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Geochemical Modelling of Fluid-Rock Interactions in the Soultz-Sous-forêts Enhanced Geothermal System

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ABSTRACT

The geochemical modeling of fluid-rock interactions has been intensively applied to the Enhanced Geothermal System (EGS) of Soultz-sous-Forets (France). Modeling was combined with experimental approaches in order to predict possible mass transfer associated to the circulated hot fluids from the granitic reservoir at a 5 km depth and 200°C, the surface power system, and in the re-injection wells at 60°C. The formation of carbonates and dissolution / precipitation of silicates were simulated as possible risks or advantages for future exploitation of the geothermal site. In the short term, the precipitation of carbonates appears to be the more important process of the two because of their kinetic properties. But in the long term, and particularly after tens of years of industrial exploitation of the geothermal system (which started in May 2008), the possible dissolution of rock-forming silicates in some areas of the reservoir and the precipitation of other minerals like clay minerals (illites and / or chlorites) in others may be significant enough to change the porosity and the permeability of the exploited reservoir. The dynamics of silicate minerals have clearly been detected with a complementary experimental approach of water-rock interaction under strong thermal gradient.

1. INTRODUCTION

During the last 15 years, the development of the Enhanced Geothermal System at Soultz-sous-Forêts (France) has yielded an interesting opportunity to use geochemical modeling of water-rock interactions based on theoretical studies with field and experimental data (geochemistry, mineralogy, petrography). The modeling and experimental approach focused on the study of the possible evolution of granitic rock during the circulation of the geothermal fluid. This fluid, initially present in the granitic body, will be pumped out the production wells, exploited for heat and power production, and re-injected into the reservoirs after cooling in the surface heat exchanger. This thermal cycle ranges from up to 200°C in the reservoir to about 65°C before re-injection in the reservoir and will create strong variations in the thermodynamic conditions of fluid-rock interactions. These variations may reactivate the possible dissolution and/or precipitation of mineral phases like carbonates and silicates. Such reactions may modify the porosity and permeability of the rock, which is important to the long term behavior of the reservoir.

2. GEOCHEMICAL MODELLING

2.1 The geothermal context

The European EGS (Enhanced Geothermal System) at Soultz-sous-Forêts is one of the most ambitious European geothermal projects and has been in its initial phase of power production tests since May 2008. Several production tests have been carried out there since 1997 in order to demonstrate that it was possible to impose the circulation of a thermal fluid through fractured granitic rock at great depths (between 3.5 km and 5km). The geothermal fluid was extracted first from the granitic reservoir through the 3876 m production well at about 140°C. An initial geochemical study was also performed during this testing phase (Jacquot 2000). In this test, the fluid produced from the reservoir was cooled to 65°C at the surface in order to simulate the stage of energy exploitation and re-injected into the granitic reservoir at the 3590 m injection well. In the Soultz-sous-Forêts EGS, the 500 m horizontal underground distance between the two wells is particularly important compared to other geothermal systems in the world. This circulation test was conducted during 4 months.

The geochemical modelling approach used was based on thermodynamic and kinetic modelling of water-rock interactions using the code KINDIS (Madé 1991, Madé *et al.* 1994a, b) to simulate these interactions.

The final aim of such a study was to estimate the geochemical risks associated with the possible dissolution and/or precipitation of minerals in the fracture network in the granite. This is described here according to Jacquot, who first defined such a "modelling strategy" (2000):

- definition of the "initial" state of the reservoir before any injection or circulation;
- evaluation of the possible thermodynamic disequilibrium states induced by the circulation of a fluid which is re- injected after cooling;
- calculation of the mineralogical consequences of these chemical disequilibrium states with feedback effects on the porosity and permeability of the reservoir.

2.2 Interpretation of the initial state of the system

The petrography and mineralogy of the granitic rock at Soultz-sous-Forêts have been intensively studied in several publications including ones by Genter (1989), Traineau *et al* (1991), Genter and Traineau (1992, 1996), Ledésert *et al* (1993a,b), Genter *et al* (1995, 1997), and Sardini et al (1997). The mineralogy of the three major rock faces are presented in Figure 1. The petrography of the core material shows clearly that the natural hydrothermal alteration of the granitic rock corresponds to a significant dissolution of K-spar and plagioclases, which is associated with the precipitation of quartz, clay minerals (mainly illites and smectites), and carbonates (calcite and dolomite). The hydrothermal fluids that caused these mineralogical transformations in the past are of course unknown but can be tested with the modelling runs.

