization model belongs to the group of models supposing that binding (functional) groups behave as independent ligands without mutual interaction and where the complexation with the metal is described using concentrations of HA functional groups and the corresponding stability constant. The model supposes the formation of 1:1 (ligand/metal) complexes and assumes that the final complex charge is zero.
State-of-the-Art and new developments	The most important experimental methods for metal-humate complexes studies include the following steps: - Ultrafiltration and dialysis - Gel permeation chromatography, Size exclusion chromatography and High performance size exclusion chromatography - Ion exchange technique (used in this study) - Electrophoretic methods - Molecular fluorescence spectrometry - Time resolved laser fluorescence spectroscopy In this study, CNM was modified for multispecies system and the new relation for loading capacity of HA was derived, namely as a function of pH and ionic strength /CER 11/.

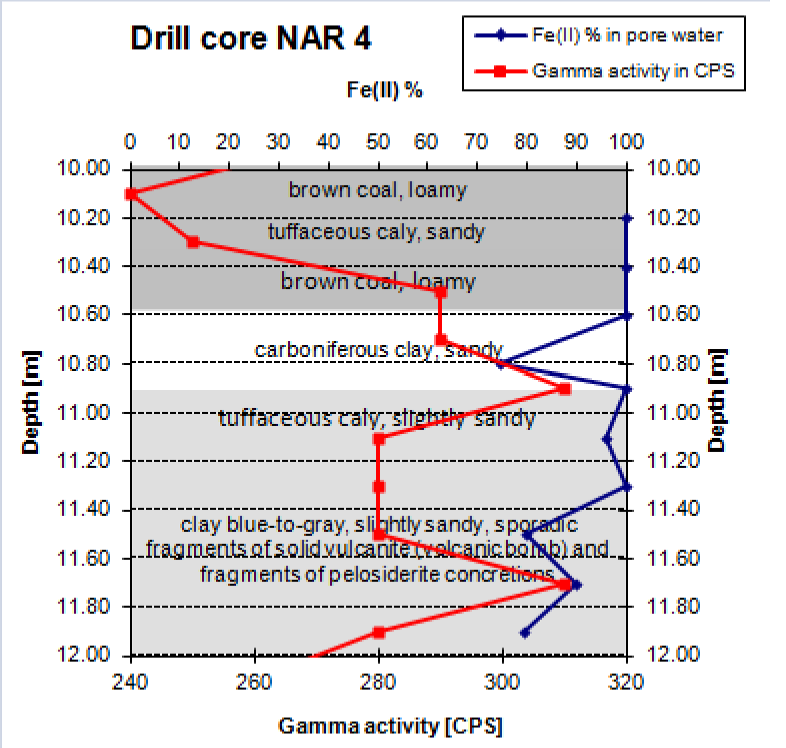
Output of the method	 *Dependence of log β (stability constant) on the molar concentration of uranium as log [U(VI)$_0$]*
Objective(s) for application in the Ruprechtov project	The study of complexation between U and HA and its extent was initiated, because organic compounds in groundwaters originate very probably from sedimentary organic matter and molecular patterns (mass/charge) of organic compound in groundwaters were similar to extracted HA from organic rich sediments (MALDI-TOF).
Practical procedure and experiences in the field	Laboratory method, no field procedure.
Applicability	The ion exchange method can be applied to the study of complexation of metals not only with HA, but also with the other types of ligands, generally it deals with anionic ligands.
Limits of application	If strongly acidic cation exchanger is used, two basic conditions have to be fulfilled: (1) the cation exchanger retains cationic forms of the given metal, and (2) the ligands and complexes, in consequence of their charge and size, remain in solution.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The uncertainties of resulting stability constant values depend above all on the analytical method used, but also on the number of experimental points and so on. As a rule, the standard deviation amounts to 5 – 10 %; evaluation procedures are based on the application of given model, corresponding code and numerical methods.
Method specific to defined boundary conditions	The defined boundary conditions (see e. g. 'Limits of application'), do not need any specific method to the fulfillment of the required experiments.
Experiences (pos. / neg., what to avoid)	There are good experiences with the ion exchange method to the study of U(VI) and Eu(III) - HA complexation (/STA 03/, /CER 11/); of course, the limits of application have to be taken into account.
Effort, comments	In the lab measurement, the study of complexation using ion exchange technique does not call for uncommon effort and costs, too.
Links, references, other sources of information	Triathler multilabel counter: http://www.hidex.com/products/triathler.aspx, 23.10.2014.
Picture of the device	 *Triathler multilabel counter (photograph: Hidex Co., Finland)*

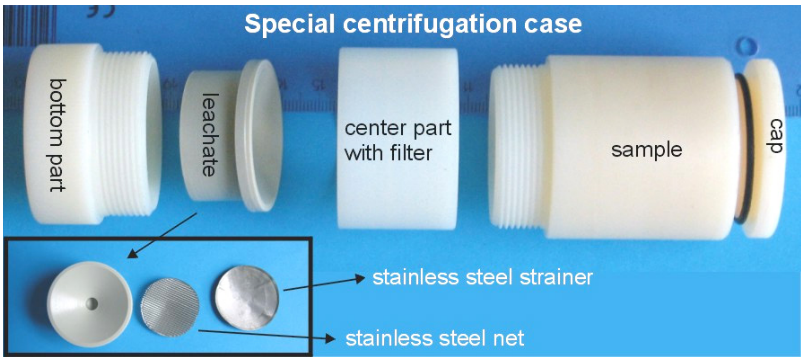
Method No. A.34: Microbial analysis (U. Noseck, R. Cervinka)

Name of method	Microbial analysis
Application in the Ruprechtov project	Identification of indigeneous microorganisms and impact of sulfate reducing bacteria on geochemistry.
Device(s) / method(s) used / applied	Growth and isolation of sulfur oxidizing bacteria, iron reducing and oxidizing bacteria as well as fungi. Batch experiments with Sulfate Reducing Bacteria (SRB)
Brief description of the functioning	For microbial growth common aerobic and anaerobic culture media on solid plates or in liquid forms are used. The sulfur oxidizing bacteria are isolated using Stakey medium /VIS 57/, fungi on DRBC medium (DIFCO) and the iron chelating microorganisms are detected on CAS medium /SCH 87/. Batch experiments with SRB: To stimulate the growth of SRB, batches of NA4-33 and NA4-36 sediments and GW6 groundwater (50 g : 500 mL) are amended with lactate (5 mM), sulfate (4 mM) and phosphate (20 mg/L). In the experiment the system is spiked with U^{6+} to reach final concentrations of about 600 µg/L.
State-of-the-Art and new developments	The study was limited and strongly focused on the role of sulfate reducing bacteria. This was done according to the state of the art /ALE 95/.
Output of the method	From microbial analysis qualitative information about the occurrence of several microorganisms. Fungi, facultative $Gram^+$ and $Gram^-$ bacteria, sulfur oxidizing bacteria, and sulfate-reducing bacteria were identified in two samples from clay/lignite horizon. In batch experiments the impact SRB (stimulated) was investigated. Examplarily the impact on geochemical conditions is shown below. By microbial degradation sulfate is reduced (concentration decrease) by simultaneously production of inorganic carbon from organic carbon degradation. The process leads to a decrease of Eh and concomitant decrease of U (very likely to reduction of U(VI) to U(IV).  *Evolution of Eh, sulfate, uranium and inorganic carbon concentrations in sediment/GW-system NA4-33. Growth of SRB was stimulated by addition of sulfate, lactate and phosphate at 22°C*
Objective(s) for application in the Ruprechtov project	Identification of the occurrence of microorganisms (particularly SRB) and characterization of the potential impact of SRB on geochemical processes with relevance for uranium mobilization / immobilization.
Practical procedure and experiences in the field	As much as possible sterile conditions have to be established during sampling. This was realized by flushing of the drilling tubes with alcohol and subsequent packaging.

