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Hydrothermal reactivity of K-smectite at 300°C and 100 bar: dissolution-crystallization process and non-expandable dehydrated smectite formation

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ABSTRACT: The hydrothermal reactivity of a smectite saturated with K was studied experimentally at 300°C and 100 bar in (Na,K) chloride solutions (Na/K = 0, 50 and 100, liquid/solid ratio = 10/1). X-ray diffraction, TEM and microprobe results show: (1) a partial to total dissolution of the initial smectite layers; and (2) the crystallization of newly-formed euhedral I-S. Random I-S is formed after 7 days, but an ordered mixed-layer I-S containing <30% expandable layers formed in the longest runs (112 days). The I-S is characterized by non-expandable layers of two distinct types: dehydrated smectite and illite. The Si content is lower in the I-S than in the initial smectite, thus creating a charge deficit, mostly compensated by the introduction of Na to the interlayer space, and yielding a silica release to the solution and subsequent crystallization of quartz and cristobalite.

Mixed-layer minerals such as illite-smectite (I-S) are very common in geologic environments. Their formation through illitization of smectite, in relation to increasing burial depth and temperature, has been extensively studied in sedimentary basins (Perry & Hower, 1970; Weaver & Beck, 1971; Hower *et al.*, 1976; Boles & Franks, 1979; Hoffman & Hower, 1979; Nadeau & Reynolds, 1981). However, recent studies have demonstrated that the illitization process is more complex than previously described. Experimental works by Eberl & Hower (1976), Roberson & Lahann (1981), Inoue (1983), Inoue *et al.* (1988), Howard & Roy (1985), Whitney & Northrop (1988), Whitney (1990, 1992), Huang *et al.* (1993), and by Cuadros & Linares (1995) have shown that several chemical and physical factors such as temperature, time, reacting fluid compositions, nature of smectite interlayer cations and rock/

water ratio may affect the course and the rate of reaction.

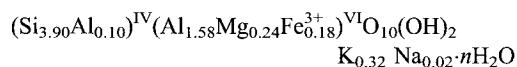
Smectite and smectite-rich rocks have been selected for nuclear waste disposal purposes as potential buffer materials (Pusch, 1978, 1980; Bird, 1979; Bird & Cameron, 1982) because of their ability to fill space between the waste canister and the host rock and to ensure an efficient permeability barrier against the incoming groundwaters. Smectite exhibits good adsorption and fixation capacities which are essential for the retardation of the eventual radionuclide migration. However, the long-term stability of the smectites under waste package conditions, e.g. under temperatures close to 100°C near the waste canister contact, under a pressure range of 50 to 100 bar corresponding to hydrostatic pressure within the 500–1000 m depth, and under solution chemistries of natural ground-

waters, is poorly documented. Most experimental works have been carried out under much higher P conditions than those expected for waste disposals, because most of them deal with the smectite–illite transition in sedimentary basins, and frequently with rather extreme solution chemistry (e.g. high K availability, to enhance illite formation).

Preliminary experiments carried out on three homoionic smectites (K , Na , Ca) under 300°C and low pressure (100 bar) have shown that the K -smectite was far more reactive than the two other end-members (Cathelineau *et al.*, 1993). In order to evaluate the maximal changes which could affect smectites, a detailed experimental study of K -smectite reactivity has been carried out under the same conditions. The main objective was to determine the nature of the mineralogical changes and to assess the effect of several variables such as fluid composition (using Na/K ratio close to those of natural fluids) and time on the rate and extent of smectite transformation. The originality of this study lies in combining the determination of the expandability of I-S by XRD, and detailed examination of the clay chemistry using TEM and microprobe analysis.

MATERIALS

The starting material was the $<2\ \mu\text{m}$ fraction of the Wyoming bentonite (SWY-1) from the Source Clay Minerals Repository collection, purified by removal of quartz and feldspar impurities and saturated with K by stirring in 1 M KCl for 72 h, followed by washing until the supernatant was chloride free. The latter procedure was chosen as saturation of the interlayer space using a common exchange process (in open systems with renewal of the solution) results systematically in alteration of the crystal chemistry of the smectite, in particular causing significant differences in the octahedral site occupancy (loss of Mg due to smectite hydrolysis (Boutiche, 1995)). The K -smectite exhibits a thickness of $16.9\ \text{\AA}$ when treated with glycol. From microprobe analyses, the structural formula of the K -smectite is:



Trace contents of the original interlayer cation (Na) are present in the initial smectite due to slightly incomplete exchange in the interlayer in the moderate conditions chosen for the exchange.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The experimental conditions are listed in Table 1. To enhance reaction rate, the temperature was fixed at $300 \pm 2^\circ\text{C}$ with the liquid/clay mass ratio (L/C) equal to 10/1, and water pressure maintained at 100 ± 5 bar, which keeps the fluids in a liquid state. The compositions of the solutions were chosen to simulate some important parameters (Na/K ratio, dominant chlorine feature, ionic strength) of natural interstitial fluids found in the Callovian-Oxfordian and Toarcian sedimentary layers of the Paris Basin. The solutions are chlorine solutions with a Na/K atomic ratio of 50 and 100 (and in some solutions, 0), and a K concentration of 100 or 300 ppm.

The hydrothermal experiments were conducted using standard cold seal vessels in horizontal resistance furnaces equipped with temperature controllers. For each run, 20–30 mg of smectite were placed in a gold capsule with 200–300 μl of the solution. After hydrothermal treatment, the vessel was placed in a vertical position and the capsule allowed to slide in the cooled part of the vessel maintained at 25°C by a constant water flow (quench).

The capsules were then cut open and the solid sample removed, washed until chloride free, dispersed in a small volume of water and transferred to a glass slide or a pure carbon slide. Each run product was dried and oriented ready to be analysed by X-ray diffraction (Jobin Yvon diffractometer, Cu anticathode, $K\alpha$ radiation), or using a Camebax-Cameca Electron Microprobe (diameter of the investigated area: $3 \pm 1\ \mu\text{m}$, analytical conditions: 10 kV, 4 to 6 nA; correction program: ZAF Cor2; and maximum analytical error: 3% of the total). Selected samples were also observed and analysed using transmission electron microscopy (JEOL JEM 2000 FX instrument operating at 200 kV) at the CRMC2-CNRS laboratory in Marseille (France). Microchemical analyses of clay particles were carried out using an EDAX energy dispersive X-ray analyser. Spectra were collected for 100 s from an area $\sim 1200\ \text{\AA}$ in diameter. Elemental composition x/Si ($x \geq \text{Na}$) was calculated assuming thin film criteria (SMTF program: semiquantitative metallurgical thin film program) and by calibration with independently analysed macroscopic micas.

The proportions of illite and smectite layer types were determined by comparison with calculated

TABLE 1. Experimental conditions and percentages of non-expandable layers of the run-products estimated from X-ray patterns of glycolated samples.

