Report on determination of Dissolution and precipitation rates of clayey materials by ^{29}Si/^{28}Si isotopic exchange. Effect of temperature.

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT

SKIN

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DETERMINATION OF DISSOLUTION AND PRECIPITATION RATES OF CLAYEY MATERIALS BY ^{29}SI/^{28}SI ISOTOPIC EXCHANGE. EFFECT OF TEMPERATURE

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1. Abstract

Surface study on illite, illite/smectite and Callovo-Oxfordian argillite clay mineral phases are performed in conditions close to equilibrium for three temperatures (35°, 50° and 90°C) in 0.01 mol/L NaCl solution. Prior the experiments, clays were purified by elutriation to remove the quartz phase. Characterization of the solids was done by SEM, XRD and XPS. Concentrations of Si, Fe and Al were measured in solution by Q-ICP-MS. Maximum concentration of Si values were determined for each solids in contact with the solution and a pseudo-equilibrium is reached after 50 days of contact time. These values ($\sim10^{-5}$ – $\sim10^{-4}$ mol/L) under the solubility of quartz values correspond to the solubility values of the clays. Concentration of Fe is 2.5×10^{-6} mol/L and Al is 3×10^{-6} mol/L in solution. After 326 - 483 days of alteration, ^{29}Si spike was added in each system studied. The results obtained for the illite/smectite system indicate that in condition close to equilibrium a dynamic exchange of ^{29}Si and ^{28}Si occurs at the interface solid/solution. The isotopic exchange was performed during 100 days with a dissolution rate of $\sim7\times10^{-15}$ mol Si/m²/s and a precipitation rate of $\sim4\times10^{-15}$ mol Si/m²/s. The XPS and XRD analyses indicate no modification for both initial and altered illite/smectite after 538 days of alteration. XRD analyses for illite and Callovo-Oxfordian argillite showed no structural modifications after 640 days of experiments.

2. Introduction

According to the French laws for the management of nuclear wastes, high level nuclear glass wastes are planned to be stored in deep geological formation. At 490 m in depth, the Callovo-Oxfordian formation presents interesting properties in terms of high retention coefficients of radionuclides, low permeability of water, large specific surface area, reactivity and pronounced sorption capacity (***ANDRA (2005), Bergaya et al. (2006)***). This geological formation is mainly characterized by the presence of illite, interstratified illite/smectite 40-45%, carbonates 30-40%, tectosilicates 20-30% and pyrite 1-2% (***Gaucher et al. (2004)***). Prior the determination and the acceptance by the public of the final site for the geological disposal CIGEO directed by ANDRA, an underground research laboratory has been built in Meuse/Haute-Marne in the Callovo-Oxfordian formation (northeastern, France) to evaluate the feasibility of disposal of radioactive wastes in a deep clay rock formation. After having filled the galleries by the nuclear waste (high level long live and intermediate level long live), the disposal locations will be sealed from access tunnels by bentonite plugs. The Callovo-Oxfordian argillite host rock and the bentonite will both become saturated with the groundwater. The increase of temperature caused by the high level nuclear waste may also change the chemical and physical properties of the clay barrier and in particular its dissolution kinetics.

In literature, a number of studies are performed on dissolution of clays minerals focusing on the temperature dependence and pH effects (eg. ***Bauer and Berger (1998); Ganor et al. (1995); Huertas et al. (2001); Köhler et al. (2003); Palandri and Kharaka (2004); Rozalén et al. (2009)***). The overall results showed a typical dissolution rates profile with an increasing of rates values in the acid and alkaline pH-range, and a minimum in near neutral pH. However, rare are the studies on understanding of clays surfaces in conditions close to equilibrium. A recent study, with illite and montmorillonite, showed that a dynamic equilibrium is established between the claystone and the porewater and is described as a dissolution/precipitation mechanism (Suzuki-Muresan et al. (2011)). Current models consider that the frayed edge sites are stable but these recent results with illite coupled to Si/^{32}Si isotopic exchange studies indicate that an ongoing dissolution/precipitation mechanism at solubility equilibrium may be related to a permanent dissolution/reconstruction on frayed edge sites.

Related to the context of nuclear waste disposal in deep geological formation, the high level nuclear waste vitrified by PUREX method will be stored in tunnels and sealed by swelling clays materials as bentonite plugs for the French programme. Considering the resaturation period and the equilibrium time with the bentonite and the Callovo-Oxfordian argillite, the concentration of Si in the porewater in equilibrium with the Callovo-Oxfordian argillite (1.8×10^{-4} mol/L, ***Tournassat et al. (2007)***) will increase to the maximum concentration of 2×10^{-3} mol/L in presence of bentonite (***Suzuki-Muresan et al. (2011)***). This later is four times higher than the solubility of the nuclear glass waste ([Si] 5×10^{-4} mol/L at 90°C; ***Daux et al. (1997); De Cannière et al. (1998)***) and may control the dissolution of the nuclear glass waste. The contribution of tectosilicates impurities in the Callovo-Oxfordian argillite may also contribute to the inventory of silicium in the porewater and may control the solubility of the clay.

The question raised in this study is how the surface of the Callovo-Oxfordian argillite will behave in presence of a source term in silicon stemming from the radioactive nuclear glass waste. For that, two clay minerals (illite and interstratified illite/smectite) considered as reference minerals are studied and compared to the Callovo-Oxfordian argillite at different temperatures. The work is focused on the close to equilibrium conditions in the experiments. The assessment of the surface reactivity is performed by the $^{29}Si/^{28}Si$ isotopic exchange.

