## SESSION IV

# REACTION OF ARGILLACEOUS MEDIA VIS-À-VIS NATURAL PERTURBATIONS AND GEOSPHERE EVOLUTION (BUFFERING)

# CLAY CLUB INITIATIVE: SELF-HEALING OF FRACTURES IN CLAY-RICH HOST ROCKS

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## Introduction

The capacity of fractures in argillaceous rocks to self-heal (or become, with the passage of time, less conductive to groundwater) is often cited as a primary factor favouring the choice of such materials as host rocks for deep disposal. The underlying processes which contribute to self-healing can be broadly subdivided into: (a) mechanical and hydromechanical processes linked to the change in the stress field, movement of porewater, swelling, softening, plastic deformation and creep, and (b) geochemical processes linked to chemical alterations, transport in aqueous solution and the precipitation of minerals. Since chemical alteration can cause profound changes to the mechanical properties of argillaceous rocks, it is often difficult to draw a firm line between these two sub-divisions. Based on the deliberations of the recent Cluster Conference in Luxembourg, there would appear to be some support for the use of the term "self-sealing" for processes affecting fracture conductivity in argillaceous rock that are largely mechanical or hydromechanical in their origin.

There are four main areas in which the self-healing capacity of the host rock becomes relevant to repository design and performance assessment:

- potential for radionuclide transport within the excavation damage zone (EDZ);
- design and performance of repository sealing systems;
- potential impact of gas migration;
- long-term performance considering erosional unloading, seismicity and fault reactivation.

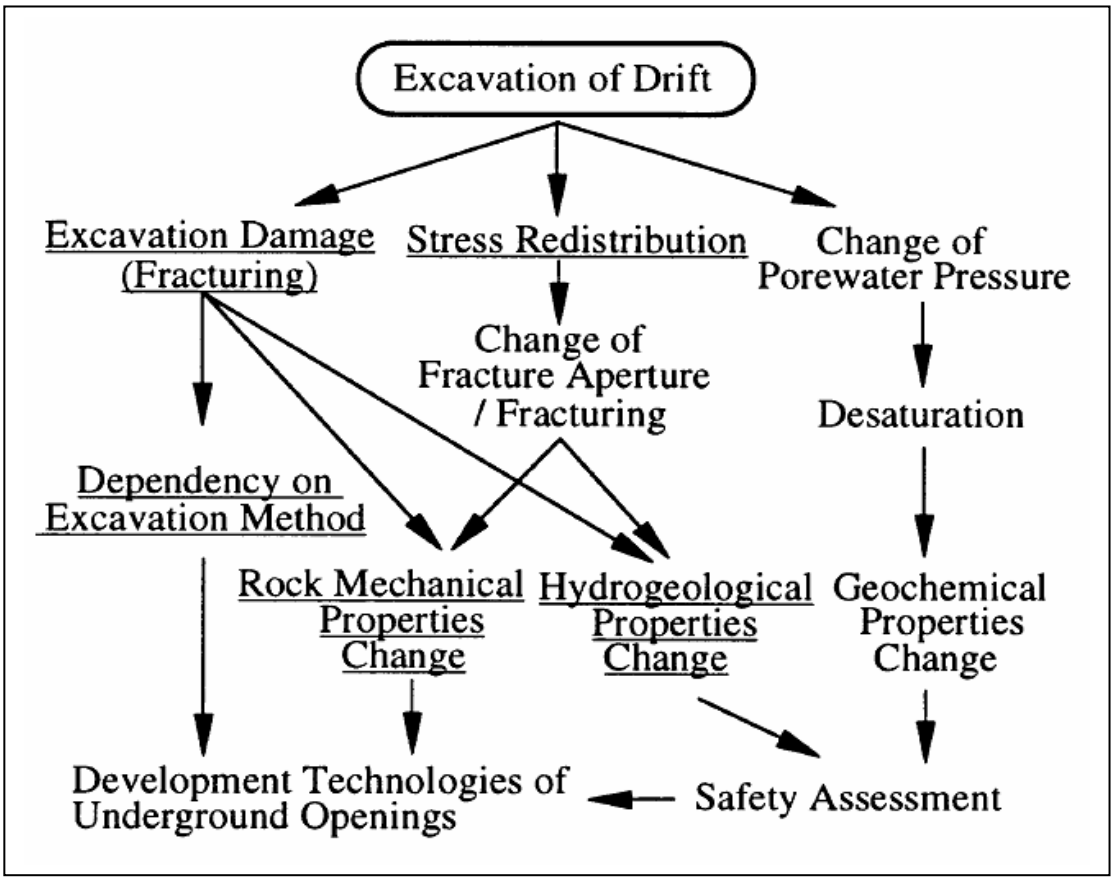
The presence of an EDZ is acknowledged to be a particularly important issue in performance assessment (Meier *et al.,* 2002). Interconnection of fractures in the EDZ could lead to the development of a preferential flow path extending along the emplacement holes, access tunnels and shafts of a repository towards overlying aquifers and the biosphere. In the preliminary French Safety Analyses, for example, the treatment of scenarios relating to early seal failure have highlighted the hydraulic role of the damaged zone as a potential radionuclide transport path (Anon, 2001).

## Excavation damage zone

Figure 1 is a schematic of processes occurring in the EDZ around a test drift. The size and the properties of the EDZ depend on the excavation method, the state of stress, the pore water pressure and the hydro-mechanical properties of the rock. Bedding plane anisotropy can be an important factor.

Blasting tends to cause more damage than other methods of excavation. Damage associated with tungsten-carbide tipped tools fitted to roadheaders and similar tunneling machines tends to be much more localised. In clays and argillaceous rocks, the most pervasive forms of damage are caused by stress redistribution and unloading. Three basic forms of fracturing may be defined: (a) shear fractures, (b) tensile fractures, and (c) extensile fractures. Recent experience during development operations in several URLs clearly demonstrate that the dominant mode of fracturing can be quite different from one mudrock to another.

**Figure 1. Processes occurring in the EDZ** (Sato *et al.,* 2000)




Conspicuous shear fracturing was observed during recent tunneling operations in the Boom Clay. It seems clear that the shear stress ahead of the tunnel face has locally exceeded the undrained shear strength of the clay. Fracturing in more indurated mudrocks such as the Opalinus Clay would appear to be more complex. Unloading fractures are fairly ubiquitous and are suggestive of a form of extensile failure (Figure 2). The rapid reduction in radial stress around an excavation leads to a stress state that approximates to one of triaxial extension. The rock therefore responds to the stress relief by stretching in the radial direction. These rocks are incapable of sustaining large extensile strains without rupturing. Unloading cracks are therefore formed normal to the minor principal stress. This mode of failure may be similar to the “core-discing” phenomenon observed during drilling. Borehole breakout has also been observed during drilling in Opalinus Clay. There is also evidence of a bedding-plane slip mechanism which would seem to be a specific form of shear failure.

**Figure 2. Extensional fracturing around the DI Niche at the Mont Terri Rock Laboratory in Switzerland**

## Dilatancy boundary

Horseman (2001) used the basic concept of the dilatancy boundary to interpret the temporal evolution of permeability along a stress path. Qualitative arguments were based on the Modified Cam-Clay Model (MCCM) which describes the deformation and failure of porous elastoplastic materials. The state boundary surface was assumed to comprise the Hvorslev Surface for material on the "dry side" of the critical state line and the Roscoe Surface for material on the "wet side" (Shah, 1997). Shear deformation on the "dry side" favours dilatant shear fracturing, whereas deformation on the "wet side" favours "contractant" behaviour. The MCCM, as currently implemented, does not adequately describe the effect of the intermediate principle stress in the development of fractures and, as a result, grossly overestimates strength in triaxial extension. Given the importance of extensile fracturing around tunnels driven in more-indurated mudrocks, this proves to be a significant handicap in the quantitative analysis of EDZ fractures in such rocks. Bardet (1990) demonstrates that it is feasible to modify the Cam-Clay approach to describe true-triaxial behaviour by invoking Lode-dependency in the specification of the state boundary surface.

## Indurated mudrocks

Research at the Mont Terri Rock Laboratory in Switzerland has revealed the main characteristics of the EDZ in moderately indurated rock-types comparable to the Opalinus Clay (Thury and Bossart, 1999; Bossart *et al*., 2002). Figure 3 shows a conceptual model of the fracturing around a tunnel. The inner zone, identified as $f_1$ extends around 1 m into the rock and consists of a network of

interconnected and air-filled unloading fracture with substantially enhanced transmissivities (values varying between $10^{-5}$ and $10^{-9}$ $m^2.s^{-1}$). The highest transmissivities are found in the first 40 cm of the tunnel wall. The second or outer zone, identified $f_2$ in the figure extends a further 2 m into the rock and consists of partially-saturated unloading fractures. These tend to be isolated and therefore have a much lower degree of interconnectivity. The transmissivities are substantially less than in the outer zone (values varying between $10^{-9}$ and $10^{-12}$ $m^2.s^{-1}$). At Mont Terri, oxidation phenomena such as gypsum spots on fracture surfaces have been observed only in the inner $f_1$ zone of the EDZ. Figure 4 illustrates the radial distribution of permeability around an excavation.

**Figure 3. Conceptual model of the excavation disturbed zone at the Mont Terri Rock Laboratory**
(Bossart *et al.*, 2002)

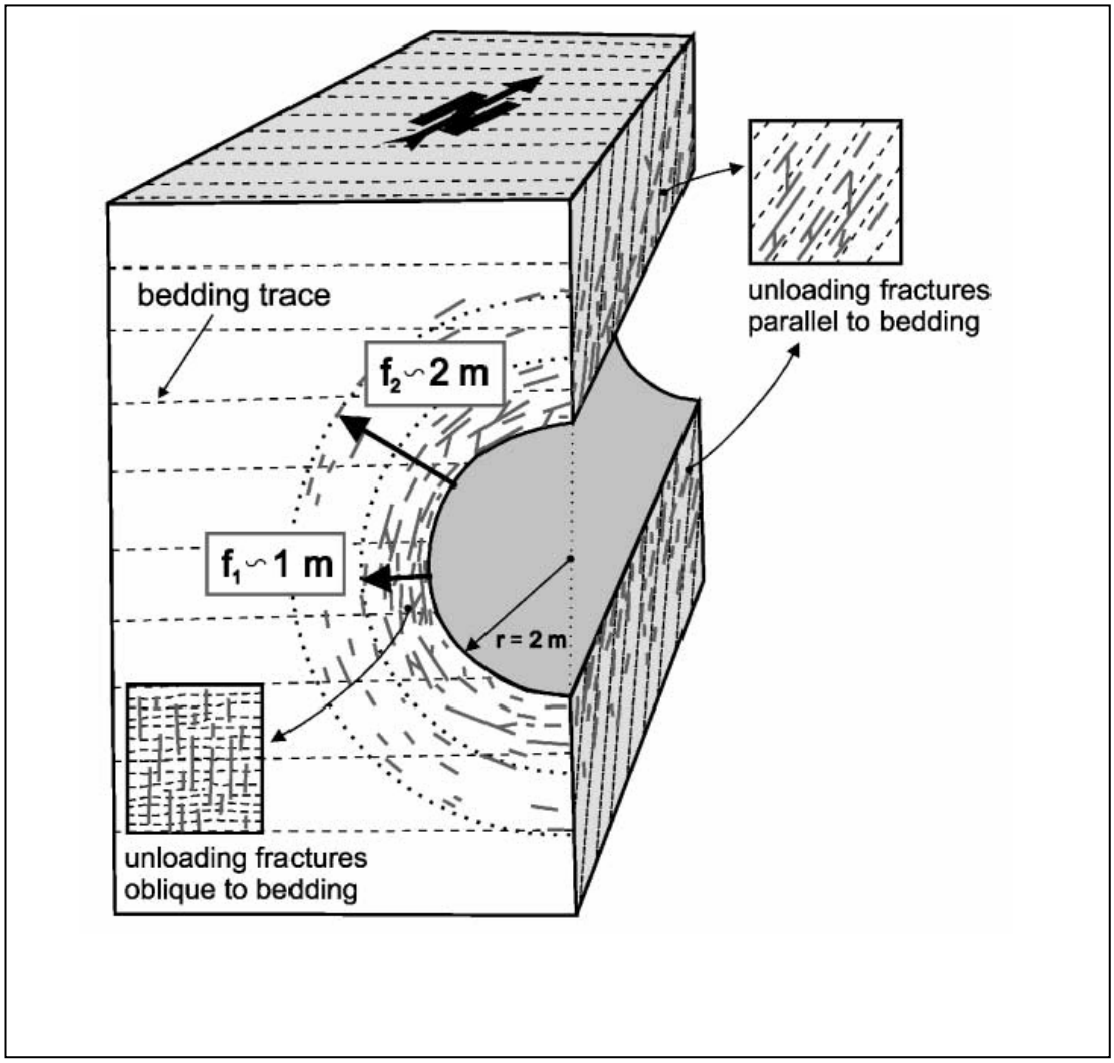
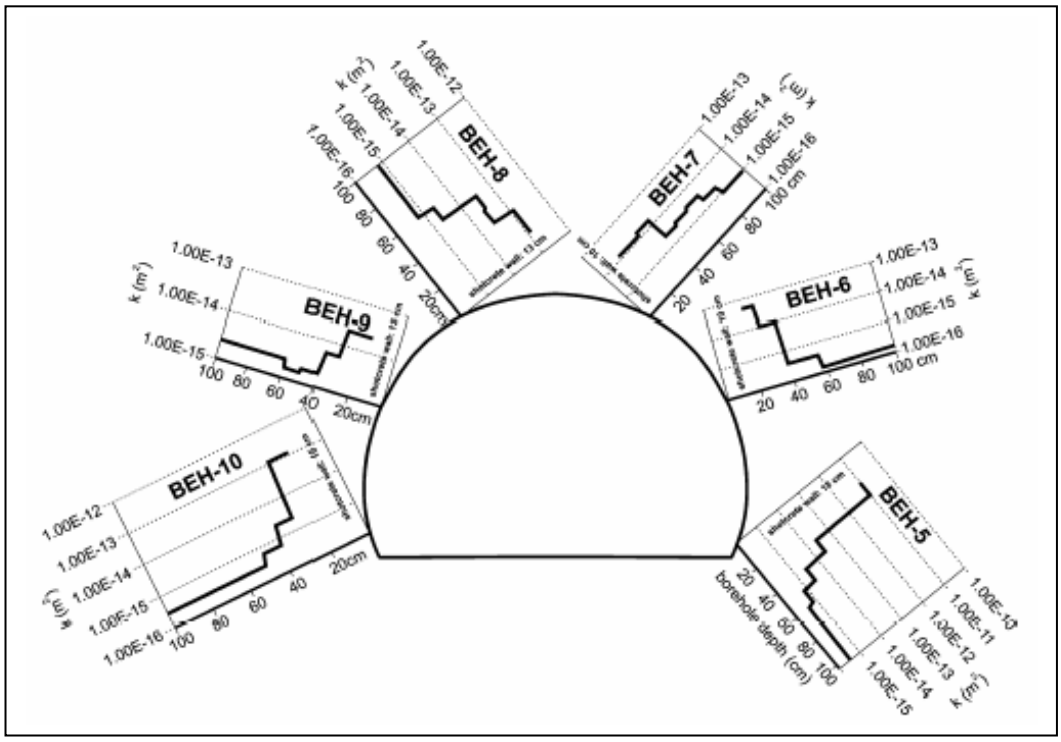


**Figure 4. Permeability to air in a section of the new gallery at the Mont Terri Rock Laboratory**
(Bossart *et al.*, 2002)




At Tournemire in Southern France, a railway tunnel built about 100 years ago is used as a laboratory for the generic scientific and geotechnical investigations related to radioactive waste disposal. The excavated disturbed zone (EDZ) around the tunnel is well expressed by a regular set of induced fractures along the vertical walls of the tunnel. The fractures are sub-vertical, parallel to the walls of the tunnel and intersect sub-horizontal fractures corresponding to open stratification beds. This results in a continuous zone adjacent to the tunnel comprising parallelepiped blocks placed side by side, generally covered by gypsum formed by oxidation (Charpentier *et al.*, 2001). The opened-fracture zone of the EDZ extends about 150 cm from the tunnel surface (Charpentier *et al.*, 2003).

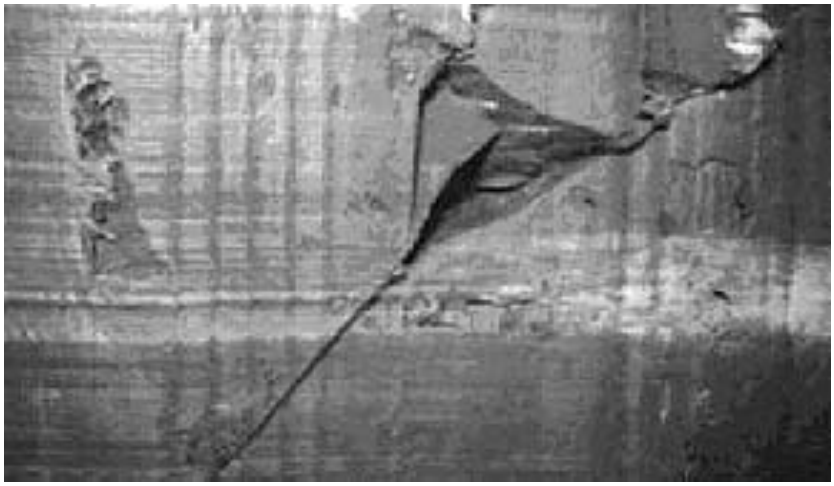
## Plastic clays

It is widely recognised that overconsolidated plastic clays exhibit inhomogeneous strains at failure, with deformation focussed along discrete macroscopic failure planes. Strain-softening is usually observed. Slickensides are a conspicuous feature of shear failure in such materials.

Shear fracturing was observed during underground development work at the Hades URL of the Belgian Nuclear Research Centre at Mol (SCK•CEN). A second shaft was sunk in 1998-1999. Two chambers were excavated in the Boom Clay at the bottom of this shaft to enable development of the horizontal gallery. Excavation of the starting chambers caused face instability problems resulting in significant fracturing of the clay to the excavation. Large fracture surfaces were visible at the face of each starting chamber, with fracture traces extending around the sidewalls. The slip surfaces consisted of an interconnected network of conjugate planes inclining at 35° towards the centre of the shaft. The circular shape of the slip surfaces indicated that they were symmetric around the shaft axis. Slickensides, visible on the slip surfaces, clearly indicated shear movement towards the centre of the

shaft (Anon, 2002). Extensive tunnel operations were undertaken 2002 to connect the URL to the new shaft. Large fractures developed in the face of the excavation side-walls and in the sidewalls (Figure 5). Blocks of clay bounded by slickensided shear planes and tension joints became detached and caused difficulties in tunneling operations (Dehandschutter, 2002). Geometric considerations suggest that most of the fracturing was caused by the process of excavation.