Time (days)	Composition of the initial chloride solution		Na/K 1-S	% non-smectite expandable layer in
	Na (ppm)	K (ppm) (atomic ratio)		
7	0	100	0	70 (o)
7	0	300	0	75 (o)
28	0	100	0	77 (o)
28	0	300	0	85 (o)
2	8820	300	50	32 (r)
7	2940	100	50	46 (r)
7	8820	300	50	50 (r)
28	2940	100	50	64 (o)
28	8820	300	50	64 (o)
112	2940	100	50	77 (o)
				+q+cr
112	8820	300	50	80 (o)
				+q+cr+chl
7	5880	100	100	55 (r)
7	17638	300	100	40 (r)
28	5880	100	100	64 (r)
28	17638	300	100	60 (r)

(o): ordered interstratification, (r): random interstratification. Other phases: q (quartz), cr (cristobalite), chl (chlorite).

XRD patterns using the computer program NEWMOD (Reynolds, 1980, 1985).

RESULTS AND DISCUSSION

The reactivity of K-smectite with time, in different solutions, was quantified using XRD and chemical data.

XRD data

The XRD results show that K-smectite transforms into several types of interstratified I-S (Table 1). A random interstratification is the most frequently found for the highest Na concentrations used for the experimental solution (Na/K = 100, K = 100 or 300 ppm), and for the shortest durations. For experiments with solutions containing only K or for the longest durations of treatment (28 and 112 days), the I-S displays an ordered interstratification of the layers. The percentage of non-expandable layers is often high in these cases (>60%). Thus, the occurrence of several types of interstratified I-S as a function of reaction time suggests a complex initiation of the reaction of illitization.

Influence of K availability and Na/K ratio. The effects of K-concentration and Na/K ratio on the rate of K-smectite reaction into I-S are shown in Fig. 1a,b,c.

In a solution containing 100 ppm of K as KCl and devoid of Na (Na/K = 0), K-smectite transforms into ordered I-S with high percentages of non-expandable layers (>60%). Increasing the amounts of K (300 ppm) in the experimental solution has little effect (<10%) on the proportion of non-expandable layers in the I-S. These results indicate that the illitization reaction has a low sensitivity to moderate changes in the K availability if the starting smectite is K saturated and the amount of K sufficient for the reactions. These results are rather different from those obtained in KCl solutions by Whitney (1992) on a bentonite standard at 300°C, 1 Kb and with L/C = 1 (Fig. 1a). Thus, in our study at 100 bar and with a liquid/clay ratio of 10, the amount of non-expandable layers is significantly greater (~ +20% to +40% depending on the considered K availability in Whitney's experiments). The lower pressure or the higher liquid/clay ratio may be the cause of the increased reaction rate, as well as the interlayer occupancy of the starting smectite.

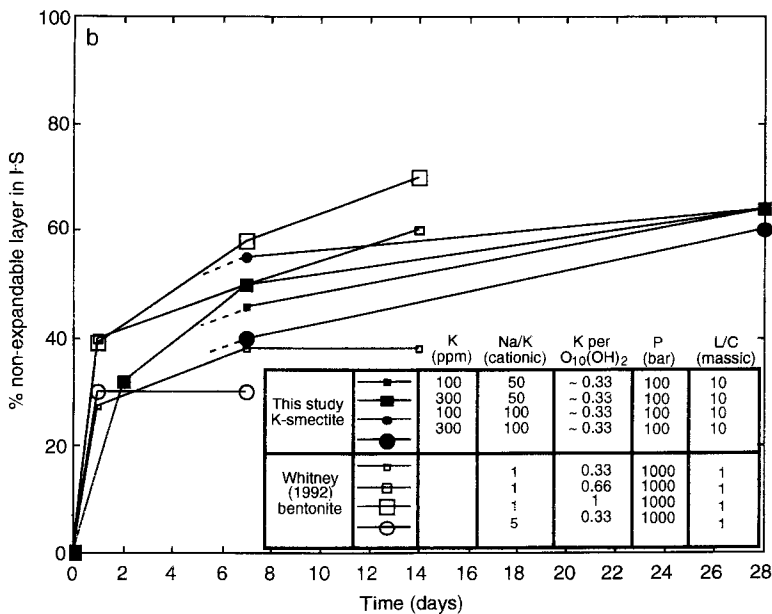
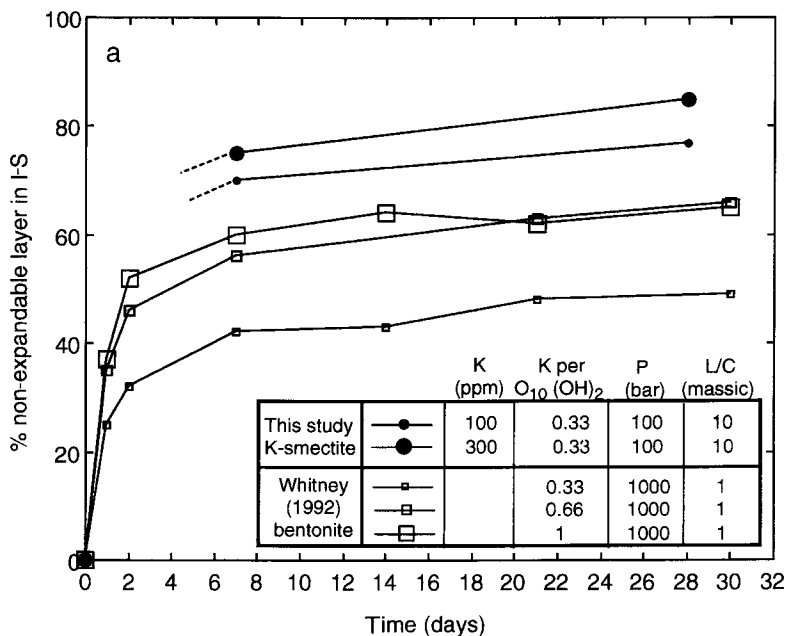


FIG. 1. Content of non-expandable layers in the interstratified 'illite'-smectite run-products (I-S) formed after treatment of the K-smectite at 300°C and 100 bar: (a) in KCl solutions, plus a comparison with results obtained on Wyoming bentonite in KCl solutions from Whitney (1992); (b) in NaCl-KCl solutions, plus comparison with results obtained on Wyoming bentonite in NaCl-KCl solutions from Whitney (1992); (c) (*opposite*) up to 112 days, in NaCl-KCl solutions plus comparison with results obtained on Smectite-K in pure water from Whitney & Northrop (1988).

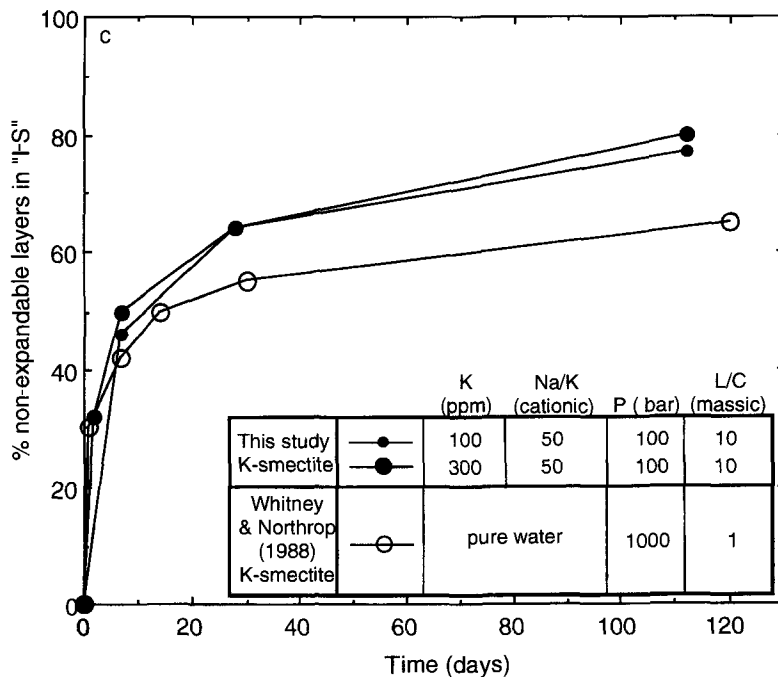


FIG. 1c.

