

EUG XI



Symposium AI02

Studies in Underground Research Laboratories
for Radioactive Waste Disposal
and Predicting the Behaviour of Engineered
and Natural Barriers for the
Geological Isolation of Wastes

Convenors

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Sunday PM Session

AI02 : SUPm25 : G3

Low-Temperature Diagenesis in Callovo-Oxfordian Shales of Haute-Marne (France): Effect on Natural Confinement Properties

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Callovo-Oxfordian argillites of eastern France were chosen for building a research laboratory to determine the physico-chemical properties of this formation for a potential underground disposal of radioactive waste. Knowledge and understanding of post-sedimentary modifications are of prime importance for definition of its properties; evaluation and quantification of the changes represent the aim of this study focusing especially on the clay material of the sequence.

Samples were taken from HTM102 drilling located about 3 km from laboratory site. Clay minerals were extracted from shales and separated into several granulometric fractions from < 0.02 µm to < 2 µm. Illite and I/S are the dominant clay components of most clay fractions. The amounts of smectite layers in the I/S were determined by comparison with computed mixtures using Newmod (Reynolds, 1985). We distinguished two populations of mixed-layers: (1) the former, in a 340-412 m depth range, is smectite-rich, with amounts of smectite layers varying from 50 to 70%, and (2) the latter, in a 418-480 m depth range, with amounts of smectite layers from 10 to 30%.

Systematic SEM and TEM observations and isotopic K-Ar, Rb-Sr and oxygen analyses pointed to diagenetic neoformations of carbonates (calcite, dolomite) and clays. For instance, veils and laths of authigenic clay particles around old detrital ones can distinctly be observed. Alternatively, FTIR spectroscopic determinations showed that the crystallographic environment of the different clay particles does not fluctuate in the whole sequence. The epoch, duration and extent of the diagenetic activity(ies) are difficult to define because of an overall detrital contribution even in the finest granulometric fractions. However, analysis of a bentonite layer in the sequence (Pellenard et al., 1999) provides a diagenetic reference for the authigenic clay material. According to K-Ar data on illite fundamental (< 0.02 µm) particles extracted from I/S and to Rb-Sr and oxygen data on < 0.2 µm, it may be suggested that the visible diagenetic modifications, at least on the clay material, occurred in a closed system, about 100 Ma ago. The diagenetic activities being limited in a restricted rock volume and having occurred long ago, the Callovo-Oxfordian sequence outlines interesting confinement properties.

Pellenard P, Deconinck JF, Marchand D, Thierry J, Fortwengler D, Vigneron G, *C. R. Acad. Sci. Paris*, **328**, 807-813, (1999).

Reynolds RC, *RC Reynolds, 8 Brook Road, Hanover, N. H. 03755, USA*, (1985).

AI02 : SUPm26 : G3

Mineralogical and Geochemical Evolution in a Fractured Zone in Shales at the Tournemire Site (Aveyron, France)

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Shales are conceivable as a natural barrier for nuclear waste disposal. The consequences of fracturing on such rocks is studied on the experimental site of the French Institute for Protection and Nuclear Safety (French acronym IPSN). Two cores drilled perpendicularly to a strike-slip structure in Toarcian shales, were investigated. Whole rock chemical composition were analysed along the cores. Furthermore, X-ray diffraction analysis on the clay fraction (< 2 microns) and thin sections observations were performed on samples from cores. Shales present a silty clay structure. No significant variations of the structure were observed along the

cores. The main fault zone consists of a 5 cm wide breccia, cemented by calcite. Diagenesis in shale is mainly occurring during an early stage, due to sulfatoreductive bacterial activity (framboids of pyrite, ankerite, dolomite). Clay minerals consist of illite, kaolinite, chlorite and illite-rich I/S. No significant changes in the mineral composition of clays were observed along the cores. Fracture plans are filled with massive pyrites and sometimes late baryte. Authigenic florencite were observed (one crystal forming around an early pyrite) in the host rock near to the brecciated zone (a few millimeters to one centimeter). There is a slight decrease of the carbonate concentration in a metric area on both sides of the main fault zone. Sulfur concentration increases in the fault plan, owing to massive pyrite precipitation. An increase of the Zn concentration is quoted in the aforesaid metric zone related to incorporation of Zn into pyrites. The concentrations of organic carbon, phosphorus, silicon, aluminium and potassium are stable along the core with the exception of the brecciated zone where they decrease due to the carbonate cement precipitation. Normalised to the host shale, Heavy Rare Earth Element are enriched relatively to Light Rare Earth Elements in the main fault zone. This relative enrichment is interpreted to be caused by carbonate cementation (as indicated by REE pattern normalised to shale in the calcite) and possibly to a depletion in LREE, as suggested by the presence of authigenic florencite in the host rock, near to the fault border. It is proposed that the host shale chemical composition is modified in a metric area on both sides of the major fault zone. Carbonates migrate from shale to the fractures, as well as S, Fe and Zn. A slight mobilisation of REE is evidenced in a metric area on both sides of the main fault zone.