Applicability	The method is applicable to all kind of rock material. A prerequisite is the provision of sterile conditions during sampling and sample handling (see above).
Limits of application	A sterile laboratory is needed. The batch experiments need to be performed in a glove box to protect the system against atmosphere.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The characterization of microbes is a qualitative method. Uncertainties are however due to the possibility to contaminate the sample with non-inidigeneous bacteria.
Method specific to defined boundary conditions	See “Applicability”.
Effort, comments	Standard methods in microbiology and hydrobiology (Institute of Microbiology of the ASCR, v. v. i., RNDr. František Nerud)
Links, references, other sources of information	- Comprehensive study on material from Mont Terri /STR 07/ - http://www.climategeology.ethz.ch/publications/2007_Stroes_Gascoyne_et_al.pdf - Overview report on the impact of microbes on the integrity of clay /MEA 11/ (http://www.grs.de/publication/GRS-291)
Picture of the device	 *SRB samples from Boom Clay cultivated in two different media /AER 09/; black colour shows precipitation of iron sulfide*

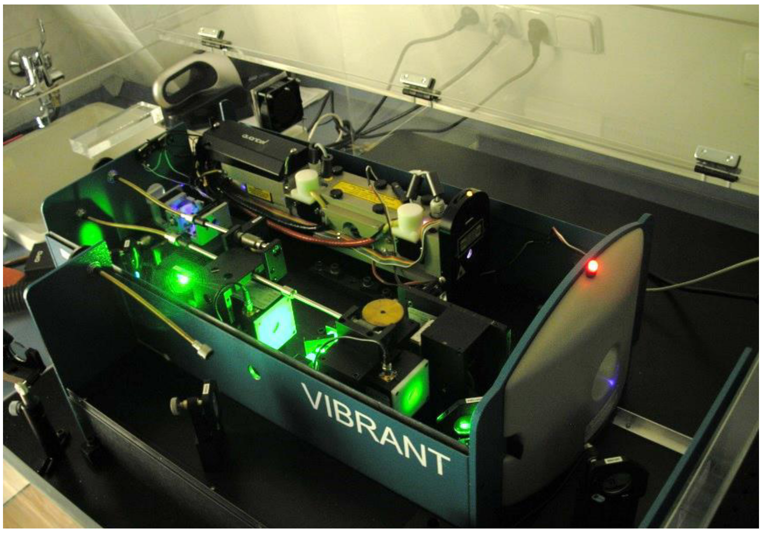
Method No. A.35: Fe(II)-Fe(III) analysis (R. Červinka)

Name of method ***Application in the Ruprechtov project***	Fe(II)/Fe(III) analysis Quantification of Fe^{2+}/Fe^{3+}-species in leachates from drill core samples and porewater samples under anaerobic conditions. Evaluation of oxidation/reduction conditions.
Device(s) / method(s) used / applied	Spectroscopic determination of Fe^{2+}/Fe^{3+} using adapted ferrozine method /VIO 00/. Special centrifugation case (see figure below).
Brief description of the functioning	Centrifugation case enables to obtain porewater from clay/sand sediments in gravitational field without influence by oxygen. The ferrozine (CAS Number 69898-45-9) reacts with divalent Fe to form a stable magenta complex /STO 70/. When Fe^{3+} is also present in solution it can react with ferrozine and interfering with the coloration of the ferrous complex. The contribution of both species is distinguished using reduction step, when Fe^{3+} reduces to Fe^{2+}. The absorbance is measured before and after the reduction step. From calibration curves and absorbances the Fe^{3+} and Fe^{2+} content can be calculated /VIO 00/
State-of-the-Art and new developments	Classically, the spectrophotometric measurement of both species is based on separate measurement of Fe^{2+} and total Fe (i. e. Fe^{2+} + Fe^{3+}). Fe^{3+} is calculated by difference. The method described here enables to measure Fe^{2+} and Fe^{3+} in one sample at submicromolal concentrations.
Output of the method	 *Depth profile of drill core NAR4 with Fe(II) content (%) in porewater and gamma activity (counts per second - CPS)*
Objective(s) for application in the Ruprechtov project	Evaluation of redox conditions in porewater of rock samples.
Practical procedure and experiences in the field	All sampling was done in a polyethylene glove bag under anaerobic conditions.

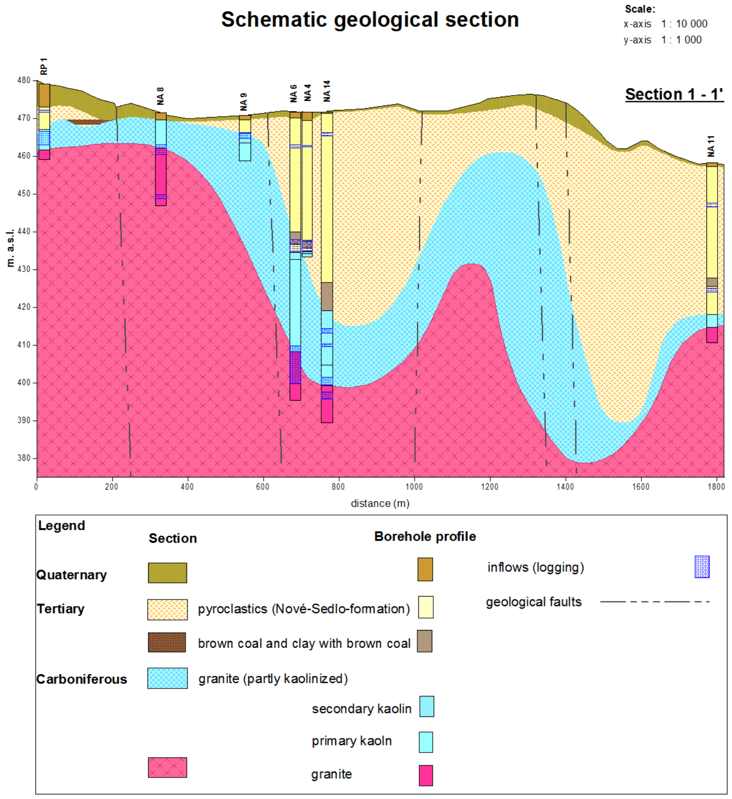
Applicability	- The drill cores have to be transported under anaerobic conditions, after centrifugation in special centrifugation case the iron is immediately measured - The ferrozine-Fe^{2+} complex is stable between pH 4 and 9 with maximum absorbance at 562 nm - Detection limit is around 1×10^{-6} mol/L
Limits of application	The maximum applicable centrifugal force is limited. As a consequence, the obtainable amount of porewater may not be sufficient for iron determination from low permeable rock samples.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Accuracy of concentration determination decreasing significantly in ratios higher than 95 % Fe^{2+} and 5 % Fe^{3+}.
Method specific to defined boundary conditions	See “Limits of application”
Experiences (pos. / neg., what to avoid)	- Fe(II)/Fe(III) analysis is reliable indicator for redox conditions - Sampling and transport have to be conducted under anaerobic conditions
Effort, comments	Spectroscopic determination is a relatively cheap method.
Links, references, other sources of information	Polyethylene glove bag (AtmosBag, Sigma-Aldrich): http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al211.pdf (10.04.2014)
Picture of the device	 *Special centrifugation case used in connection with Fe(II)/Fe(III) analysis*