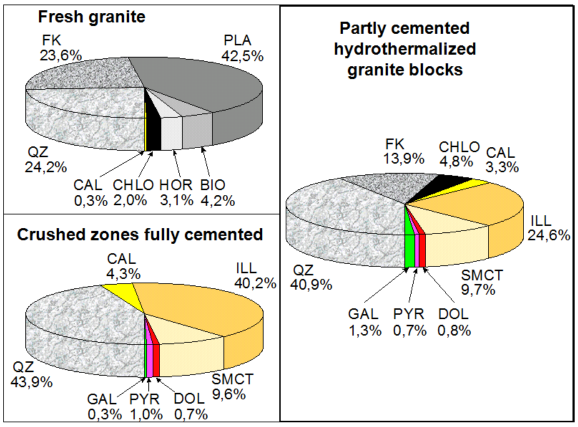

Figure 1: Quantitative mineralogy (volume %) of the three main faces of the granitic basement on the Soultz-sous-Forêts EGS site. ILL = illite ; SMCT = smectite ; CAL = calcite ; DOL = dolomite ; PYR = pyrite ; GAL = galena

The fluids present today in the reservoir have been sampled and analyzed by several authors (Pauwels *et al.* (1992, 1993), Aquilina *et al.* (1997), Komninou and Yardley (1997)).

As a complementary tool, geochemical modelling has been used to test the composition of geothermal fluid in equilibrium with the granitic rock at Soultz at reservoir temperature (165°C). In 1997, the EGS was only drilled to 3.9 km, but it has since been extended to 5 km. The calculations allow the testing of in situ chemical variables which are not precisely determined in the laboratory because of the possible evolution after sampling (Al, Fe2+, Fe3+, Eh) due to cooling effect. The recalculated composition of the fluid is given in Table 1. During the 1997 circulation tests, a pH value of 4.8 was measured directly in the fluid circulating in the pumping pipes while avoiding any contact between the fluid and atmosphere, thus preventing possible oxygen dissolution or CO_2 degassing.

2.3 Quantification of the thermodynamic disequilibrium state at 60°C after cooling.

The rapid cooling of the geothermal fluid in the thermal exchanger between 165°C and 60°C creates a disequilibrium state at 60°C as shown in Figure 2 by the saturation states for major minerals of interest.

The large over-saturations predicted for galena and pyrite are in good accordance with observations of the circulating fluid made during the 1997 circulation tests. Metallic sulfides may precipitate rapidly from these oversaturated fluids as described by Rickard (1988, 1995).

2.4 Simulation of the geochemical evolution of the reservoir during exploitation

After this first cooling step in the geothermal cycle, the geothermal fluid, oversaturated with respect to several minerals (as shown in Figure 2), is re-injected into the granitic reservoir and through the fracture network.

Table 1: Chemical composition of the hydrothermal fluid at 3500 m depth and 165°C calculated at thermodynamic equilibrium with mineral phases of the partly cemented hydrothermalized granite.

Element	Molality (mMol/kg H_2O)
Na	1190
Ca	166
K	65.5
Mg	4.17
Si	1.80
Fe	0.116
Al	7.44 E-03
Pb	0.035 E-03
Cl	1580
S	3.22
F	0.171
pH	4.8
Alkalinity	15 meq.kg^{-1}
Eh	-245 mV