AI02 : SUPm27 : G3

Fluid-Granite Interactions along Fault Surfaces: Geochemical Modelling of Meteoric Alteration (Albala Granite, SW Variscan Iberian Massif)

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The interaction of granitic rocks with meteoric fluids is instrumental in understanding the pore fluids chemistry and alteration mineralogy in groundwater circulation systems in the continental crust. The existence of mineral and textural alterations along fault surfaces evidences that fracture zones and open brittle structures are the major groundwater conducting features within a granitic massif. A detailed mineralogical and geochemical study of cores using SEM, XRF, ICP-MS, electron microprobe and conventional light optic techniques, has been carried out to assess the alteration history of the Albala Granite Pluton (SW Central-Iberian Zone, Variscan Iberian Massif). Fault surfaces with altered igneous feldspar and secondary clay minerals are present throughout the drilled granite. The results of these studies have been used, together with analyses of rainwater and present-day pore fluids within fault-rocks, to geochemically model the alteration process along transmissive faults.

Modelled fluids are alkaline (pH=7-8.5), reduced (pE=2.8/-4.5) and of low salinity. The dissolution of feldspars, the oxidation of igneous biotite and hydrothermal chlorite, and the growth of kaolinite, calcite and Fe-Mn oxides dominated mineral-fluid reaction. Final fluids were saturated with respect to quartz and unsaturated with respect to dolomite, gypsum and fluorite. During the alteration, simulated concentration of the chemical components showed a net decrease in Fe and K; a light increase in Si, Al and Na; and conservative Ca, Mn, Mg, C and anions (Cl, F, Br). Alteration mineralogy from simulations compared with that present as natural fracture infills from Albala granite, and associated with the later stage of alteration, reveals a closed similarity. Also, there is good agreement between F-Q properties and element concentrations of the modeled groundwater with those of the water observed in pores of fault-rocks. Since few of the minerals used in the simulations are close to saturation, fault alteration in the granite may have been produced by a flow regime similar to that prevailing today.

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Role of the Alteration Gel in Remobilization of Contaminants from Ultimate Glassy Wastes

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Management of ultimate wastes requires the prediction of the long-term behavior of the containment matrix and the evaluation of the potential release of hazardous species in the environment. High level radioactive wastes are currently incorporated in a glass matrix before storage. Vitrification is also used to stabilize waste incinerator fly ashes that concentrate heavy metals (Zn, Cu, Pb, Sn, Cr and Ni). Prediction of remobilization of chemical species from the alteration of vitrified waste requires the determination of the release kinetics of the elements incorporated into the matrix according to the geochemical context of the storage site (pH and Eh conditions, temperature, solution chemistry and geology). In particular, a better understanding of physico-chemical processes at the liquid-solid interface has to be achieved. For instance a glass altered in a solution develops a gel that can prevent the further diffusion of elements. In this work the remobilization behavior of heavy metals and Rare Earth Elements, used as geochemical analogues for radionuclides, from glassy wastes was investigated in relation with the alteration of the matrix. Several representative vitrified waste materials, nuclear glass waste simulants and domestic vitrified wastes, were selected. Dynamic leaching experiments were carried out to simulate weathering in different environmental conditions (aqueous, oxidizing or reducing). Physico-chemical processes at the solid surface were investigated with an integrated approach. Altering solutions were analyzed in real time to monitor remobilization of elements from the matrix. Alteration features of the matrix and the elemental distribution (metals, matrix elements and light elements) in the interface were studied with solid and surface characterization techniques operating at the nanoscale, respectively Electron Transmission Microscopy and Glow Discharge Optical spectroscopy. The influence of the alteration of the matrix on the potential mobility of the heavy elements was then discussed. The leaching behavior of the matrix elements and metals trapped in the matrix was assessed together with their diffusion kinetics. The development of an interphase, created by the leaching agent at the interface of the solid and the liquid, was observed. The diffusion of the leaching agent into the vitreous matrix could be estimated using hydrogen as a tracer. The migration of the heavy elements in the alteration gel was also shown. The results suggested complex remobilization and trapping mechanisms occurring at the interphase.

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Motelica-Heino M, Le Coustumer P, Thomassin J-H & Donard O, *Talanta*, **46**, 407-422, (1998).

AI02 : SUPm29 : G3

Mobility of REE in Hydrothermal Uranium Deposits as Natural Analogue of HLWR

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Mobility of The REE in hydrothermal systems is of interest as these elements are often used as chemical analogues for trivalent actinides in HLWR. Important part of hydrothermal uranium mineralization in the Bohemian Massif (Czech Republic) is bounded on large shear zones of the Late Variscan age in the Moldanubian zone. Uranium mineralization is hosted within the high-grade metamorphosed complex composed of migmatized biotite or sillimanite-biotite gneisses, with intercalations of amphibolites, marbles and calc-silicate rocks. Uranium mineralization in the Rožná ore deposit in eastern part of the Moldanubian zone is bounded on the system of NW-SE shear zones. Thickness of shear zones with chloritized, graphitized cataclasis is from some metres to 30 m. In the deeper parts of this deposit intensively albitized and carbonatized bodies of original metamorphic rocks are evolved. The uranium ore deposit Okrouhlá Radoúš is evolved on NE part of smaller

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granite Klenov massif of Variscan age that belong to the South Bohemian batholith. Uranium mineralization occurs in two NNE-SSW shear zones, which are 2-8 m thick. The part of these shear zones is evolved in two-mica granites, which are altered to albitites. For other parts of shear zones, which are evolved in biotite gneisses and migmatites of the Moldanubian zone is also characteristic intense albitization and carbonatization of original rocks. For both deposits is characteristic disseminated uranium mineralization with variable content of coffinite and uraninite.