Method No. A.36: TRLFS (D. Vopálka, A. Zavadilová)

Name of method ***Application in the Ruprechtov project***	Time resolved laser induced fluorescence spectroscopy (TRLFS) Determination of uranium hydroxocomplexes and carbonate species in natural waters.
Device(s) / method(s) used / applied	- Tunable laser system based on flash lamp pumped Q-switched Nd: YAG laser is used as fluorescence excitation source (repetition rate 10 Hz, pulse length < 2 ns, wavelength 416 nm) of TRLFS measurements - Measurements are performed at temperature range of 13 – 20 °C of the studied solution. Emitted fluorescence is detected using monochromator and imaging spectrograph - The focus of the work consists of evaluating spectral characteristic corresponding to observed form for sets of solutions, whose composition differed mainly in the calcium concentration and pH
Brief description of the functioning	- In each measurement the fluorescence intensity is summed over preset number of laser pulses for every gate. Dependence of the sum of fluorescence intensity for each gate time versus time enable to determine decay curve and then by fitting calculate the lifetime of the complex - Spectral characteristics of fluorescent signals of different forms were determined
State-of-the-Art and new developments	The method is based of known principles of TRLFS. The realization of method needed a specific approach related to TRLFS system available, see /MOU 03/, /GEI 08/, /BER 96/.
Output of the method	Four uranyl-carbonate ($(UO_2)_3(OH)_5^+$, $(UO_2)_2(CO_3)(OH)_3^-$, $Ca_2UO_2(CO_3)_3$ and $UO_2(CO_3)_3^{4}$) were identified in modelled Ruprechtov water and their lifetimes were determined. Model speciation diagrams with adequate representation of species were generated using the calculations performed in the program PHREEQC using database HATCHES. The equilibrium reaction constant of $Ca_2UO_2(CO_3)_3$ species was determined for two temperatures relative to the zero ionic strength. Results were obtained by evaluating ratios of fluorescent signals corresponding to the solutions with different Ca^{2+} concentration by method based on the speciation calculations in PHREEQC program. Log K_0 of $Ca_2UO_2(CO_3)_3$ was determined as 30.65 ± 0.45 for 20°C and 31.43 ± 0.25 for 13°C, and standard reaction enthalpy ($\Delta H° = 179.3$ kJ mol^{-1}) was calculated.
Objective(s) for application in the Ruprechtov project	The methodology of differentiated time resolved laser fluorescence spectroscopy (TRLFS) allows studying speciation of uranium, which in turn effects its migration behaviour.
Applicability	TRLFS method can be used only for species with luminescence properties.
Limits of application	TRLFS is a very sensitive method and can be used only for “clean” solutions which are not polluted e. g. by organics.
Uncertainties / accuracy (devices, methods, evaluation procedure)	The standard uncertainties of experimental procedures and analytical methods are in the order of 5 %. The uncertainty of results which are obtained by fitting and using mathematical models is from 5 – 30 %, depending on the fluorescence signal intensity, signal noise and background effects.

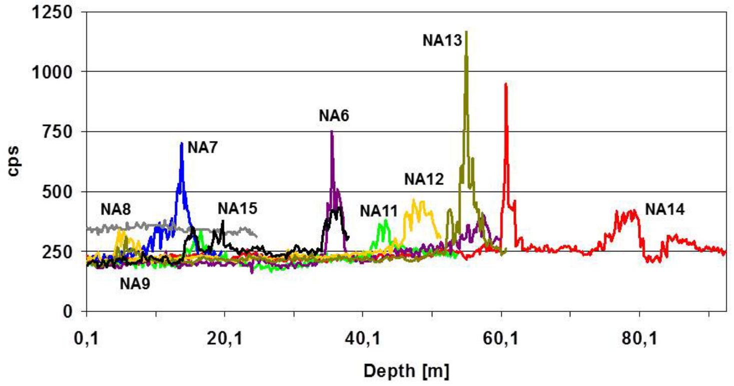
Method specific to defined boundary conditions	The method is applicable for natural waters containing uranium. So far, the measurements were performed only for laboratory prepared analogs of natural samples.
Effort, comments	Determination of uranium speciation in natural waters in connection with the study of the migration for the compounds showing luminescence properties.
Links, references, other sources of information	Fundamental article: /MOU 03/
Picture of the device	 *View on the TRLFS system in CTU's laboratory in Prague*

Method No. A.37: Drill core description (R. Červinka, F. Woller)

Name of method ***Application in the Ruprechtov project***	Drill core description Basic petrographical description of drill cores and basis for geological cross-sections.
Device(s) / method(s) used / applied	Classical observation with basic tools (meter rule, knife, axe, geologist's hammer, acid, camera).
Brief description of the functioning	Visual observation of drill cores, petrographical description and classification of rocks, preliminary assignment of rocks to stratigraphic units.
State-of-the-Art and new developments	Yes, classical geological procedure.
Output of the method	 *Geological cross-section (SE-NW) at Ruprechtov site, derived from drill core description*
Objective(s) for application in the Ruprechtov project	Data from drill core description support mainly: - Stratigraphic orientation (during drilling) - Identification of permeable zones - Interpretation of logging data - Following micro-structural studies - Compilation of a geological model of the site (stratigraphic correlation, morphology)
Practical procedure and experiences in the field	Description of drill cores is done immediately after drilling. Drill core sections with higher uranium content were just quickly described but preserved against oxygen contact by special, tightly sealed tubes at once (see /NOS 06/ for photodocumentation).
Applicability	Applicable to all drill cores.
Limits of application	- Drill core quality (see "Experiences") - Visual inspection has limitation in resolution (cm)

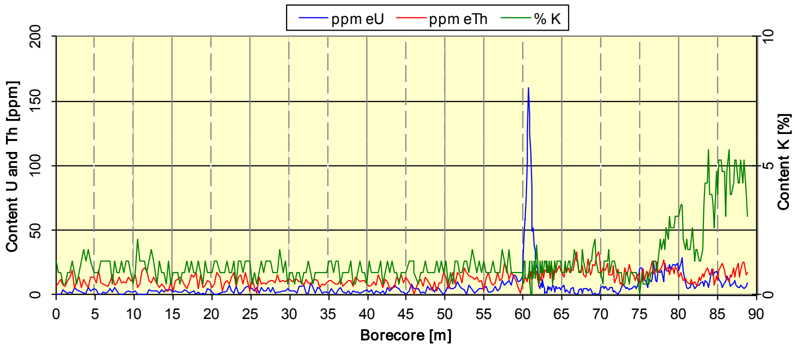
Uncertainties / accuracy (devices, methods, evaluation procedure)	Uncertainties can be connected with actual knowledge about the lithostratigraphic units (e. g. member), which can be changed in future due to new stratigraphic understanding of the area.
Method specific to defined boundary conditions	Applicable to all kind of rock, but observed features can differ with type of rock (sedimentary, igneous, metamorphic rocks).
Experiences (pos. / neg., what to avoid)	Drilling without fluid distorted drill cores and made desription partly impossible (especially in plastic clayish sections, see Method No. 8.5: Drilling technology). Personal experience with local geology is important for description of drill cores.
Effort, comments	- For data evaluation special software is used (e. g. LogPlot by RockWare) - Costs of procedure is app. 2,00 € / m
Links, references, other sources of information	LogPlot and Surfer software by RockWare: http://www.rockware.com (27.02.2014)
Picture of the device	 *Visual observation and description of drill cores in the field*