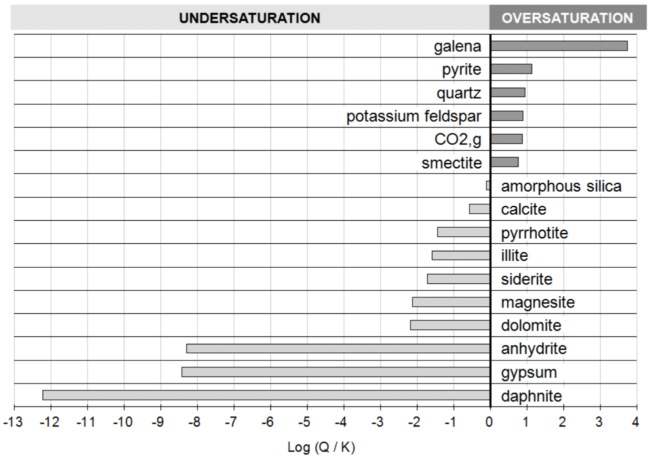

Figure 2 : Saturation states Log(Q/K) of minerals in the hydrothermal fluid after cooling to 60°C at the outlet of the heat exchanger (Q is the ion activity product and K is solubility product of the mineral).

The numerical code KINDIS (Madé (1991), Madé *et al.* (1994a,b) allows one to predict the geochemical evolution of the fluid during this process, but each calculation run is isothermal (at any temperature between 0 and 300°C). This a limitation in the modelling approach because the re-injected fluid is progressively heated in the geothermal reservoir. In order to bypass this problem, a successive sequence of simulations has been performed with isothermal calculation at every ten degrees between 60 and 160°C. The results of these calculations are shown in Figure 3. The kinetic code KINDIS was therefore combined with the code THERMAL

(Fritz (1981)), which calculates the thermodynamic evolution of an aqueous solution between two temperatures.

Different petrographic faces were identified in the granite, as shown in Figure 1. The so-called "hydrothermalized granite" is vital to the circulation of injected fluids because of its high permeability as compared to "fresh granite" and to the "crushed zones," which are totally cemented. Jacquot (2000) only considered the hydrothermalized granite in his modelling of the evolution of physical properties of the reservoir. The sequence of dissolution and precipitation processes detected by the modelling are given in Figure 4 as a function of the progressive temperature increase of the fluid.

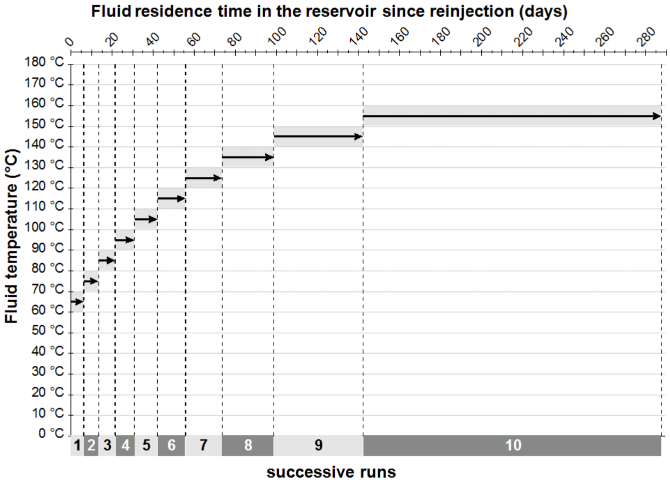

Figure 3: Sequence of calculations (temperature / time) developed for simulating the water-rock interactions during fluid re-injection in the geothermal reservoir during the 1997 circulation test.

The volumetric balance between dissolved and precipitated minerals was calculated for the ten successive simulations at increasing temperatures. This underlines the tendency of the system to open or close the fracture network and is directly related to the different behaviors of carbonate and silicate minerals.

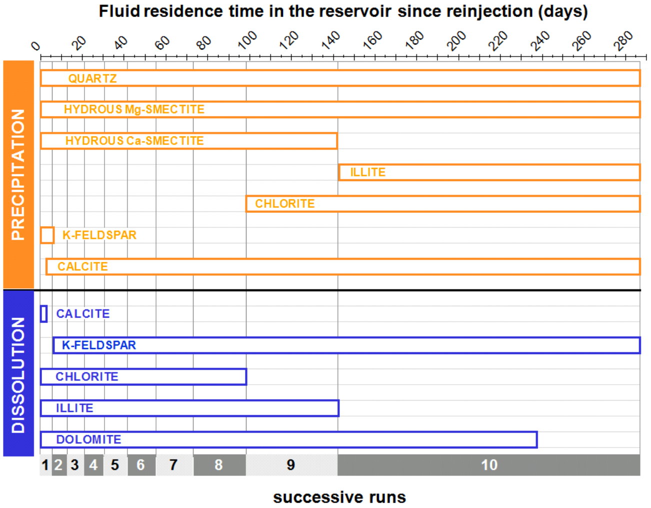

Figure 4: Qualitative sequence of mineral dissolution and precipitation during fluid re-injection in the geothermal reservoir during the 1997 circulation test.