In Na-K solutions, the reaction rates are decreased (Fig. 1b) as the amount of the non-expandable layers in the I-S is lower (~20% non-expandable layers) than in the KCl solutions. In addition, at $t = 7$ days the percentages of non-expandable layers show slight differences as a function of the initial Na concentration, and are the lowest in solutions richer in Na. However, after 28 days, whatever the Na concentration in solutions, they are $\sim 60 \pm 5\%$, and after 112 days $\sim 80\%$ whatever the initial K concentration in solution.

Results show that in Na-K solutions, the reaction rates are increased with respect to experiments conducted with pure water such as those carried out by Whitney & Northrop (1988) on K-smectite (Fig. 1c).

Kinetics of transformation. The advancement of the reaction, as defined by the percentage of the non-expandable layers in the I-S (Fig. 1a,b), depends, to a small extent, on the K concentration, but mostly on the Na/K ratio. Thus, the presence of Na inhibits the illitization reaction, thereby confirming the results of Whitney & Northrop (1988) and Whitney (1992). However, results obtained for Na/K ratios close to those found in nature (50, 100) indicate that the inhibiting effect of

Na at 300°C is moderate, as the amount of the non-expandable layers in the I-S obtained after 118 days' experiment for Na/K solutions (around 80%) is rather close to those found for K solutions after 28 days' experiment. Thus, in both cases, after 118 days' experiment, an I-S, rather rich in non-expandable layers is found.

If the reaction is a first-order one, it satisfies the differential equation:

$$dX/dt = KX \quad (1)$$

where X is the percent of non-expandable layers/100, t is time and K is kinetic constant. The kinetic equation calculated for a ratio Na/K of 50 and 300 ppm of K in the starting solutions, is the following: $y = 100(1 - \exp(-0.33x^{0.34}))$. Time calculated for a total transformation of smectite into 'illite' (or mineral composed of non-expandable 10 Å layers) range from 2 to 4 years, for 95% to 98% yield.

TEM observations

The I-S products display flakes with island-and-step patterns indicative of a dissolution-precipitation process (Fig. 2c). In the longest run, the initial

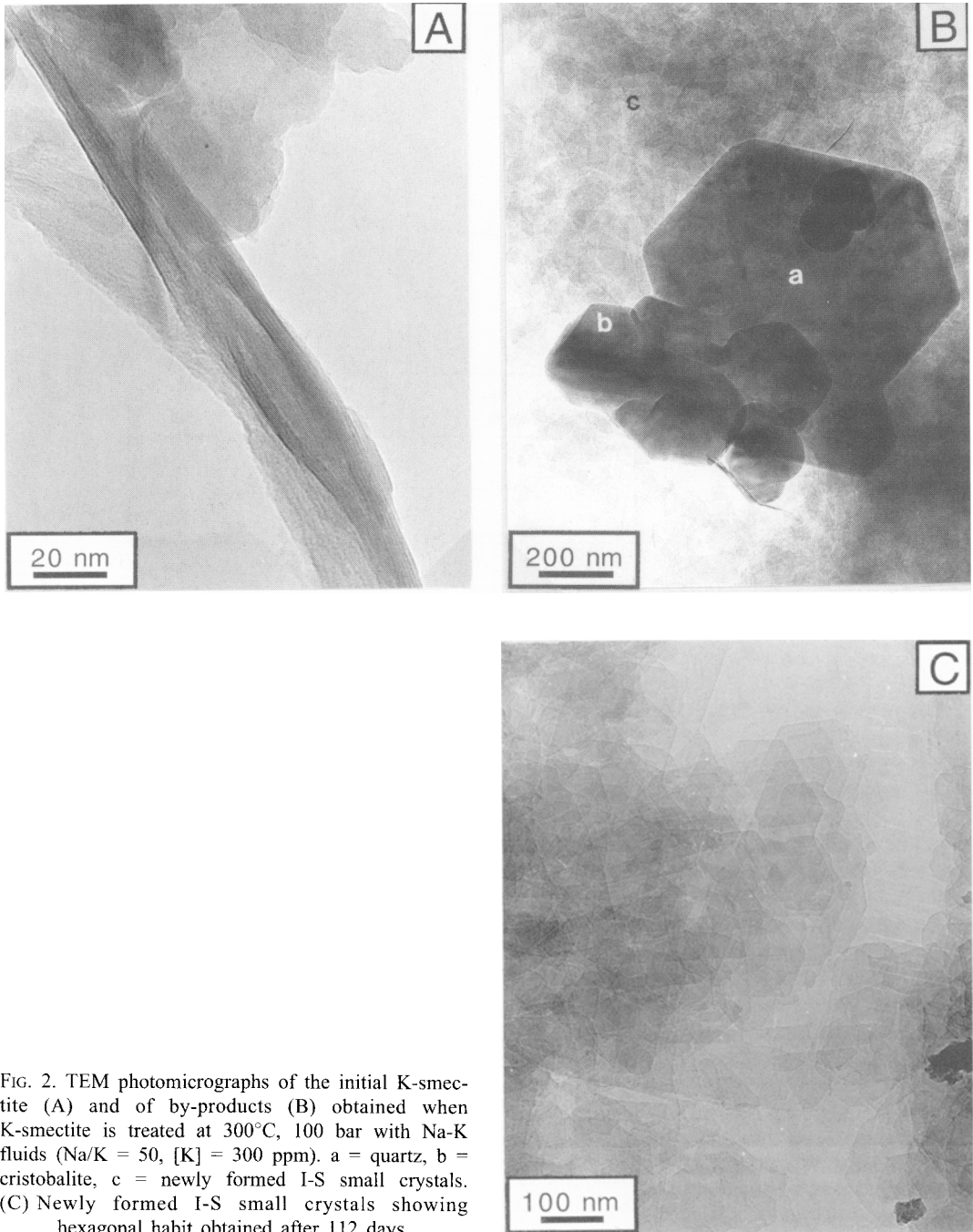


FIG. 2. TEM photomicrographs of the initial K-smectite (A) and of by-products (B) obtained when K-smectite is treated at 300°C, 100 bar with Na-K fluids (Na/K = 50, [K] = 300 ppm). a = quartz, b = cristobalite, c = newly formed I-S small crystals. (C) Newly formed I-S small crystals showing hexagonal habit obtained after 112 days.

smectite flakes (long rolled-up flakes of a few hundred nm in length, Fig. 2a) are absent from the experimental end-products. Newly-formed plates of I-S, 50 to 100 nm in width, and displaying a

polygonal habit are observed in place of the initial smectites (Fig. 2c). The I-S plates display, in some instances, a geometric arrangement (complex pseudohexagonal textures) similar to the figures

identified during experimental growth of micas (Baronnet *et al.*, 1976).