Materials and methods

Solid materials

Natural clayey samples were used for this project: (i) illite/smectite ISCz1 provided by Clay Mineral Society (C.M.S.) (0.5 wt% quartz, 1 wt% kaolinite) and (ii) illite IMT2 from C.M.S. (7.5% quartz, 2% microcline); (iii) Callovo-Oxfordian argillite from the Underground Research Laboratory at Bure (40–45% illite, interstratified illite/smectite, 20-30% quartz, 30-40% carbonate, 1-2% pyrite (***ANDRA (2005b); Gaucher et al. (2004)***). Samples contain a fraction of quartz phase for which the proportions could be considered as none neglectable for the experiments. The clayey samples were therefore purified by the method of elutriation defined as “*the process of separating the lighter particles of a powder from the heavier ones by means of an upward directed stream of fluid (gas or liquid)*” (***IUPAC (1997)***).

Batch experiments

The experiments were performed in batch systems for three temperatures studied 35°, 50° and 90°C. The solution composition is a solution of NaCl 0.01 mol/L with an initial pH of 5.5. The aqueous solution is then filled into PFA Teflon reactors (Savillex, 250 mL) containing 1 g of solid. One reactor contains only one type of solid. This operation is repeated for each temperature at 35°, 50° and 90°C. For each set of temperature, one reactor containing only a solution of NaCl is prepared as blank experiment (free of solids). A total of 12 reactors were prepared (4 reactors × 3 temperatures) with a solid/solution (m/V) ratio of 6.7 g/L. The temperature of the ovens was controlled by a digital system. Before sampling, the reactors were taken out of the ovens and quenched at room temperature and filtered at 0.45 µm (Q-ICP-MS) or ultrafiltrated at 5 kDa (HR-ICP-MS). Solution aliquots were taken, measured for pH (pHC3006 Ag/AgCl, Radiometer), acidified with HNO_3 2% for ICP-MS analyses.

Initial dissolution rates (expressed as Si release rates in mol Si/m^2/s) were calculated from the variation of aqueous silicon concentrations far from the equilibrium at very early time in all systems.

$$R_{\mathrm{dissolution}} = \frac{[\mathrm{Si}]_t - [\mathrm{Si}]_0}{\frac{m}{V} \times SA/m \times t}$$

where $[\mathrm{Si}]_t$ and $[\mathrm{Si}]_0$ (mol/L) stand for the final and initial silicon concentrations in solution, m/V (g/L) for the ratio of the solid mass onto the solution volume, SA/m (m^2/g) for the specific surface area and t (s) for the reaction time.

Isotopic exchange experiments

The stable isotope of silicon ^{29}Si was used to study the isotopic exchange between ^{28}Si and ^{29}Si at the interface solid/solution. The tracer supplied by Euriso-top® as solid SiO_2 form with an enrichment of ^{29}Si up to 99.9% was prepared on the base of the procedure of Van den Boorn et al. (2006) (***Van den Boorn et al. (2006)***). The tracer was prepared gravimetrically and dissolved in $NaOH.H_2O$ (99.99% Suprapur) at 200°C in a PFA pressure vessel. The working tracer solution was obtained after taking up the residue in Milli-Q water and then adding a 10mol/L HCl solution in order to get a final concentration of silicon equal to 459.2±1.2µg/g (1 sigma) in 0.25 mol/L NaOH and pH 13.4. The stable tracer was added when the conditions close to equilibrium were reached i.e. after 399 days of contact from the beginning of the experiments for Illite, 483 days for Illite/Smectite and 326 days for Callovo-Oxfordian argillite.

From the mixed isotope ratio determined experimentally by HR-ICP-MS, the relative proportions of $\delta^{29}/^{28}$Si in comparison to the IUPAC reference standard value were calculated according to the following relation (***Handler et al. (2009)***):

$$\delta^{29/28}\mathrm{Si}(‰) = \left(\frac{\left(\frac{^{29}\mathrm{Si}}{^{28}\mathrm{Si}}\right)_{\mathrm{mix}} - \left(\frac{^{29}\mathrm{Si}}{^{28}\mathrm{Si}}\right)_{\mathrm{natural}}}{\left(\frac{^{29}\mathrm{Si}}{^{28}\mathrm{Si}}\right)_{\mathrm{natural}}} \right) \times 1000$$

where $\left(\frac{^{29}\mathrm{Si}}{^{28}\mathrm{Si}}\right)_{\mathrm{mix}}$ and $\left(\frac{^{29}\mathrm{Si}}{^{28}\mathrm{Si}}\right)_{\mathrm{natural}}$ are the isotope ratio in the mixture determined experimentally and the isotopic ratio given by the IUPAC reference standard, respectively.