Among silicates, the volumetric balance is mainly controlled by quartz, K-spar and the hydrated magnesium rich smectite. However, despite their abundance of contact with the hydrothermal fluid in the fractures of the granitic body, the contribution of silicates to the volumetric balance of dissolved and precipitated minerals remains very small. Therefore, the dissolution of dolomite and the precipitation of calcite explain the major part of the porosity evolution in the geothermal reservoir during exploitation. As shown in Figure 5, the major part of the volume of minerals dissolved or precipitated concerns these carbonates.

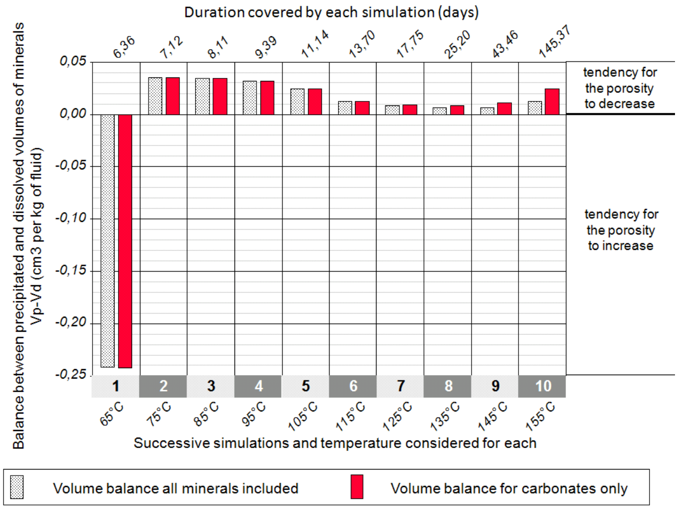

Figure 5: Volumetric balance between dissolution and precipitation for the successive simulations at increasing temperatures.

Carbonates represent the majority of the volume of minerals dissolved or precipitated, despite their small contribution to the composition of the granitic rock (< 5%). This is due to the difference in reactivity between silicates and carbonates. Carbonates dissolve and precipitate several orders of magnitude more rapidly (e.g. 7 orders of magnitude at 25°C and near neutral pH values) (White *et al.* 1999).

2.5 Fluid – rock interactions in the granitic body: quantification and modeling of mass transfers.

In addition to its interest as a geothermal site, the Soultz-sous-Forêts granite is an interesting example of a system where paleofluid circulation along the fractures has induced mineralogical and chemical transformations in the granitic basement and in the overlying terrains (triassic sandstones in particular) as well (Ledésert *et al.*, 1993a,b). The fluid circulation in the future geothermal system will obviously induce new transformations as shown above. These changes might be short term (mainly carbonates) or longer term (silicates, clay minerals). Paleo-transformations may be detected in the granite and can be used as indicators of what may occur during future exploitation. Jacquemont (2002) made a complete petrographic study of the various alteration faces of the Soultz-sous-Forêts granite on core samples using the Gresens method of mass transfer quantification (Gresens 1967, Potdevin and Marquer 1987). This method is focused on the characterization of the behaviour of chemical elements during alteration in order to establish the mass balance during alteration at three different levels (i.e. the mineralogical reaction cells, the alteration horizons and the whole granite body). This allowed for the quantification of the mass transfer in the granitic rock resulting from successive hydrothermal circulations at temperatures ranging from 100°C to 300°C. Some results are particularly interesting in the context of the geothermal system: (1) titanium and aluminium were immobile elements at the mineral grain level, (2) calcium, manganese, iron and magnesium were widely exchanged through the different faces but remained more stable at the scale of the entire granitic body, (3) silicium, potassium and sodium were mobile at the various scales, (4) silica and potassium contributions from sedimentary fluids were demonstrated, (5) sodium coming from plagioclase alteration could have been exported from the system.