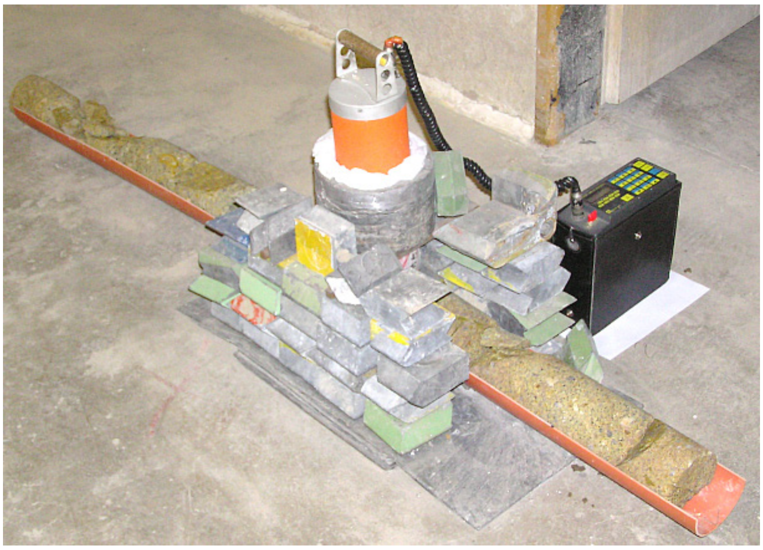
Method No. A.38: Field γ spectrometry (T. Brasser)

Name of method ***Application in the Ruprechtov project***	Field gamma spectrometry Gamma scanning of drill cores in the field (on-site).
Device(s) / method(s) used / applied	Differential Gamma Ray Spectrometer, Type GRS-500 (EDA-Instruments Inc., Canada - taken over by Scintrex Ltd., Canada).
Brief description of the functioning	Portable, five-channel wide energy band spectrometer for measuring all terrestrial gamma radiation; device used contains a thallium-activated, sodium iodide crystal with a volume of 124 cm²; the NaI (TI)-crystal being coupled to a high-stability photomultiplier tube (PIT) to form the detector, magnetically shielded by Mu-metal.
State-of-the-Art and new developments	Yes - comparable devices on the market (from multiple manufacturers).
Output of the method	 *Total gamma ray activity, displayed as "cps" (counts per second) in different boreholes at Ruprechtov site*
Objective(s) of application in the Ruprechtov project	- Immediate identification of Uranium-enriched layers in drill cores in order to protect them against air-contact at once - Assistance in addressing the drilled stratigraphic layers and control of drilling activity - Correlation of real vs. core length
Practical procedure in the field	- Device' energy window switch to "tc1" (total counts above 80 keV = most sensitive position) - Measurement of background radiation on surrounding soil - Scanning of the drill cores (in core boxes) app. each 20 cm, manual entry in a table, possibly in a graph - measured values above background indicate U-enrichment in drill core
Applicability	- Normalized display up to 99,999 cps - Operating temperature -10°C to +50°C
Limits of application	- High background radiation (> layer, to be detected) - Very low anomalies (in the range of surface background)
Uncertainties / accuracy (devices, methods, evaluation procedure)	Smudging of stratigraphic boundaries, resp. U-enriched layers by drilling mud is possible; in general only a resolution in the 10 cm range is feasible (sufficient for identifying one-meter portions of the drill core).

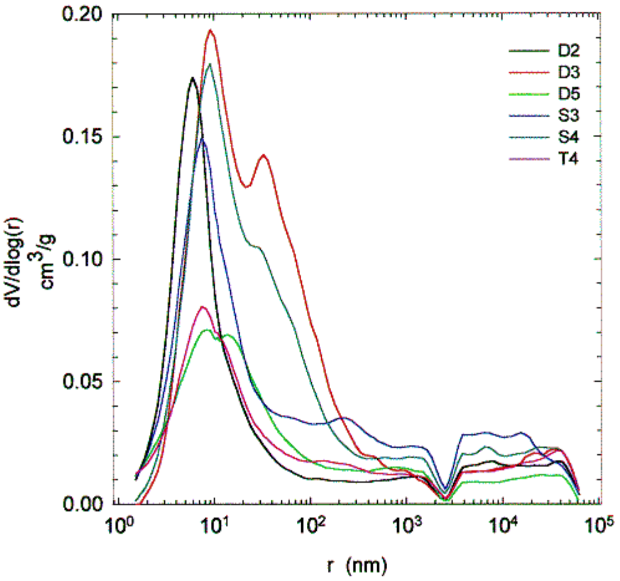
Method specific to defined boundary conditions	No, as a field device it can be used under almost all relevant conditions; measurement of gamma radiation is independent from rock type.
Experiences (pos. / neg., what to avoid)	Reliable method for field use with sufficient accuracy.
Effort, comments	- No sample preparation needed - Very fast measurement(s) [seconds] - No need for exact data evaluation (for field decision) - Maintenance-free device (except for occasional calibration-checks)
Links, references, other sources of information	- Manufacturer homepage (EDA's successor Scintrex): http://www.scintrexltd.com/ - Operational manual: /EDA 80/ - Review article: /MAK 95/
Picture of the device	 *Differential Gamma Ray Spectrometer, Type GRS-500 (EDA-Instruments Inc., Canada)*

Method No. A.39: Lab γ spectrometry (R. Červinka, M. Matolín)