**Figure 5. Excavation-induced fracture in the side-wall of the connecting gallery in the Hades URL at Mol in Belgium** (Dehandschutter, 2002)



## Desaturated zone

The combined effect of extensile and shear-induced dilatancy in undrained situations is a significant reduction in the pore pressure. It seems probable that pore pressures can actually become negative in sign (i.e. a state of suction) close to the walls of a repository excavation, leading to localised desaturation. Ventilation can also cause localised desiccation, and increase in suction and further desaturation. The aperture of EDZ fractures is sensitive to variations in the humidity of the air. Rock properties such as shear strength will change with change in the suction.

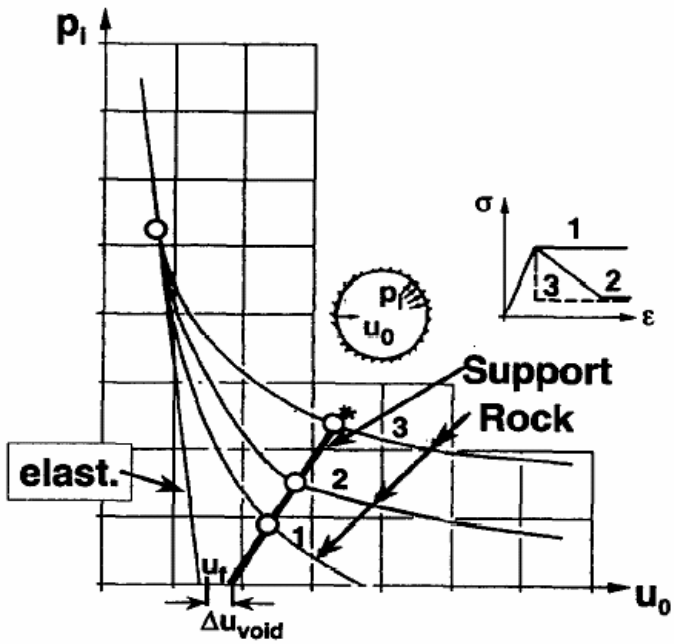
## Support and backfilling

The provisions for made long-term support of repository excavations are of first order importance in assessing the capacity for EDZ self-healing. Various systems of support systems proposed including: sprayed concrete (shotcrete), steel arches with concrete lagging, concrete block linings, cast iron tubbing and cast-in-place monolithic concrete linings. Prior to repository closure, the void spaces will be backfilled with clay (e.g. bentonite) or a mixture of clay and sand. In some repository designs, temporary support will be provided using steel-fibre-reinforced shotcrete in combination with rockbolts and weldmesh. Long-term support will be assured by filling the tunnel section with a swelling clay backfill which will also serve to minimise groundwater movements. If this backfill is formulated to have a significant swelling pressure, then as it hydrates it will exert a radial stress on the shotcrete and the surrounding rock.

Force transference between the rock to the support system is a matter of central concern in tunnels engineering. One approach to the design of a tunnel lining uses the so-called "Convergence-Confinement Method". This involves the calculation of a "ground response curve" (or rock characteristic line) and a "support response curve". Convergence is expressed in terms of the radial displacement of the tunnel wall. The ground response curve is a plot of the convergence against a hypothetical pressure applied uniformly to the tunnel wall, known as the confinement. The ground response curve is calculated using a model for the strength and deformation of the rock. For concrete linings the support response curve is usually calculated assuming linear elastic stress-strain behaviour. By superimposing the response curve for the lining on that for the lining and making allowances for any overbreak (or gap) behind the lining and the rock, it is possible to estimate the maximum radial stress that will be carried by the lining.

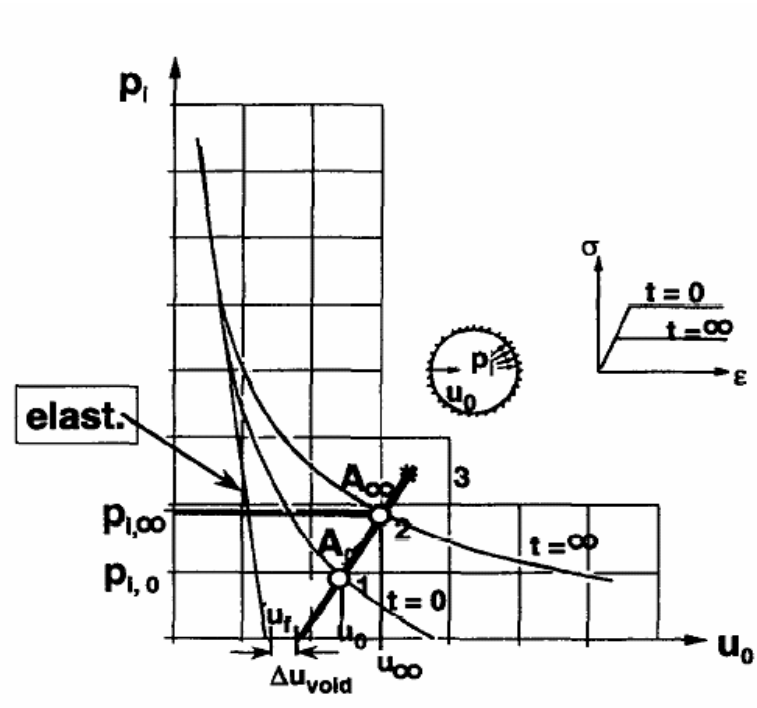
Tunnel engineers frequently assume that soft rocks exhibit either: a) perfectly elasto-plastic; b) strain-softening elasto-plastic; or c) elasto-plastic-brittle behaviour. The constitutive model is usually formulated in terms of total stresses and therefore neglects the effect of pore pressure dissipation on the redistribution of stress. Figure 6 shows a schematic of the ground response curves based on the assumption of elasto-plastic behaviour.

**Figure 6. Convergence-confinement analysis of the interaction between the rock and the tunnel support system, based on: (1) elasto-perfectly-plastic rock deformation; 2) elasto-plastic strain softening deformation and 3) elasto-plastic brittle deformation**




The argillaceous rocks of interest as potential host-rocks in radioactive waste disposal show a pronounced rate-dependency in their stress-strain behaviour. Creep deformation (see below) is very important in such rocks and the ground response curve therefore changes progressively over time. Figure 7 illustrates this for a rock in which creep is only significant when the deviatoric stress is larger than a specific threshold value. The stress acting on the lining is predicted to rise asymptotically with time up to some maximum limiting value.

**Figure 7. Convergence-confinement analysis of the interaction between the rock and the tunnel support system based on the assumption of creep deformation above a threshold stress**

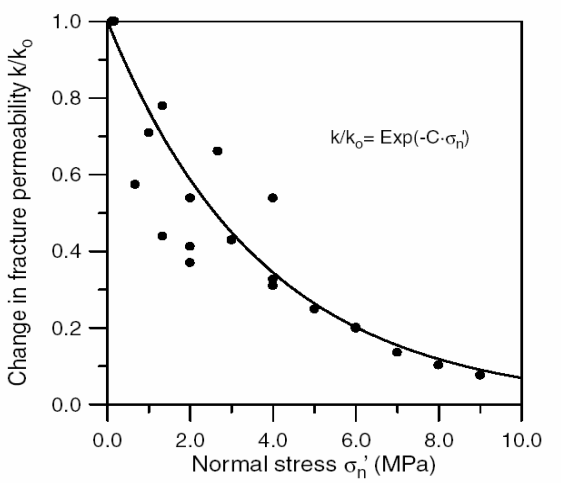



In the context of self-healing it is important to remember that any stress acting on the tunnel lining must be transmitted by the EDZ. If the rock exhibits creep then the EDZ will experience a time-dependent build up in the radial stress after installation of the support system. The magnitude of this build up will depend in part on the rigidity of the support. One possible effect of this increase in radial stress will be to cause the stress path of the rock within the EDZ to move progressively away from the failure (or yield) surface. The general movement of the stress path will be towards the "wet side" which favours contractancy over dilatancy.

## Effect of normal stress

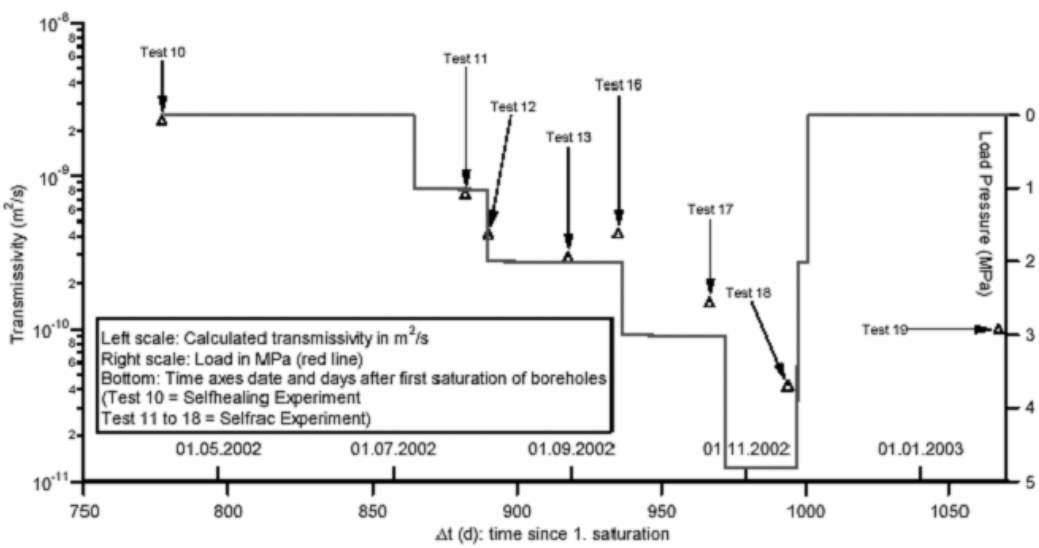
The hydro-mechanical behaviour of an extensional fracture in shale under normal and shear loading has been investigated experimentally by Gutierreza *et al*. (2000). The samples were obtained by de-mineralising cemented natural fractures in block samples of Kimmeridge Shale. These are believed to be representative analogues of hydraulic fractures in shaly formations. Increasing the normal stress across the fracture reduced the fracture permeability. This behaviour could be represented by an empirical exponential law (Figure 8). However, loading the sample to an effective normal stress twice equivalent to twice the intact rock unconfined compressive strength did not completely close the fracture. The fracture permeability was reduced by an order of magnitude after loading to an effective normal stress of 10 MPa. The measured fracture permeability was still eight orders of magnitude larger than the permeability of the intact shale.

**Figure 8. Effect of normal stress on the permeability of a de-mineralised fracture in Kimmeridge Shale**
(Gutierreza *et al.*, 2000)




Many of the extensile (unloading) fractures observed around openings in argillaceous rock are orientated more or less parallel to the tunnel surface. The radial component of stress around the tunnel therefore acts normal to many of these fractures. Re-application of normal stress to the EDZ should therefore lead to at least partial closure of EDZ fractures. In the SELFRAC Experiment at the Mont Terri Laboratory, the arrangements were made to reload the EDZ using hydraulic rams (Trick, 2003). Transmissivity measurements of were made before reloading and at various levels of applied stress. Figure 9 is a summary of the results. Loading the EDZ caused the transmissivity to drop from around 2 x $10^{-9}$ $m^2.s^{-1}$ at the start of loading to 4 x $10^{-11}$ $m^2.s^{-1}$ at an applied stress of 3.75 MPa. After complete removal of load, the transmissivity was 1 x $10^{-10}$ $m^2.s^{-1}$ showing that the effects of re-stressing the EDZ are largely irreversible.

**Figure 9. Summarised results of the SELFRAC Experiment at Mont Terri Rock Laboratory showing the effect of reloading on the transmissivity of the EDZ**



**Viscoplastic deformation**

Creep is time-dependent deformation of a material when subjected to sustained loading. In porous materials it is possible to distinguish two main types: (a) creep in shear governed by the deviatoric component of the stress tensor and (b) volumetric creep governed by the spherical component of the effective stress tensor. Consolidation of clay-rich materials is a time dependent change in volume and is considered to have a hydrodynamic component (primary consolidation) and a creep component (secondary consolidation). Most of the research in rock mechanics has focused on creep in shear. Since creep strains are largely non-recoverable on unloading, they are best described as viscoplastic strains. A variety of modelling approaches are available, including mechanical analogues assembled from basic rheological elements (e.g. the Kelvin model), empirical formulations and phenomenological approaches. Models are calibrated using laboratory data from multistage triaxial creep tests, relaxation tests or constant strain-rate tests or from field data by the back-analysis of monitored tunnel convergence or extensometer measurements. Possible scale effects have been observed in creep measurements on argillaceous rocks suggesting that over reliance on laboratory test data is inadvisable (Boidy *et al*., 2002).

Fundamentally important issues in the specification of constitutive models for the creep are: (a) nonlinearity of the relationship between viscoplastic strain rate and deviatoric stress and the possibility of thresholds; (b) volumetric response of the material during creep deformation; (c) long-term extrapolation of creep test data and the existence or otherwise of steady-state creep under constant deviatoric stress. In contrast to evaporites such as rock salt, argillaceous rocks are only weakly nonlinear with a stress exponent only slightly greater than unity. Also in contrast to salt, argillaceous rocks can undergo substantial volumetric creep when mean effective stress is raised. Since creep models are seldom formulated in terms of effective stresses, volumetric creep behaviour is usually ignored. Coupling between shear and volumetric behaviour is likely in clay-rich rocks. Extrapolation of creep test data presents a significant problem and there are very few data sets of a quality or duration adequate to define long-term behaviour. It is necessary to compare numerical simulations with measurements obtained from monitored tunnels over long periods. Such data are very scarce.

Boidy *et al.,* (2002) present a back-analysis of the time-dependent behaviour of the reconnaissance gallery of the Mont Terri Tunnel in Switzerland. The study examined a specific section of the gallery which was excavated in Opalinus Clay and left without any support system for approximately 3 months, after which a stiff lining consisting of concrete rings was installed (Kohler, 1995; 1997). Numerical modelling was undertaken using the Lemaitre creep law. This is a total stress approach based on the assumption of isovolumetric viscoplastic behaviour. Pore pressure effects and volume-change phenomena such as consolidation and swelling are therefore ignored. Initial estimates of the parameters of the model were obtained from triaxial creep tests data supplied by the École Polytechnique Fédérale de Lausanne (EPFL) and reported in Kharchafi and Descoeudres (1995). Figure 10 shows the results of a typical laboratory test. Using the convergence measurements from the gallery, a parametric study was made on the Lemaitre parameters with particular attention to the viscosity term A. Figure 9 shows a comparison between the viscoplastic simulations and the measured convergence data. Parameter set no. 2 gives the best representation of the measured convergence. The viscosity term A is substantially smaller than that the value obtained by fitting the laboratory test results.

**Figure 10. Lemaitre creep model fitted to undrained triaxial creep data for the Opalinus Clay**
(test data from Kharchafi and Descoeudres, 1995; and data fits from Boidy *et al.*, 2002)

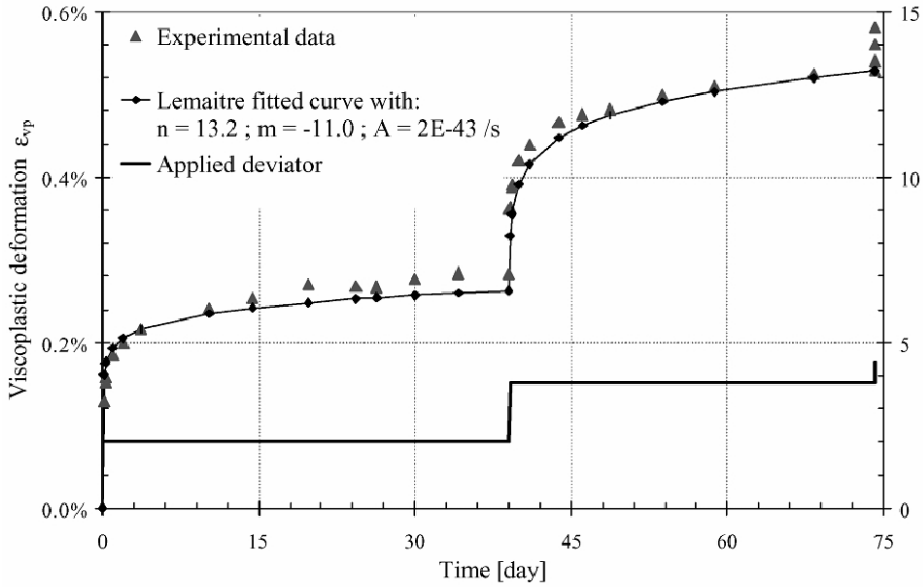
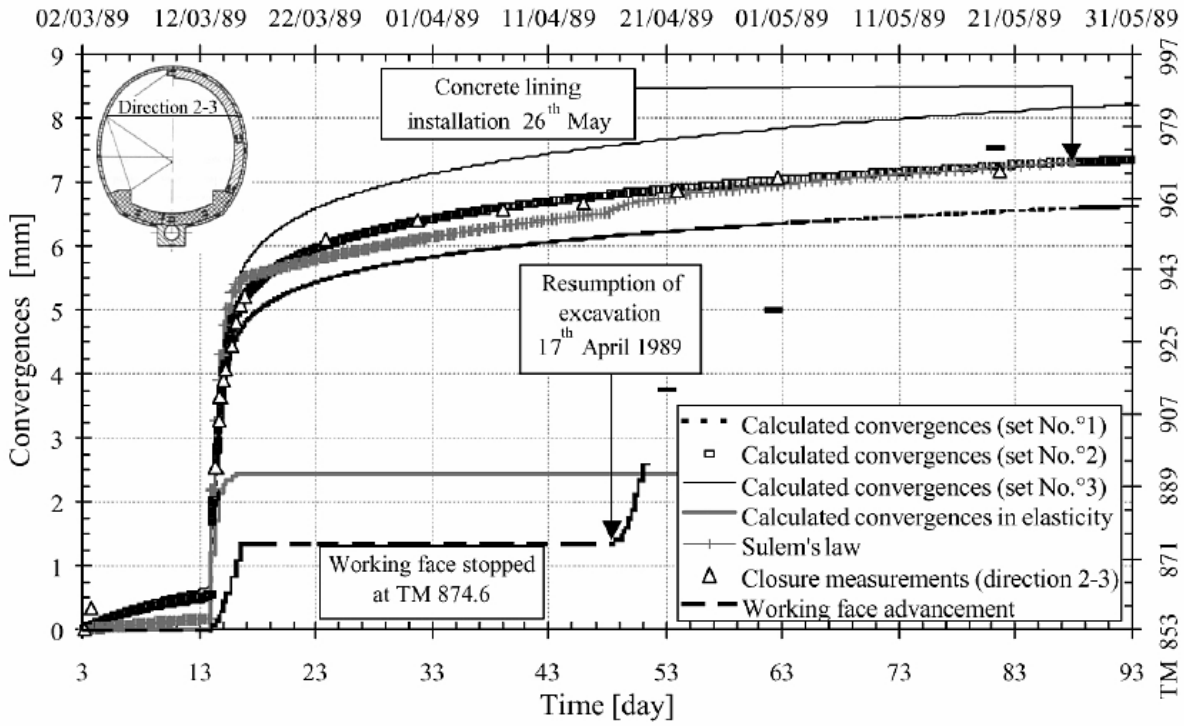
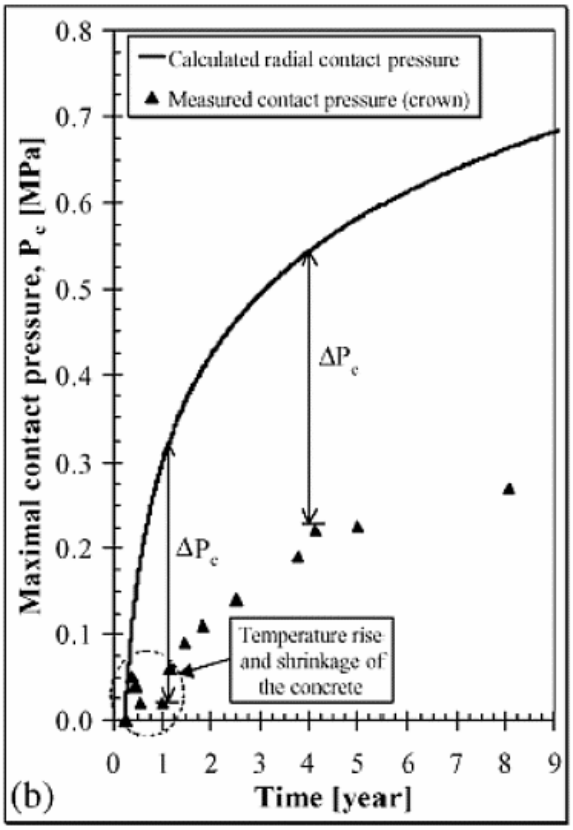



**Figure 11. Measured and computed convergence for different sets of creep parameters**
(measurements from Kohler, 1995; 1997; and modelling results from Boidy *et al.* 2002)



The build up of radial contact pressure is interesting from the point of view of EDZ self-healing. Figure 12 shows the measured and calculated response at the crown. The overburden stress is estimated to be 6.35 MPa. The actual contact pressure is around 0.27 MPa after 8 years showing that only a small proportion of the overburden stress is tranferred to the lining in this time period as a result of creep deformation of the formation.