The percent of Si atom exchanged was calculated from the expression below (***Handler et al. (2009)***):

$$\text{percent exchanged} = \frac{\delta_t - \delta_i}{\delta_e - \delta_i} \times 100$$

where the δ_t, δ_i and δ_e are the isotopic composition at time t, the initial isotopic composition of the phase and the equilibrium isotope composition, respectively (***Gorsky et al. (2012)***). The later δ_e is calculated from the mass balance-weighted isotopic composition of the two-components system silicon in silicate and silicon in spike:

$$\left(\delta^{29/28}\mathrm{Si}_{\mathrm{mix}}\right)\left[\mathrm{Si}_{\mathrm{silicate}} + \mathrm{Si}_{\mathrm{sp}}\right] = \left(\delta^{29/28}\mathrm{Si}_{\mathrm{silicate}}\right)\left[\mathrm{Si}_{\mathrm{silicate}}\right] + \left(\delta^{29/28}\mathrm{Si}_{\mathrm{sp}}\right)\left[\mathrm{Si}_{\mathrm{sp}}\right]$$

Dissolution rates and precipitation rates were calculated after addition of ^{29}Si spike according to the quantity of Si released from illite/smectite, and the precipitation rates have been calculated by considering the quantity of ^{29}Si-spike in solution. The rates values are compared with those calculated at the beginning of the experiments far from equilibrium.

Analytical methods

Determinations of element concentrations in solution were carried out by plasma based techniques, namely Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q-ICP-MS, X Series, Thermo Electron Corporation) and sector field High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS, Thermo Scientific Element-XR instrument).

Q-ICP-MS. Aliquots sampled during the experiments were prepared for concentration measurements of silicon, iron and aluminum by Q-ICP-MS using external calibration with ^{45}Sc and ^{115}In as internal standards for signal drift correction. The quantification limit calculated as ten times the standard deviation of the blank (i.e. 0.2% HNO_3 solution) is equal to 7×10^{-7} mol/L for silicon, 7×10^{-8} mol/L for iron and 4×10^{-8} mol/L for aluminum. Multi-Element calibration standard and sample solutions for analysis were prepared in 2% HNO_3. The ^{45}Sc-^{115}In mixed internal standard solution at 20ppb was introduced on-line in all solutions. Any residual signal drift was corrected from the measurement of the “quality-check” multi-element standard performed every five samples. All standards used during the course of the study were supplied by Scp Science, ultrapure water was obtained with a Milli-Q water purification system and HNO_3 acid was purified by sub-boiling distillation.

HR-ICP-MS. Si isotope ratios were measured on the SEM in analog mode using a mass resolution of 4000 ($\Delta m = 0.007$ u.m.a. for m = 28, 29, 30) for complete removal of isobaric spectral interferences on ^{28}Si, ^{29}Si and ^{30}Si. The use of a free-Si liquid sample introduction device with PFA Teflon nebulizer and spray chamber but also an injector torch made of platinum as well as purified reagents will greatly improve the silicon instrumental background and as a consequence the accuracy and reproducibility of Si isotopic ratios after ^{29}Si tracer addition. The instrument sensitivity is around 20000 cps/ppb and the detection limit for silicon is equal to 1.3×10^{-7} mol/L - 6×10^{-8} mol/L. Working matrix-matched standard solutions of silicon were prepared in 0.01 mol/L HCl using 1000 mg/l silicon and sodium stock solutions purchased by SCP Science and Alfa Aesar, respectively. All samples and standards were diluted to a final Si concentration ranging from 100 ppb to 500 ppb. During the analysis session, five samples are bracketed by a silicon working solution and a 0.01N HCl blank solution in order to correct raw isotope data from blank (blank/sample ratio less than 15%) and mass bias using the mass fractionation exponential law. Every sample and standard measurements are followed by a 5 min wash of the complete sample introduction system using 0.01N HCl. The acquisition procedure allows the collection of one hundred measurements of each silicon isotope ratios in 3min20s with in-run precision around 0.1-0.2% $(1\sigma/\sqrt{10})$ for ^{29}Si/^{28}Si.

Characterization methods

BET. The surface area of illite, interstratified illite/smectite and Callovo-Oxfordian argilite samples were determined from N_2 adsorption isotherms at 77 K experiments and obtained with a Micromeritics ASAP 2010 M. Prior to analyses, the samples were outgassed in vacuum overnight. Surface area of illite is 50.9 m^2/g, interstratified illite/smectite 82.3 m^2/g and Callovo-Oxfordian argillite 92.8 m^2/g.

Granulometry. The particle size was determined by means of the particle sizing system (PSS) from CAD instrumentation. Size distributions (volume based) from 1 to 100 µm diameter range were determined by single-particle optical sensing using an AccuSizer$^{\text{TM}}$ 780 optical PSS.

SEM. Surface morphology were observed by scanning electron microscopy and the chemical composition was determined by energy dispersive spectroscopy (EDS) with a JEOL 5800-LV using a PGT IMIX-PTS (Princeton Gamma-Tech, Energy Dispersive Spectrometer with germanium) probe operating at 15 kV.

XRD. Patterns were collected with a Bruker-AXS D5000 (Bragg-Brentano geometry Advance diffractometer (Bragg^{+}Brentano geometry) equipped with a Cu anticathode under the following experimental conditions: 0.2 mm receiving slits and 1 mm divergence slits for radial divergence, a 16 mm-high receiving slit, and a 2.3° Soller slit. X-ray powder diffraction data were collected with a step size of 0.02° 2θ over the angular range from 10-60° 2θ. MAUD program (***Luterroti, 2000***) with the full pattern XRD Rietveld fitting procedure combined with a Fourier analysis were used to describe the broadening of peaks (***McHale et al, 1997***). This method consists in refining the experimental diffractograms from the structural model of the phases.