Name of method	Laboratory gamma-ray spectrometry
Application in the Ruprechtov project	Gamma-ray spectrometric measurement of the content of natural radionuclides K, U, Th in drill cores.
Device(s) / method(s) used / applied	Portable gamma-ray spectrometer GS-256 with scintillation detector NaI(Tl) 76x76 mm, 256 channel energy analyzer, energy resolution 7.5 % (662 keV) and spectrum stabilization.
Brief description of the functioning	Drill cores with or without transportation case are measured in a Pb-shielded area (Pb-segments) using a gamma-ray spectrometer, step 0.1 m and exposure time 2 minutes.The correction for drill core geometry is determined by measuring the IAEA standards (RG-set: RGK-1, RGU-1 and RGTh-1) and correction on attenuation of transportation tubes is accounted. Measured energies: ^{40}K 1461 keV, ^{214}Bi 1764 keV (for U), ^{208}Tl 2615 keV (for Th). Weight concentrations are expressed in units % K, ppm eU and ppm eTh (e denotes the concentration under assumption of radioactive equilibrium in decay-series of U and Th). Conversion relations: 1 % K = 313 Bq/kg ^{40}K, 1 ppm eU = 12.35 Bq/kg ^{226}Ra i. e. ^{238}U, 1 ppm eTh = 4.06 Bq/kg ^{232}Th.
State-of-the-Art and new developments	Comparable devices on the market (from various manufacturers).
Output of the method	 *Depth profile of drill core NA14 with K (%), eU (ppm) and eTh (ppm) content*
Objective(s) for application in the Ruprechtov project	- More precise detection of natural radionuclides enrichments with identification of their proportion on gamma-ray activity - Correlation of borehole depths vs. core length (prolongation of plastic rock core during the drilling)
Practical procedure and experiences in the field	Measurements were performed under laboratory conditions (inside a building basement).
Applicability	Analyses of all rock materials with natural radionuclides (and daughter products) detected by gamma-ray spectrometry.
Limits of application	Minimum content (not specified) of natural radionuclides needed; extremely low concentrations are not detectable.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Accuracy of measurement depends on: calibration of gamma-ray spectrometer, geometry correction, correction for gamma-ray absorption, effectivity of background radiation shielding.
Method specific to defined boundary conditions	Usage as portable device is possible under almost all relevant conditions. Values from drill core head pieces and broken drill cores are measured in non-standard geometry (deficit of mass of drill cores) and therefore may be distorted.

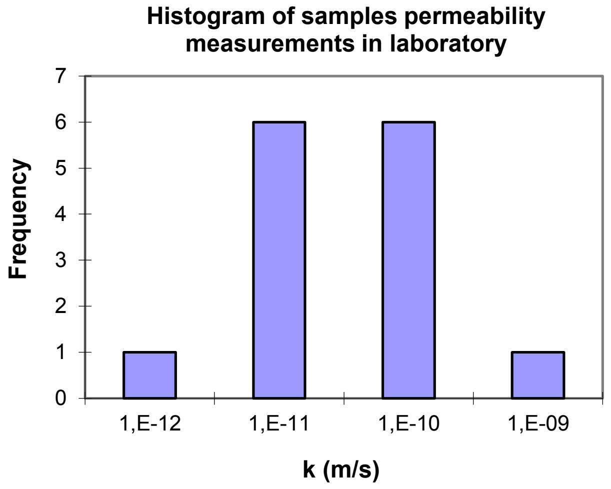
Experiences (pos. / neg., what to avoid)	No special experiences gained.
Effort, comments	- No sample preparation; quantitative and qualitative assays - Quality of measurement corresponds to measurement (exposure) time
Links, references, other sources of information	- Performed by Institute of Hydrogeology, Engineering Geology and Applied Geophysics, Geology, Charles University in Prague - Various producers of portable gamma-ray spectrometers - IAEA documents: /IAEA 03/, /IAEA 10/, /IAEA 13/ - Other documents: /MAT 05/
Picture of the device	 *Setup of laboratory gamma-ray spectrometry*

Method No. A.40: Hg porosimetry (R. Červinka)

Name of method ***Application in the Ruprechtov project***	Hg-porosimetry Size and distribution of pores in selected rock samples.
Device(s) / method(s) used / applied	AUTOPORE III (Micromeritics, USA) - high-pressure mercury porosimeter, high-pressure mercury intrusion up to 400 MPa (corresponds to pore radii of 1.5 nm).
Brief description of the functioning	Hg porosimetry /GIE 06/ is based on the capillary law governing liquid penetration into small pores. This law, in the case of a non-wetting liquid like mercury and cylindrical pores, is expressed by the Washburn equation $D = -(1/P)4\gamma \cos\varphi$ where D is pore diameter, P the applied pressure, γ the surface tension and φ the contact angle, all in consist unit. The volume of mercury V penetrating the pores is measured directly as a function of applied pressure. This P-V information serves as a unique characterization of pore structure
State-of-the-Art and new developments	Hg-porosimetry is performed nearly exclusively on automatic commercial instruments that differ mainly in the highest operative pressure, which determines the size of smallest attainable pores. The highest pressure is limited by the uncertainty about the validity of the Washburn equation, which forms the basis of data evaluation. In pores with sizes similar to the mercury atom the assumption that physical properties of liquid mercury (surface tension, contact angle) are equal to bulk properties is, probably, not fully substantiated. For this reason the up-to-date instruments work with pressures up to app. 4,000 bar.
Output of the method	 *Pore size distribution/frequency for NA5 drill core samples. X-axis: pore radius, Y-axis: change in volume intrusion divided by change in pore radii (log)*
Objective(s) for application in the Ruprechtov project	- Detailed information about pore size distribution - Support for hydrodynamical measurements (e. g. permeability measurements)
Practical procedure and experiences in the field	Lab-method; no specific preparation in the field is necessary.
Applicability	Applicable to all relevant rocks.

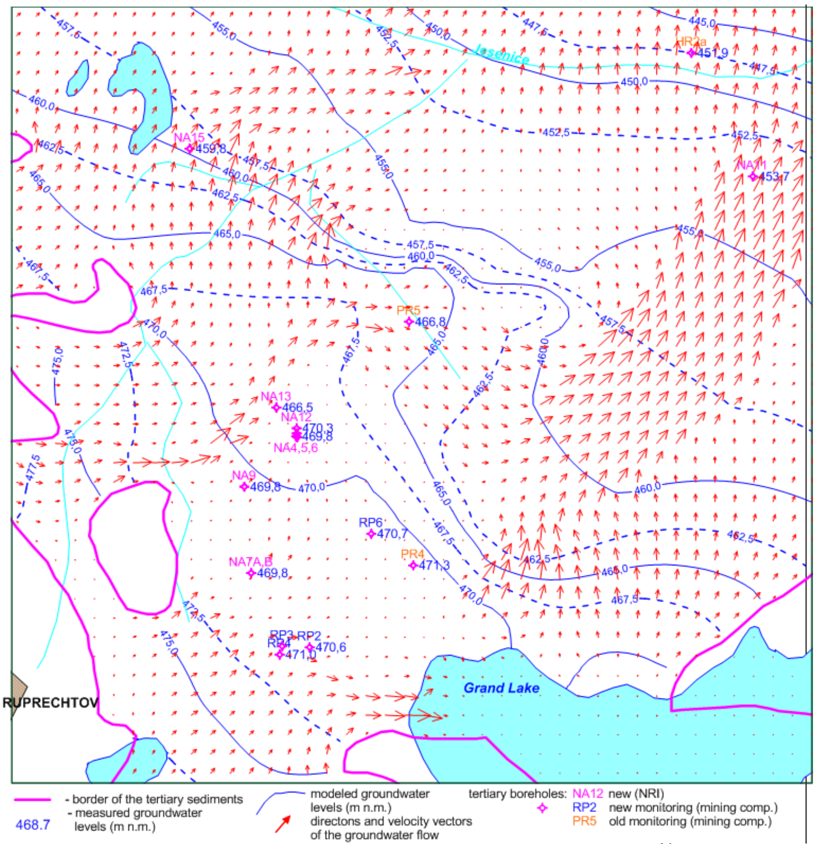
Limits of application	Method allows to measure pore diameters from 0.003 to 360 µm.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Collects extremely high-resolution data; better than 0.1 µL for mercury intrusion and extrusion volume.
Method specific to defined boundary conditions	In general, no; - Sample requirements: bulk or powder material which does not interact with mercury - Maximum size of the cylindrical sample is 2.5 cm in diameter and a height of 2.5 cm
Experiences (pos. / neg., what to avoid)	Standard laboratory method, no specific experiences.
Effort, comments	- Standard technique - Institute of Chemical Process Fundamentals of the ASCR, v.v.i., CZ, app. 75 € per sample
Links, references, other sources of information	- Micromeritics, USA, http://www.micromeritics.com/, 12.06.2014 - Device documents, http://www.micromeritics.com/product-showcase/AutoPore-IV.aspx, 12.06.2014
Picture of the device	 *AUTOPORE III - high-pressure mercury porosimeter (Micromeritics, USA)*