**Figure 12. Measured and computed build up of radial contact pressure on the concrete rings in the reconnaissance gallery at the Mont Terri Tunnel**
(Boidy *et al.*, 2002)




In this respect the Opalinus Clay differs considerably from the Boom Clay. Measurements of the build-up of load on the concrete segmental lining of the connecting gallery in the Hades URL show that lining load reaches 3 to 3.5 MPa after a comparatively short period of time. The calculated vertical overburden stress is around 4.2 MPa, showing that a significant fraction of the total stress is transferred to the lining. The reapplication of this normal stress to the EDZ is likely to promote permeability decrease and self-sealing.

## Swelling

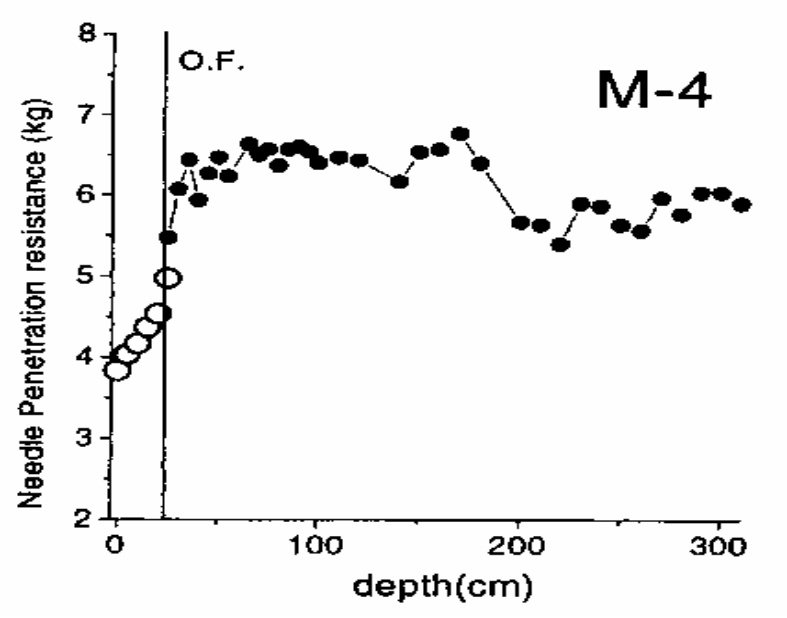
The capacity of an argillaceous rock to swell when exposed to free water depends on: (a) clay mineralogy; (b) cementation; (c) stress history and (d) water chemistry. Water is drawn into the clay fabric by physico-chemical forces and this inward movement of water molecules into the interparticle spaces between platy clay minerals causes the fabric to expand. The presence of an interparticle cement can inhibit swelling of the clay fabric. However, cementing agents such as calcite and silica

are brittle and easily damaged by shear deformation and it seems likely that fabric damage is a necessary prerequisite for swelling in some of the more indurated argillaceous rocks. This form of fabric damage is sometimes referred to as bond degradation (Vaunat and Gens, 2003).

## Softening

Many argillaceous rocks also exhibit a progressive process of fabric breakdown referred to as softening. This is a gradual alteration of a hard rock into a plastic soil-like clay material with substantially reduced shear strength (Botts, 1986). The water content of a softened argillaceous rock is significantly larger than that of the parent material showing that swelling and softening are closely linked. Softening usually commences around fissures and fractures. Figure 13 illustrates the process of softening around a tunnel.

**Figure 13. Variation of needle penetrometer resistance with distance from a tunnel surface showing softening of the rock in the oxidised zone**
(Oyama and Chigira, 1999)

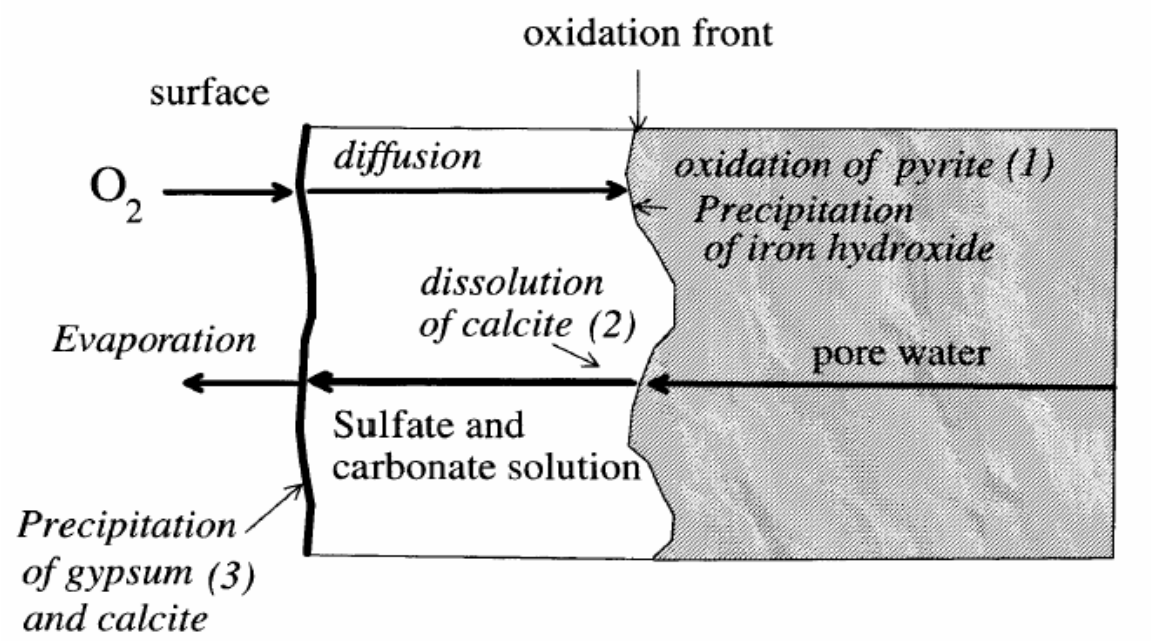



## Chemical weathering

Geochemical processes play an important role in the progressive alteration of argillaceous rock in the walls of underground excavations. For example, the oxidation of pyrite can leading to acidification of the porewater. The sulphuric acid thus formed can react with calcite to form gypsum. This process is not exclusively chemical. Autotrophic bacteria obtain their energy from the oxidation of inorganic compounds and atmospheric oxygen is consumed. Proteinaceous body materials are produced from atmospheric $CO_2$ and nutrients such as nitrogen are usually available in pyritic shales to support bacterial growth and reproduction.

It was recently discovered that the unlined walls of road tunnels excavated 45-85 years ago in central Japan have maintained their original cut surfaces over several decades; offering suitable locations to study the long-term effects of chemical weathering on mudstones and tuffs (Oyama and Chigira, 1999). The tunnel walls are assumed to have been saturated with water before the excavation and to have become desaturated by natural ventilation. White gypsum crusts about 0.5-2 mm thick, together with powdery gypsum were found to have precipitated on the wall surfaces. Prior to tunnel excavation, the water-saturated mudrocks were in a reducing environment. After excavation, the tunnel walls became dry and desaturated by ventilation, and oxidation started from the walls and moved inward. Oxygen diffused from the surface walls to the interior through the interconnected pore-space of the rock (Figure 14). This resulted in oxidation of pyrite at the oxidation front, and the generation of sulphuric acid. FeO present in the clay minerals was oxidised. The sulphuric acid released by oxidation dissolved certain components of the rock, in particular carbonate in the mudstones and glass in the tuffaceous samples. As a consequence, rock present within the oxidised zone softened and weakened.

**Figure 14. Mechanism of chemical weathering of the mudstone tunnel wall**
(Oyama and Chigira, 1999)




Growth of gypsum crystals can also force shale layers apart (Figure 15). This process is similar to the formation of ice lenses in soils (Penner *et al.,* 1972). Oyama and Chigira (1999) suggest that diffusion of oxygen is the limiting factor in determining the rate of advancement of the weathering front into the rock (Figure 16). Isotopic studies at the Tournemire Tunnel in southern France indicate that oxygen isotopes are disturbed at more than 10 m indicating air diffusion around this old tunnel at a significant distance from the tunnel wall (Charpentier *et al*., 2003).

**Figure 15. The growth of gypsum crystals tends to force shale layers apart. This process is similar to the formation of ice lenses in soils.**
(Penner *et al.*, 1972)

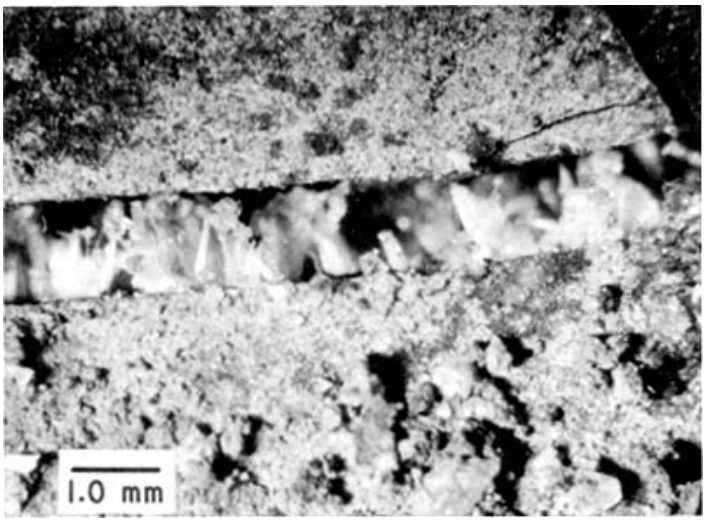
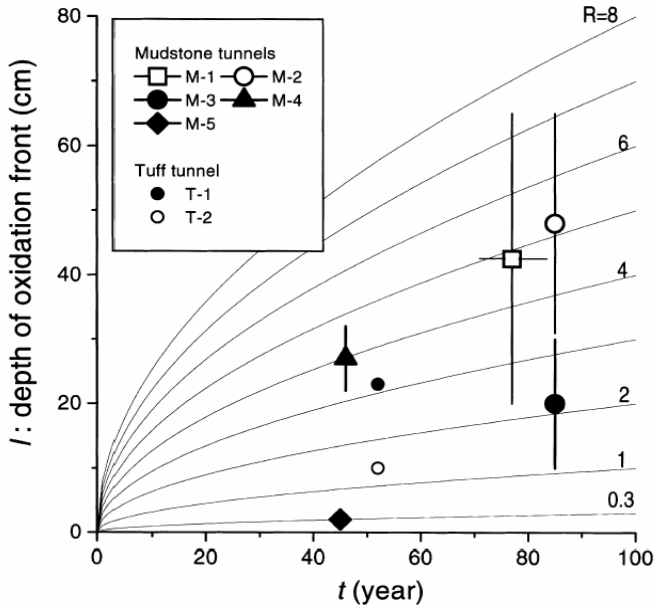



**Figure 16. Advancement of the chemical weathering front into the tunnel wall. Error bars relate to various measurements of diffusivity.**
(Oyama and Chigira, 1999)




It is conceivable that, under very specific circumstances, gypsum precipitation might contribute to a lowering of fracture conductivity. It is also possible that the chemical breakdown of interparticle cements could initiate the swelling and softening mechanisms discussed above. Geochemical changes might result in alteration of the retention capacity of the damaged rock.

## Long-term geochemical evolution

The tunnel lining will impede the diffusion of oxygen into the wall rock. After backfilling of the excavations and closure of the repository any remaining residual air will eventually be consumed by chemical reactions and biological activity. The EDZ will then enter an anoxic phase. The long-term geochemical evolution of damaged rock and its effect on the transport properties of the EDZ remain to be elucidated. In the specific case of repositories containing large amounts of cementious materials, the precipitation of cementing minerals from a hyperalkaline plume is anticipated. Fracture sealing by this form of mineralisation has been observed at the Maqarin natural analogue site in Jordan (Alexander, 1995; Smellie, 1997).

## Conclusions

The capacity of fractures in argillaceous rocks to self-heal (or become, with the passage of time, less conductive to groundwater) is often cited as a primary factor favouring the choice of such materials as host rocks for deep disposal. The underlying processes which contribute to self-healing can be broadly subdivided into: (a) mechanical and hydromechanical processes linked to the change in the stress field, movement of porewater, swelling, softening, plastic deformation and creep, and (b) geochemical processes linked to chemical alterations, transport in aqueous solution and the precipitation of minerals. Since chemical alteration can cause profound changes to the mechanical properties of argillaceous rocks, it is often difficult to draw a firm line between these two sub-divisions.

Provisions for made long-term support of repository excavations are of first order importance in assessing the capacity for EDZ self-healing. One approach to the design of a tunnel lining uses the so-called “Convergence-Confinement Method”. This involves the calculation of a “ground response curve” and a “support response curve”. The ground response curve is a plot of the convergence against a hypothetical pressure applied uniformly to the tunnel wall, known as the confinement. The ground response curve is calculated using a model for the strength and deformation of the rock. The argillaceous rocks of interest as potential host-rocks in radioactive waste disposal show a pronounced rate-dependency in their stress-strain behaviour. Creep deformation is very important in such rocks and the ground response curve therefore changes progressively over time. The stress acting on the lining is predicted to rise asymptotically with time up to some maximum limiting value.

If the rock exhibits creep deformation then the EDZ will experience a time-dependent build up in the radial stress after installation of the support system. The magnitude of this build up will depend in part on the rigidity of the support. Many of the extensile (unloading) fractures observed around openings in argillaceous rock are orientated more or less parallel to the tunnel surface. The radial component of stress around the tunnel therefore acts normal to many of these fractures. Re-application of normal stress to the EDZ should therefore lead to at least partial closure of EDZ fractures. The hydro-mechanical behaviour of an extensional fracture in shale under normal and shear loading has been investigated experimentally. In Kimmeridge Shale, loading to an effective normal stress twice equivalent to twice the intact rock unconfined compressive strength did not completely close the fracture. Fracture permeability was reduced by an order of magnitude after loading to an effective normal stress of 10 MPa.

Measurements of the build-up of load on the concrete segmental lining of the connecting gallery in the Hades URL show that lining load reaches 3 to 3.5 MPa after a comparatively short period of time. The calculated vertical overburden stress is around 4.2 MPa, showing that a significant fraction

of the total stress is transferred to the lining in the Boom Clay. The reapplication of this normal stress to the EDZ is likely to promote permeability decrease and self-sealing.

It seems likely that the combined processes of chemical weathering, swelling and softening will lead to a gradual decrease in the amount of water flowing through interconnected fractures. The presence of an interparticle cement can inhibit swelling of the clay fabric. However, cementing agents such as calcite and silica are brittle and easily damaged by shear deformation and it seems likely that some form of mechanical damage or chemical alteration is a necessary prerequisite for swelling in some of the more indurated argillaceous rocks. It has been suggested that suggest that diffusion of oxygen is the limiting factor in determining the rate of advancement of the weathering front into the rock. It is conceivable that gypsum precipitation might contribute to a lowering of fracture conductivity.

After backfilling of the excavations and closure of the repository any remaining residual air will eventually be consumed by chemical reactions and biological activity. The EDZ will then enter an anoxic phase. The long-term geochemical evolution of the damaged rock and its effect on the transport properties of the EDZ remain to be elucidated.

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# HYDRO-MECHANICAL ASPECTS: GLACIAL LOADING/EROSION – THE OPALINUS CLAY STUDY

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## 1. Introduction

In Nagra's high level waste programme the future geological evolution of the investigation area in the Zürcher Weinland (NE Switzerland) is considered over a time period of around 1 Ma. Uplift, erosion and climatic changes were identified as processes that may affect the long-term performance of a repository for spent fuel (SF), vitrified high-level waste (HLW) and long-lived intermediate-level waste (ILW). The possible impact of those long-term processes on the barrier function of the host rock formation (Opalinus Clay) comprises: (i) the change of the vertical hydraulic gradient caused by changing recharge/discharge conditions in the regional aquifer systems; (ii) permeability enhancement of the host rock formation due to the uplift process; and (iii) expulsion of contaminated porewater from the disposal area as a result of repeated glacial loading.