In addition to the production of I-S, the major by-products are quartz and cristobalite (high-temperature form), and are especially observed for the longest runs when K-smectite is treated with a Na-K fluid. Quartz displays sub-hexagonal crystals of variable width, ranging from 100 to 600 nm (Fig. 2), scattered within the I-S plates.

Microchemical data

The initial and final materials were analysed using a CAMEBAX microprobe, following appropriate preparation of the sample and suitable measuring conditions (Debrabant *et al.*, 1985). Formulae calculated on a basis of 10 oxygens and 2 OH, from microprobe analysis in wt%, are listed in Table 2. Total iron is converted to Fe³⁺.

The run-products obtained after experiments on K-smectite in Na-K solution (Na/K = 50, [K] = 300 ppm), e.g. the solution having the Na/K ratio closest to the natural Na/K ratios have been analysed by electron microprobe.

The run-products display a decrease in Si(IV) correlated to an increase of the interlayer charge (Na+K+2Ca), except for the 2 day experiment (Fig. 3a) for which the apparent interlayer charge decrease could be interpreted as a consequence of partial K⁺-H₃O⁺ exchange, a frequent process in hydrolysis reactions of smectites. For durations of 7 days and 28 days, the Si (IV) decrease is low (-0.03 to -0.06) but for the 112 day experiments, the Si content decreases more significantly.

The octahedral site occupancy of I-S run-products shows little change whatever the experiment duration (Table 2). The mean values are 0.25 ± 0.01 for Mg, 0.17 ± 0.02 for Fe³⁺ (Fig. 3b) and 1.56 ± 0.02 for Al_{V1} (Table 2). The slight Fe increase in the 2 day and 7 day run-products is linked to the presence of trivalent iron oxides (observed by SEM), which are intimately associated with the I-S and analysed together. These oxides seem to represent temporary mineralogical phases which have not been observed during longer experiments.

In the interlayer space (Fig. 3c), K⁺ is partially replaced by Na⁺ from the solution. The interlayer charge increases progressively with time. In all cases, the increase in the interlayer charge by incorporation of Na⁺ and K⁺ balance sufficiently the tetrahedral substitutions. The octahedral occupancy remains stable, this being explained in part

by the lack of electric unbalance due to the tetrahedral/interlayer substitutions, but also by the incorporation of the same amount of Al, Fe and Mg in the octahedral sites of the I-S.

Figures 3a and 3b compare microprobe data with mean values and standard deviations of Si, Fe and Mg deduced from analyses obtained by TEM, listed in Table 3. As Na and K concentrations were not determined quantitatively by this method, the total interlayer charge of the structural formula was calculated by difference between the layer charge (tetrahedral and octahedral) and the total charge of 22. These graphs display a good agreement between microprobe and TEM analyses, in particular for Si and Fe. The slight overestimation in Si(IV) content sometimes obtained by microprobe is probably linked to the presence of newly-formed quartz crystals (a few hundred nm), frequently observed by TEM within the run-products. Magnesium is overestimated by TEM, probably because of interference between the Mg and Al spectral lines.

Comparison of the chemical analysis and XRD data

The microprobe analyses of the I-S run-products have shown that the transformation of the K-smectite into I-S proceeds through very slight modifications of the octahedral composition (Table 2). Accordingly, the transformation of K-smectite into I-S would involve only Si⁴⁺-Al³⁺ substitutions in the tetrahedral sites, thus creating a positive charge deficiency compensated by the introduction of Na and K in the interlayer space. Therefore, the expandable layers in I-S remain low-charge smectites, and do not involve high-charge smectites which are necessarily characterized by higher R²⁺ octahedral occupancy and Si contents. If non-expandable layers in the I-S have an interlayer charge of 0.87 — a value close to those defined by Eberl & Środoń (1988) or by Meunier & Velde (1989) — and the same octahedral composition as the initial K-smectite, their tetrahedral Si content is 3.37 Si (in respect to electric balance), similar to the value determined by Meunier & Velde (1989).

Using the percentages of non-expandable layers, calculated using NEWMOD, and assuming that: (1) they are of illite type with 3.37 Si per O₁₀(OH)₂ and an interlayer charge of ~0.87; and (2) the expandable layers of the I-S have the same composition as the initial ones (3.91 Si and an interlayer charge of 0.35), it is possible to calculate

TABLE 2. Half-structural formulae ($O_{10}OH_2$) calculated from microprobe analyses for run-products obtained after treatment of the K-smectite under 300°C and 100 bar in a mixed Na-K fluid (Na/K = 50, [K] = 300 ppm).

	Si	Al (IV)	Al (VI)	Fe ³⁺	Mg	Mn	Ca	Na	K	Ti	Interlayer charge	
K-Sm	3.90	0.10	1.58	0.16	0.26	—	—	0.03	0.32	—	0.35	
	3.91	0.09	1.56	0.18	0.23	—	—	—	0.39	—	0.39	
	3.88	0.12	1.58	0.18	0.25	—	—	0.02	0.31	—	0.33	
	3.90	0.10	1.59	0.16	0.24	—	—	0.03	0.32	—	0.35	
	3.88	0.12	1.59	0.18	0.24	—	—	—	0.32	—	0.32	
	3.90	0.10	1.59	0.16	0.24	—	—	0.03	0.30	—	0.34	
	3.89	0.11	1.58	0.18	0.23	0.01	—	0.03	0.32	—	0.36	
	3.91	0.09	1.56	0.18	0.27	—	—	0.02	0.31	—	0.33	
	3.89	0.11	1.53	0.21	0.24	—	0.01	0.02	0.34	0.01	0.37	
	3.92	0.08	1.58	0.18	0.24	—	0.01	0.01	0.28	—	0.31	
	3.91	0.09	1.57	0.18	0.22	—	0.01	0.02	0.32	0.01	0.36	
	Mean	3.90	0.10	1.58	0.18	0.24	—	—	0.02	0.32	—	0.35
	Standard deviation	0.01	0.01	0.02	0.01	0.01	—	—	0.01	0.03	—	0.02
2 days	3.87	0.13	1.55	0.20	0.28	—	—	0.08	0.21	0.01	0.30	
	3.88	0.12	1.57	0.20	0.26	—	—	0.08	0.19	—	0.28	
	3.89	0.11	1.59	0.20	0.24	—	—	0.06	0.19	—	0.25	
	3.90	0.10	1.59	0.19	0.24	—	0.01	0.09	0.16	0.01	0.28	
	3.90	0.10	1.54	0.22	0.24	—	0.03	0.11	0.12	0.02	0.27	
	3.87	0.13	1.56	0.19	0.23	—	0.01	0.08	0.18	0.03	0.27	
	3.88	0.12	1.55	0.23	0.26	—	0.01	0.11	0.12	—	0.24	
	3.87	0.13	1.56	0.21	0.24	0.01	0.00	0.08	0.18	0.01	0.26	
	3.91	0.09	1.55	0.23	0.25	—	—	0.07	0.16	0.01	0.24	
	3.88	0.12	1.53	0.23	0.25	0.01	0.01	0.08	0.21	—	0.32	
	Mean	3.89	0.11	1.56	0.21	0.25	—	0.01	0.08	0.17	0.01	0.27
	Standard deviation	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.03	0.01	0.02
	7 days	3.89	0.11	1.54	0.19	0.23	—	0.01	0.24	0.22	—	0.48
3.86		0.14	1.56	0.18	0.21	—	0.01	0.21	0.23	0.01	0.47	
3.83		0.17	1.52	0.21	0.25	—	0.01	0.22	0.24	—	0.47	
3.84		0.16	1.52	0.22	0.24	—	0.01	0.20	0.22	—	0.44	
3.86		0.14	1.56	0.18	0.24	—	—	0.19	0.22	—	0.42	
3.90		0.10	1.56	0.16	0.22	—	—	0.23	0.23	—	0.48	
3.87		0.13	1.54	0.20	0.24	—	0.01	0.21	0.23	—	0.45	
3.84		0.16	1.57	0.16	0.26	—	—	0.23	0.19	—	0.41	
3.89		0.11	1.57	0.17	0.24	—	—	0.17	0.23	—	0.40	
3.86		0.14	1.57	0.17	0.25	—	0.01	0.17	0.22	0.01	0.41	
3.89		0.11	1.54	0.19	0.26	—	—	0.17	0.22	—	0.40	
3.87		0.13	1.50	0.25	0.23	—	—	0.20	0.22	—	0.42	
3.87		0.13	1.58	0.15	0.25	0.01	0.01	0.16	0.21	0.01	0.39	
3.89	0.11	1.58	0.16	0.24	—	0.01	0.16	0.21	—	0.39		
Mean	3.87	0.13	1.55	0.19	0.24	—	0.01	0.20	0.22	—	0.43	
Standard deviation	0.02	0.02	0.02	0.03	0.01	—	—	0.03	0.01	—	0.03	