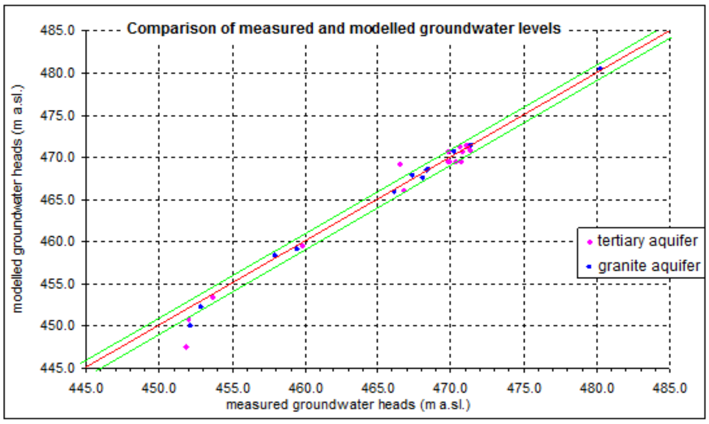
Method No. A.41: Permeability measurements (R. Červinka, T. Brasser)

Name of method ***Application in the Ruprechtov project***	Permeability measurements Lab measurements of permeability (hydraulic conductivity - k) and porosity.
Device(s) / method(s) used / applied	Permeability meter based on Czech technical standard /ČSN 05/, non-commercial apparatus, manufacturer Petr Brůha - MONITORING servis, Czech Republic.
Brief description of the functioning	Laboratory determination of permeability is based on the application of permanent pore (saturation) pressure on the front of a sample (adjusted to a cylinder); measuring of volume of pure water flowed through the sample over a distinct time interval. From the height, cross-section area and the difference of pressure heights the hydraulic conductivity is calculated.
State-of-the-Art and new developments	In general, from Darcy's law equation the hydraulic conductivity [m/s] can expressed as follows: $$k = -\frac{Q}{A \cdot \left(\frac{\Delta h}{\Delta l}\right)}$$ where Q is volume per time, A is cross-section and dh/dl is hydraulic gradient. The hydraulic conductivity is a function of fluid and porous media properties. The measurements of hydraulic conductivity are performing in two main modes: with constant gradient or non constant gradient. A lot of national and international standards are available for methodology of measurement.
Output of the method	 *Laboratory measurements of permeability k ranges from* 2×10^{-12} *to* 7×10^{-9} *m/s (NA4, NA6, NA7, RP3)*
Objective(s) for application in the Ruprechtov project	- Hydraulic conductivity of specified layer/sample - Comparison of hydrodynamical measurement in-situ (wells) and in laboratory
Practical procedure and experiences in the field	Laboratory measurements.
Applicability	Applicable to all relevant rocks.
Limits of application	- The diameter of core has to fit to the apparatus - Degassed water should be used - Before the test procedure the sample has to be fully saturated

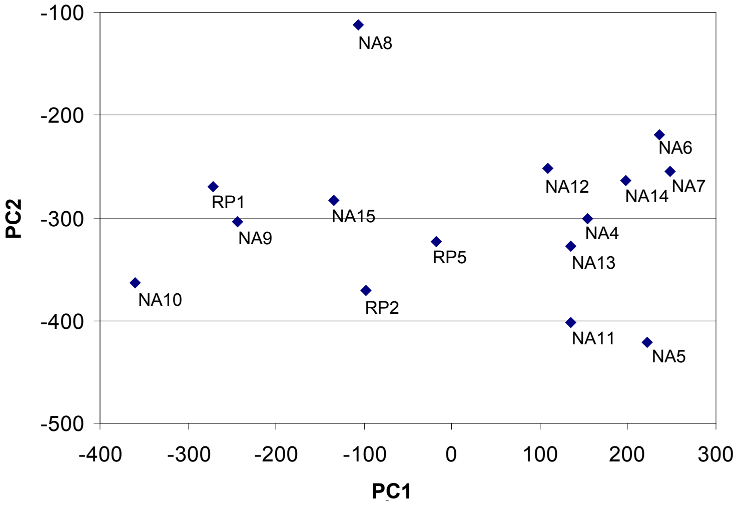
Uncertainties / accuracy (devices, methods, evaluation procedure)	Technical parameters: - Max. pressure of saturation 300 kPa - Usable water volume without refilling 450 mL - Accuracy for volume measurement 0.001 mL - Accuracy for pressure difference 0.1 mm of water column - Accuracy for temperature measurement 0.01°C - Accuracy for saturation pressure measurement 0.01 kPa - Datalogger capacity 5,485 values - Frequency of measurement from 1 sec to 24 hours
Method specific to defined boundary conditions	See “Limits of application”
Experiences (pos. / neg., what to avoid)	Standard laboratory method with good interlaboratory comparison.
Effort, comments	- Standard laboratory method - Low cost
Links, references, other sources of information	See Czech technical standard /ČSN 05b/ or ISO/TS 17892-11.
Picture of the device	 *Permeability meter - manufacturer Petr Brůha - MONITORING servis, Czech Republic*

Method No. A.42: Hydrogeological modelling (M. Milicky)

Name of method ***Application in the Ruprechtov project***	Hydrogeological (hydraulic) modelling Evaluation of the groundwater flow and groundwater mass balance.
Code(s), version(s) and database(s) used	Computer codes: MODFLOW 2000 /HAR 00/; Groundwater Vistas, version 4 /RUM 04/,.
Brief description of the code(s)	MODFLOW is a 3D finite-difference groundwater model with a modular structure. MODFLOW 2000 simulates steady and non-steady flow in an irregularly shaped flow system with confined / unconfined aquifers. Flow from external stresses, such as flow to wells, areal recharge, evapotranspiration, flow to drains, and flow through river beds, can be simulated. Hydraulic conductivities or transmissivities for any layer may differ spatially and be anisotropic (restricted to having the principal directions aligned with the grid axes), and the storage coefficient may be heterogeneous. Groundwater Vistas (GV) is a Windows graphical user interface for 3D groundwater flow & transport modelling in MODFLOW MODPATH (both steady-state and transient versions), MT3DMS, MODFLOWT, MODFLOW-SURFACT, MODFLOW2000, GFLOW, RT3D, PATH3D, SEAWAT and PEST software.
State-of-the-Art and new developments	New Modflow version 2005 and Groundwater Vistas, version 6 are available.
Output of the method	 *Groundwater flow and it´s mass and directions in the 1^{st} model layer - Tertiary sediments (uninfluenced flow)*