Due to the fact that the discharge level of the regional aquifer systems is defined by the Rhine valley and the regional recharge areas are characterised by moderate elevations (typically <200 m above the level of the Rhine valley) the present day *vertical hydraulic gradient* between the regional aquifers is <1; hydraulic gradients >2 are not expected within the next several million years. Hence, the topography of NE Switzerland together with the favourable hydraulic properties of the host rock formation prevent efficiently the vertical exchange of groundwater between the regional aquifer systems. Even on geological time scales of millions of years the expected vertical porewater flow through the host rock formation is in the order of $10^{-14}$ m/s and lower.

At present, the Opalinus Clay forms a perfect hydraulic barrier. The process of ongoing uplift, however, may give rise to embrittlement of the rock, entailed by *permeability enhancement*. Evidence for permeability enhancement of Opalinus Clay in shallow depth was observed by Hekel (1994). On the other hand, regional studies confirmed the low permeability of the Opalinus Clay formation in greater depth – even when fractured (Gautschi, 2001; Marschall *et al.,* 2003). Such evidence, together with conceptual considerations concerning the rock deformation behaviour (Horseman, 2002) leads to the conclusion that the onset of significant dilatancy phenomena in the host rock is restricted to burial depths <200 m (Nagra, 2002). Given the moderate uplift rates in the area of interest, permeability enhancement due to embrittlement of the Opalinus Clay is not expected within the next million years.

During glacial periods, ice cover and partial permafrost affect both, local and regional groundwater flow. An ice cover of several hundred metres thickness may impose a transient increase in effective stress in the host rock formation and *excite the expulsion of contaminated porewater* from the disposal systems. For such scenarios, mass fluxes and transport paths of the expulsed porewater

were inferred by hydrodynamic modelling. This paper summarises key result of modelling, which are presented in greater detail in Nagra (2002).

## 2. Geological setting and long-term evolution of the investigation area

The Opalinus Clay was deposited some 180 million years ago in a shallow marine environment over a large area in northern Switzerland and southern Germany. In the Zürcher Weinland the Opalinus Clay is part of the sedimentary sequence of the Molasse basin with a uniform thickness of 80-120 m over many kilometres, almost flat-lying (dipping gently to the south east) and little affected by faulting. The burial and compaction history of the sedimentary formations is complex, including two major phases of subsidence during the Cretaceous and the Miocene. From about 10 million years ago, uplift processes brought the Opalinus Clay progressively up to its present burial depth of about 650 m in the region of interest. The Zürcher Weinland is characterised by a low uplift rate of about 100-200 m/Ma (Nagra, 2002).

At present, the Opalinus Clay is a slightly overconsolidated claystone formation with an overconsolidation ratio between 1.5 and 2.5. Its hydraulic conductivity is very low-recommended values for horizontal and vertical hydraulic conductivity are $2\times10^{-14}$ and $1\times10^{-13}$ m/s, respectively (Nagra, 2002). The major principal stress at Benken is approximately horizontal ($S_H$=22.6 MPa, $S_h$=15.1 MPa, $S_v$=15.9 MPa at reference depth 650 m).

Several glaciations are expected to take place during the next 1 Ma (Nagra, 2002). The typical duration of the glacial periods is 10 000-50 000 a, followed by interglacial periods of roughly the same duration. During the glacial periods an ice cover of 200-400 m is assumed to increase vertical stress within the Opalinus Clay by 2-4 MPa.

## 3. Results of hydrodynamic modelling

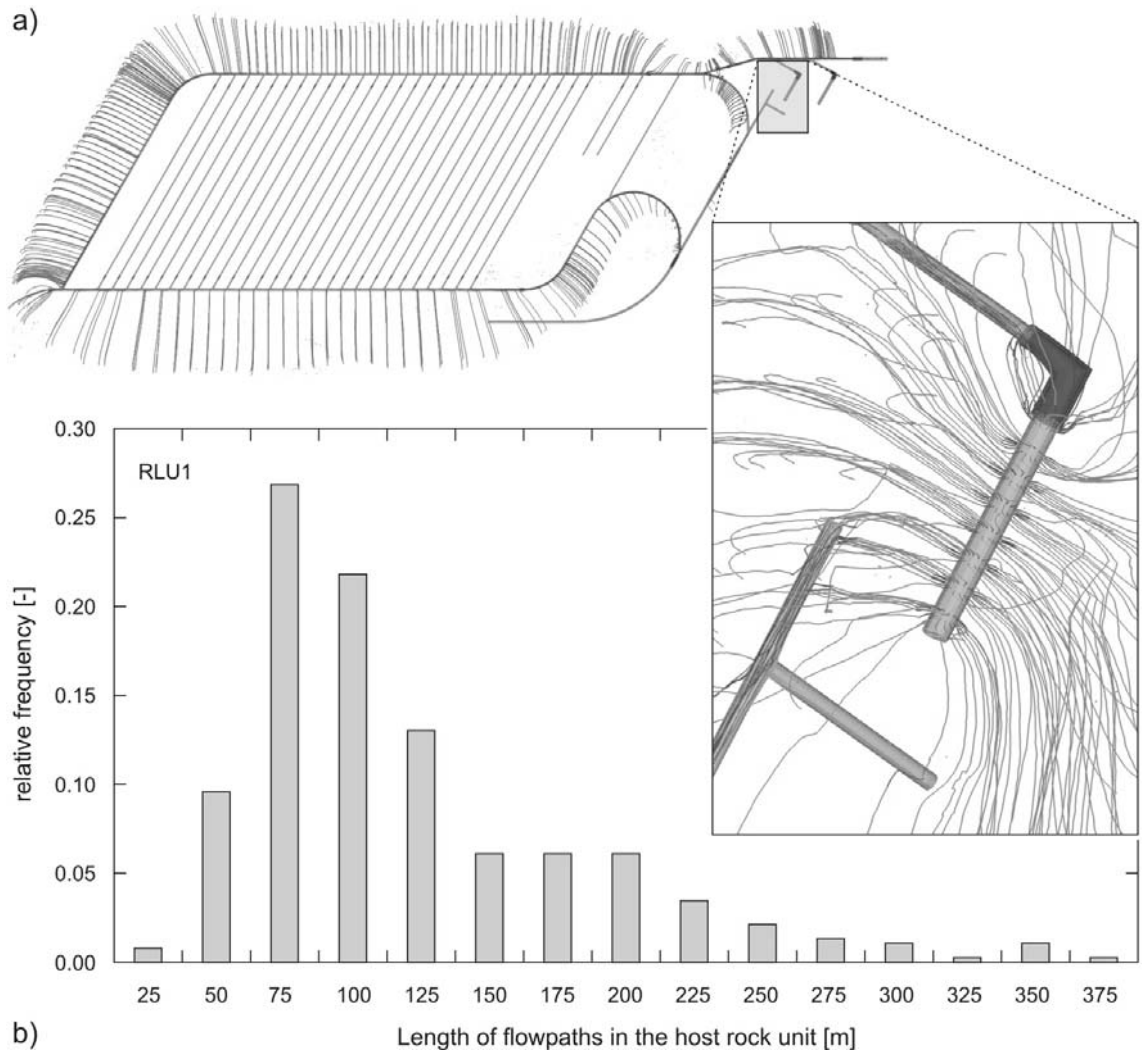
The emphasis of hydrodynamic modelling as part of the geoscientific site characterisation process has been on the understanding of both the natural, undisturbed groundwater flow in the investigation area as well as the repository-induced perturbations. The undisturbed hydrogeological system was simulated in a local scale model with a lateral extension of 10×10 km (Kuhlmann *et al.,* 2002). The repository-induced perturbations were assessed with a repository model (Kuhlmann & Marschall, 2002), which was embedded in the local model. Among the repository-induced perturbations the overpressurisation of the disposal systems (SF/HLW and ILW), entailed by the expulsion of porewater formed the most important modelling cases. Overpressurisation could be caused by the generation of repository gas or by an increase of vertical stress as a consequence of a glacial ice load. The assumed upper limits for gas-induced and ice load-induced overpressures in the disposal areas are 7.5 and 4 MPa, respectively. It is further assumed that the maximum glacial ice-load would act for a time period of about 20 000 a.

Simulations of the undisturbed hydrogeological system (local model) indicate an upwards directed vertical flow of $2\times10^{-14}$ m/s through the host rock. Consideration of the backfilled underground excavations (repository model) does not significantly change porewater flow through the host rock formation – the flow direction is still vertical and the length of the flow paths from the disposal area through the host rock to the adjacent formation (Wedelsandstein) is about 40 m; the flow magnitude is indistinguishable with respect to the undisturbed conditions. Porewater overpressures in the disposal areas, however, give rise to marked changes of flow conditions in the vicinity of the backfilled underground excavations. As seen in Figure 1 the flow paths are no more vertical but

diverge radially into the host rock formation. Furthermore, for the ILW disposal tunnels the length of the flow paths through the host rock increases substantially (histogram in Figure 1). Porewater flow into the Wedelsandstein formation is enhanced: for the case of unlimited overpressures of 7.5 MPa, the flow into the Wedelsandstein formation is $2\times10^{-13}$ m/s and for the modelling run with overpressures of 4 MPa and limited duration (20 000 a) maximum flow rates of $1\times10^{-13}$ m/s were determined.

As shown in Nagra (2002), diffusion is the dominating transport process in the host rock formation, when the advective flow component is in the order of $10^{-13}$ m/s or lower. Therefore, it is concluded that the ice load during glacial periods does not substantially affect the barrier function of the host rock formation. The unloading process during the interglacial periods may give rise to sub-hydrostatic pressures in the Opalinus Clay, resulting in a reversal of the hydraulic gradient towards the repository.

**Figure 1. Expulsion of porewater from the disposal areas of an SF/HLW/ILW repository that may be caused by glacial loading** (Kuhlmann & Marschall 2003)
(a) flow patterns and (b) length of flow paths in the host rock formation (ILW disposal tunnel)



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# GEOCHEMICAL STABILITY OF CLAY-RICH ROCK FORMATIONS: EVIDENCE BASED ON NATURAL TRACER PROFILES

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## 1. Introduction

In comparison to many other rock types, clay-rich formations have high water contents and porosities. However, hydraulic conductivities measured on core samples and in boreholes are mostly very low, which is due to the extremely small apertures of individual pores (predominantly in the range of nanometers). By consequence, specific mineral-surface areas with which water molecules and solutes interact are very large. Knowledge of the microscopic characteristics of the pore space is the key to the understanding of several macroscopic properties, such as the commonly observed insignificance of advection and the large chemical buffering capacity.

Given the generally long residence times, the chemical composition of pore waters in clay-rich formations is controlled by equilibria with mineral phases, such as carbonates and silicates, and ion-exchange reactions with clay minerals (Beaucaire *et al.*, this volume). The generally reducing conditions are strongly buffered by pyrite, siderite and/or organic matter.

Some constituents of the pore water are conservative, i.e. not buffered by minerals, and can move in the interconnected pore space. These constituents include:

- the $H_2O$ molecules of the pore water;
- halogens (e.g. Cl, Br); and
- noble gases (e.g. He, Ne, Ar).

$H_2O$ of the pore water and dissolved noble gases can move in the entire physical porosity of a rock, provided the pore space is interconnected. The movement of water molecules can be monitored by using their stable isotopic signatures, expressed as $\delta^{18}O$ and $\delta^{2}H$. In clay-rich formations, halogens can only move in a fraction of the physical porosity due to anion exclusion effects.

The conservative constituents can be used as tracers of migration processes in clay-rich formations, such as diffusive exchange with the embedding aquifers and advection across the formation. They are archives of migration processes that occurred in the formation over geological time scales in the past. If these processes are understood quantitatively and if the evolving geological boundary conditions can be constrained, predictions of future evolution can be made.

## 2. Available data base and interpretation

The geochemistry of several clay-rich formations has been investigated in the recent past, and a selection is listed in Table 1. These formations were subjected to different degrees of burial and induration, reflected by the wide range of water-accessible porosity of 8-40%. Based on laboratory measurements, pore-diffusion coefficients for water in these formations are within the narrow range $8\text{-}20*10^{-11}$ $m^2/s$ (direction normal to bedding), whereas for anions (Cl, I), they are smaller and scatter more widely ($0.5\text{-}13*10^{-11}$ $m^2/s$).

All formations considered are marine sediments, but their current pore-water salinity is generally lower than that of sea water. Some of the formations lost most of their marine signature, others preserved it at least in the central parts of the formation. Curved profiles of tracers in pore waters, such as $\delta^{18}O$, $\delta^{2}H$, Cl, I, Br and He, were observed in several formations. Model calculations indicate that many of the observed profiles are consistent with diffusive exchange between the clay-rich formation and the surrounding aquifers, whereas advective transport in the vertical direction must be very limited or absent.

In addition to the identification of the relevant transport process, model calculations can also provide constraints on diffusion times and/or on large-scale diffusion coefficients. The most difficult part of such calculations is the definition of initial and boundary conditions, because this requires knowledge on the paleohydrogeological evolution of the clay formation and the surrounding aquifers. Available results indicate that model calculations based on laboratory-derived diffusion coefficients are consistent with the hydrogeological evolution constrained by independent evidence, suggesting that the laboratory data are applicable to the whole formation. Some cases where this is not so, or where the constraints are not sufficient, need further evaluation.

**Table 1. Selection of sites where data of natural tracers are available**

| Formation | Site | Country | Reference |
|---|---|---|---|
| Callovo-Oxfordian | Bure (Meuse/Haute Marne) | France | Andra (1999a) |
| Toarcian-Domerian | Tournemire | France | Boisson *et al.* (1998), Cabrera *et al.* (2001) |
| Couche silteuse | Marcoule/Gard | France | Andra (1999b) |
| Boom Clay | Mol | Belgium | Ondraf/Niras (2002) |
| Opalinus Clay | Benken | Switzerland | Nagra (2002), Gimmi & Waber (2003) |
| Opalinus Clay | Mont Terri | Switzerland | Pearson *et al.* (2003) |

## 3. Example 1: Couche silteuse at Marcoule, France

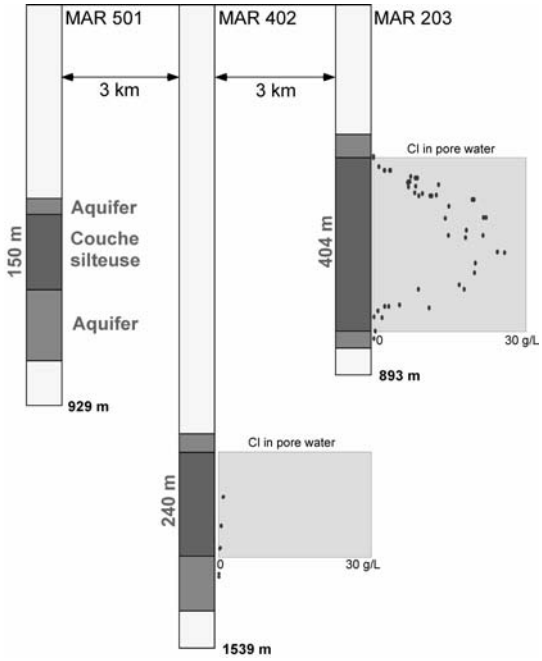
The Marcoule site lies in SE France and was investigated by Andra (1999b). The target formation, the Couche silteuse, is embedded between two regional aquifers. Within a small horizontal distance (few km), three boreholes penetrating the whole sequence have been drilled, and in two of them, Cl contents in pore water have been analysed in vertical profiles (Figure 1). The interesting point is that over the short distance of 3 km, the thickness of the formation varies substantially between 150 and 400 m. In borehole MAR 203, the Cl contents show a regular, symmetric profile, with Cl contents close to the marine value in the centre of the formation but strong decrease towards

the boundaries.[1] In borehole MAR 402, where the formation is only 240 m thick, Cl contents are very low throughout the profile, even though still higher in the centre than at the lower boundary. The question is whether the Cl distributions in both boreholes can be explained as diffusion profiles using the same dataset (formation properties, initial and boundary conditions), the only difference being the variable formation thickness. A simple analytical solution for time-invariant boundary conditions (Carslaw & Jaeger, 1959) was used for the calculations:

$$C(x,t) = C_0 + (C_1 - C_0)\left( (1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\left[\frac{(-1)^n}{2n+1}\exp\left\{\frac{-Dp\,(2n+1)^2\pi^2 t}{4L^2}\right\}\cos\left\{\frac{(2n+1)\pi x}{2L}\right\}\right]\right)$$

with L = half thickness of the clay layer, [m];
Dp = pore-diffusion coefficient for Cl, [m $s^{-2}$];
$C_0$ = initial tracer concentration in the clay layer, [mg $L^{-1}$];
$C_1$ = tracer concentration at the boundaries, [mg $L^{-1}$];
C(x,t) = tracer concentration at time t and location x in the clay layer, [mg $L^{-1}$];
t = diffusion time, [s];
x = spatial coordinate (-L < x < L), [m].

**Figure 1. Overview of borehole data from the Marcoule site (Gard, SE France)** (Andra, 1999b)

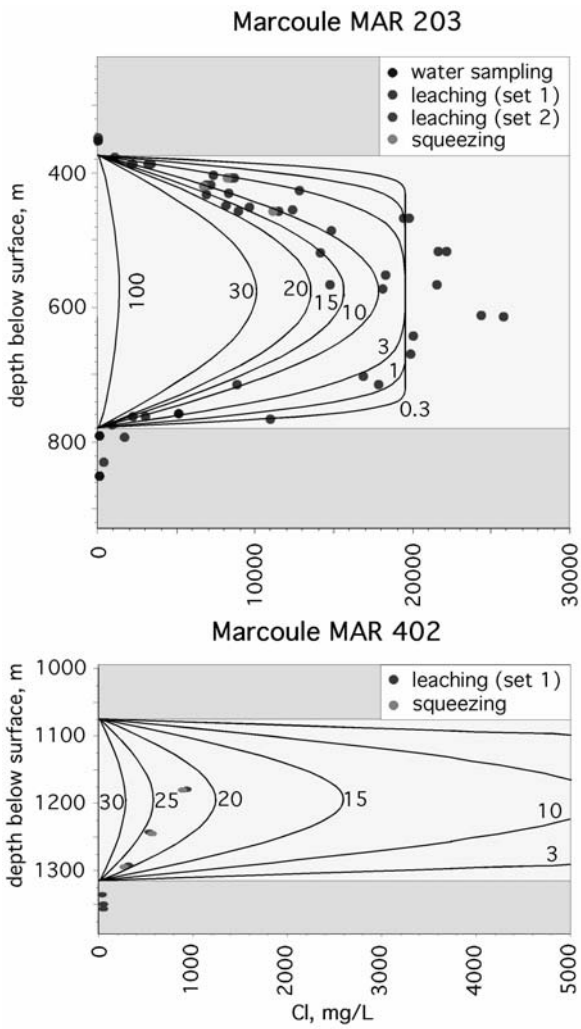



1. Some values lie above the sea-water value and are most likely related to data uncertainties, for example in the knowledge of Cl-accessible porosity. The original data set in Andra (1999b) contains Cl concentrations mostly based on aqueous leaching experiments, and the conversion of concentrations per volume of rock to aqueous concentrations was done using porosity values measured by conventional techniques such as water loss upon heating. These techniques characterise the porosity accessible to water, while Cl-accessible (geochemical) porosity is smaller due to anion exclusion effects (Pearson, 1999). A limited number of Cl concentrations based on porewater squeezing are also given in Andra (1999b) and yield higher values. In the present paper, the leaching data were corrected in order to be consistent with the squeezing data, which are considered to best represent in situ concentrations in the Cl-accessible porosity.