the Si contents in I-S run-products. The results show that calculated Si contents are lower than those obtained by the microprobe analyses (Fig. 4, open triangles). This indicates that another type of

non-swelling layer, richer in Si and diffracting as illite, is present. According to Ransom & Helgeson (1994), partially dehydrated K-smectites generate XRD patterns similar to those of randomly

Table 2 (continued)

	Si	Al (IV)	Al (VI)	Fe ³⁺	Mg	Mn	Ca	Na	K	Ti	Interlayer charge
28 days	3.82	0.18	1.57	0.17	0.23	—	0.03	0.13	0.28	0.01	0.47
	3.82	0.18	1.58	0.17	0.24	—	0.03	0.16	0.24	—	0.47
	3.82	0.18	1.55	0.19	0.26	—	0.03	0.11	0.26	—	0.44
	3.84	0.16	1.53	0.17	0.25	0.01	0.04	0.20	0.25	0.01	0.53
	3.80	0.20	1.55	0.16	0.27	0.01	0.04	0.15	0.27	—	0.50
	3.82	0.18	1.56	0.16	0.25	—	0.03	0.16	0.27	0.01	0.50
	3.81	0.19	1.55	0.18	0.27	—	0.03	0.13	0.27	—	0.46
	3.83	0.17	1.57	0.16	0.25	—	0.02	0.16	0.28	—	0.48
	3.82	0.18	1.53	0.20	0.25	—	0.04	0.15	0.29	—	0.51
	3.85	0.15	1.57	0.17	0.26	—	0.02	0.11	0.25	—	0.41
Mean	3.82	0.18	1.56	0.17	0.25	—	0.03	0.15	0.27	—	0.48
Standard deviation	0.01	0.01	0.02	0.01	0.01	—	0.01	0.02	0.01	—	0.03
112 days	3.74	0.26	1.58	0.19	0.24	—	0.02	0.10	0.32	—	0.45
	3.74	0.26	1.55	0.19	0.27	—	0.02	0.09	0.33	—	0.47
	3.78	0.22	1.57	0.15	0.27	—	0.02	0.12	0.32	—	0.48
	3.78	0.22	1.57	0.16	0.27	—	0.03	0.10	0.31	0.01	0.46
	3.77	0.23	1.60	0.16	0.23	—	0.02	0.10	0.30	0.01	0.45
	3.73	0.27	1.60	0.16	0.26	—	0.01	0.12	0.33	—	0.47
	3.75	0.25	1.60	0.15	0.23	—	0.02	0.11	0.35	0.01	0.51
Mean	3.75	0.25	1.58	0.17	0.25	—	0.02	0.11	0.33	—	0.47
Standard deviation	0.02	0.02	0.02	0.02	0.02	—	0.00	0.01	0.01	—	0.02

interstratified mixed-layer clays. So, we propose that among non-expandable layers of the I-S run-products, there are dehydrated smectites (with Si_{3.91}) which have the same XRD response as illite layers.

Despite the observations of Whitney & Northrop (1988) that the non-expandable layers can re-expand after Na saturation, non-expandable layers are generally considered as illite. Therefore, it appears particularly interesting to evaluate among the non-expandable layers, the amount of true 'illite' and dehydrated smectites, by a means other than XRD. Using microprobe analysis and the mean formula of the I-S run-product, it is possible to estimate the percentage of illite (x) and dehydrated K or Na-smectite (y).

$$y = \frac{Si_{(I-S)} - [(Si_{(I)}) \cdot \% \text{ non-exp}] + (Si_{(Sm)} \cdot \% \text{ exp})}{(Si_{(Sm)} - Si_{(I)})} \quad (2)$$

% non-exp and % exp are determined by XRD (NEWMOD program)

Si_(I-S) = Si content of the I-S determined by microprobe analysis

Si_(I) = 3.37 and Si_(Sm) = 3.91

x = % non-exp - y

z = % exp = 100 - (x + y)

For all experiments, x and y have been determined using eqn. (2) and are plotted in Fig. 5. The proportions of dehydrated smectite are significant for all the run-products, even after 112 days of heating at 300°C (>50%). Assuming that the illite layers in the I-S are only potassic, with 0.87 of interlayer charge, the values of x , defined by eqn. 2, allows us to calculate the amounts of K attributable to the illite layer in the I-S run-products. They can be compared to the total abundances of K obtained by microprobe analysis (Fig. 6). The positive difference between total K analysed in the run-products and K in the illite fraction of the I-S indicates that K is also present in the interlayer space of the smectite layers, in association with Na (Fig. 6). However, it is not possible to determine the distribution of interlayer K and Na cations among the hydrated or dehydrated smectite layers of the I-S run-products. Nevertheless, the K/Na ratio in hydrated or dehydrated smectite layers of the I-S (Fig. 6), is relatively constant, in the