This description of the long-term elemental behavior in the granitic system appeared to be totally consistent with the short-term predictions as modeled by Jacquot (2000), particularly for the dynamics of carbonates and silicates. Additionally, the results of the mass balance calculations on the core samples showed that major elemental transfers were detected in the fractured zones. This caused intense alteration and produced secondary illitic clayey phases.

In a geochemical modelling approach, Jacquemont (2002) showed that the hydrothermal alteration in initially fractured and unaltered granite by a fluid with a chemical composition close to that of the present-day fluid in the reservoir could explain the mineralogical compositions observed in the different alteration faces. He confirmed that plagioclase alteration resulting in illite was the most important alteration process in up to 1000 years of alteration.

This modelling approach appeared to be complementary to the previous one as it considered the effect of very long term processes on a geological time scale. In that situation, the mass transfer is much more dependent on the dynamics of silicates. If carbonates may be active phases on short processes, when the system is more or less open to atmosphere and CO_2, this is not the case in the granitic body.

3. EXPERIMENTAL APPROACH : THE STABILITY OF PHYLLOSILICATES IN A STRONG THERMAL GRADIENT

If the dynamics of silicates are the major concern for long term behavior of the reservoir, the precipitation of silicate minerals and particularly of clay minerals has to be well documented in order to validate the geochemical models that combine thermodynamic and kinetic properties of the mineral phases to predict their long term dynamics in a geothermal system. In many experimental studies, like those conducted by Oelkers et al. (1994), the research is focused on the kinetics of dissolution processes. Only a few studies concern the precipitation of secondary phases. This is essentially because it is much more difficult to detect the minor secondary phases in short term reactions, particularly for low temperature processes (<150°C). In the case of strong thermal gradients, the mineral evolution (dissolution and/or precipitation) can be studied experimentally with the 'tube-in-tube' design as used by Goffé et al. (1987) and Robert and Goffé (1993). This design is illustrated in Figure 6. In this experimental approach, the initial mineral products are enclosed in a capsule. This capsule has drilled walls and is located at one end of a 10 cm gold tube containing only an aqueous solution at the beginning of the experiment (no minerals). This apparatus was then placed in a thermal gradient. During these experiments (Vidal (1997), Vidal et al. (1995), Baldeyrou-Bailly (2003), Baldeyrou *et al.* (2003), the initial mineral products may dissolve in the aqueous solution if unstable, and the aqueous species will diffuse toward the opposite side of the tube through the imposed thermal gradient. Saturation, which is a function of the change in mineral solubility with temperature, may be reached in the solution at specific steps along the tube. Thus, secondary precipitated phases will be observed in the tube, which was free of solids at the beginning of the experiment.

Using powdered granite as the material placed in the initial capsule, Baldeyrou et al. (2003) showed that albite, orthose and sometimes saponite could be observed precipitating at the hot extremity of the system (300°C), whereas interlayered illite/smectite and/or dioctahedral smectites were observed with quartz at the cold extremity. Complementary experiments were conducted with different starting assemblies, different fluid compositions, and different temperature ranges (Fritz et al. (2009b))

3.1 Experimental method

The experiments were conducted by successively using powdered granite and separated rock-forming phases in the molar proportions given in Figure 7. The granite used originated in the Flamanville area (France) and has a similar composition to the Soultz-sous-Forêts granite (Baldeyrou et al. (2003)).

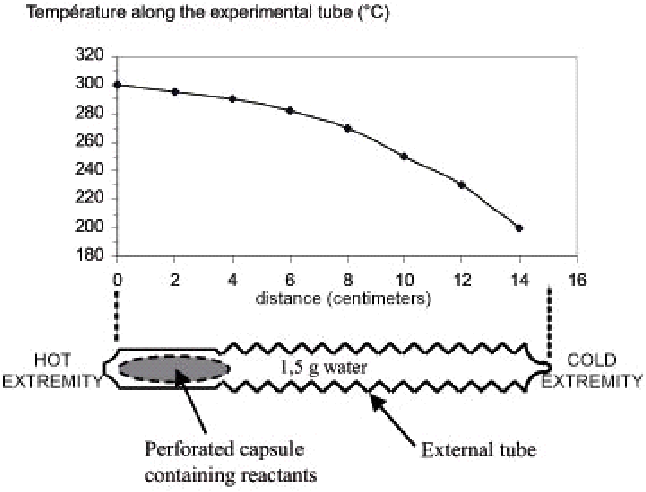

Figure 6: Experimental protocol in one-capsule experiments.