Boundary conditions were assumed to be represented by the present-day Cl contents of the embedding aquifers. The marine Cl concentration of 19 350 mg/L was taken as the initial condition. Pore-diffusion coefficients Dp were derived from laboratory measurements of De of I (Andra, 1999b), recalculated to Dp using the estimated geochemical porosity and corrected for in situ temperature.

The results of the calculations are shown in Figure 2. Diffusion times that best fit the tracer distribution in borehole MAR 203 are in the range of 3-15 Ma, compared to 20-25 Ma for borehole MAR 402. These values are similar, considering the uncertainties related to the incomplete dataset for borehole MAR 402 and other data uncertainties (e.g. geochemical porosity, spatial heterogeneity). It is concluded that diffusion alone can at least roughly explain the very different tracer concentrations in both boreholes. Further studies are needed to evaluate possible 2- or 3-D effects, i.e. horizontal diffusion within the formation between the two sampling localities, and the (in)compatibility of the observed Cl concentrations with alternative conceptual models considering other processes.

**Figure 2. Measured (circles) and calculated (lines) Cl contents of porewater in the Couche silteuse in boreholes MAR 203 and MAR 402 at Marcoule (Gard, SE France)**
Measured data are recalculated values from Andra (1999b)
and refer to Cl concentrations in the Cl-accessible porosity



## 4. Example 2: Opalinus Clay at Mont Terri, Switzerland

A profile of Cl contents (and several other tracers) in pore water was acquired from boreholes drilled from the Mont Terri rock laboratory tunnel (Swiss Jura Mountains), which penetrates Opalinus Clay in an anticlinal structure (Pearson *et al.,* 2003). As shown in Figure 3, the anticline has been partially eroded since the end of the major thrusting/folding events at ca. 3.5 Ma b.p. According to a preliminary and simplified erosion scenario, the limestone aquifer overlying the Opalinus Clay was exhumed ca. 2.5 Ma b.p., while the underlying aquifer was exposed on the surface only at later times, ca. 0.35 Ma b.p. Thus in the case of Mont Terri, there is independent evidence that the onset of flushing with meteoric water occurred at different times at the two boundaries.

The distribution of Cl in pore water across the Opalinus Clay is shown in Figure 4. The striking feature is the asymmetry of the profile, with a smoother gradient towards the upper aquifer and a steeper gradient downwards. Calculations considering diffusive exchange of Cl with the aquifers were performed separately for both aquifers, and the results are also shown in Figure 4. These calculations used Dp = 3.4E-11 $m^2/s$, a value based on laboratory-derived De values for Cl (Nagra, 2002; Table 5.10-1), a geochemical porosity based on Pearson *et al.* (2003, Table A10.3), and a correction for in situ temperature. The best-fit diffusion time for the onset of exchange with the upper aquifer is ca. 5 Ma, the one for the lower aquifer ca. 0.3-1 Ma. The shapes of the measured and the calculated Cl distributions are remarkably consistent, while the calculated diffusion times exceed those derived from erosion scenarios by about a factor 2. Potential explanations can be the choice of the diffusion coefficient for the calculations or, more likely, the assumptions regarding the erosion scenario.

**Figure 3. Cross-section through the Mont Terri anticline (Jura Mountains, Switzerland).** Stippled lines and ages indicate a rough estimation of the erosion history of the anticline (Pearson *et al.* 2003)

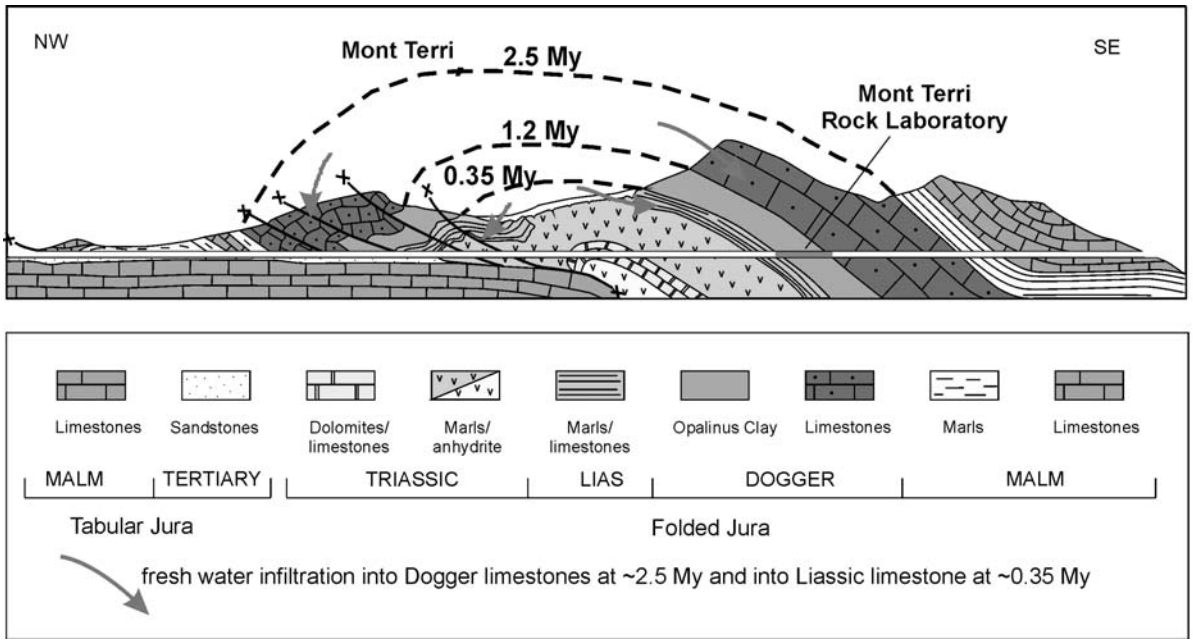
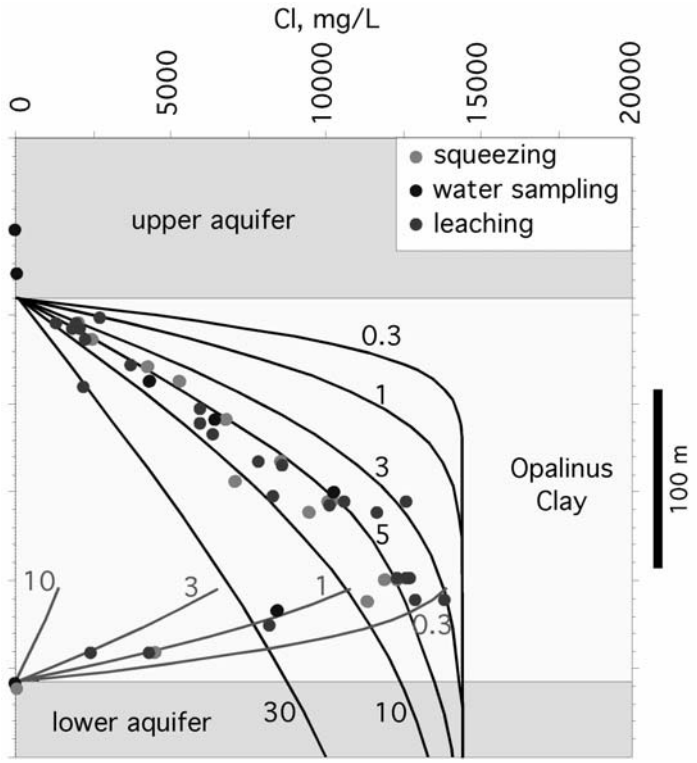


**Figure 4. Measured (circles) and calculated (lines) Cl contents of porewater in the Opalinus Clay at Mont Terri (Jura Mountains, Switzerland)**




## 5. Conclusions

In the examples above, only Cl data were discussed, even though data on other tracers are available and should be investigated in a next phase. The simultaneous consideration of all available data increases the confidence in the interpretation.

Diffusion profiles may develop in relatively thin clay-rich units over time scales that are short compared to the age of the formation (order of 0.1-1 Ma for a 100 m thick layer), provided marked chemical gradients to the aquifers are established. Very long diffusion times (tens of Ma or more) reported in the literature are not independent model results in most cases but a priori assumptions, often combined with a poorly constrained hydrogeological evolution. Overall, the study of natural tracer profiles is an important contribution to the understanding of the long-term evolution of clay-rich formations because such profiles represent long-term and large-scale natural experiments that can be used for the upscaling of laboratory data in space and time. Natural tracer profiles can contribute to the identification of the dominant transport process, to the quantification of maximum advective fluxes that are compatible with the spatial distribution of tracers. Tracer profiles crossing faults can provide additional information concerning paleofluid flow events along preferential pathways.

When the past evolution of the observed tracer profile is quantitatively understood, quantitative predictions are possible regarding the further evolution (e.g. loss of salinity to the embedding aquifer). Alternative scenarios for future development can also be explored by varying the boundary conditions.

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# CHEMICAL BUFFERING CAPACITY OF CLAY ROCK

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## 1. Introduction

The long-term performance of a nuclear waste repository is strongly dependent on the chemical properties of the host rock. The host rock establishes the chemical environment that determines such important performance attributes as radionuclide solubilities from the waste and the transport rates from the repository to the accessible environment.

Clay-rich rocks are especially favourable host rocks because they provide a strong buffering capacity to resist chemical changes prompted either internally, by reactions of the waste itself and emplacement materials, or externally, by changes in the hydrologic systems surrounding the host rock.

This paper will focus on three aspects of the stability of clay-rich host rocks: their ability to provide $pCO_2$ and redox buffering, and to resist chemical changes imposed by changes in regional hydrology and hydrochemistry.

## 2. $CO_2$ buffering

It is well known that there are multiple sources for $CO_2$ in ground water. However, it has been demonstrated that there is a relationship between $pCO_2$ and temperature of formation waters in sedimentary rocks indicating a possible control of $CO_2$ by a mineral assemblage (Hutcheon *et al.,* 1993). This relationship seems to be independent of the sources of $CO_2$ and cannot exist in an open system.

A geochemical system can be defined involving a large number of constituents (H, O, C, Al, Si, Ca, Mg, K, Na) which are in equilibrium simultaneously and are representative of the local conditions in the aquifer. Mass transfer of chemical elements and the evolution of the rock porosity can be calculated using this approach to local equilibrium, as shown by Gouze and Coudrain-Ribstein (2002). In this study, a compilation of ground waters in sedimentary rocks showed that over a temperature range from 40°C to more than 200°C, $pCO_2$ appears to be controlled by equilibrium of the solution with calcite, dolomite and a set of hypothetical silicates including chlorite. For the chlorite-kaolinite-chalcedony-calcite-dolomite assemblage (Hutcheon *et al.*, 1993), $pCO_2$ can be calculated using the following relation:

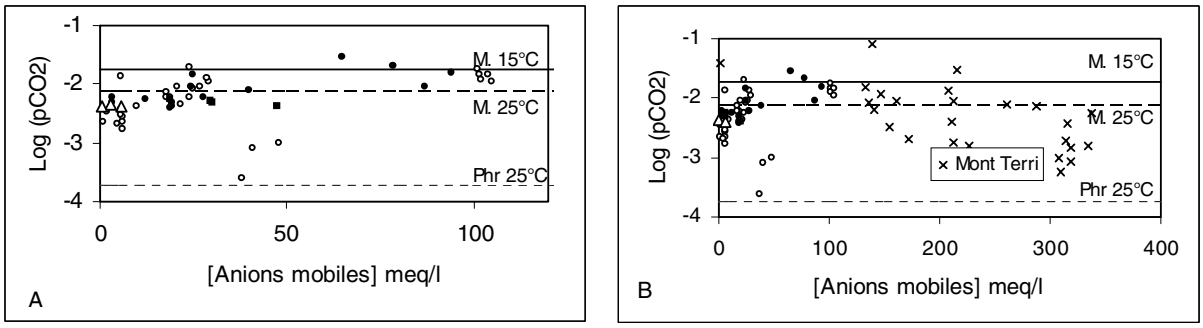
$$pCO_2 = [H_2O]^{2/5} \frac{K_{calcite} \times K_{1/5\,chlorite}}{K_{CO_2(g)} \times K_{1/5\,chalcedony} \times K_{1/5\,kaolinite} \times K_{dolomite}}, \qquad (1)$$

where K corresponds to the formation constants of the different minerals and $CO_2$.

This relation implies that some mineral assemblages can buffer $CO_2$ concentrations against additional $CO_2$ produced by bio-degradation or thermal degradation of organic matter, for example. In scenarios of waste disposal in geological formations, $CO_2$ production may be expected during the thermal phase. Equation (1) indicates that $CO_2$ concentrations can be predicted with changing temperatures regardless of the amounts of $CO_2$ added to the system by thermal reactions. To be generalised, the applicability of Equation (1) must be confirmed and it must be demonstrated that the masses of the reactive minerals included in Equation (1) are great enough to provide a buffer capacity sufficient to accommodate all $CO_2$ produced. This will be site specific, but in general the clay-rich rocks of interest here contain enough of these minerals to buffer large quantities of $CO_2$.

The observations supporting Equation (1) extend to temperatures as low as 40°C. While this is close to the ambient temperatures of certain proposed repositories (*e.g.* 38°C for Benken – Zürcher Weinland, Nagra, 2002a), it is also important to decide if such equilibria can be achieved in clay rocks at even lower temperatures and therefore can actually be observed in lower temperature, natural systems.

**Figure 1. Evolution of Log ($pCO_2$) vs the sum of mobile anions in different sedimentary formations**
A: Mol: interstitial fluids (triangles) and aquifers (empty and filled circles); Tournemire (squares);
B: Mol, Tournemire and Mont-Terri (crosses). Lines represent equilibrium with respect calcite-dolomite-chalcedony-chlorite-kaolinite, at 15 and 25°C for two formations constant of chlorite
(Phr: PHREEQC data; M: Michard's data)




In support of this conclusion, we summarise water chemical data obtained from several clay rocks in different sedimentary contexts: interstitial waters from the Boom Clay (Beaucaire *et al.*, 2000), ground waters from the aquifers surrounding the Boom clay (Marivoet *et al.*, 2000), fracture fluids from Tournemire (Cabrera *et al.,* 2000; Beaucaire *et al.*, in prep.) and interstitial waters from Mont-Terri drill-holes (Pearson *et al.* 2003). All these formations are characterised by a predominance of clay minerals in the rock and a low matrix permeability. $pCO_2$ values calculated from pH and alkalinity measurements for the different ground waters are plotted on Figure 1.

The same figure shows $pCO_2$ values calculated according to Equation (1) at 15 and 25°C and for two values of the chlorite formation constant. From the different chlorite dissolution constants in the literature, we have chosen two limiting values of log K, 16.16 and 23.98, from Michard and the PHREEQC data base (Parkhurst and Appelo, 1999), respectively. In these conditions, it appears that the range of variation of log ($pCO_2$) does not exceed a factor of 2.0 and that all the studied waters fall within this range. In order to fully validate the model, it is necessary to verify that solutions are equilibrated with respect to the involved mineral phases.

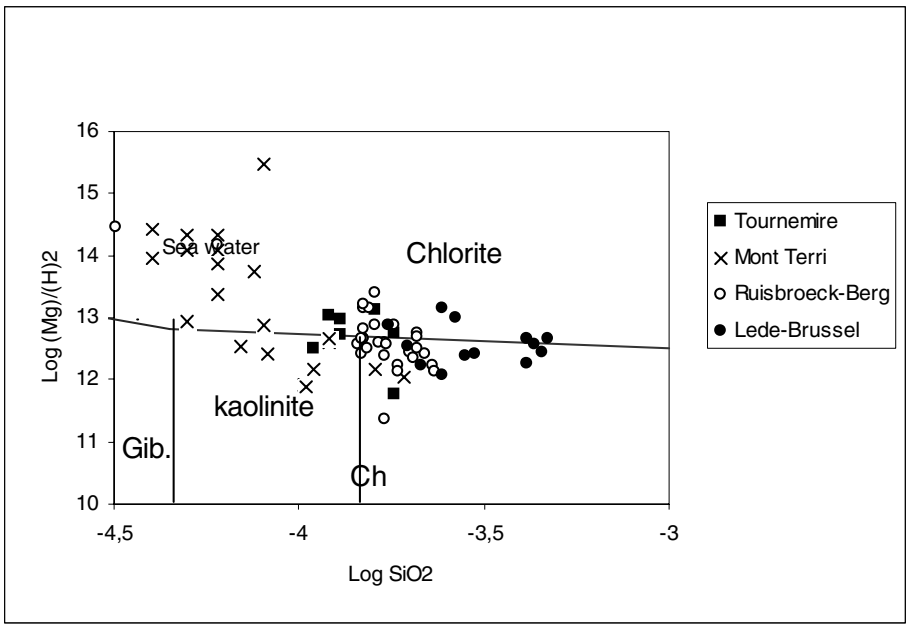
The thermodynamic behaviour of clay minerals is a continuous topic of discussion regarding the question of whether a solution can be equilibrated with respect to clay minerals. Recent laboratory studies of the dissolution of chlorite affirm that it is possible to describe the evolution of solutions at

equilibrium with the kaolinite-chlorite assemblage from 25 to 175°C (Aja *et al.,* 2002). If it is the case, natural solutions must also show a relationship between $\log(Mg^{++})/(H^{+})^2$ and $\log(H_4SiO_4)$ corresponding to the equilibrium of the solution with the kaolinite-chlorite assemblage according to the schematic reaction:

$$\underset{\text{chlorite}}{Mg_5Al_2Si_3O_{10}(OH)_8} + 10H^+ + 2H_2O = 5Mg^{++} + \underset{\text{kaolinite.}}{2Al_2Si_2O_5(OH)_4^-} + H_4SiO_4$$

Figure 2, is a plot of the data corresponding to samples from the Ruisbroeck-Berg and Lede-Brussel aquifers associated with the Boom Clay, from Boom Clay and Mont Terri interstitial waters and from Tournemire fracture fluids. The majority of samples except some of the Mont Terri fluids are close to a horizontal line limiting kaolinite and chlorite fields.