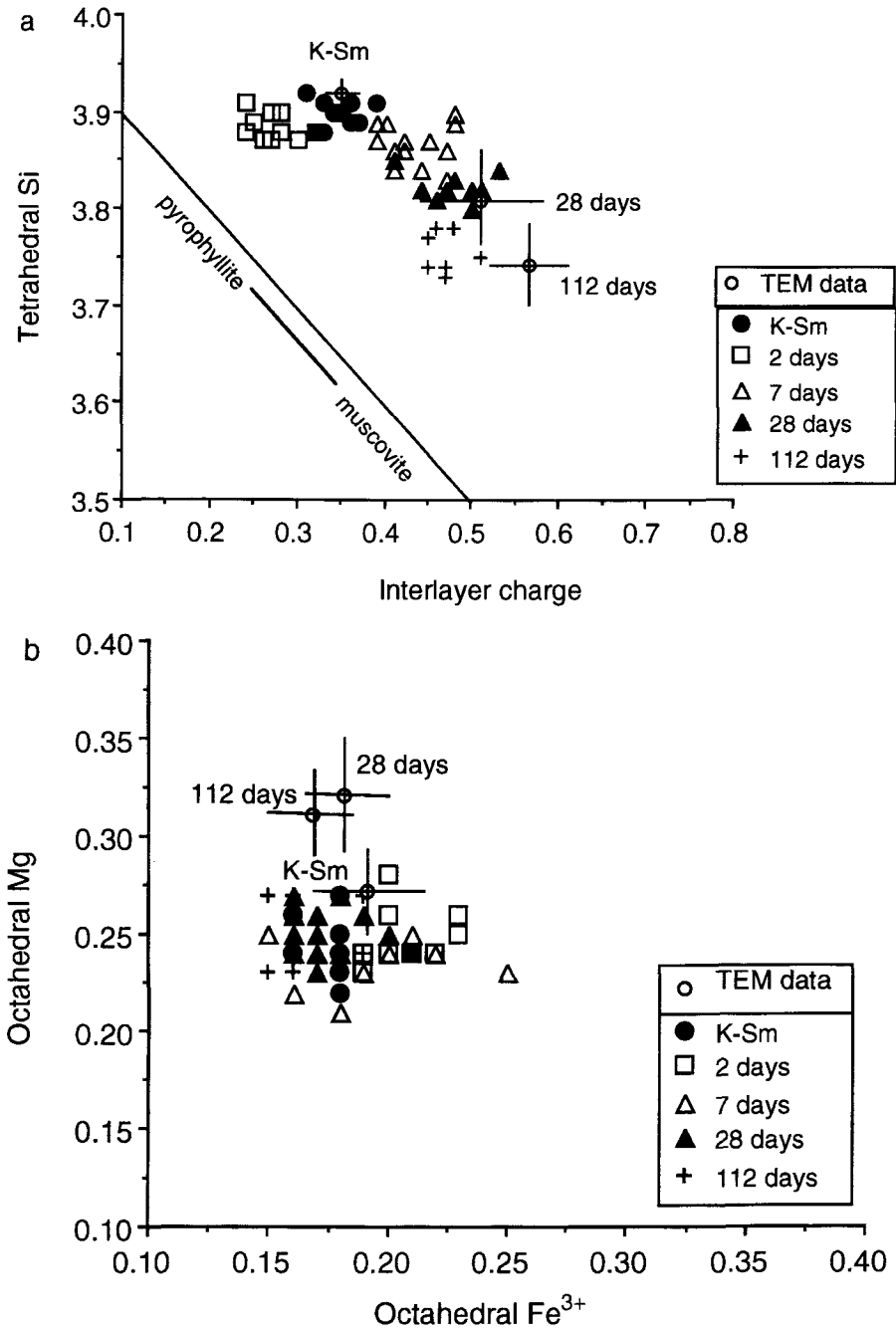


FIG. 3. Evolution of the composition of the run-products when K-smectite (K-Sm) is treated at 300°C and 100 bar in a mixed Na-K fluid (Na/K = 50, [K] = 300 ppm). Microprobe results are compared with TEM data represented as open circles (mean value), the bar giving the standard deviations. (a) Si vs. interlayer charge (Na+K+2Ca). Line indicates the location of the pyrophyllite-muscovite tie-line delimiting the field of dioctahedral clays; (b) Mg vs. Fe; (c) (*Opposite, upper*) K vs. Na. Lines indicate the boundaries of the main domain of low charge K-Na smectites.

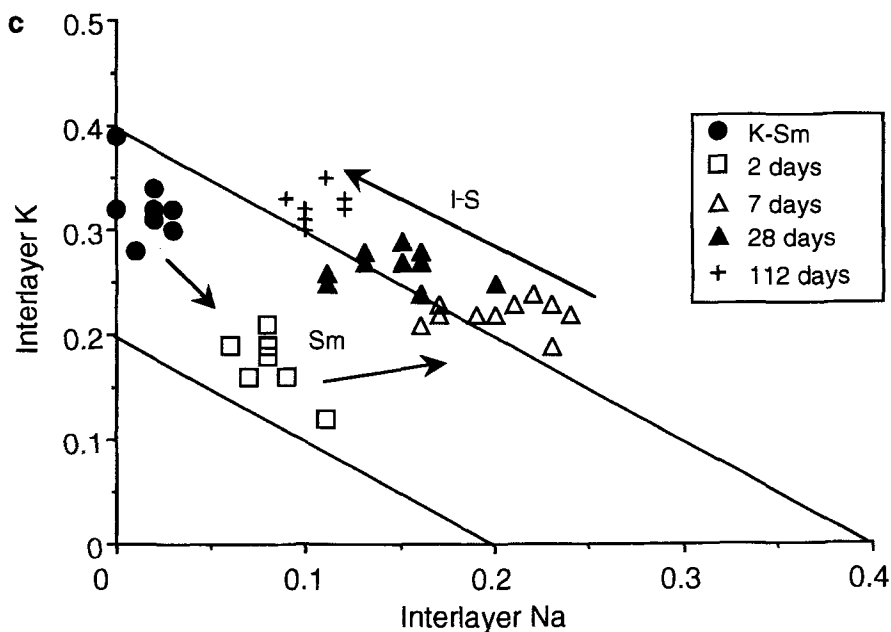


FIG. 3c.