About 20 mg of the starting materials were sealed in a gold capsule with drilled walls. In this system, dissolved species may migrate into the aqueous solution contained in the gold tube, but the solids cannot. The capsule was oriented at the hot extremity of the gold tube (length = 10 cm, diameter = 4 mm) containing 1.5 ml bi-distilled water or a solution having the composition of the brine analysed in the Soultz-sous-Forêts geothermal system as described by Pauwels *et al.* (1993), and Aquilina *et al.* (1997). The composition of this brine is described in detail in Table 2. The closed tube was placed in a horizontally oriented cold seal autoclave.

The cold extremity of the autoclave was in contact with ambient air, and the other extremity was centered in the oven. At the end of the run, the gold tube was removed from the autoclave and immersed in liquid nitrogen in order to freeze the solution and to avoid any displacement of the newly formed phases. The tube containing frozen water was heated to 80°C for 12 hours to evaporate the solution, and its walls were observed with a scanning electron microscope (SEM). When possible, the products were collected after the SEM observations for XRD or TEM characterization.

Table 2: composition (mmol/Kg H_2O) of the salted fluid used in the experiments SEL and gradT4 (see Fig. 7)

Na	Ca	K	Mg	SiO2	Cl	Al	Fe
1134	147.7	95.1	3.92	6.48	1590	1	2

3.2 Results of the experiments

The experimental conditions and results are shown in Figure 7, from the studies of Baldeyrou-Bailly (2003) and Baldeyrou *et al.* (2003, 2004)). The major results of these experiments were the high chemical reactivity of the systems: in the thermal gradient created in the cells, the water-rock reaction occurred significantly. Between 30% and 70% of the reacting mineral phase (located initially in the capsule) was dissolved, and the corresponding elements were transferred to the solution in the tube, precipitating pro parte in secondary phases and particularly at the cold end of the tube. Enough material was generally available for XRD detection and SEM observation and analysis.

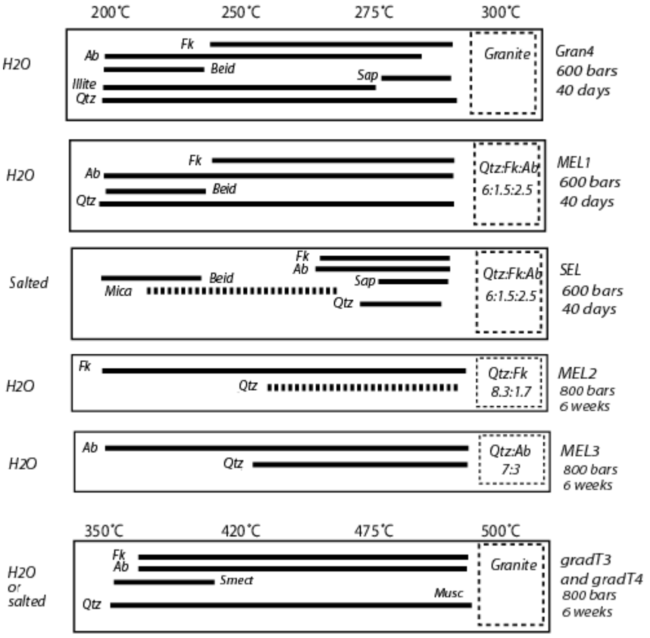

Figure 7: Experimental results of the tube-in-tube experiments under thermal gradient. Dashed outlined boxes represent the capsules containing the starting material (molar proportions). The type of reacting fluid is indicated on the left side. Bars show the temperature ranges where the precipitated phases were observed.

The composition of the smectites varied with temperature, as shown in Figure 8:

- At the cold point, the composition was found to be close to the beidellite end-member, and few intermediate compositions were observed between saponite and K-feldspar.
- At intermediate temperatures (middle part of the tube), the analyses plot was close to K-feldspar.
- At the hot point, few intermediate compositions were observed between saponite and K-feldspar.