**Figure 2. Isothermal (15°C) ion activity diagrams showing the variation of aqueous Mg and Si species in solution. Comparison with stability of kaolinite-chlorite assemblage.** Ch: chalcedony; Gib: gibbsite




Samples from Ruisbroeck Berg aquifer, Tournemire and Boom Clay fluids can be considered as equilibrated with respect to chlorite, kaolinite and chalcedony, while Lede-Brussel fluids evolve toward silica enriched fluids. This silica enrichment was attributed to the occurrence of opal in this sedimentary horizon. It is also important to indicate that the temperatures of the studied waters are ranging from 13 to 25°C.

Mont Terri fluids present have the most variable silica concentrations and $\log(Mg^{++})/(H^{+})^2$ values ranging from 12.7 for the less concentrated ground waters to 14.5 for the more concentrated waters. The latter waters maintain the characteristics of the sea water originally present in the formation while the more "diluted" waters of the series seem to have evolved towards equilibrium with the mineral assemblage.

In conclusion, the residence time of interstitial waters and the very low permeability of clay rocks are in favour of the establishment of chemical equilibria. Many observations in sedimentary aquifers at

low temperature and in interstitial waters within clay rocks seem to indicate that the behaviour of $CO_2$ continues to be constrained: $pCO_2$ in such formations generally ranges between $10^{-2}$ and $10^{-3.5}$ atm. However, the validation of such an approach must be supported by further mineralogical and thermodynamic studies: observation of the involved mineral phases and their chemical variability in the different natural contexts, and therefore evaluation of their relative stability.

Other conceptual models of controls on $pCO_2$ are also used. $pCO_2$ values in the Opalinus clay at Mont Terri and in the Callovo-Oxfordian have been modelled considering equilibria among cation-exchange reactions and carbonate minerals (Gaucher *et al.*, 2000; Motellier *et al.*, 2003, Pearson *et al.*, 2003). In this model, the predictability of $CO_2$ in interstitial fluids depends on the stability of the chemical properties of the clayey-exchanger with time, which is itself function of temperature, rate of diffusion of the species in the formation and other all chemical reactions induced by the presence of nuclear waste (pH perturbation, thermal or bio- degradation of organic matter, …). However, in the long term, we could expect $CO_2$ buffering by silicate-carbonate mineralogical assemblages.

Finally, the calculated chemical buffer capacity will differ depending on whether one considers the $CO_2$ regulation in interstitial fluids to be by mineral buffering, exchange reactions or external constraints. Thus, it will be important in the future to evaluate the buffer capacities of systems by all possible models.

## 3. Redox buffering

The redox buffering capacity of a clay rock can be illustrated by data from the Mont Terri Underground Research Laboratory. Geochemical studies at Mont Terri have been summarised by Pearson *et al.* (2003). The following discussion is based on that report and references below to Section, Figure and Table numbers refer to that report, unless otherwise indicated.

Chemical analyses of several samples of Opalinus Clay and adjacent claystones at Mont Terri show that the major redox-active elements present are C, Fe, Mn and S (Section 5.2.3.4). The formation mineralogy is such that Fe(II) would be present in pyrite and carbonates, Mn(II) in carbonates, Fe(III) in silicates, principally chlorite, and S both in $SO_4^{2-}$ and reduced sulphur minerals, principally celestite and pyrite. Carbonate and silicate minerals are dominant in the Opalinus Clay. Celestite is present in veins in undisturbed Opalinus Clay samples and in the bulk formation as well, but only at trace levels. The formation also contains more than one percent pyrite which accounts for virtually the entire analysed S content of the formation.

The redox buffer capacity of the Opalinus Clay depends principally on the $SO_4^{2-}$ content of the system to buffer reducing tendencies and on the reduced S, Fe(II) and reduced C contents to buffer oxidising tendencies. The water itself has virtually no capacity to resist oxidation because it has only vanishingly small concentrations of reduced substances. On the other hand, the Opalinus Clay itself is strongly resistant to oxidation.

The total reduction capacity (TRC) of a formation is a measure of its resistance to oxidation. It can be measured directly using a strong oxidising agent such as permanganate or dichromate or calculated from the concentrations of reduced materials. Calculated TRC values of Opalinus Clay samples range from 2.0 to 4.7 meq/g, in good agreement with a measured value of 4.9 meq/g (Table A9.7). Half or more of these TRC values represents the contribution of organic C in the formation.

Mäder (2002) gives a detailed description of the oxidation of Opalinus Clay. This is based on petrographic and chemical studies of samples exposed to oxidising conditions for periods from days, in the laboratory, to years, centuries and millennia, in the Mont Terri and railroad tunnels and in exposures in quarries and outcrops. From his observations, Mäder concludes that during periods of up to at least a few hundred years, pyrite oxidation will dominate according to the generalised overall reaction:

$$FeS_2 + \frac{15}{4}O_2 + \frac{15}{2}H_2O + 2CaCO_3 \Leftrightarrow Fe(OH)_3 + 2CaSO_4 \cdot 2H_2O + 2H_2CO_3 \qquad (2)$$

In addition, birnessite is observed associated with pyrite oxidation (Mazurek *et al.* 1996), indicating that Mn(II) oxidation also occurs. Although Mäder does not report any observations suggesting the oxidation of Fe(II) in siderite nor of organic C, Mazurek *et al. op. cit.* report siderite dissolution with oxidation to Fe(III) to form Fe-hydroxides in oxidation rims around fractures in an open clay pit.

Mäder concludes that pyrite oxidation will dominate the redox behaviour of the Opalinus Clay for periods of the order of hundreds to perhaps thousands of years. However, at full equilibrium, as might occur during prolonged exposure to $O_2$, additional oxidation of the organic C and siderite could also occur. The organic C of the Opalinus Clay is refractory and not easily oxidised. However, Petsch *et al.* (2001) have recently shown that even highly refractory organic carbon, such as the kerogen found in Palaeozoic shales, can be used as a substrate for growth and thereby oxidised by certain microbes during prolonged weathering. In addition, work in progress at Mont Terri (PC Experiment) shows that bacterially mediated sulphate reduction coupled to organic C oxidation takes place in anaerobic boreholes in the Opalinus Clay.

**Figure 3. Masses of minerals, in mol per kg porewater, and pe for Opalinus Clay as $O_2$ is added to system. System is at equilibrium with calcite, dolomite and $pCO_2 = 10^{-3.5}$**

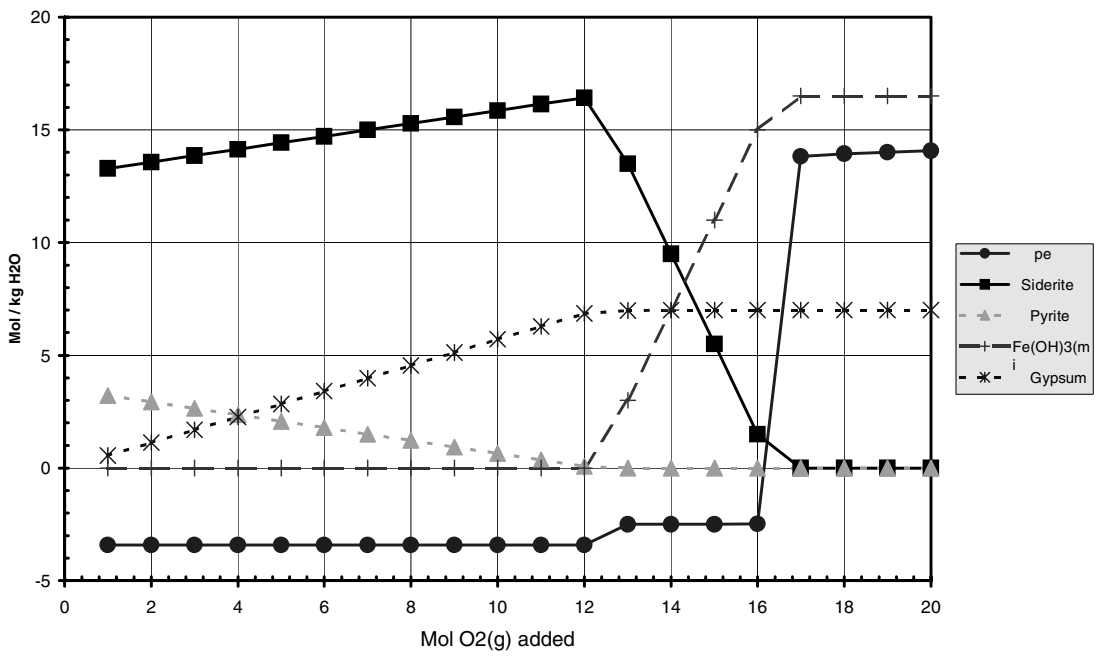


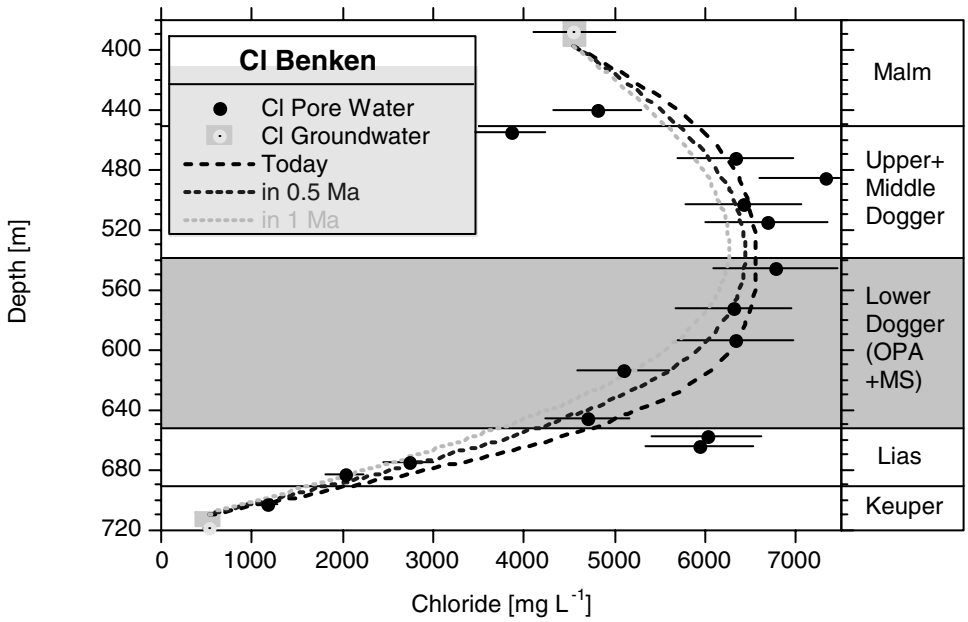

Figure 3 shows the results of equilibrium modelling of the change in mineralogy and redox potential (pe) as $O_2$ gas reacts with rock of the composition of the Opalinus clay. The reactions are

those expected from field observations: Pyrite oxidation increases the Fe(II) concentration leading to siderite and gypsum precipitation. When pyrite disappears, there is a slight increase in the pe as siderite begins to dissolve leading to Fe(III) formation and the precipitation of $Fe(OH)_3$. Finally, as siderite is exhausted, the pe rises steeply. Note that the formation is able to absorb 16 mol $O_2$ per kg formation water before there is a significant increase in pe. This illustration does not include oxidation of organic C which makes up at least half the total reduction capacity of the Opalinus clay.

## 4. Capacity to buffer external changes

The only constituents of clay porewater that are not chemically buffered by the rock are chloride and trace components like bromide, iodide, and noble gases. Their distribution within the formation is strongly influenced by the composition of ground waters in adjacent aquifers and is therefore site-specific (see for example Mazurek *et al.*, this volume, and references cited therein). However, due to the fact that diffusion is the dominant transport process in these very low permeability rocks, long-term changes are extremely slow, even in the case of relatively large concentration gradients.

**Figure 4. Evolution of the Cl profiles at Benken under the assumptions of diffusive transport and constant boundary conditions at the aquifers with values as today** (Nagra, 2002a; Gimmi & Waber, 2003) The indicated times are based on a diffusion coefficient $D_p = 5 \cdot 10^{-11}$ m$^2$ s$^{-1}$. Changes within the potential host rock remain relatively small (≤ about 20%) within this time span.




Nagra has recently completed a safety analysis of a potential repository in the Opalinus Clay in the Zürcher Weinland (Nagra, 2002b). A scenario tested as part of this analysis was the effect on chemistry at the repository horizon of continuing diffusive exchange between Opalinus Clay porewater and water in the aquifers overlying and underlying the Opalinus Clays for a time of up to 1 My (Nagra, 2002a; Gimmi & Waber, 2003). Based on palaeohydrogeological considerations these assumptions are reasonable, even though future glaciation might increase the influence of advection slightly during relatively short time periods of glacial load. Direct infiltration of water during a glacial period is not expected. There is no isotopic evidence that one of the 13 Pleistocene glaciations has influenced the porewater composition of the Opalinus Clay. The results of the diffusion calculations for the long-term evolution of Opalinus Clay porewater are shown in Figure 4. They show that for

times of the order of 1 My the effects of diffusive changes propagating to the repository horizon are very small and illustrate the strong buffering effect of clay rocks.

## 5. Conclusion

Studies of several European clay rocks illustrate their capacity to buffer changes in pH and redox potential and to resist changes in concentrations of non-reactive solutes like chloride. $pCO_2$ (and consequently pH) appears to be controlled by reactions among formation silicate and carbonate minerals, with the buffer capacity dependent on the abundance of these minerals. Oxidation of clay rocks are buffered by reactions with such reduced substances as pyrite, siderite and organic C. The reduction capacity depends on the concentrations of these substances. Finally, changes in non-reactive solutes in indurated clay rocks like the Opalinus Clay occur only slowly in response to external concentrations because solute transport takes place predominantly by diffusion.

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# SOME ELEMENTS OF UNDERSTANDING OF ARGILLACEOUS MEDIA STABILITY

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## 1. Introduction

In the absence of tectonic or metamorphism influence, the argillaceous formations can be stable over very long periods of time: 150 million years for the Callovian-Oxfordian formation (COX, Bure Site, France), 180 million years for the Opalinus Clay (OPA, Mont Terri, Switzerland), 420 million years for the Silurian formation of the Arabic platform. The aim of this paper is to highlight three aspects that provide a better understanding of the stability of this type of formations in the context of their potential for the disposal of nuclear waste:

1. Favourable liquid/solid ratio, allowing very strong buffering effects.
2. Progress in the understanding of the clay stability.
3. Experimental evidence that the carbonate system is controlled internally by the mineralogy.

## 2. Favourable liquid/solid ratio

The very fine granulometry of the clay minerals leads to the formation of rocks with very low porosities. This porosity is typically water-saturated and therefore the water content is very low. For the COX, the water contents range between 6 and 9 ml for 100 g of dry rock (Gaucher *et al*, 2004). In other words, the masse of rock per litre of porewater ranges between 11 and 16 kg. Some major rock minerals are therefore: 18 mol/l illite, 8 mol/l montmorillonite, 34 mol/l calcite, 1.6 mol/l pyrite. The number of exchange sites is also very large (around 3 mol/l), the rock can be thus considered as a "super-exchanger". In this context, it is easy to understand that the liquid/solid ratio is extremely favourable and that infinitesimal rock dissolution leads to thermodynamic equilibrium between water and solution in static conditions.

Another consequence of this low porosity is the very low rock permeability and therefore the major transport mechanism is molecular diffusion. A low diffusion coefficient is the parametre that permit a very long water residence time. This is the ideal situation for equilibrium between solid and solution. This equilibrium is clearly imposed by the rock.

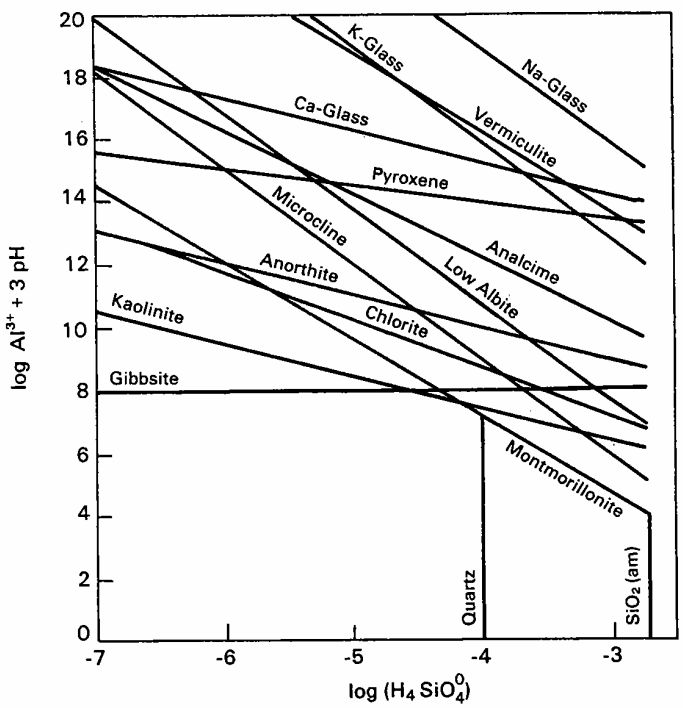
Consequently, the liquid/solid ratio is a key parameter for modelling chemical perturbations in clayey systems. It is essential that the water/rock interaction model take into account the major phases (in %) in order to be able to model the influence of buffering. The illite and smectite that are the major phases in the claystones should be considered as exchangers and as well as soluble phases.

## 3. Progress in the understanding of clay stability

The stability of the clay minerals is a key question is the context of nuclear waste disposal. It is a difficult question due to of the controversial nature of the clay minerals. This is illustrated, for example, by the comments of Kittrick and Peryea (1989): "For complex minerals of variable composition [clays], the present issue is not their exact stability, but whether or not their stability can be determined".

In order to compare the solubilities of clays minerals with those of other aluminosilicates, activity diagrams have been used extensively (Sass *et al,* 1987). The clays are hydrous minerals with a high exchange capacity and, in our opinion, they cannot be included in activity diagrams considering alkaline or alkaline-earth cations, for example: $Log(H_4SiO_4)$ vs $Log(K^+)/Log(H^+)$. In stability diagrams, the slopes of lines represent mineral-solution equilibria. However, for the 2:1 clays, the $Log(K^+)/Log(H^+)$ axis is more related to ion exchange reactions than to clay mineral stability. Consequently, interpretations of porewater evolution made using this type of diagram are misleading. Such stability diagrams for clay minerals should consider the major ions of the mineral structure, i.e. Al and Si. Rai and Kittrick (1989) have published a very interesting diagram in the system $SiO_2$-$Al_2O_3$-$H_2O$ at pH 7 for $log(Mg^{2+})=log(Na^+)=(log\ K^+)=-3$ mol/l, $log(Ca^{2+})=-2.5$ mol/l and $log(Fe^{3+})$ in equilibrium with hematite (Figure 1). In this diagram, the mineral that maintains the lowest log $Al^{3+}$+3 pH activity at a given $H_4SiO_4$ activity is the most stable. For example, at $log(H_4SiO_4)$ of -3.5, the minerals in order of increasing stability are Na-glass, vermiculite, Ca-glass, K-glass, pyroxene, analcime, anorthite, low-albite, gibbsite, chlorite, microcline, kaolinite, montmorillonite. It is interesting to notice, that for the range of $H_4SiO_4$ activity considered for a nuclear waste disposal in argillaceous media ($10^{-4}$ to $10^{-2.5}$ mol/l), the montmorillonite is the more stable phase of the list.