Total content of REE in unaltered biotite gneisses is on ore deposit Rožná 132-169 ppm, on uranium deposit Okrouhlá Radouš is their content 306-312 ppm. Their ratio LREE/HREE is for unaltered gneisses from ore deposit Rožná 2.9-10.5 (La_N/Yb_N) and for unaltered biotite gneisses from Okrouhlá Radouš is this ratio 7.6-7.9. Hydrothermally altered rocks are obviously depleted more in LREE as in HREE. The most intensive depletion of REE is characteristic for albitized biotite gneisses from ore deposit Okrouhlá Radouš (Total content of REE 152-322 ppm). Value of La_N/Yb_N in hydrothermally formed chlorite rocks (chlorite, plagioclase, quartz, accessory minerals) from uranium deposit Rožná is 2.7-4.7, in albitized gneisses is this ratio only 1.2-3.4. The REE patterns, normalised to PAAS of chlorite rocks from Rožná display HREE enrichment, which is possible associated with alteration products (chlorite). For albitized metamorphic rocks from both uranium deposits is also very typical significant negative Eu anomaly ($Eu/Eu^* = 0.33-0.64$). It seems most likely that REE were transported in a hydrothermal fluid as soluble carbonate complexes. This work is part of the GACR project (No 205/00/0212).

AI02 : SUPM30 : G3 Fracture Systems in Deep Underground Granitic Sites

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In order to evaluate and simulate the 3D fracture systems of granitic rocks prior to fluid flow modelling in the vicinity of underground sites, several granite massifs were investigated by means of drillhole, outcrop survey or aerial photograph analysis. The Soutz granite (Rhine graben, France), a possible target for geothermal energy exploitation, was penetrated by three main boreholes, which reached 2200, 3600 and 5100 m depth. Another granite site, located near Poitiers (Charroux, France) and investigated for the appraisal of an underground research laboratory, was penetrated by 16 fully cored boreholes of various depths ranging between 200 and 1000 m. Field survey and/or aerial photograph analysis were conducted on well exposed granites outcropping in southern France (Pyrénées), northern Sardinia (Italy) and close to the borders of the Red Sea (Saudi Arabia, Egypt).

Based on extensive geological investigations (core analyses, borehole image logs, structural field works), several scales of fractures were evidenced: small-scale fractures and fractured zones. Small-scale fractures correspond to primary joints or Mode I fractures; those that were reactivated during later fracturing episodes are shear-fractures or Mode II fractures. Fractures were systematically sealed by hydrothermal products (quartz, carbonates, clay minerals, Fe-oxides). During the Soutz drilling operations, some fractures showed some evidence of natural permeability with an outflow of natural brine (100 g/l) which correlated with the occurrence of secondary quartz deposit. Fractured zones correspond to large-scale fractures such as normal faults (Soutz, Egypt), shear faults (Charroux, Pyrénées, Sardinia), or joint clusters (Saudi Arabia). They delineate large-scale blocks in which are embedded the small-scale fracture patterns.

Fracture organisation in boreholes shows that small-scale fractures are concentrated in clusters with linear fracture density of about 4 fract/m both at Soutz and Charroux. 2D fracture networks surveyed in relevant analogue granites provide fracture maps about the large-scale fracture patterns as well as orders of magnitude about fracture length, those data being not easily accessible by means of boreholes.

A 3D simulation procedure of the Soutz fracture network was designed. It is based on the combination of a probabilistic simulation of small-scale fractures with a determin-

istic modelling of the large-scale fractures. Geometrical modelling of fractures was done by combining the multi-scale fracture data. Fractures are mostly organised in clusters and form several directional sets, whose parameters were derived from observations. Fractures are assumed to be disk-shaped and their lateral extension is taken as a function of their sealed width, measured on the cores. Only the quartz-filled fracture population was simulated, aiming that they represent a possible connecting fracture network.

AI02 : SUPM31 : G3 The Mobility of Depleted Uranium in the Balkan Wars Zone of 1999