XPS. The spectra were collected on an XPS apparatus (KRATOS Nova). The source of photons is a monochromatized AlK_α lamp (1486.6 eV) and a FWHM at 0.26 eV. The charge effects were corrected using the 1s line at 284.6 eV (***Moulder et al. (1993)***) of the contaminant carbon (C–H species species). The XPS spectra are fitted with the software CasaXPS Version 2.3.16 PR 1.6 program (Copyright © 1999-2011 Casa Software Ltd). The precision on binding energy values is ± 0.2 eV.

Results

Dissolution of clays.

The results of the dissolution of illite/smectite, illite and Callovo-Oxfordian argillite are shown in Figures 1, 2 and 3, respectively, and present the concentration of Si (mol/L) measured in solution against the contact time (days) at 35°, 50° and 90°C. From a general observation, the concentrations at 35° and 50°C are very similar and different to that of at 90°C. After about 50 days, a maximum of Si-concentration is reached. The concentrations of Si in presence of illite and illite/smectite are higher at 35° and 50°C by a factor 2 compared with the Callovo-Oxfordian argillite. At 90°C the concentrations in all the systems are similar. At low temperature, the dissolution of illite and/or illite/smectite seems not to participate to the dissolution of the Callovo-Oxfordian argillite due to the lower concentration of the later. The presence of muscovite and kaolinite in the Callovo-Oxfordian argillite request more investigation to assess the influence of each of the clay mineral phases present. At 90°C, the results indicate clearly that illite and/or illite/smectite may control the dissolution of the Callovo-Oxfordian argillite.

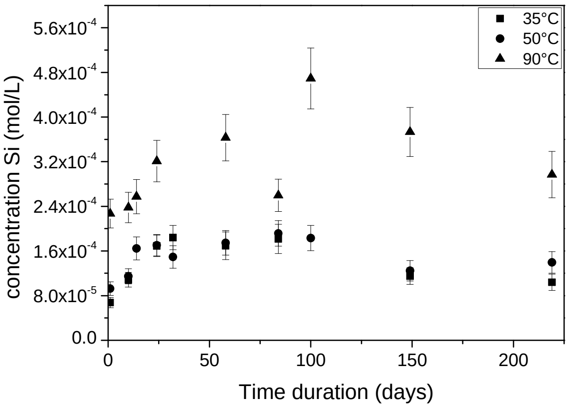

***Figure 1**: Evolution of Si-concentration in solution versus time for different temperatures (35°, 50°, and 90°C) for illite/smectite: m/V = 6.7 g/L, SA/m = 82.3 m²/g, NaCl 0.01 M, pH 5.6 – 6.3*

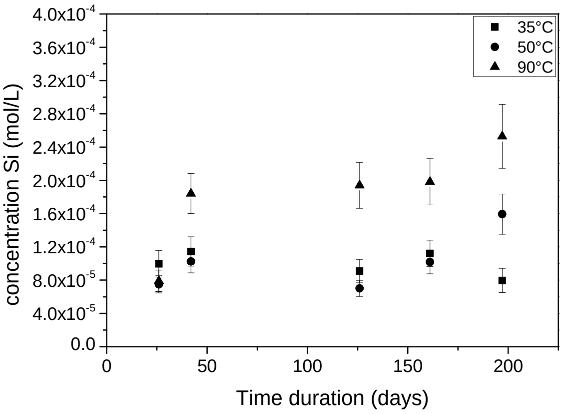

Figure 2*: Evolution of Si-concentration in solution versus time for different temperatures (35°, 50°, and 90°C) for illite: m/V = 6.7 g/L, SA/m = 50.9 m²/g, NaCl 0.01 M, pH 6.1 – 5.8*

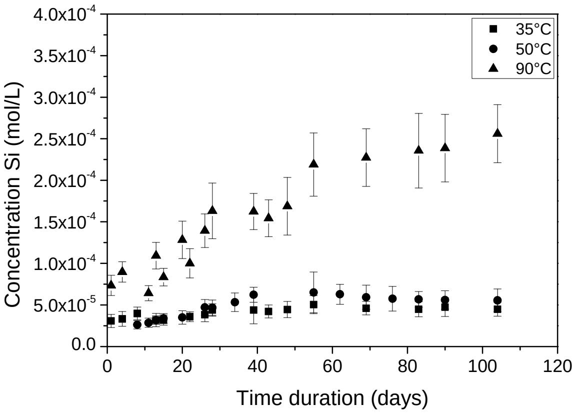

Figure 3*: Evolution of Si-concentration in solution versus time for different temperatures (35°, 50°, and 90°C) for Callovo-Oxfordian argilite: m/V = 6.7 g/L, SA/m = 92.8 m²/g, NaCl 0.01 M, pH 8.0 – 8.2*

Comparing to the data published in Suzuki et al., the concentrations of Si in solution for the Callovo-Oxfordian argillite sample is lower in this study by a factor 2. This could be explained by the presence of quartz fraction existing in the study of Suzuki et al. which has been removed by purification in this study (***Suzuki et al. (2011)***). In this work, we have assessed the maximum concentration values of Si for the Callovo-Oxfordian argillite in conditions close to equilibrium. This implies that the quartz fraction in the geological disposal will be a key fraction and may compete with the dissolution of the nuclear glass waste.

From the results (Figures 1 – 3), the initial dissolution rates R_{diss} (mol Si/m²/s) were calculated between 0 and 25 days or 0 – 50 days depending on the clayey systems and the temperature. The results are presented in Table 1. The general observations show an increase of the dissolution rates with the temperature and the rate values for the Callovo-Oxfordian argillite are lower than that of illite and illite/smectite by 0.8 to 0.3 orders of magnitude. The dissolution rate values are almost similar between illite and illite/smectite at 35° and 50°C, while at 90°C the values are close for the three clays.