**Figure 1. Relative solubility in the system $SiO_2$-$Al_2O_3$-$H_2O$ of selected primary and secondary minerals**
(Rai and Kittrick, 1989)

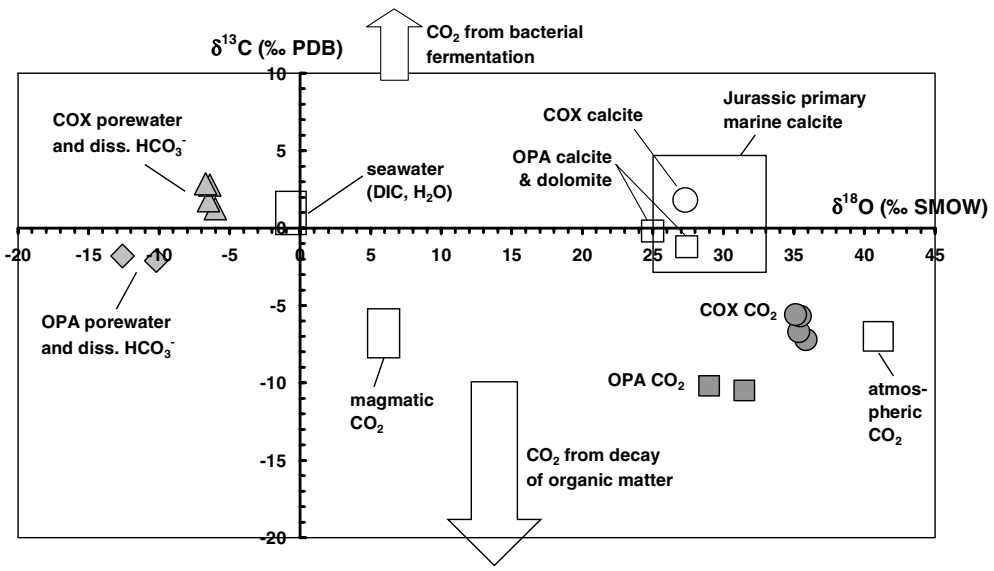


For the solubilities of 2:1 clay minerals, it is important to use a system of equations that link the solubility of the structure to the ion exchange properties and to some extent to clay mineral hydration reactions. To introduce the solubility of montmorillonite or any other mineral having an important exchange capacity in a numerical model of water/rock equilibrium, the software PHREEQC (Parkhurst and Appelo, 1999) presents a new interesting option. With this software it is possible to introduce a system of equations that accounts for the solubility of the structure of the mineral (with Si, Al, Fe, Mg, …, in tetrahedral and octahedral positions) and all the ion exchange reactions. The total solubility of the phase is defined by this system of equations and this representation is believed to be very relevant to the natural processes.

## 4. Evidence for carbonate system control

The argillaceous media are very often also carbonaceous media. In the COX and in the OPA formation, calcite and dolomite are present in large amounts. These minerals strongly influence the buffer capacity of the rock as a whole. It is therefore important to understand how the carbonate system functions. For this system the $pCO_2$ is a key parameter, which contributes to determine the pH of the porewater. In a sedimentary rock, the $pCO_2$ can be fixed externally by diffusion of $CO_2$ coming from the atmosphere, the mantle of the earth, the degradation of organic matter and the bacterial activity. Coudrain-Ribstein *et al.* (1998) have developed a model that considers an internal origin for the $pCO_2$. The partial pressure of $CO_2$ is determined by the equilibrium between the solution, calcite, dolomite and a Mg-aluminosilicate (chlorite or montmorillonite). The minerals control Ca, Mg and $HCO_3$ in this system and the $pCO_2$ is fixed by the mineralogical assemblage.

**Figure 2. $\delta^{13}C$-$\delta^{18}O$ plot showing measured isotopic compositions of COX (filled circles) and OPA (filled squares) outgassed $CO_2$, and calculated isotopic compositions of porewater ($\delta^{18}O$ water) and dissolved bicarbonates ($\delta^{13}C$ diss-bicarb) for COX (filled triangles) and OPA (filled diamonds) interstitial water. Measured isotopic compositions of solid carbonates (calcite and/or dolomite) occurring in each of the two argillites (open circle and squares) and compositional fields of main sources of $CO_2$ are also shown.**



At BRGM, we have developed a novel approach based on the measurement of the gas partial pressures where the gases are out-gassed from a core sample confined within a hermetically cell (Gaucher *et al.,* 2003). Isotopic analyses of $CO_2$ naturally released from the cores have also been performed (Girard *et al.*, 2004). The method was developed with the primary aim of avoiding any physical/chemical disturbance of the argillite sample that might affect porewater isotope composition. It provides indirect determination of the $\delta^{18}O$ and the $\delta^{13}C$ of dissolved carbon.

The log $pCO_2$ in the two systems (OPA -2.88 to -2.22 bar, COX -2.5 to -2.14 bar) are in the range foreseen by Coudrain-Ribstein *et al.* (1998) for sedimentary rocks. And the measure of the isotopic composition of the $CO_{2(g)}$ allows the calculation of the isotopic composition of the aqueous $HCO_3$ (pH between 7 and 8). The figure 2 shows clearly that the $\delta^{13}C$ of $HCO_3$ corresponds to the $\delta^{13}C$ of the carbonaceous minerals of the rocks. This demonstrates that the $pCO_2$ of the OPA and of the COX is regulated internally by the minerals of the rock and this constitutes a strong buffer for any acid-base perturbation.

## 5. Conclusion

The argillaceous rock appears to be a very stable media if the range of temperature and pressure do not evolved significantly during long periods of time. The characteristics of a high rock/water ratio, clay mineral stability and carbonate system auto-regulation are particularly favourable to chemical perturbation buffering in such geological formations.

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# CHEMICAL BUFFERING/MINERALOGICAL ASPECTS: MINERALOGICAL STABILITY

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## Part 1: Temperature effects on clay rocks in natural systems

In natural systems, the heat that leads to the conversion of clay minerals may proceed from three sources:

- The burial under sediment layers that produces diagenetic conversions and may locally reach stages of burial metamorphism; in this system, continuously heated, the duration of reactions may reach values over ten million years.
- Volcanic or igneous intrusions that induce a contact metamorphism in the surrounding rocks; the duration of reactions may vary from a hundred to a million years; heating is also progressive and continuous.
- Hydro-thermal fluid flows in fractured or porous environments (geothermal systems) are more superficial expressions of thermal transfers; the duration of reactions in that case are much shorter, ranging from a few hours to a few thousand years in thermal systems that can be pulsed. Ranges of temperatures covering the stability fields of minerals are available in the literature for hydro-thermal systems.

Clay minerals can not be considered reliable geothermometres because they are often not in chemical equilibrium with the surrounding fluids. Reactions appear to be controlled, by kinetics, and this makes it difficult to transpose temperatures from one system to another.

The most widespread occurrences of clay minerals are part of the dioctahedral smectite→IS →illite and trioctahedral smectite→CS→chlorite conversion series. Their spatial distribution in a given system is connected to the kinetics of conversion reactions rather than by equilibrium of thermodynamically stable phases. Nevertheless, the spatial distribution of these clay minerals may reveal a thermal gradient, but the temperature associated to a given mineral is not necessarily transposable to another system.

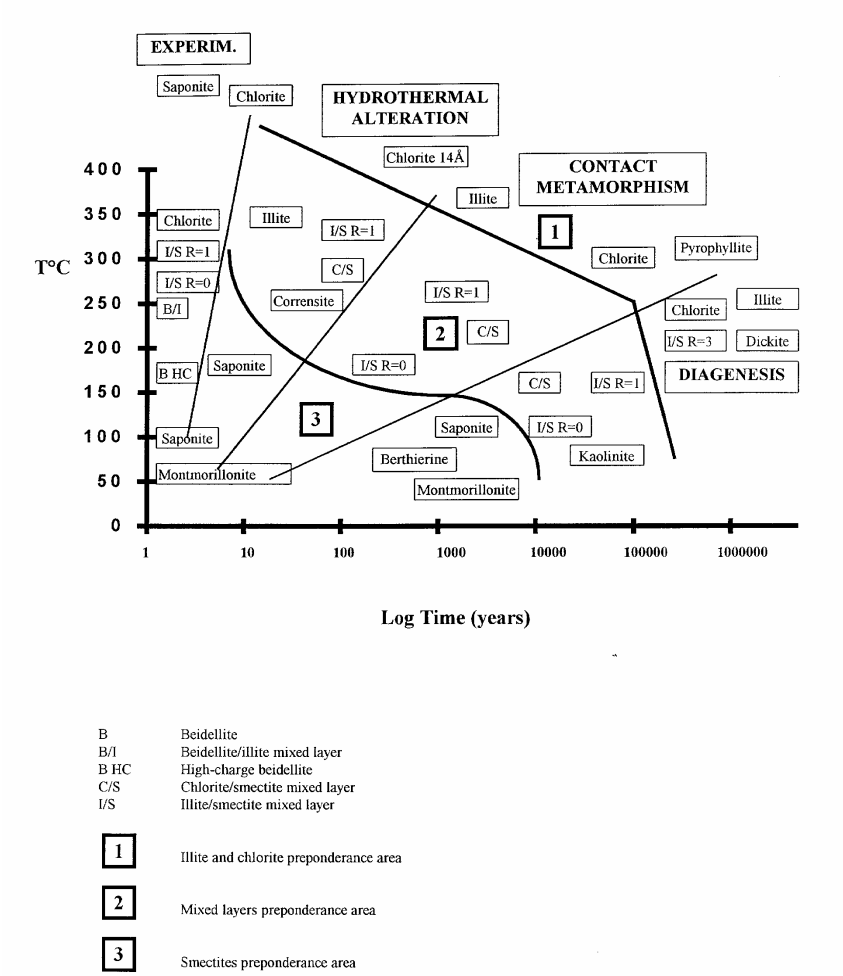
The most often described occurrences of clay minerals are summarised in the following time-temperature schematic diagram (Figure 1). This presentation does not take into account the fact that these minerals might appear in other zones and in specific conditions.

Overall, what emerges from the schematic diagram below is that the higher the temperature of a system, the shorter the period of time necessary to the formation of a phase. This is best illustrated by the experimental formation of saponite in two days at 800°C (Iiyama, J.T. and R. Roy (1963). It appears that smectites are a dominant reaction produced over shorter timescales, even at high temperature. So during the first thousand years smectitic minerals should be stable at temperatures

near 100°C. However, with increasing time a tendency to the interstratification with illite or chlorite is seen.

It can be concluded that study of an intrusion into surrounding clays allows the detection of transformations occurring on a very short period of time (ten to thousand years). This is relevant for performance assessment of a nuclear waste storage. It seems that even with high temperature input the effect on clay is spatially limited.

**Figure 1. Clay minerals stability in time-temperature diagram** (Pellegrini R. *et al.,* 1999)

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**Part 2: A new approach to assess the mineralogical organisation and stability in clay rocks, construction of a tri-dimensionnal structure model at a micrometric scale**

Long term evolution of the clay mineralogy and their associated chemical retention capacity is mainly controlled by the microstructure of the clay matrix. Indeed, microstructure governs possible interactions at the level of clay mineral surfaces and also is modified by them. Here, microstructure defines the complex spatial arrangement of the porosity and the minerals, from the scale of clay particles to that of laboratory samples. Characterizing microstructure allows therefore to define the sample mineralogical heterogeneity and the distribution of fluid pathways as compared to the geochemical porosity where fluid - mineral interactions occur (Pearson, 1999).

It is now commonly accepted that rock physical properties are mainly function of the microstructure (Guéguen *et al.,* 1997). Furthermore, their characterization is partly realized in laboratories in order to determine parameters used in models. Comparing experiments results with model one's often underscores discrepancies that are partly attributed to the unknown of microstructure characterictics (Gens *et al.,* 2002).

Since several years, ERM and HYDRASA have developed a new petrographic approach based on multiscale imaging techniques:

- minerals and porosity mappings of areas of several millimeter sizes with a Scanning Electron Microscope or an Electron Probe MicroAnalyser (EPMA) (Prêt *et al.,* 2003), and three-dimensional reconstruction with high resolution X-ray microtomography,
- porosity mappings by autoradiograph of sample sections of several centimeter sizes (Sammartino *et al.,* 2002; Prêt *et al.,* 2002).

Comparing these images by superimposition with the help of specicific imaging tools allows to locate quantitatively porosity related to mineral spatial distribution.

Two examples are presented: a three-dimensional reconstruction of argillite sample by X-ray microtomography and a two-dimensional mapping of bentonite minerals by combination of chemical element maps obtained with EPMA.

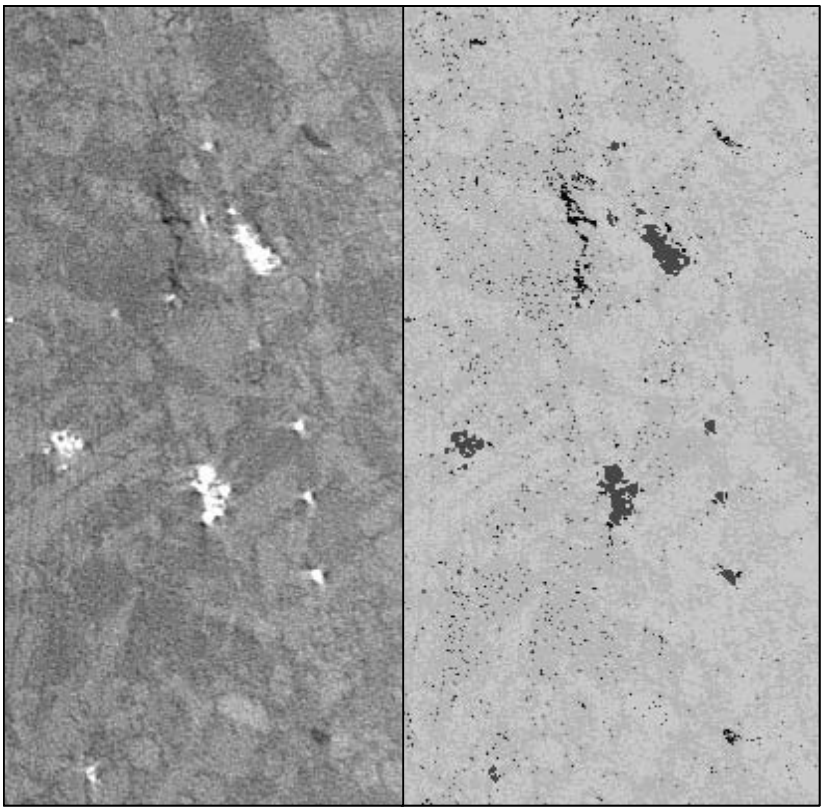
**Three-dimensional reconstruction of argillite sample by X-ray microtomography**

Microtomography is based on X-ray beam attenuation through a rock sample. It is similar to medical tomography but with a better contrast and an infra-micrometric resolution. X-ray attenuation coefficient is calculated for each voxel of the sample volume, by knowing initial and transmitted beam intensities regarding each section with beam multi-directional azimuths. The attenuation coefficient of each voxel is a function of the local bulk density and the average atomic number.

A three-dimensional reconstruction of an argillite sample of Bure site (ANDRA, Underground laboratory) was realized at the ESRF (European Radiation Synchrotron Facility). One section of the reconstructed volume is shown in the following figures. These images reveal the organisation of macropores and minerals in terms of bulk density variations in the sample volume.

This two-dimensional representation seems to be convenient for the reconstruction of the three-dimensional microstructure of the rock that should be suitable for the application of future modellings of transport properties (Delay *et al*., 2002). Sample volumes will be presented during the communication.

**Figure 2. Image selection (200*400 pixels) of a reconstructed slice of a compacted argillaceous sample, pixel size is 1.4 microns. X-ray beam energy was 25.6 keV and transmission ratio about 16%.** On left, raw image in grey levels. On right, thresholded image to highlight the microstructure spatial distribution: light grey as carbonates, medium grey as the porous clay matrix, dark grey as pyrite and black as macroporosity.

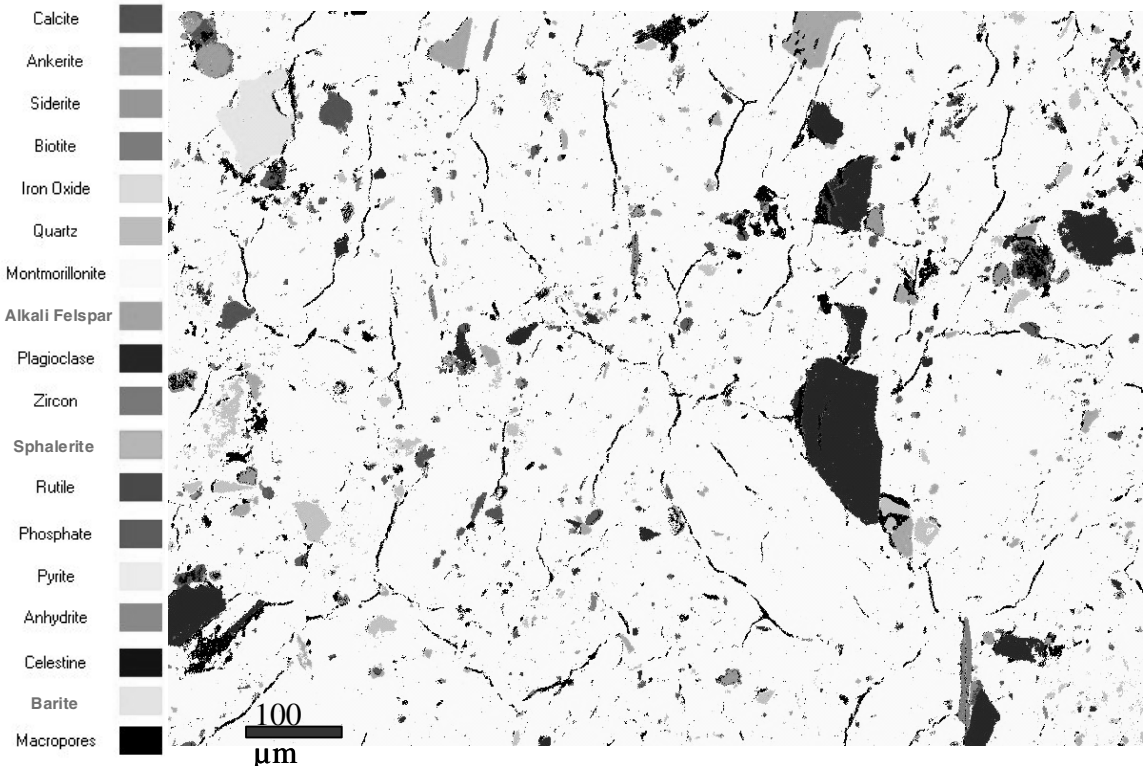


## Mineral and porosity mapping using EPMA

Quantitative chemical element maps are obtained using EPMA. Until 16 elements are mapped with a spatial resolution close to one micrometer and image size of 1 024 per 768 pixels. The analysed area is thus pluri-millimetric. The identification and the spatial distribution of all mineral species is then performed thanks to a specific software, developed for the analysis of each pixel chemistry. The sum of oxide weight percentages measured for each pixel is also exploited in order to estimate the local porosity.