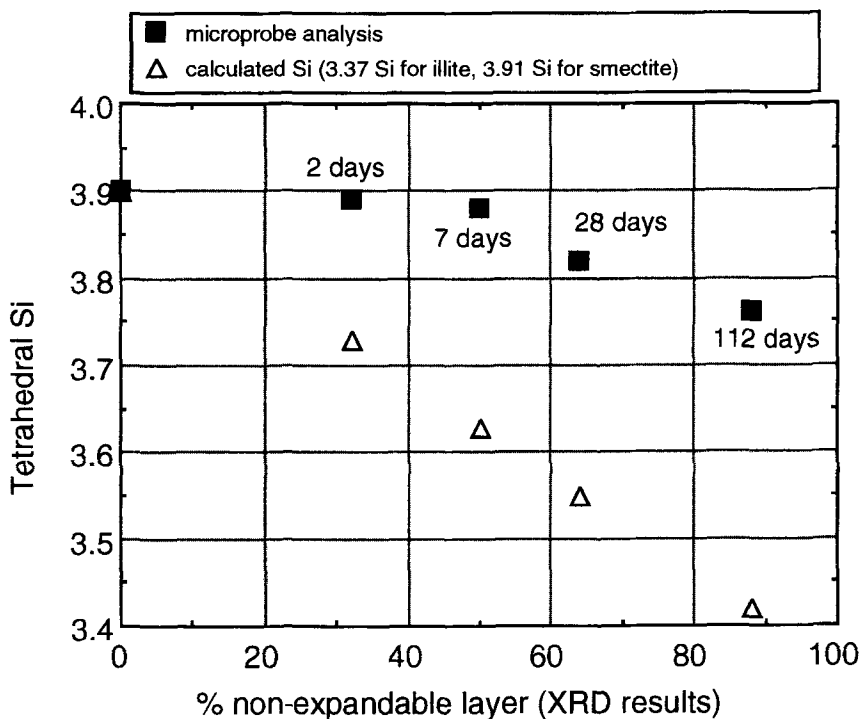


FIG. 4. Tetrahedral Si vs. the proportion of non-expandable layers in the I-S for the data obtained after treatment at 300°C and 100 bar of the K-smectite in Na/K = 50 and K = 300 ppm solution. Comparison of the microprobe analysis and the calculations of tetrahedral Si assuming that illite layers in I-S contain 3.37 tetrahedral Si.

TABLE 3. Representative half-structural formulae ($O_{10}OH_2$) and mean analyses calculated from TEM analyses for run-products obtained after treatment of the K-smectite under 300°C and 100 bar in a mixed Na-K fluid (Na/K = 50, [K] = 300 ppm).

K-smectite												
% Si	%Al	%Mg	%Fe	Σ cation	Si	Al(IV)	Al	Al(VI)	Fe ³⁺	Mg	Interlayer charge	
62.11	25.72	4.69	2.72	95.24	3.91	0.09	1.62	1.53	0.17	0.30	0.38	
62.15	25.05	4.32	3.86	95.38	3.91	0.09	1.58	1.49	0.24	0.27	0.36	
64.08	26.4	4.96	2.73	98.17	3.92	0.08	1.61	1.53	0.17	0.30	0.39	
63.85	26.65	3.78	3.08	97.36	3.93	0.07	1.64	1.58	0.19	0.23	0.30	
63.37	28.03	4.36	2.55	96.31	3.95	0.05	1.62	1.57	0.16	0.27	0.32	
				Mean	3.92	0.08	1.61	1.54	0.19	0.27	0.35	
				Standard deviation	0.01	0.01	0.02	0.03	0.03	0.02	0.03	
28 days												
% Si	%Al	%Mg	%Fe	Σ cation	Si	Al(IV)	Al	Al(VI)	Fe ³⁺	Mg	Interlayer charge	
59.51	26.44	5.45	2.83	94.23	3.79	0.21	1.68	1.47	0.18	0.35	0.56	
59.82	28.41	4.88	3.52	96.63	3.71	0.29	1.76	1.48	0.22	0.30	0.59	
59.38	27.61	4.83	2.62	94.44	3.77	0.23	1.75	1.53	0.17	0.31	0.53	
63.52	27.1	4.07	4.04	98.73	3.86	0.14	1.65	1.51	0.25	0.25	0.39	
62.75	27.62	4.77	2.98	98.12	3.84	0.16	1.69	1.53	0.18	0.29	0.45	
				Mean	3.81	0.19	1.69	1.50	0.18	0.32	0.51	
				Standard deviation	0.05	0.05	0.04	0.02	0.03	0.03	0.07	
112 days												
% Si	%Al	%Mg	%Fe	Σ cation	Si	Al(IV)	Al	Al(VI)	Fe ³⁺	Mg	Interlayer charge	
59.02	29.65	5.19	2.77	96.53	3.67	0.33	1.84	1.51	0.17	0.32	0.65	
61.29	28.11	5.22	2.46	97.08	3.79	0.21	1.74	1.53	0.15	0.32	0.53	
60.99	28.95	4.94	2.6	97.48	3.75	0.26	1.78	1.54	0.16	0.30	0.55	
80.27	27.06	5.51	3.16	96	3.77	0.23	1.69	1.46	0.20	0.34	0.58	
60.25	29.75	4.53	2.57	97.1	3.72	0.28	1.84	1.56	0.16	0.28	0.56	
				Mean	3.74	0.26	1.78	1.52	0.17	0.31	0.57	
				Standard deviation	0.04	0.04	0.06	0.03	0.02	0.02	0.04	

0.78–0.92 range. This high K/Na value in smectite, despite the low K/Na ratio in the solution, is probably partly controlled by the exchange constant $K_{Na/K}$ of the smectite at 300°C, which is in favour of K in smectite, and this is in agreement with thermodynamic predictions (Fritz, 1981). Therefore, these data can be tentatively explained by the co-existence of both (Na, K) hydrated and dehydrated smectite layers.

From these results, and the calculated percentages of real illite layers, the kinetics equation of total transformation of the K-smectite into illite can be estimated (Fig. 7, fitting curve b). Compared to

kinetic fitting curve a (Fig. 7), plotted using the percentages of non-expandable layers deduced from XRD results and composed of dehydrated smectite and illite, the duration for a complete transformation of the K-smectite layers into illite is much longer: from 8–12 years for 95–98% of yield, and in the conditions of our experiment, e.g. Na/K = 50, K = 300 ppm and L/C = 10.

The two curves show that the amount of illite in I-S can be easily overestimated if additional data such as the crystal-chemistry data in our case, or XRD data after saturation tests (Whitney & Northrop, 1988) are not available.

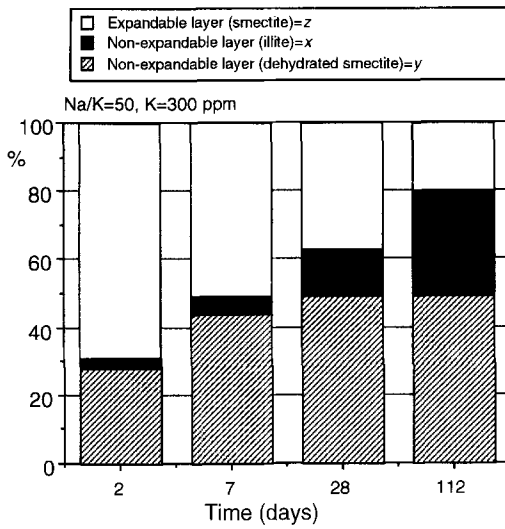


FIG. 5. Estimation of the proportions of illite (x), non-expandable dehydrated smectite (y) and expandable hydrated smectite (z) from microprobe analysis and with hypothesis that illite contains 3.37 tetrahedral Si. Treatment at 300°C and 100 bar of the K-smectite in Na/K = 50 and K = 300 ppm solution.

DISSOLUTION/DEHYDRATION OF SMECTITES AS PRECURSOR PROCESSES OF I-S FORMATION: A DISCUSSION

The overall examination of the results yield a stepwise model of transformation of the K-smectite at 300°C in a mixed Na-K fluid. Three main distinct processes can be distinguished: the dissolution of the starting smectite, and the crystallization of interstratified non-swelling layer/smectite minerals, and the dehydration of smectite layers.