All the results indicate that the behavior of the dissolution of the Callovo-Oxfordian is a function of temperature. Illite and illite/smectite may not control the dissolution of the Callovo-Oxfordian argillite at low temperature but may influence at 90°C. At 35° and 50°C, other mineral phases such as kaolinite (for e.g.) may expect to be in competition with the two other clays.

In addition to the data collected on the concentration of Si measured in solution, aluminum and iron were measured in solution. The results are given in the 2nd annual workshop proceedings (***Bosbach et al. (2012)***).

Table 1: *Dissolution rates R_{diss} (mol Si/m²/s) illite/smectite, illite and Callovo-Oxfordian argillite (COx) at 35°, 50° and 90°C.*

	Log R_{diss} (mol Si/m²/s)		
	Illite	**Illite/smectite**	**COx**
35°C	-13.6	-13.4	-14.2
50°C	-13.5	-13.4	-13.7
90°C	-12.7	-13.1	-13.4

Isotopic exchanges.

Experiments of isotopic exchange were performed in all systems in which the stable isotope ^{29}Si was added in solution after 399 days of equilibrium between illite and solution, 483 days for illite/smectite and 326 days for Callovo-Oxfordian argillite. The results obtained for the interaction ^{29}Si with illite/smectite are detailed in this paper.

The Figure 4 shows the evolution of total Si-concentration in solution after addition of spike. At 35° and 50°C, the total Si-concentration remains constant indicating an equilibrium between illite/smectite and solution ($(1.4 \pm 0.1)\times10^{-4}$ mol/L (35°C and 50°C)), whereas at 90°C the addition of spike has disturbed the system with an increase of the concentration to stabilize at $(6.3 \pm 0.6)\times10^{-4}$ mol/L. This increase may stem from the increase of pH from 6.3 to 7.5 at 90°C related to pH of the ^{29}Si-spike solution while an increase of pH at 35° and 50°C to 7.5 was also measured.

The quantification of the mix isotopic ratio ^{29}Si/^{28}Si was determined in solution by HR-ICP-MS and the results are presented in Figure 6. The limit range of the isotope ratios is 0.05080 for the natural abundance and 2497.5 for the ^{29}Si-spike solution. Experimentally, the range of the mix isotopic ratio is 0.14046 (35°C) and 0.07684 (90°C) at the beginning and 0.10048 (35°C) and 0.06823 (90°C°) after 98 days of isotopic exchange. These values are to be compared with the IUPAC reference value of 0.0508. From this result, we notice that the mix isotopic ratios are close to the IUPAC reference which indicates a low disturbance of the system studied. Moreover, the mix isotopic ratios decrease against the time reaching a stable value higher than the IUPAC reference value. This indicates an exchange of Si between solid and solution. It may also mean that the isotopic ratio ^{29}Si/^{28}Si has reached a new value characteristic of the studied system. If this value came to evolve, it will take a long time to recover the reference value of natural ^{29}Si/^{28}Si isotopic ratio. The quantity of Si exchanged between illite/smectite and solution has been calculated. About 46% (35° and 50°C) and 35% (90°C) of Si have been exchanged and half of this quantity has been exchanged after 18 days. The Figure 6 presents the results.

Dissolution rates and precipitation rates were calculated on the base of the results given by the isotope ratios measurements. In particular, the dissolution rates have been calculated by taking into account the quantity of Si released from illite/smectite, and the precipitation rates have been calculated by considering the quantity of ^{29}Si-spike in solution. The results give dissolution rates of 7.83×10^{-15} mol Si/m²/s (35°C), 4.59×10^{-15} mol Si/m²/s (50°C) and 6.54×10^{-15} mol Si/m²/s (90°C) and precipitation rates of 3.89×10^{-15} mol Si/m²/s (35°C), 4.59×10^{-15} mol Si/m²/s (50°C) and 5.90×10^{-15} mol Si/m²/s (90°C). These values are in good agreement with the data of literature. Figure 7 reports the experimental data of the dissolution rates obtained from the Q-ICP-MS and HR-ICP-MS compared with the literature data. The results indicate that, for the case of illite/smectite, the dissolution rates values are in good agreement with literature data and the presence of quartz as accessory phase in clay mineral should not be neglected for the evaluation of the uncertainties in solubility value of clay minerals (***Suzuki et al. (2011)***). Dissolution rates calculated in conditions close to equilibrium as well as the effect of temperature give results less scattered than those calculated far from equilibrium (initial dissolution rates). Considering the dissolution rates vs. precipitation rates (Figure 8), the experimental results determined in this work are compared with those obtained in a previous work. On the base of the results obtained for the illite/smectite system, the data indicate that a dynamic equilibrium of dissolution/precipitation exists in the studied system with a dissolution rates slightly higher than the precipitation rates of about 1 order of magnitude.