As an example, minerals and macropores of a compacted MX80 bentonite sample are presented in Figure 3. This imaging technique also provides the mineral contents and the mineral specific porosities. One of the main information was to quantify the mean porosity of clay aggregates and to identify the macropore network. These results are of great importance for the understanding of transport processes in this clay matrix which was long time considered as homogeneous.

**Figure 3. Mineral and macropores mapping of compacted MX 80 bentonite**
(density = 1.58 g/cm$^3$)




## Conclusion

These methods are suitable to characterize textural and mineralogical transformations due to any physico-chemical impact affecting rocks constituted by swelling clay minerals.

In particular they are enough sensitive to discriminate clay mineral changes subsequent to a thermal event or a chemical perturbation (alkaline or iron plume) where mineralogical transformations inevitably induce textural modifications.

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# NATURE AND REACTIVITY OF ORGANIC MATTER IN ARGILLACEOUS FORMATIONS: EXAMPLE OF THE CALLOVO-OXFORDIAN OF BURE (FRANCE)

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In carbon cycle models, it is admitted that less than 1% of produced organic carbon is transferred to the geological cycle as sedimentary organic matter (Tissot and Welte, 1984). Although, coal or petroleum source rocks are most well known, sedimentary organic matter also occurs in various concentrations throughout many different rock facies. Organic matter is therefore a witness of the record of environmental changes as well as biomass evolution through time. It is also a reliable tracer of diagenetic conditions, from sediment deposition to metamorphism and subsurface alteration.

Especially in the case of argillaceous sediments, known for their potential proneness of organic matter, the study of fossil organic matter is able to unravel a large amount of information concerning the geological past (depositional conditions and preservation, palaeoenvironment, burial, thermal history) as well as the future (effects of induced thermal perturbation, oxidative alteration, biodegradation). We are presenting here data obtained on the Callovo-Oxfordian argillaceous formations of Bure (France), which are the target layers for the installation of a future laboratory.

## 1. Analytical methods

Organic matter from ancient sediments is an association of kerogen (organic matter insoluble in usual solvents, Durand, 1980) and extractable organic matter (aliphatic and aromatic hydrocarbons as well as macromolecules: asphaltenes and resins). The nature of this organic material necessitates the use of specific analytical equipment. In our study we used:

I. organic petrography and palynology using visible as well as UV light, completed with SEM coupled to X-ray spectrofluorescence and imaging;

II. elemental analysis, Rock-Eval pyrolysis;

III. spectroscopic methods (micro-Fourier Transform Infrared Spectroscopy);

IV. gas chromatography coupled to mass spectrometry for molecular analysis.

Some of the information concerning the geological history of sedimentary organic matter is only revealed if its reactivity is studied. Among specific methodologies, we used artificial maturation (Landais *et al.,* 1989). This technique allows to reproduce in the laboratory the major steps of organic matter thermal alteration and leads to the determination of kinetic parameters as well as reaction pathways.

## 2. Petrographic, palynologic and geochemical characteristics of the organic matter from Callovo-Oxfordian argillaceous formations of Bure (France)

Rock-Eval data indicate that the sediments from the Callovo-Oxfordian of Bure contain less than 1% Total Organic Carbon. Hydrogen Index varies between 50 to 300mgHC/gTOC and Tmax from 422 to 430°C.

Petrographical analysis reveals the presence of: 1) macerals (vitrinite, inertinites) mostly identified as plant remains, often oxidized, with evidence of significant transport; 2) amorphous macerals, sometimes UVfluorescent (liptinites). Palynological analysis reveals the presence of significant amounts of acritarchs associated to amorphous organic matter. Dinoflagellates and sporomorphs are less abundant, but frequently encountered.

Dichloromethane extractible organic matter represents from 0.04 to 0.3mg/g of rock. It is composed of 60wt% polar compounds (asphaltenes and resins), 22 to 46wt% of aromatic hydrocarbons and 16 to 34wt% of aliphatic hydrocarbons. Chromatographic traces of aliphatic hydrocarbons indicate compounds in the $nC_{15}$ to $nC_{35}$ range, which can be roughly described in two parts: 1) The aliphatics of the $nC_{15}$ to $nC_{25}$ range are often composed of an unresolved hump of cyclo and iso alcanes, together with well resolved alcanes; 2) The aliphatics of the $nC_{25}$ to $nC_{35}$ range present n-alcanes with odd predominance as well as cyclo-alcanes typical of biomarkers. The relative proportions of the hydrocarbons of the $nC_{15}$-$nC_{25}$ range compared to $nC_{25}$-$nC_{35}$ range (n-alcanes and biomarkers) varies significantly throughout the sedimentary column. The pristane/phytane ratio varies from 1.5 to 3 (the stronger values corresponding to the samples with higher sulfur content). Aromatic hydrocarbons are mainly represented by series of alkylnaphthalenes, alkylphenanthrenes, alkyldibenzothiophenes and aromatic steroids.

All the above mentioned features of the organic matter from the Callovo-Oxfordian of Bure indicate a mixture between marine (acritachs, dinoflagellates, algal macerals, typical biomarkers) and continental sources (vitrinite and inertinite, recognizable plant remains with typical oxidation and transport features, sporomorphs, n-alkanes with odd predominance, biomarkers).

## 3. Heterogeneity of the organic matter within the sediment and throughout the argillaceous formations

### *3.1 Organic-mineral association at the microscale*

The extremely fine texture of the claystone and macerals necessitates the use of SEM coupled with X-ray fluorescence imaging in order to visualize organic matter distribution. This technique used on polished sections of sediments shows that organic matter occurs as aggregates (local concentrations, fine layers parallel to bedding are not rare), but also as very fine particles disseminated through the rock. The distribution of the kerogen within the rock is therefore very heterogenous at the few micrometer scale. Although association between organic matter and pyrite is common, systematics and statistics of organic-mineral associations in terms of reaction micro-sites have yet to be determined.

### *3.2 Distribution of the organic matter in the sedimentary series: a record of environmental changes during deposition*

Our data show a clear evolution of the geochemical characteristics of the organic matter from Callovian to Oxfordian. A remarkable change is noticeable during the Callovian-Oxfordian transition. The Callovian is characterized par molecular signatures dominated by marine input, while evidence of continental input significantly increases in the Oxfordian. A similar change is noticed by palynological analysis (decrease of the contribution of acritarch and increase of the spore-pollen input from Callovian to Oxfordian) (Huault *et al.,* 2003). We are currently conducting research in order to have more detail on paleoenvironmental changes during the Callovian to Oxfordian transition.

## 4. Maturity of the organic matter and impact on the determination of paleothermicity and paleoburial

All data collected on the organic matter of the Callovo-Oxfordian from Bure indicate a thermal immature sediment. More specifically, the presence of biomarkers (triterpanes for instance) bear biological conformation and contain double bonds which can only subsist since the Callovo-Oxfordian if the sediment never experienced a significant heating. We used artificial maturation (Landais *et al*., 1989) in order to study the thermal behaviour of the organic matter. Experiments allowed to study the thermal stability of the triterpane assemblage and determine their maturation kinetic parameters. Modeling of the biomarker behaviour as a function of heat lead to the conclusion that the organic matter from the Callovo-Oxfordian of Bure did not experience temperatures higher than 40°C. Similar conclusions were reached by fluid inclusion and clay geochemistry studies. Moreover, the maturity modeling of the biomarkers using today's heat flux of 33°C/km and a surface temperature of 10°C allowed to reconstruct the theoretical maturity/depth relationship for the Callovo-Oxfordian. Comparison with the actual maturity of the organic matter in wells located in the east of the Paris Basin indicates a shift of 400-600 m. This shift corresponds to the thickness of eroded sediments since the beginning of uplift of this part of the basin.

## 5. Conclusions

The study of the organic matter from the Callovo-Oxfordian claystones of Bure brings interesting information and both the sedimentological and diagenetic history of this part of the Paris Basin. Combined techniques allowed to identify and describe the various aspects of the organic matter intimately associated to the sediment. Although present in low amount (less than 1wt% of rock), its distribution is heteregenous at all scales, from the sedimentary pile to the microscale.

The combined use of facies sedimentology, sequence stratigraphy and organic geochemistry is an efficient tool to investigate the heterogeneity of argillaceous formations (Fleck, 2001; Fleck *et al*., 2001a, b; 2002). As a matter of fact, argillaceous series are often "monotonous" on a sedimentological perspective (rare sedimentological structures, often destroyed by bioturbation, almost constantly fine layered sediments) and remain difficult to investigate through conventional sedimentological approaches. By combining sedimentological information with Organic Geochemistry, it is possible to more precisely distinguish depositional and diagenetic changes in argillaceous formations.

The study of the potential reactivity of the organic matter associated to clays using artificial maturation and kinetic modeling of biomarker transformation allows to determine maximal paleotemperature and burial. This information is an important constrain to the reconstruction of the geological history of argillaceous formations. In regards to the past conditions of burial of the Callovo-

Oxfordian and the uplift context at which this part of the Paris Basin will evolve from today to the next 1 My, it is most likely that the organic material will thermally not evolve further.

Our experimental work on the organic matter from Bure also demonstrated a significant potential reactivity towards oxidation (Faure *et al*., 1999; Elie *et al*., 2000) and biodegradation. This reactivity is very much conditioned by the organic-mineral associations (catalysis of low temperature oxidation of the organic matter by clays for instance: Faure and Landais, 2000; Faure *et al*., 2003). Organic matter in argillaceous sediments can therefore also be used as tracer of human induced perturbations.

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# EARLY FRACTURATION IN ARGILLACEOUS MASSIFS AND RELATED CARBONATE TRANSFER

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To be sure of the stability in the future of underground storage in argillaceous massifs needs to understand the present-day properties of the sediment in the light of its history. It is why early fracturation and associated carbonate transfer in shaly-marly massifs is one of the major themes of the *MINANDRA Partnership* (École des Mines de Paris + Andra + some collaborators). That joint program involves tens of geoscientists, and we would like to present here the main objects we study and the methods we apply.

The base of the project is made of selected large reference-outcrops where an early fracturation is undoubtedly visible in the field. Two sets of such outcrops are presently worked in south-eastern France:

- Aptian-albian marls (*Marnes Bleues*), at *Bevons* (near 04-Sisteron) and *Saint-André de Rosans* (W. of 05-Serres).
- Domerian marls, at *Clue du Vançon* (E. of 04-Sisteron).

Both are made of thick marls and intercalated limestone beds and nodules.

## Early fracturation: sandy dykes and sills

Recognized since the 80s, the sandy dykes and sills of the *Marnes Bleues* of *Bevons* and *Saint André de Rosans* record an early fracturation *per descensum* (Beaudoin et Friès, 1982; Beaudoin *et al*., 1983; Parize, 1988; …): hydraulic fracturation by a sudden sandy turbidity current led to the development of huge vertical and lateral injections in the submarine marly massif. Present depth of the dykes below the feeder channels reaches 250 m (decompacted: more than 400 m) and some sills may be followed laterally on more than 1 km; thickness of the dykes varies from 1 m (near the paleo-seafloor) to some cm, thickness of the sills is frequently plurimetric!

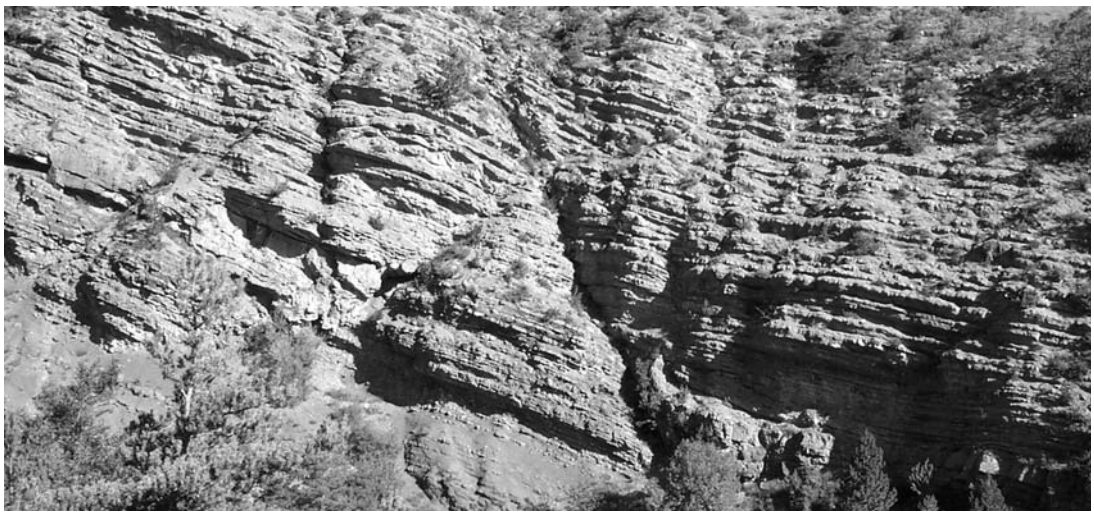
We study the present-day geometry of these fractures, their dimensions, spatial orientation and distribution (clustering? …), the relations with metric and decimetric lithology (limestone and carbonate nodules/marls), anisotropy (relations with the paleo-slope?) and heterogeneities (such as bentonites).

**Figure 1. At *Bevons*, sandy dykes (1) and sills (2) cut the upper albian marine regular alternation sills and dykes (limestone/marlstone); the sand has filled *per descensum* early potential fractures by sudden hydraulic fracturation**

## Synsedimentary faulting and double stratification

The domerian marls of *Clue du Vançon* offer a unique example of double stratification (Beaudoin *et al.*, 1989; Maillart, 1989): the outcrop shows a series of faults between tilted blocks (Figure 2), affecting domerian marls and limestones but sealed by a condensed toarcian level (Coadou & Beaudoin, 1973); these early faults are not planar, but deformed by later compaction.

**Figure 2. The Clue du Vançon outcrop, with the synsedimentary faults**



In such a context, the peculiarity is the presence of decimetric to metric limy nodules. Recent observations (Moreau, 2001) allowed to characterize a litho-stratigraphic succession affected by normal faults; two sets of nodules may be then recognized: one is banal, according to the general stratification; the other is made of parallel *nodular pseudo-beds*, distant of some meters, and along one family of syn-sedimentary faults (Figure 3).

**Figure 3. The two sets of nodules of *Clue du Vançon*: According to the stratification (horizontal) and along syn-sedimentary faults**

## Early fracturation

Based on these field observations, we try to elucidate the genesis and the propagation of the fractures, the timing regarding the age of the marly massif, the (paleo)mechanical properties of the sediment at different scales, the relations with anisotropy and heterogeneities.

In such early fracturation processes, we try to decipher the role of true tectonics and of differential compaction, to observe traces of later reactivation.

A special effort is presently made on mechanical numerical simulations in diverse static and dynamic configurations.

## Compaction

As we work with early fracturation, compaction has obviously to be taken in account. Not only as a cloudy concept, but as an inescapable process recorded in the sediment (Figure 4).

**Figure 4. Compacted dyke in the aptian marls of Bevons**
The post-injection compaction rate
($\tau = h_0/h$) may be directly measured

Bevons outcrop is a remarkable support for such studies: as the injection of sand (as deep as 400 m below the sea-floor) was instantaneous, it as in a way taken a photo of the compaction state of the massif, as a {$\tau$=f(z)} law, were z is the burial depth. Later compaction led to complete compaction of the sediment. So we can estimate the compaction before and after fracturation.

The values of $\tau$ depend on the facies and the carbonate content and reflect the evolution of porosity with depth. The geometry of the dykes when cutting marls or limestones, at time of injection and after later compaction, records the geomechanical properties of the sediment during burial and related progressive compaction, but also the progressive differentiation due to carbonate transfer. Moreover fractures were deformed by later compaction.

## Carbonate transfer

The presence of carbonate nodules in shales implies obviously carbonate transfer. In our cases, because of the unusual exposed processes (sand injection in the *Marnes Bleues*, double stratification in the domerian marls), we can go further: carbonate migration may be studied in time and space with the use of carbonate content in an adapted sampling.

Following Lippmann (1955) and Seibold (1962), one can imagine an instantaneous birth of the nodule (or part of such a nodule) by filling the porosity of the sediment by carbonate: if so, we can write a series of relations such as:

$$I_0 + \acute{U}_0 + C_0 = 1 \qquad I_0 / C_0 = I / C$$

where $I_0$, $C_0$, $\acute{U}_0$ are the insoluble and carbonate contents and the porosity at time of nodulisation, I and C the present day values.

$I_0$ is known (in the nodule), and then $C_0$ and the porosity $\acute{U}_0$.

For example, in the *Clue du Vançon* nodules, we obtain:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ($I_0$) | 29% | 32 | 37 | 39 | 41 | 47 | 51 | 56 | 60 |
| ($\acute{U}_0$) | 62% | 58 | 51 | 49 | 46 | 38 | 33 | 26 | 22 |

for nodules of one family or the other.

These porosity values at the moment of carbonatation, from 60% to 25%, suggest burial depths from some tens of meters to 400-500 m. These results are in agreement with the early (and shallow) timing of the faults given by de-compaction.

After carbonatation of the nodules, the marly massif has still undergone compaction. The geometry of the nodular pseudo-beds was affected, even with fault-like shifting and related re-fracturation.

## Further developments

The ultimate goal of the project is to elaborate methods of investigations allowing to reveal early fractures in shaly massifs and to consider their possible reactions to future solicitations.

It is why the inter-acting processes during early diagenesis and burial are approached at different scales, from outcrop (tens, hundred of m, km …) to selected samples and sets of samples, in relation with field observations: some preliminary results will be given as examples.

The next step will obviously be to apply validated methods to samples of the Underground Laboratory.

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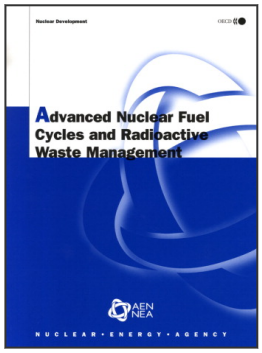


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