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The fate and transport of uranium has taken on a new significance (Ragnarsdottir and Charlet, 2000) because in recent armed conflicts, such as in the Gulf and Balkan areas, depleted uranium (DU) was introduced to the surface environment (UNEP/UNCHS 1999a,b). DU is a dense waste product of the natural uranium enrichment process which can be used to strengthen the tips of bullets and missile nose cones. Natural abundance of uranium isotopes is 98.28% ^{238}U , 0.72% ^{235}U and 0.056% ^{234}U . Depleted uranium, on the other hand, has had the majority of ^{235}U and ^{234}U removed, resulting in DU containing 0.2-0.3% ^{235}U and 99.7-99.8% ^{238}U . In the environment, DU can thus be used as an isotopic tracer for uranium mobility. In November, 2000, the United Nations Environment Programme (UNEP - of which we were part) ended an assessment in Kosovo of several sites where depleted uranium (DU) was used during last year's conflict. In total 31000 rounds of DU containing bullets were used, amounting to 10 tons of DU. The aim of the UNEP assessment is to determine whether the use of DU during the Kosovo conflict has resulted in any current or future health or environmental risks. The UNEP team visited 13 sites in Kosovo where, according to information supplied NATO, DU munitions were used. At these sites, radiation activity measurements were taken as well as samples of soil, water, vegetation and cow's milk. The team also collected several DU munitions (penetrators and sabots) used during the conflict and at these specific locations slightly higher radioactivity than normal was measured. Results of laboratory analysis of field samples will be presented and an assessment made of the mobility of uranium in affected areas. The potential risk to the population of affected areas will also be evaluated.

Ragnarsdottir KV & Charlet L, *Environmental Mineralogy: Microbial Interactions, Anthropogenic Influences, Contaminated Land and Waste Management*, 9, 333-377, (2000).
UNEP/UNCHS, *The Kosovo Conflict. Consequences for the Environment & Human Settlements*, 104, (1999a).
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AI02 : SUPM34 : G3 Migration of Fissionogenic REE within the Groundwater Table of Bangombe (Gabun)

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The natural nuclear fission reactor of Bangombe is located at only 12 m depth and is subjected to supergene weathering and to chemical exchange with the groundwater. This study evaluates the REE (Rare Earth Element) patterns and their isotopic composition of whole rocks and fractures and the hydrochemistry of REE in groundwater samples around the site. ICP-MS and TIMS measurements were performed on rocks, fractures, suspended loads and water. A relative loss of heavy REE (HREE) is observed in whole rock in the upper layer of the FB formation, which lies above the reactor zone. This indicates supergene weathering effects assuming preferential removal of HREE over light REE (LREE) and other minerals (Salah et al, this volume). Strong isotopic anomalies were found in whole rocks and fractures of the FA formation below the reactor zone, which

indicates REE migration from the fission reaction zone as well as neutron, capture reactions. Timing of migration of fissionogenic REE is not known. Water samples taken from the reactor site show small isotopic anomalies of $^{143}\text{Nd}/^{146}\text{Nd}$, $^{145}\text{Nd}/^{146}\text{Nd}$ and $^{149}\text{Sm}/^{147}\text{Sm}$ of 0.7235, 0.4933 and 0.843 respectively (normal: 0.7094, 0.4828 and 0.9173). This suggests that only 2.3% of the dissolved Nd is of fissionogenic origin. The leachate of the suspended load shows similar isotopic anomalies. The water samples and suspended loads as well as the leachate collected outside of the reactor zone have normal isotopic composition. The concentration of REE in the water samples, especially at the reactor site, is rather low (1.9 ppt Nd and 0.15 ppt Sm) considering the huge availability of REE in the reactor zone (e.g. 1078 ppm Nd and 215 ppm Sm). The prevailing physico-chemical conditions within the current water table did not allow detectable long-distance migration (< 4 m) of fissionogenic REE.

Salah S, Del Nero M & Gauthier-Lafaye F, *this volume*

AI02 : SUPM35 : G3 Detection and Quantification of Groundwater Flow: Geothermal Scanning of the Sub-Surface for Temperature Residuals of Advective Origin

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In the context of the search for areas suitable for safe radioactive waste disposal, more than 8000 existing borehole sites in Germany with temperature data at depths > 2000 m will be used to construct a 3D image of subsurface temperatures. For a pilot area not yet chosen, advective residuals will be estimated. This implies the successive elimination of effects like borehole-related disturbances, paleoclimatic signal, and heterogeneities. To achieve this, existing data will be reevaluated and additional geothermal and petrophysical information will be collected, including extensive measurements on cores. In a second step, the advective signals identified will be used to construct a detailed model of the areas considered. Methods used and first results from this project will be presented.

AI02 : SUPM36 : G3 Behavior of Si and O during Hydrothermal Alteration of Nuclear Waste Glass, using ^{29}Si and ^{18}O Isotope Tracing and Ion Probe Depth Profiling

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Storage of radioactive waste glasses in geological repositories require the understanding of corrosion mechanisms and their kinetics in aqueous medium. In contact with water, the surface of the glass develops a leached layer. In order to model the mechanisms (hydrolysis, precipitation, condensation...) responsible for the formation of this altered layer, we performed leaching experiments using a solution highly enriched in ^{29}Si and ^{18}O under dynamic conditions. Such isotopic tracing was aimed at: i) understanding reactions involving silicon and oxygen, the two main constituents in the leached layer, ii) following the real exchange between solution and glass during alteration processes. The $^{29}\text{Si}/^{28}\text{Si}$ and the $^{18}\text{O}/^{16}\text{O}$ ratios of the solution were respectively 1.13 and 1.10-2, largely in excess to the natural ratio of pristine glass ($^{29}\text{Si}/^{28}\text{Si} = 5.10-2$ and $^{18}\text{O}/^{16}\text{O} = 2.10^{-3}$). Glass samples were removed from the solution after 1 week, 2 weeks, 1, 3 and 6 months. Element and isotope variations in the altered glass layer were measured with the CRPG Cameca IMS 3f ion-probe using in depth profiling technique. Aliquots of leachates were sampled every 2 weeks, and were analyzed by ICP-MS and ICP-AES. Using both element and isotopic analyses of leachates, the real exchange between the solution and the glass as alteration proceeds can be evaluated. While element analysis displays a loss of Si from the glass to the solution, isotopic measurements reveal, in contrast, a gain of ^{29}Si in the glass. In depth