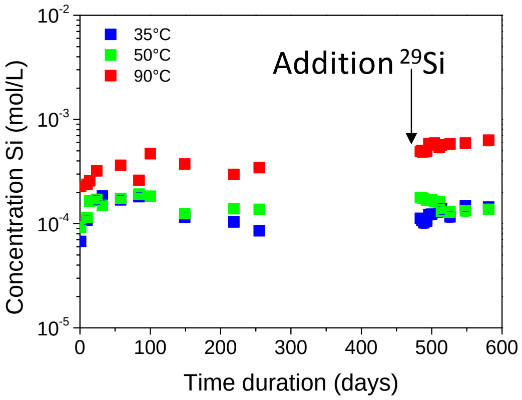

Figure 4*: Evolution of total-Si-concentration in solution in presence of ^{29}Si spike versus time for different temperatures (35°, 50°, and 90°C) for illite/smectite: m/V = 6.7 g/L, SA/m = 82.3 m²/g, NaCl 0.01 M, pH 7.5*

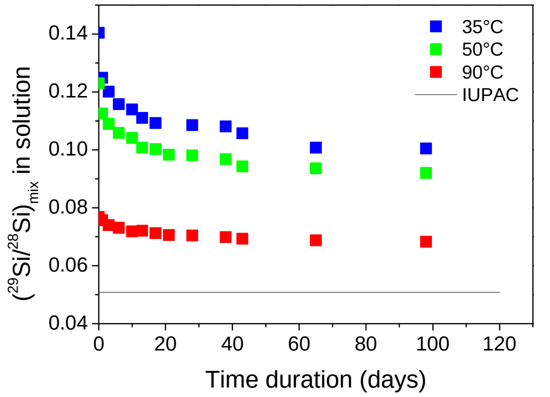

***Figure 5**: Evolution of the isotope ratio $^{29}Si/^{28}Si$ in solution versus time for different temperatures (35°, 50°, and 90°C) for illite/smectite: m/V = 6.7 g/L, SA/m = 82.3 m²/g, NaCl 0.01 M, pH 7.5. The straight line corresponds the natural isotope ratio taken as reference and determined by IUPAC (**IUPAC (1997)**).*

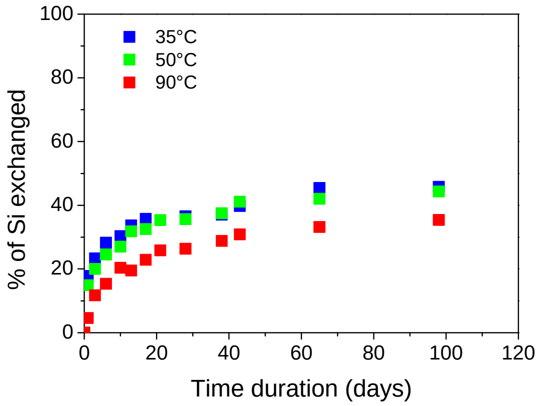

***Figure 6**: Evolution of the percent of Si exchanged between solid and solution versus time for different temperatures (35°, 50°, and 90°C) for illite/smectite: m/V = 6.7 g/L, SA/m = 82.3 m²/g, NaCl 0.01 M, pH 7.5*

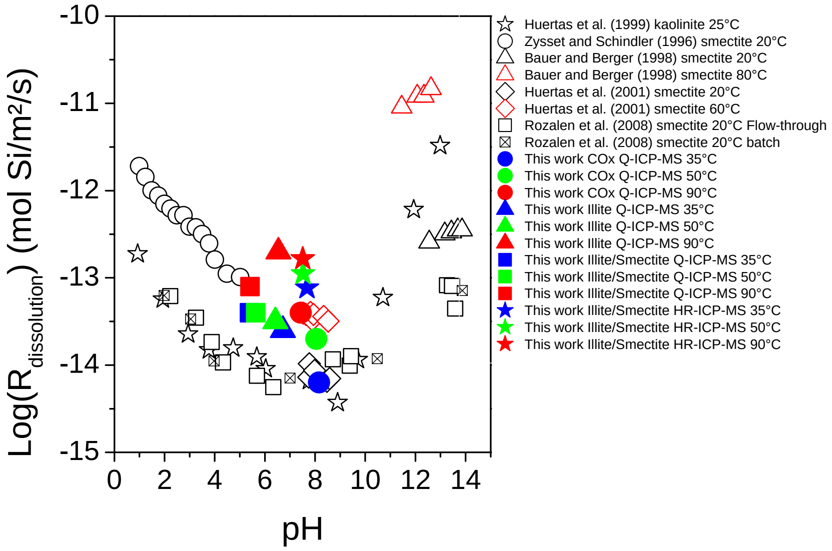

***Figure 7**: Comparison of the experimental dissolution rates determined by isotopic exchange and initial dissolution rates calculations versus pH with the literature data for different temperatures (35°, 50°, and 90°C) for illite/smectite, illite and Callovo-Oxfordian argilite: m/V = 6.7 g/L, NaCl 0.01 M.*