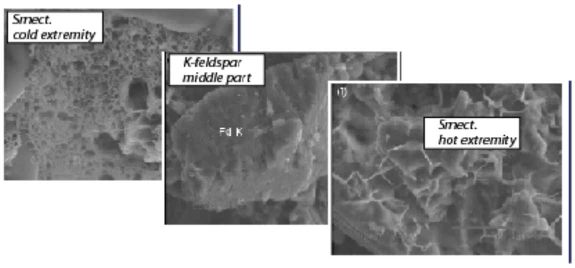

Figure 8: SEM micrograph of the run products from the experiment « SEL »

The products of the rock-water interaction were characterized in all experiments by the XRD (except MEL2 and MEL3, in which the amounts of newly formed phases were too small). The two types of fluid provided similar results for the two temperatures:

- K-Spar or albite were observed at the hot extremity.

- Al-rich smectite (beidellite composition) was observed at the cold extremity of the experiments with granite or two feldspars as reactant phases.

- A Mg-rich smectite of saponite composition was also detected at the hot extremity.

The production of smectite is obviously strongly controlled by the availability of aluminium. This was observed in experiments MEL2 and MEL3, in which the reactants were poor in Al and no smectite was detected after SEM observation. These results are consistent with low aqueous Al concentration controlling aluminous silicates in most water-rock systems (Ransom and Helgeson (1995),Vidal and Durin (1999)).

3.3 Simulation of the experimental processes

The results of these experiments were compared with the results of the fluid-rock interaction modelling using the numerical codes THERMAL (Fritz (1981), and KINDIS (Madé (1991), Madé *et al.* (1994a,b)). The code KINDIS calculates the dissolution/precipitation of minerals reacting with an aqueous solution at a given temperature (up to 300°C). This code works isothermally. The code THERMAL was used to calculate the effects of temperature variations during the heating or cooling steps. The combination of these two codes allowed reproducing steps of heating or cooling typically by 10°C. The calculation indicated the possible dissolution of the initial minerals introduced in the capsule and the precipitation of minerals in the tube in the ranges 100-200C and 200-300°C (Baldeyrou *et al.* (2003)). The calculated saturation index of the different phases detected in the experiments MEL1, MEL2 and SEL are shown in Figure 9.

In agreement with the experimental observations, the results of the simulations indicated that the fluid was either very close to saturation (MEL 1) or oversaturated (MEL2 and SEL) with respect to feldspar at high temperature, and it became saturated with respect to smectite as temperatures decreased. The temperature range of the mineral stability along the temperature gradient depends on the composition of the reacting mineral in the capsule at the hot extremity. Feldspars were restricted at the hot end of the tube in the simulation of experiment SEL, whereas it was stable or very close to stability in the other simulations. This result was in good agreement with the experimental results shown in Figures 7 and 8. Smectite precipitated in the simulations at around 250°C in both SEL and MEL 1, which is in the temperature range of the cold extremities of tube. In contrast, smectite is predicted to be unstable above 150°C in MEL 2 (i.e. at the temperature of the cold extremity of the experimental system). These results were in good agreement with the occurrence of smectite in MEL1 and SEL and its absence in MEL2.

The good agreement between this thermodynamic modelling and the experimental results suggests that the experimental results can be interpreted in terms of local thermodynamic equilibrium along the thermal gradient in the reactive cells as proposed by Thompson (1959). The diffusion of elements in the solution from the capsule occurred where they were produced by the dissolution of the reactant minerals, then along the tube. This tube-in-tube experimental approach is a very efficient tool for detecting the potential sequence of precipitation of minerals in a thermal gradient. It confirms the dynamics of water-rock interactions between two temperatures as it occurs in a geothermal reservoir. In the particular case of the Soulz-sous-Forêt EGS, it can be predicted that the precipitation of quartz and feldspars is more likely at high temperature (around 200°C), while clay minerals may be expected at “low” temperatures (< 150°C) and will partially control the porosity in the granitic reservoir.