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profiles of $^{29}\text{Si}/^{28}\text{Si}$ and $^{18}\text{O}/^{16}\text{O}$ ratios, and of elemental concentrations (including major, transition and REE elements) in the altered glasses allow 1) to discriminate three main zones: an ion exchange zone in contact with the pristine glass, a hydrous silicate gel, a precipitated phase layer at the surface (smectite like precipitates), and 2) to specify elemental partitioning between these different layers and the solution. Profiles recorded at different times of alteration show an increase of the depth of the altered layer as time increases. For both isotopic systems, the highest values of the ratio are observed at the surface of the leached glass. From rim to core of the glass, each profile shows a decrease in $^{29}\text{Si}/^{28}\text{Si}$ and $^{18}\text{O}/^{16}\text{O}$ ratios, with a sigmoidal shape, which approach values representative of the pristine glass. These results confirm a transport of ^{29}Si and ^{18}O from the solution into the altered glass and show a similar behavior for the two elements, Si and O. This isotopic tracing demonstrated that, during glass alteration, Si exchange is a reciprocal process between the solution and the glass, in agreement with a dissolution-condensation model.

AI02 : SUPm37 : G3 Leaching of Concrete by Waters Little Mineral-Bearing and Sulphated Waters

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Concrete is commonly used as protecting barrier for isolating wastes. But the behaviour of the healthy concrete in prolonged contact with waters of rains and rivers is not well known. These achieved at the CEA permitted to acquire fundamental experimental data on behaviour of cement pastes (Adenot, 1992 ; Faucon, 1997) and of mortars (Bourdette, 1994) in contact with pure water under inert atmosphere. These works propose also models based on diffusion / dissolution / precipitation for understanding the observed changes.

Cement manufacturers are interested in the durability of their product too. In collaboration with two manufacturers, Calcia and Vicat, we work on two projects at the department of geochemistry of the School of Mines of Saint-Etienne :

The first project is about leaching of cement pastes and mortars. Samples are placed in open reactors filled with water during two months. Three conditions of leaching are achieved: continuous leaching with pure water under inert atmosphere; continuous leaching with pure water under N_2+CO_2 atmosphere; continuous leaching with pure water acidified with H_2SO_4 (pH = 4).

The second project is about leaching of mortars by sulfated solutions. Samples of mortars are placed in closed reactors which are filled with $\text{H}_2\text{O}+\text{Na}_2\text{SO}_4$. The solution is changed every month during one year.

We focus on the chemical and mineralogical modifications of each sample. Our tools of investigation are X ray diffraction, backscattering electron microprobe and electronic microbeam. We use thermodynamic equilibrium diagrams for understanding the observed mineralogical zonations. Diagrams are built with ZEN+k, a computer code (Guy and Pla, 1997) which is based on the concept of Affigraphy (Guy and Pla, 1997).

Adenot F, *Thesis of University of Orléans*, (1992).
Bourdette B, *Thesis of INSA Toulouse*, (1994).
Faucon P, *Thesis of University of Cergy Pontoise*, (1997).
Guy B, Pla JM, *CRAS*, **324 IIa**, 737-743, (1997).
Guy B, Pla JM, *International Conference Calphad XXVI, T. Anderson Editor*, D5, (1997).

AI02 : SUPm38 : G3 Coupled ESEM and Digital Image Analysis for Qualitative and Quantitative Study of Bentonite Swelling

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Bentonite physical-chemical properties are subject to many studies as one of their main interests is in barriers for nuclear waste deposits. The study of interaction between clay and fluids and especially swelling properties, is of crucial importance in the knowledge of clay behavior in these environments submitted to heat.

Varying standard methods can be used to approach swelling properties as X-ray diffraction (XRD), small angles X-ray diffusion, transmission electron microscopy, and isothermal adsorption. Among them only transmission electron microscopy gives visual information on swelling. However this technique needs a preliminary treatment of the sample which may modify the structure and texture of the clay.

In this study we use an Environmental Scanning Electron Microscope (ESEM) whose major advantage is to allow the observation of clay in controlled atmosphere, in this case at different relative humidities. In this way swelling can be observed from the dry to the fully hydrated states without any treatment of the sample. Texture and structure modifications can be qualitatively and quantitatively underlined.

We studied a bentonite already characterized by X-ray diffraction, Scanning Transmission Electron Microscopy (STEM), Scanning Electron Microscopy (SEM) and Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). Swelling was directly observed at high magnification (10000x). Experiences of hydration/ dehydration and/or condensation/ evaporation were carried out in a range of relative humidity from 0 to 100% and temperatures from 4 to 55°C. Water condensation and evaporation are controlled solely by changing the temperature and water pressure conditions in the microscope.