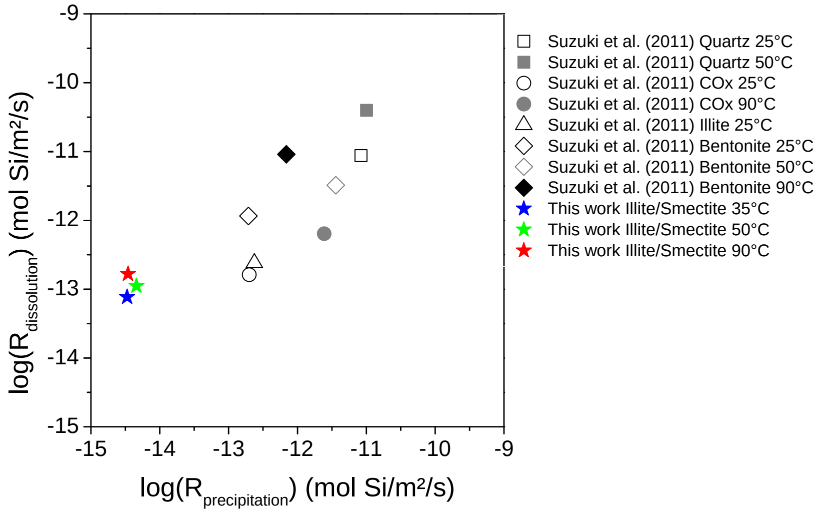

Figure 8*: Precipitation rates versus dissolution rates calculated by isotopic exchange of* ^{29}*Si/*^{28}*Si. Results compared with the dissolution/precipitation rates calculated by* ^{32}*Si/Si exchange (****Suzuki et al. (2011)****) for different temperatures for illite/smectite, illite, bentonite, quartz and Callovo-Oxfordian argilite, NaCl 0.01 M.*

Finally, distribution coefficient Kd was calculated according to the relation

$$\mathrm{K_d} = \left(\frac{\left({}^{29}\mathrm{Si}_{\mathrm{t=0}}\right) - \left({}^{29}\mathrm{Si}_{\mathrm{t=eq}}\right)}{\left({}^{29}\mathrm{Si}_{\mathrm{t=eq}}\right)}\right) \times \frac{\mathrm{V}}{\mathrm{m}}$$

where $\left({}^{29}\mathrm{Si}_{\mathrm{t=0}}\right)$ and $\left({}^{29}\mathrm{Si}_{\mathrm{t=eq}}\right)$ are the quantity of 29Si in solution at the beginning and the end of experiments, m (g) the solid mass, V (mL) the solution volume.

The experimental calculation gives distribution coefficient of 100 mL/g (35°C), 93 mL/g (50°C) and 44 mL/g (90°C) which are in the same order of magnitude with those given in literature (Kd 11–93 mL/g for Boom Clay (***De Cannière et al., (1998)***), Kd 500 mL/g for montmorillonite (***Tan (1982)***)). Although the Kd-values should increase with temperature, at 90°C the low value indicates the existence of a competition between the dissolution and precipitation of Si. As the results of the dissolution rates shown (Figure 5), the increase of the concentration of Si in solution may be correlated with the decrease of the Kd-values.

Characterization of the solids.

The characterizations by X-Ray diffraction of Callovo-Oxfordian argillite and illite were performed before and after purification of the clays, respectively. The method of purification by elutriation has allowed to remove 76% and 63% of quartz fraction from the the Callovo-Oxfordian argillite and illite, respectively. For the illite/smectite, almost 100% of the quartz fraction has been removed. This method has not completely removed all quartz fraction although sonification has been used to separate the secondary mineral phases from the clayey materials. This method has not allowed the complete removal of the quartz phase but it’s a compromise between the decrease as much as possible of the quantity of quartz phase and the preservation of the structure of the clays. The granulometry of the clays after purification give a median diameter of particles of 1.0 ± 0.1 µm. The detailed results are showed in the second annual workshop proceedings (***Bosbach et al. (2012)***). The XRD-patterns of illite and Callovo-

Oxfordian argillite after 559 days of experiments and 643 days of experiments for illite/smecte do not show structural modification compared with the initial solid.

The binding energies of A12p (E_b 74.7 (1.7) eV), Si2p (E_b 103.0 (1.7) eV) and Ols (E_b 532.0 (2.1) eV) peaks were found to be similar for both the initial, altered and ^{29}Si exchanged illite/smectite, suggesting that no significant interaction between the surface and the solution occurred after 538 days of contact or 52 days of contact with ^{29}Si tracer. The binding energy position of the Ols peak was nearly the same in both spectra obtained. The experimental value obtained is likely due to oxygen ions in the strongly bound water of the interlayer cations (***Moulder et al. (1993)***). Finally, the carbon peak, Cls, was due to carbon contamination in XPS measurements and was observed in every spectrum obtained. Ratio of Al/Si was calculated from the quantitative data obtained by XPS. The results give a ratio of 0.36 for both initial and altered illite/smectite at 35°, 50° and 90°C. This value is in good agreement with the literature data (montmorillonite (***He et al. (2007)***) confirming the weak change of the chemical environment of Si and Al against the temperature and the alteration duration. Complementary analyses by ^{29}Si-NMR will give additional data on the chemical environment of silicon in solids.

3. Conclusions and final work

The dissolution of illite, illite/smectite and Callovo-Oxfordian were perfomed at 35°, 50° and 90°C in NaCl 0.01 mol/L solution in batch system. Concentrations of Si, Fe and Al were measured in solution with a strong influence of temperature on the release rates and the maximum concentration in solution. The dissolution behaviour of the Callovo-Oxfordian argillite could be explained by the dissolution of the various mineral phases existing in argillite. Less than 90°C, mineral phases such as kaolinite and/or muscovite could influence the dissolution behaviour whereas at temperature higher than 90°C, illite and/or illite/smectite may control the dissolution of the argillite. The efficiency of the purification of clayey materials allows to consider that the quartz fraction is present in the minerals as impurities. The concentrations of Si measured in the experiments are lower than the solubility of quartz. This indicates that the influence of the quartz fraction contained in the clayey materials is neglectable in this study.