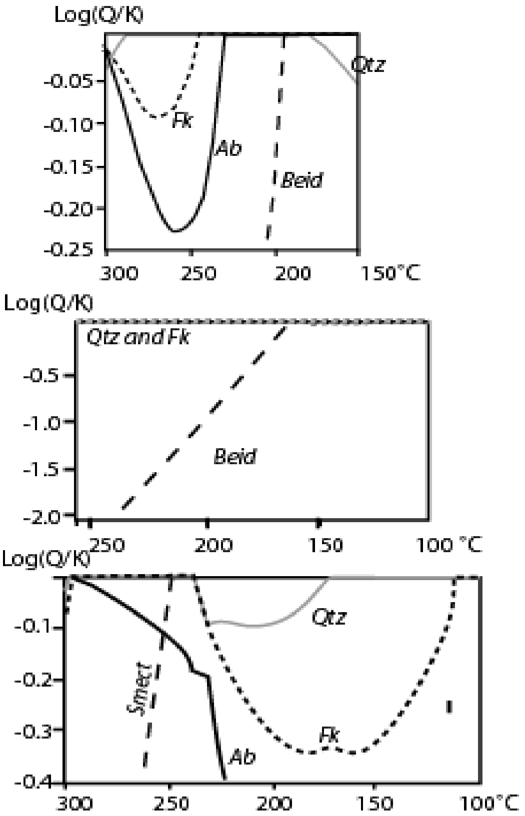

Fig. 9 - Saturations states of major minerals in the simulated aqueous solutions (Minerals may precipitate if Log(Q/K) >0). Top to bottom: runs MEL1, MEL2, SEL.

One may comment that this experimental approach has been used at higher temperatures and stronger temperature gradients than expected in the geothermal reservoir. However, these results give a clear indication of the tendency of the chemical dynamics in the system.

4. CONCLUSION

In the context of the Enhanced Geothermal System of Soultz-sous-Forêts, the geochemical modelling approach was based on a database of field and experimental data. This modelling and experimental approach helped to predict possible dissolution or precipitation processes which may occur during the circulation of the geothermal fluid, at surface in the exchanger, and in the reservoir after re-injection.

This study clearly underlined the importance of kinetic effects on the considered fluid-rock interaction processes. Silicate minerals represent about 95% of the volume of the rock in the reservoir at depth. However, they only play a minor role in the short term evolution of the porosity. However, minor carbonates may play an important role in controlling the evolution of the porosity and therefore the permeability and are thus important to the long term evolution of the system during heat exploitation. This is due to the fact that kinetic rate laws are significantly different for these mineral phases: carbonates dissolve and precipitate faster in a water-rock interaction. This result is particularly important if a complex model coupling fluid transport and chemical reactions is developed. Coupled models will help to predict the localization in space and time in the geothermal reservoir of the feedback effects of the induced mineralogical evolutions on porosity. Such models are developed as numerical codes like KIRMAT (Gérard *et al.* (1998) and have already been applied on a small scale to nuclear waste storage systems (Marty (2006), Marty *et al.* (2009)).

In the short term, neglecting the effect of silicate dissolution/precipitation is only a first approximation. Experimental results help to document this problem for dissolution processes (Vidal *et al.,* (1995), Oelkers *et al,* (1994). The simulation of the precipitation of secondary clay phases in alteration processes creates new perspectives for the simulation (Sausse *et al.* (2001), Fritz *et al.* (2009a). The simulations already performed show clearly that even if the re-injected fluid is able to produce swelling hydrous smectites, the evolution of the reservoir porosity is essentially controlled by the carbonate phases. This is due to the fact that the dissolution and precipitation kinetics of these phases are very fast compared to those of the silicate minerals, even if they do not represent major phases in the granitic rock. This result has been confirmed by Durst (2002) using a more complex modelling approach that combines fluid-rock interactions and heat and fluid transport, showing that calcite and dolomite presented the maximum potential for precipitation or dissolution compared to quartz and pyrite. A significant dissolution of carbonates should occur at re-injection zone (positive effect for porosity-permeability) and secondary precipitation should occur later in the re-injection path in the reservoir (negative effect). This was obtained using the code FRACHEM, a 2D simplified reservoir model (Durst (2002), Portier and Vuataz (2009)).

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