A quantitative treatment was made by Digital Image Analysis (Visilog) which enables to characterize porosity and bentonite swelling. The method is based on digital analyses of images at different magnifications in the ESEM mode.

Sunday PO Session

AI02 : SUPo01 : PO Space-Time Features of Changes in the Condition of the Rock Massif

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The processes resulting in restructuring of local stress fields and structural discontinuity of rocks around mine openings and producing force effect on rock massif composed of structural blocks of different hierarchy have been studied. Results are presented of the study of the effect of explosion mining of ores on rock distribution in dynamic representation. Force effects of explosion mining as well as natural tectonic processes are manifested as stepped in spatial and cyclic in time dislocation of zones of relative packing and failing towards the worked out room. The developed methods of geophysical observation of the effect of space-time changes on stress fields in the contour zone of a blocks rocks during explosion mining of ores can be applied for solution of a wide range of practical problems in the mining industry. The established time regularities in geophysical fields and in the deformation of rock massif, parameters like the velocity of dislocation of failure zones, effective radius of their development in the massif, the distance to the packing zone shield, especially when predicting rock bump strength, and geometrical parameters of sites where the changes of geophysical fields characterizing the condition of separate structural blocks of the massif occur can serve as prognostic criteria for dynamic destruction of rocks. New data have been obtained on the deformation in the contour zone of large-diameter chambers in which hazardous techniques are used under prolonged effects of high temperature and rock pressure.

AI02 : SUPo02 : PO Geochemical Monitoring of the Unsaturated Zone at the Sur-Frètes Tunnel: A Tool for the Understanding of the Seismic Cycle and the Hydrogeochemistry of Waste Disposal Sites

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The Sur-Frètes experiment is located in the French Alps in the vicinity of two artificial lakes at the edge of the Belledone crystalline basement. Part of the experiment takes place in a 128 m-long dead-end tunnel, ca. 40 m below the ground surface and ca. 10 m above the water table. The experiment demonstrated the association of radon emanation and electric potential variations with transient rock deformation due to the seasonal variation of lake water level (Trique et al., 1999), and brought important results on the understanding of the physics of earthquake precursors. A monitoring station for the chemistry of water has thus been set up in order to increase our knowledge of an often-cited precursor type and of the dynamics of the unsaturated zone. Results on the chemical monitoring of water from the unsaturated zone are rare and share important connections with the safety of waste disposal sites. Known driving forces of fluid flow in this context are the rainfall (modulated by snow) and the rock deformation due to the time variation of the lake level. Dripping waters from the tunnel roof over 6 m² surface areas have been collected automatically every 4 days during more than 1 year from two geologically contrasting zones: the host foliated gneiss, and a zone with dm-wide quartz veins. Flow rates of water from the two zones are accordingly contrasted, and vary with time, respectively from 3 (summer-fall) to 14 (winter-spring) ml/hour in the host gneiss, and from 200 to 1200 ml/hour in the veined zone. The $\delta\text{D}-\delta^{18}\text{O}$ signature of waters shows their meteoric origin. During wet periods the isotope compositions shift toward those of a nearby spring, or snow, while during dry periods the isotope compositions shift opposite toward an unidentified pole. The major element chemistry of waters are dominated by HCO_3^- , SO_4^{2-} , Ca, Mg, and Na. Waters from the host gneiss show little chemical variations with time, whereas waters from the quartz veined zones show contrasted compositions with large variations. SO_4^{2-} shows the largest contrast between the two rock zones and its variations with time are anti-correlated with those of the lake water level, known to modulate microcracks development. Other ions show such variations but with less amplitude. The quartz veins that locally contain abundant pyrites and chalcopyrites may be the

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place for enhanced chemical reactions due to higher flow rates and micro-ruptures. Unsaturated fluid flow is heterogeneous in heterogeneous rocks, so is the chemistry of the circulating waters. Chemical variations are amplified in high permeability zones. High flow rates and microcracks can lead to detectable variations in major element concentrations in water. Monitoring of water major element chemistry thus appears to be a good tool to characterize underground sites in the unsaturated zone.

Trique M, Richon P, Perrier F & Avouac JP, *Nature*, **399**, 137-141, (1999).

AI02 : SUpo03 : PO Diagenetic and Post-Diagenetic Exchanges between Minerals and Fluids in the Clayey/Silty/Carbonated Callovo-Oxfordian Rock from East of Paris Basin

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The callovo-oxfordian formation of the Paris Basin has been the subject of many studies for several years. This clayey rock was selected to receive an underground research laboratory for the assessment of feasibility for disposal of radioactive wastes. The study of diagenetic and post-diagenetic evolutions of the callovo-oxfordian formation is essential to understand the nature and behaviour of the fluids in contact with the rock 160 My ago up to now. It can also allow to evaluate the extent of chemical exchanges. Stable isotopes have been used to trace water-rock interactions.

The mineralogy corresponds to 30-40% of clay minerals and 30% of carbonates.