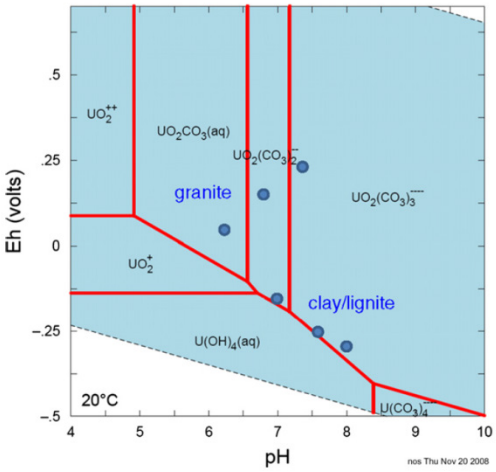
<table>
<tr><td></td><td>
</td></tr>
<tr><td><i>Objective(s) for application in the Ruprechtov project</i></td><td>Groundwater flow directions is generally from south-west to north (in all model layers), dominantly under influence of hydraulic conductivity (particularly zones with high or low permeability (water blocking zones). The smallest groundwater flow is through Tertiary volcano-detritic sediments (particularly in 1st model layer is negligible). Total balance:
<table>
<tr><th>Inflows</th><th></th><th></th><th>Outflows</th><th></th><th></th></tr>
<tr><td>rainfall infiltration</td><td>(l/s)</td><td>11.90</td><td>drainage into rivers</td><td>(l/s)</td><td>0.68</td></tr>
<tr><td>lake Velky rybnik</td><td>(l/s)</td><td>0.14</td><td>lake Velky rybnik</td><td>(l/s)</td><td>1.73</td></tr>
<tr><td></td><td></td><td></td><td>fault zone Krusne Hory</td><td>(l/s)</td><td>6.20</td></tr>
<tr><td></td><td></td><td></td><td>quarry Hajek</td><td>(l/s)</td><td>3.42</td></tr>
<tr><td>TOTAL</td><td>(l/s)</td><td>12.04</td><td>TOTAL</td><td>(l/s)</td><td>12.03</td></tr>
</table>
Groundwater flow quantity is higher through granite rocks (particularly through fissure zones) - third model layer.</td></tr>
<tr><td><i>Applicability</i></td><td>- Input data: → Hydraulic conductivity, recharge, porosity
- Boundary conditions: → Drainage into the streams and springs; Cauchy 3rd type</td></tr>
<tr><td><i>Limits of application</i></td><td>Knowledge of the input data.</td></tr>
<tr><td><i>Uncertainties / accuracy (devices, methods, evaluation procedure)</i></td><td>Uncertainties during the evaluation of the measured data (esp. hydraulic conductivity from pumping tests). Degree of schematization is needed. Input data for each model element in the mesh were evaluated from point measurements (boreholes). Uncertainties of the boundary condition - esp. river bank conductance. Lack of the measured data for calibration - esp. the drainage into rivers</td></tr>
<tr><td><i>Method specific to defined boundary conditions</i></td><td>The methods are applicable to all geological formations. Possibility to define calibrated rainfall infiltration.</td></tr>
<tr><td><i>Experiences (pos. / neg., what to avoid)</i></td><td>- Lack of input data (only local information) to model the groundwater flow in low permeable rocks
- Possibility to get mass balance of the groundwater</td></tr>
<tr><td><i>Effort, comments</i></td><td>- Difficult data inputs preparation and calibration of the model (at least two months), computer model calculation (few minutes)
- MODFLOW: freeware; Groundwater Vistas software: app. 2,500 US$</td></tr>
<tr><td><i>Links, references, other sources of information</i></td><td>- MODFLOW: http://water.usgs.gov/nrp/gwsoftware/modflow2000/modflow2000.html
- Groundwater Vistas: https://www.rockware.com/product/overview.php?id=147&gclid=CKr2uZTjl78CFevpwgodmHAAdw</td></tr>
</table>

Method No. A.43: PCA (U. Noseck, E. Hofmanová)

Name of method ***Application in the Ruprechtov project***	Principal Component Analysis - PCA PCA was used for statistical evaluation of large data sets (chemistry of groundwater analysis and results from sequential extractions).
Device(s) / method(s) used / applied	Free statistical software Past /HAM 01/ was used for PCA on groundwater analysis data set and The Unscrambler® v9.2 (software from CAMO) was applied on sequential extractions data set.
Brief description of the functioning	PCA is a statistical technique for analyzing data sets with a large number of variables. This method reduces the number of variables to relevant variables describing the variability of the data with minimum loss of information. This leads to the reorganization of information in the data set and can search the data structure. The technique is based on orthogonal linear transformation that transforms the data to a new coordinate system (PC - principal components). The first PC covers the greatest data variability. The second and each subsequent PC is orthogonal (perpendicular to all foregoing PC´s) and describe the maximum of remaining variability.
State-of-the-Art and new developments	The mathematical transformation in PCA is unchanged since its introduction in 1901. PCA is one of the oldest and most widely used methods of multivariate analysis. At present, the new software are developed for new applications (particularly face recognition) in order to be faster and more user friendly.
Output of the method	A typical output is shown in the figure below. The method was applied to identify the most important factors controlling the groundwater geochemistry. The results show that most information is covered by two components: Principal Component 1 (PC1) accounts for 80.6 % and Principal Component 2 (PC2) accounts for 15.3 % of the variability in the data set. PC1 is well defined and has a highly positive loading for HCO_3, positive loadings for Ca, Na, and Mg and a highly negative loading for the redox potential, i. e. samples with low Eh are covered by this component. It represents a geochemically evolved reducing groundwater. PC2 is not that well defined and has a positive loading for Si, highly negative value for HCO_3 and negative values for Na, and Mg. This component represents immature groundwater, probably dominated by the dissolution of silicates close to recharge areas. The results indicate a progressive geochemical evolution from the left to the right.  *Results of Principal Component Analysis: plot of PC1 vs. PC2*

Objective(s) for application in the Ruprechtov project	PCA was mainly applied to: - Identify the most important factors controlling the groundwater geochemistry - To analyze the correlation between elements to each other and their influence in determining the new coordinate system for sequential extractions
Practical procedure and experiences in the field	Not relevant for this method.
Applicability	PCA is applicable to any multivariate data set. Some data pre-treatment is important before use of the method (e. g. standardizing). In some cases, the pre-treatment procedure is inclusive in the software method. The first PCA analysis has to be focused on data analysis from the perspective of number of PC´s and which portion of variability is captured by these PC´s. Then it can be concluded that the data set can contain some information describing the studied problem. Further attention has to be paid to the presence of outliers.
Limits of application	Outliers can contain important information; by elimination of outliers the main information is lost. Large or small amount of PC´s can lead to misrepresentation of results interpretation. Therefore, the specialist from statistical branch is needed.
Uncertainties / accuracy (devices, methods, evaluation procedure)	Due to large limits of application, results of PCA analysis should be always controlled by another independent multivariate method.
Method specific to defined boundary conditions	No, but the data set should be integral and large enough.
Experiences (pos. / neg., what to avoid)	For assessing of large amount of data sets, the use of multivariate methods is an appropriate tool in comparison with laborious one-dimensional evaluation.
Effort, comments	- Data preparation is time consuming - PAST is free statistic software; price of The Unscrambler® app. 650 €
Links, references, other sources of information	- PAST free statistic software: http://folk.uio.no/ohammer/past/, 13.06.2014 - The Unscrambler®: http://www.camo.com/rt/Products/Unscrambler/unscrambler.html, 13.06.2014