Dissolution

The first process, occurring early, consists of the partial dissolution and/or hydrolysis of several smectite layers. Iron oxides precipitated on the clay layers (shown by SEM analysis for the 2 day experiment) are evidence that elements such as Fe issued from smectite dissolution reprecipitated as transitory phases. This first mechanism probably corresponds to the necessary chemical equilibrium between the smectite and the solution at the beginning of an experiment. For the longest duration of experiment, the disappearance of the

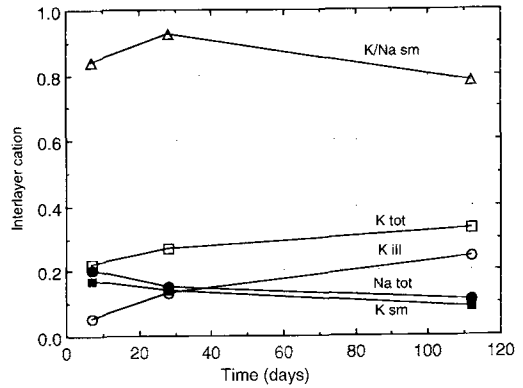


FIG. 6. Distribution of interlayer K and Na cations in the different kinds of layers of the I-S run-products. Total K and Na content: K tot and Na tot (analysed by microprobe); calculated contribution of K from illite in I-S: K ill; calculated K content in smectite: K sm; calculated K/Na ratio in the smectite layers: K/Na sm.

initial smectite flakes, and the lack of any contribution of fully expandable layers (initial smectite) in the XRD patterns tend to indicate that the starting material has been entirely dissolved to form the new I-S.

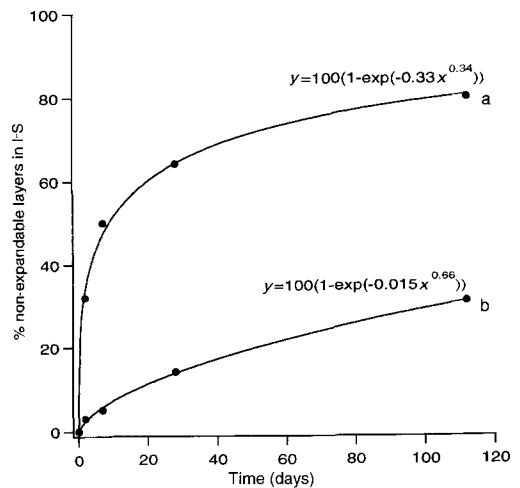


FIG. 7. Kinetics of non-expandable layers formation in I-S for experiments on K-smectite with K = 300 ppm and Na/K = 50 in the starting experimental solution. (a) Non-expandable layers determined by the NEWMOD program (XRD data) and including both dehydrated smectite and illite. (b) Illite layers defined by equation 2 (microprobe data).

Formation of the I-S

Illite-smectites precipitate from the solution as shown by the crystallization of newly-formed polygonal euhedral crystals. They are dominant after the longest (112 days) experiment. This observation shows that within an unconsolidated medium, and for high fluid/clay ratio, the polygonal crystals of I-S formed after extensive dissolution, convective transport and precipitation, and do not nucleate necessarily onto or within smectite plates. In addition, the newly formed I-S display a mica-like habit. This observation is rather distinct from that of Small (1994) who considered the formation of euhedral illite as scarce under a high liquid/clay ratio of 70 or 700, but at 200°C and after shorter runs. Therefore, the nucleation of discrete euhedral I-S seems to be highly dependent on kinetic factors, and temperature.

Illite-smectites are poorer in silica but richer in Al issued from the layers that dissolved during the previous steps of the evolution of the K-smectite. Silica, which is not fully incorporated within the I-S crystallizes as sub-euhedral quartz or cristobalite crystals. Semi-quantitative estimation of the volume of quartz produced by the reaction, using TEM images, is in good agreement with the calculated volume of quartz, which can be formed after release of silica during the dissolution-crystallization process. Equations written at constant Al and using the structural formulae of the starting and run products indicate that after the 112 day experiment, one mole of K-smectite may transform into ~0.9 moles I-S and 0.5 moles of quartz.

The interlayer charge of the I-S run-products increases proportionally to the decrease in tetrahedral Si, through the partial replacement of K by Na, which is by far the dominant cation in the solutions. The competition between K and Na to enter the interlayer space is probably directly related to the ion-exchange properties of the smectite layers within I-S minerals which are still poorly known at high temperature.

Dehydration of the smectite layers

The discordance between the Si content of the newly formed I-S clay, estimated by electron microprobe analysis, and the percentage of illite layers estimated by XRD suggests that the illitization process would begin with the dehydration of K or Na smectite layers. The first

'dehydrated smectite'-smectite mixed-layer clays are random and contain <60% of non-expandable layers. After a longer duration of experiment (>28 days), the precipitated I-S minerals display an ordered interstratification and a significant proportion of non-expandable layers, composed both of illite layers and dehydrated smectite.

The dehydration of a part of the smectite layers can be considered as a transition stage in the illitization process. It is important to note that the dehydration is probably partly reversible, as the swelling properties of the run products can be partly recovered after ion exchange (Whitney & Northrop, 1988).

CONCLUSIONS

The results presented have been obtained for particular experimental conditions, simulating hydrostatic pressure, and natural fluid-like solution (in great abundance) with a Na/K ratio close to most interstitial groundwaters in sedimentary basins. The chosen temperatures are extreme conditions for a deep waste repository, but have successfully accelerated the reactions with no inhibiting defect such as the formation of other mineral assemblages than those obtained at lower temperatures (I-S clay minerals).

The progressive dissolution of smectite, the formation of disordered I-S, and finally, the crystallization of newly-formed I-S is rather similar to the processes found in some natural hydrothermal or experimental systems under distinct *P-T* conditions and solution chemistry (Inoue *et al.*, 1988; Small, 1994). Such a process is rather distinct from the solid-state transition (Hower *et al.*, 1976), or from the 'cannibalization' process (Pollastro, 1985), generally invoked for the smectite-illite transition in sedimentary basins. Concerning the inhibiting effect of Na, and the more reactive behaviour of K-smectite, they are in good agreement with previous data obtained under distinct experimental conditions (Eberl & Hower, 1976, 1977; Eberl, 1978; Lahann & Roberson, 1980; Roberson & Lahann, 1981).

The novelty and originality of these results lie in the fact that TEM and microprobe chemical data complete the XRD approach of the smectite-to-illite transformation, and allow refinement in the understanding of the illitization processes. The Si content in the I-S may be considered as a rather good indicator for the interstratification of I-S and the

comparison of our microprobe analysis and XRD results yield similar conclusions to those of Ransom & Helgeson (1994), e.g. the formation of dehydrated smectite layers in the I-S. It can be also concluded that the amount of illite in I-S can be easily overestimated if crystal-chemistry is not studied.

Thus, the kinetics of the reaction can be interpreted by two distinct processes: (1) the formation of true illite layers; and (2) the smectite layer collapse within the newly formed I-S. These results are particularly important in the estimation of: (1) the stability of natural clay barriers; and (2) the reversibility of reactions, especially the dehydration process, occurring through a temperature cycle which could include a heating stage followed by a cooling stage.

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