Isotopic compositions of carbonates are very homogeneous in the whole sequence (130 m) of the clayey rock ($\delta^{18}\text{O} = 27.2 \pm 0.8\text{‰}$ / SMOW et $\delta^{13}\text{C} = 1.7 \pm 0.52\text{‰}$ / PDB). The $\delta^{13}\text{C}$ variations follow the sea-level changes. It thus looks like that the marine isotopic signature has been preserved. Early and late diagenesis marks cannot be distinguished.

The clay fraction contains 30% of illite-smectite mixed-layers and 40% of illite. Their oxygen and hydrogen isotopic compositions ($\delta^{18}\text{O} = 19.7 \pm 1.1\text{‰}$ / SMOW, $\delta\text{D} = -67.1 \pm 3.6\text{‰}$ / SMOW) do not vary on the whole profile and point out to a detritic origin. This indicates that no major thermal or chemical process has occurred since diagenesis.

In the same way we have studied chlorine (extracted by leaching) isotopic compositions of pore-water. This part of the study should detect fluid movements or diffusion processes in the clayey rock. The first results ($-0.2\text{‰} < \delta^{37}\text{Cl} < +0.9\text{‰}$ / SMOC) show very small variations which could point out to diffusion processes.

The whole of our results shows that the callovo-oxfordian clays have evolved in a low water/rock ratio context which was little affected by diagenetic and post-diagenetic interactions.

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AI02 : SUpo04 : PO Borehole Geophysical Logs in the Characterization of Petrophysical Properties, Fracture Patterns and Stress Indicators of Granites in an Old Mining Area

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A complete set of geophysical logging data acquired in 5 holes up to 500 m was analyzed and interpreted in order to characterize petrophysical properties, fracture patterns and present-day stress indicators. This characterization is part of a multidisciplinary approach to investigate subsurface fluid flow paths and patterns in granites of an old mining area. The main purpose of this study is the identification of the relationship between fractures and preferred permeability.

The geophysical logging program included borehole televiewer, sonic full waveform and dipmeter measurements in addition to conventional geophysical logging measurements. A detailed characterization of fractures and the identification of stress indicators was mainly conducted on high resolution televiewer borehole images. The multiphase deformation tectonic history of the area has resulted in a complex distribution of fracture sets including both high angle and low angle fractures, whose orientation, spacing and aperture could be measured on borehole images. Different fracture patterns have been identified by applying statistical structural analysis methods to fracture populations (3.336 fractures in total). The structural interpretation of fracture patterns measured on borehole images and dipmeter logs indicate that these are consistent with different deformation episodes as characterized in previous field geology and regional studies.

A specific goal of this study was to unravel the role of individual fractures and potential preferred permeability and fluid flow in the subsurface. High resolution borehole televiewer images, acoustic full waveform data and additional borehole measurements were applied to identify the relationship between individual and preferred fracture orientations and zones of increased permeability, as indicated by other downhole measurements. A certain number of stress indicators (tensile fractures and borehole breakouts) could be identified on borehole televiewer images. The relationship of favourably oriented fractures and present-day stress indicators was also analyzed.

AI02 : SUpo05 : PO Characterization of Cs Sorption Mechanisms onto an Organic Soil

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Radiocaesium from nuclear weapons and nuclear accidents is reported as a major source for environmental radioactivity. A reliable modelling of the migration of radioactive pollutants in the environment requires thus a thorough understanding of processes controlling Cs mobility in soils. Although many studies focused recently on retention / migration mechanisms of radiocaesium deposited in soils, further work is needed to fully characterize the complex interactions of Cs with the organic and inorganic soil components. Our study deals with the retention mechanisms of Cs on a "hot-spot" soil sample collected in the Massif du Mercantour (SE part of french Alps), which displays a higher ^{137}Cs activity than in common mountain soils. Mineralogical investigations show that the dominant mineral is illite.

The aim was to get insights into Cs retention mechanisms by investigating: (i) the efficiencies of the organic and inorganic soil components for Cs trapping and (ii) the effect chemical parameters upon which Cs sorption may depend (pH, ionic strength, Cs aqueous concentration). The partition of Cs between solutions and soil was measured with pH as a master variable (3-9) by performing batch experiments of the sorption of ^{137}Cs on the bulk soil and on subsamples in which organic acids have been removed ($\text{Na}_2\text{P}_2\text{O}_7$ pretreatment). The percentage of Cs sorbed does not vary significantly upon pretreatment, which suggests a minor contribution of organic acids to Cs retention. The experimental data indicate the occurrence of high-affinity and lower-affinity sites for Cs sorption. The data are consistent with (i) an incorporation of Cs into a limited number of sites such as narrow parts of wedge zones of illites, reported to be highly Cs-specific in the literature, (ii) further Cs sorption, as Cs concentration increases, on lower-affinity sites via ion exchange on clays (chlorite, wide parts of wedge zones of illite...) and partly adsorption at clay surfaces. Our study provides valuable information on processes which control Cs mobility in an organic soil. Complementary desorption / ion exchange experiments of Cs previously sorbed on the soil are now being conducted to gain knowledge on the reversibility of Cs sorption and on the nature of sites, and to provide reliable extrapolation to field conditions for prediction of Cs migration.