In this proceeding, the results of ^{29}Si/^{28}Si isotopic exchange between illite/smectite and solution have been shown and compared with literature data. The main results indicate a dynamic exchange between the clay mineral and solution with a dissolution rates higher of 1 order of magnitude than the precipitation rates. About 40% of the initial ^{29}Si spike solution has been exchanged with illite/smectite after 98 days and half of it have been exchanged after 18 days of contact. The results will be compared in the final work with the data from the isotopic exchange experiments in presence of illite and Callovo-Oxfordian argillite.

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4. References

ANDRA (2005). Dossier ANDRA argile: Evaluation de la faisabilité du stockage géologique en formation argileuse

Bauer, A. and Berger, G. (1998). Kaolinite and smectite dissolution rate in high molar KOH solutions at 35° and 80°C. Applied Geochemistry, 13, 905–916

Bergaya, F., Theng, B.K.G., Lagaly, G. (2006). Handbook of Clay Science, Developments in Clay Science. Elsevier, Amsterdam

Bosbach D., F. Brandt, L. Duro, B. Grambow, D. Kulik, T. Suzuki-Muresan (2013). 2nd Annual Workshop Proceedings (SKIN project), 7th EC FP - SKIN, 21th - 22th November 2012 Villigen PSI, ed. Institut für Energie- und Klimaforschung, Nukleare Entsorgung und Reaktorsicherheit (IEK-6), July 2013, ISSN 0944-2952.

De Cannière, P., Moors, H., Dierckx, F., Gasiaux, F., Aertsens, M., Put, M., Van Iseghem, P. (1998). Diffusion and Sorption of ^{32}Si-labelled silica in the boom clay. Radiochimica Acta, 82, 191–196

Daux, V., Guy, C., Advocat, T., Crovisier, J.-L., Stille, P. (1997). Kinetic aspects of basaltic glass dissolution at 90°C: role of aqueous silicon and aluminium. Chemical Geology, 142, 109–126

Ganor, J., Mogollón, J.L., Lasaga, A.C. (1995). The effect of pH on kaolinite dissolution rates and on activation energy. Geochimica Cosmochimica Acta, 59, 1037–1052

Gaucher, E., Robelin, C., Matray, J.M., Négrel, G., Gros, Y., Heitz, J.F., Vinsot, A., Rebours, H., Cassagnabère, A., Bouchet, A. (2004). ANDRA underground research laboratory: interpretation of the mineralogical and geochemical data acquired in the Callovian-Oxfordian formation by investigative drilling. Physics and Chemistry of Earth, Parts A/B/C 29, 55–77

Gorski, C.A., Handler, R.M., Beard, B.L., Pasakarnis, T., Johnson, C.M., Scherer, M.M. (2012) Environ. Sci. Technol., 46, 12399−12407

Handler, R.M., Beard, B.L., Johnson, C.M., Scherer, M.M. (2009). Atom exchange between aqueous Fe(II) and goethite: an Fe isotope tracer study. Environ. Sci. Technol., 43, 1102–1107

He, H., Q. Zhou, R. L. Frost, B. J. Wood, L. V. Duong and J. T. Kloprogge (2007). A X-ray photoelectron spectroscopy study of HDTMAB distribution within organoclays Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 66(4-5): 1180-1188.

Huertas, F.J., Caballero, E., Jiménez de Cisneros, C., Huertas, F., Linares, J. (2001). Kinetics of montmorillonite dissolution in granitic solutions. Applied Geochemistry, 16, 397–407

IUPAC (1997). Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford

Köhler, S.J., Dufaud, F., Oelkers, E.H. (2003). An experimental study of illite dissolution kinetics as a function of ph from 1.4 to 12.4 and temperature from 5° to 50°C. Geochimica Cosmochimica Acta, 67, 3583–3594

Lutterotti L. (2000). MAUD program, CPD, Newsletter (IUCr) No. 24. 2000, http://www.ing.unitn.it/~maud/.

McHale J.M., Auroux A., Perrotta A.J., Navrotsky A. (1997). Science, 1997, 277, 788.

Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D. (1993). in: J. Chastain, R.C. King, Jr. (Eds.), Handbook of X-ray Photoelectron Spectroscopy, Physial Electronics, Inc.

Palandri, J.L. and Kharaka, Y.K. (2004). A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modelling, US GEOLOGICAL SURVEY

Rozalén, M., Huertas, F.J., Brady, P.V. (2009). Experimental study of the effect of pH and temperature on the kinetics of montmorillonite dissolution. Geochimica Cosmochimica Acta, 73, 3752–3766.

Suzuki-Muresan, T., et al. (2011). Solution controls for dissolved silica at 25°, 50° and 90°C for quartz, Callovo-Oxfordian claystone, illite and MX80 bentonite. Physics and Chemistry of the Earth, Parts A/B/C 36(17-18): 1648-1660

Tan, K.H. (1982). The effect of interaction and adsorption of silica on structural changes in clay minerals. Soil Sci. 136, 300–307.

van den Boorn, S. H. J. M., P. Z. Vroon, C. C. van Belle, B. van der Wagt, J. Schwieters, M. J. van Bergen (2006). Determination of silicon isotope ratios in silicate materials by high-resolution MC-ICP-MS using a sodium hydroxide sample digestion method. Journal of Analytical Atomic Spectrometry, 21(8): 734-742