Method No A.44: Geochemical modelling (U. Noseck)

Name of method ***Application in the Ruprechtov project***	Geochemical modelling Evaluation of geochemical conditions and element speciation in groundwater, evaluation reaction pathways, saturation of minerals, solubility limiting U minerals, and evolution of isotope signatures.
Code(s), version(s) and database(s) used	Computer codes: - PHREEQC, Version 2 /PAR 99/ - Geochemists Workbench (GWB), Version 9.0 /BET 13/ - NETPATH Database: - Updated NEA TDB database /GRE 92/, /GUI 03/, /YOS 04/
Brief description of the code(s)	The programs PHREEQC and GWB are based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. They have evolved to model kinetic reactions and 1D (one-dimensional) transport. NETPATH is an interactive Fortran 77 computer program used to interpret net geochemical mass-balance reactions between initial and final water along a hydrologic flow path. Alternatively, NETPATH computes the mixing proportions of two to five initial waters and net geochemical reactions that can account for the observed composition of final water. The program utilizes previously defined chemical and isotopic data for waters from a hydrochemical system. For a set of minerals and (or) gas phases hypothesized to be the reactive phases in the system, NETPATH calculates the mass transfers in every possible combination of the selected phases that accounts for the observed changes in the selected chemical and (or) isotopic compositions observed along the flow path.
State-of-the-Art and new developments	PHREEQC is continuously further developed and regularly updated. Currently, version 3.1 is available; improved features can be found at the USGS website (see link below) /PAR 13/. There are several database projects aiming at improvement of thermodynamic data. One example is the German project THEREDA focusing on high saliniferous solutions /MOO 15/.
Output of the method	Geochemical speciation of chemical elements (especially U, see Eh-pH diagram below), saturation indices of mineral phases, evolution of water chemistry along reaction path water evolution including involved reactions, and isotope signatures. 

Objective(s) for application in the Ruprechtov project	- Identification of the relevant geochemical reactions during water evolution - Determination of redox conditions, equilibrium between redox pairs (redox controlling parameters), uranium redox state, uranium speciation and solubility determining mineral phases at Ruprechtov site - Interpretation of ^{14}C and $\delta^{13}C$ data by inverse geochemical modelling with respect to carbon reactions and groundwater ages
Applicability	The methods are applicable to all geological formations. Concerning the data basis specific ion-interaction models need to be used for high saline solutions (for Ionic strength > 0.55: Specific Ion Interaction Theory (SIT); for solutions at/near saturation: Pitzer)
Limits of application	Databases are limited for temperatures higher than 25°C.
Uncertainties / accuracy (devices, methods, evaluation procedure)	- Uncertainties in thermodynamic data - Uncertainties in experimental data. Major uncertainties origin from redox values due to uncertainties in the determination method (see table 10.2)
Method specific to defined boundary conditions	See "Applicability".
Experiences (pos. / neg., what to avoid)	Need for confidential input parameters and sufficient quantity of data, especially for - Eh, pH - Isotope ratios The quality of input data impacts the strength / weakness of statements. Inverse geochemical modelling: The results give good indications for reactions. However, due to the high heterogeneity in flow and petrography the evolution of water from an upstream to a downstream borehole is probably influenced by additional mixing, which impedes evaluation.
Effort, comments	Main effort is needed to establish a sound database and to evaluate experimental data, to get a sound data set. - PHREEQC: freely available (see link below) - Geochemists Workbench: app. 200 € per license (see link below) - NETPATH: freely available (see link below)
Links, references, other sources of information	Fundamental information: e. g. /BET 08/ - PHREEQC: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/ - Geochemists Workbench: http://www.gwb.com/ - NETPATH: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/netpath/

List of abrreviations

AES	Atomic Emission Spectrometry
AGH	AGH University of Science and Technology (Akademia Górniczo-Hutnicza), Kraków
AMS	Accelerator Mass Spectrometry
ANKA	Angströmsource Karlsruhe
AR	Activity Ratio (for $^{234}U/^{238}U$)
ASEM	Analytical Scanning Electron Microscopy
BGS	British Geological Survey
BSE	Backscattered Electrons
CA	Component Additivity approach
CNM	Charge Neutralization Model
CPS	Counts per Seconds
CTU	Czech Technical University
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EDS	Energy Dispersive Spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
FA	Fulvic Acid
FAAS	Flame atomic absorbtion spectroscopy
FE-EPMA	Field-Emission Electron-Probe Microanalysis
FEP	Features, Events and Processes
FFF	Flow Field Fractionation
FIB	Focused Ion Beam
FTIR	Fourir Transform Infra Red
GC	Generalized Composite Approach
GFZ	Helmholtz Centre Potsdam - GFZ German Research Centre for Geosciences (Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum GFZ)
GRS	Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH
GW	Groundwater
HA	Humic acid
HAADF	High-Angle Annular Dark-Field Detector
HD-B1	Heidelberg Biotite (Internal standard for Ar analysis)

HDPE	High Density Polyethylen
HRSF	High Resolution Sector Field
HRTEM	High Resolution Transmission Electron Microscopy
IAEA	International Atomic Energy Agency
ICP-MS	Inductiv Coupled Plasma Mass Spectrometry
ICP-OES	Inductiv Coupled Plasma
IHSS	International Humic Substances Society
IRMS	Isotope Ratio Mass Spectrometer
IUGS	International Union of Geological Sciences
KPA	Kinetic Phosphorescence Analysis
LBB	Landeslabor Berlin-Brandenburg
LIBD	Laser Induced Breakdown Spectrometry
MALDI	Matrix Assisted Laser/Desorption Ionization
MC	Multi Collector
MS	Mass Spectrometry
NAWG	Natural Analogue Working Group
NEA	Nuclear Energy Agency (OECD subdivision)
OM	Organic Matter
PCA	Principal Component Analysis
PCS	Photon Correlation Spectroscopy
PTKA	Project Management Agency Karlsruhe (Projektträger Karlsruhe am Karlsruher Institut für Technologie (KIT)
QMS	Quadrupole Mass Spectrometer
REE	Rare Earth Elements
SEM	Scanning Electron Microscopy
SFMS	Sector Field Mass Spectrometry
SIC	Sedimentary Inorganic Carbon
SOC	Sedimentary Organic Carbon
SOM	Sedimentary Organic Matter
SÚRAO	Správa úložišť radioaktivních odpadů
TC	Total Carbon
TDB	Thermodynamic Data Base
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
TOF MS	Time of Flight (Mass spectrometry)
TRLFS	Time Resolved Laser Fluorescence Spectrometry
ÙJV	ÚJV Řež, a. s.

US	University of Silesia in Katowice (Uniwersytet Śląski w Katowicach)
USGS	United States Geological Survey
VCDT	Vienna Canyon Diablo Troilite
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
WMWL	World Meteoric Water Line
XANES	X-ray Absorption Near Edge Structure
XRD	X-ray Powder Diffraction
XRF	X-ray Fluorescence

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