AI02 : SUpo06 : PO Characterization and Migration of Atmospheric REE in Soil Profiles

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The knowledge of the transport processes of rare earth elements (REE) at the atmosphere-soil interface is of importance because some REE isotopes occur as fission-derived longlived radionuclides in nuclear waste and because the trivalent REE are considered as good analogues for the trivalent actinides. But only few studies deal with distributions and origin of REE in surface waters and especially in rainwater or snow because of their very low concentrations (ppt) in aquatic systems. We therefore applied a liquid-liquid extraction method that allows to enrich the REE. Our study focus on soils and waters which have partly been contaminated by atmospheric fallouts of fission products (Pourcelot *et al.*, 2001).

Rainwater and snow collected at three different sites (Aubure, Vosges mountains ; Mercantour, French Alps; Strasbourg) show as a whole the same distribution patterns. Rainwater from Strasbourg is the more REE enriched whereas precipitation from the rather unpolluted areas are less concentrated ; especially those from Aubure are very close to seawater REE concentrations.

The Vosges rainwater normalised REE patterns of the solutions sampled in the Mercantour watershed (snow, interstitial, puddle and stream water) are similar, show LREE enrichment (La to Nd) but are MREE and HREE depleted. The snow collected in February has been for long time in contact with the atmosphere and shows therefore higher HREE contents than the fresh snow collected in October. Interstitial waters appear to be the most REE enriched solutions.

At Aubure, REE are more enriched in throughfall than rainwater probably due to the leaching of atmospheric particles deposited on the foliage. Throughfall is like lichens LREE enriched and slightly HREE depleted. Both of them contain REE of only atmospheric origin. Similar REE distribution patterns are observed in fertilisers suggesting that they are the most important providers of REE in the atmosphere. Also the soil solutions, stream and spring waters show the LREE enrichment but MREE and HREE are less depleted.

Leaching experiments on two soil profiles with diluted HCl or acetic acid (0.01 N) have been performed in order to separate the adsorbed REE from the solid phases of the soil. The leachates of samples from close to the surface (5 cm depth) show an atmospheric REE distribution pattern whereas leaching of samples from deeper soil horizons show increasing Eu anomalies and Gd contents reflecting the enhanced importance of mineral dissolution with depth as previously demonstrated (Aubert *et al.*, in press).

Thus, it was possible to trace the transport of atmospheric REE up to depths of 180 cm in soil profiles and the data yield important information about the exchange processes of these REE with the soil particles. Sr, Nd and Pb isotope measurements will yield additional information about the transport processes.

Pourcelot L, Louvat D, Gauthier-Lafaye F, Del Nero M & Stille P, *J. Conf. Abs.*, **6**, 39, (2001).

Aubert D, Stille P & Probst A, *Geochim. Cosmochim. Acta*, (in press).

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AI02 : SUpo07 : PO The Orciatico Natural Analogue Site for the Study of the Thermal Response of Clay Barriers

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The physical properties of clay offer the possibility to consider argillaceous formations as geological barriers to radionuclide migration in high-level radioactive-waste isolation systems. As laboratory simulations are short term and numerical models always involve assumptions and simplifications, natural analogues are extremely attractive surrogates for the study of long-term isolation. In the Orciatico area (Tuscany, Central Italy) a small, outcropping subvolcanic intrusion has induced metamorphic effects in the host Pliocene clay. These conditions represent a natural model of a heat source which acted on argillaceous materials for times similar to those expected for a nuclear-waste repository. The study of this natural analogue has been performed through detailed electrical, gravity and soil-gas surveys in order to define both the geometry of the Selagite intrusion and the gas permeability of a clay unit characterised by different degrees of thermal alteration.

Radon and carbon dioxide soil-gas anomalies are concentrated in zones where the Selagite intrusion outcrops and where thermally altered clays may be inferred, while further from these fractured zones no appreciable soil gas anomalies occur for these gases due to the sealing of these intact clays. This distribution is likely due to intense fracturing of clays along the laccolith boundary, as it is reasonable to suppose that the intrusion of the laccolith caused mechanical stress and contact metamorphism in the clay. This observation indicates that the clay sequence, in spite of its thickness and plasticity, is far more permeable to naturally migrating gas if it is fractured and metamorphosed. In addition, the association of a trace gas (radon) with CO₂ suggests that the latter acts as a carrier gas of the former; if the pressure of carbon dioxide is sufficient, it can form a free gas phase (i.e. bubbles) and advect rapidly within the rock, scavenging Rn as it rises through groundwater up to the unsaturated horizon.

Helium concentrations locally reach values which are significantly above the atmospheric content, suggesting a deep origin. Positive anomalies in apparently-intact clays infer the presence of buried deep structures linked to regional faulting that favoured gas migration toward the surface. Although without isotopic analyses it is not possible to define the origin of the other analysed soil-gas species (CH₄, COS, C₃H₈), it is likely that their distribution was also influenced by the contact metamorphism because the highest values are present over the metamorphosed clays. Geophysical lineaments, which represent highly permeable zones within the clays, correspond to where the highest Rn, CO₂, CH₄ and COS soil-gases anomalies occurred.