

Experimental alteration of Mg-vermiculite under hydrothermal conditions: formation of mixed-layered saponite-chlorite minerals

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(Received 29 January 2002; revised 13 January 2003)

ABSTRACT: The hydrothermal reactivity of a Mg-vermiculite from Santa Olalla (Spain) was studied experimentally at 150 and 300°C, 75 and 100 bars, respectively, in (Na,K,Ca,Mg) chloride and sulphate solutions (liquid/solid ratio = 10). The formation of mixed-layer clays is demonstrated by FT-IR spectroscopy, X-ray diffraction (XRD) and electron microprobe. The gradual decrease of the 3220 cm⁻¹ infrared band intensity, characteristic of free water, is interpreted as the dehydration of the interlayer Mg cation of the vermiculite. The presence of ‘brucite type’ sheets is also observed by the increase of 3555 cm⁻¹ and 3420 cm⁻¹ band intensities. The XRD results show that run products are able to expand when glycolated. Microprobe analyses document the decrease of ¹⁴Si content and a significant enrichment in Mg in the run products. The formation of a mixed-layer clay comprising saponite and chlorite layers is proposed.

KEYWORDS: vermiculite, chlorite, saponite, XRD, microprobe data, FT-IR.

The behaviour of vermiculite, a common constituent of soils and siliciclastic sediments, has rarely been studied under hydrothermal conditions. Most studies concern the thermal stability of vermiculite under atmospheric pressure at low *a*H₂O (Barshad, 1950; Roy & Romo, 1957; Walker, 1961; Bobrov *et al.*, 1970). The latter show that at 300°C and for experiments of short duration (several hours or days), vermiculites (Mg or Ca or Na saturated) are relatively stable. Roy & Romo (1957) showed that for long runs (two weeks), the changes in vermiculite occur gradually, becoming significant above 300°C with a redistribution of Mg²⁺ between octahedral and interlayer crystallographic sites and the formation of a ‘chlorite-like’ phase (at 550°C). The formation of the latter phase causes a strong change in X-ray

intensities of reflections, the *d* spacings being unaffected. Nevertheless, the formation of chlorite *sensu stricto* is rejected by these authors because of the lack of availability of Mg in the structure. Above 550°C, a new phase characterized by a broad 10.4 Å basal spacing, which expands to the 14.4 Å spacing when water is added, is interpreted as a mixed-layer chlorite-montmorillonite.

Vermiculite, like smectite, saponite or berthierine, is considered as a potential precursor of chlorite during diagenetic or metamorphic processes (Berner, 1980; Iijima & Matsumoto, 1982; Shau *et al.*, 1990; Meunier *et al.*, 1991; Ehrenberg, 1993; Hornibrook & Longstaffe, 1996; Bettison-Varga & Mackinnon, 1997; Aagaard *et al.*, 2000). The gradual or continuous transformation of precursors to chlorite has been largely studied in metabasites (Bettison & Schiffman, 1988; Bevins *et al.*, 1991) and sediments (Helmold & Van de Kamp, 1984; Chang *et al.*, 1986). In the case of smectite, a discontinuous decrease in smectite

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DOI: 10.1180/0009855033830097

proportion, from smectite (with <20% chlorite), to corrensite and chlorite (with <10% smectite) occurs with increasing temperature, and has been reported from diagenetic and hydrothermal environments (Inoue *et al.*, 1984; Inoue, 1987; Inoue & Utada, 1991; Schiffman & Staudigel, 1995).

A small amount of vermiculite, considered as a potential buffer material for nuclear waste disposal, was detected by XRD in shales of the Paris basin, and so the purpose of this paper is to examine the behaviour of a standard vermiculite under hydrothermal conditions simulating those of a disposal facility. The possible formation of chlorite from vermiculite, which is sometimes described in natural environments was also studied at temperatures of 150 and 300°C, and pressures of 75 and 100 bars respectively. The present study combined hydrothermal experiments and a multi-technique characterization of the run products, using XRD, Fourier transform infrared spectroscopy (FT-IR), Transmission electron microscopy-electron energy loss spectroscopy (TEM-EELS) and electron microprobe analysis.

ANALYTICAL TECHNIQUES

Sample preparation was similar for all analytical techniques. Sample suspensions in water were dried and oriented with 00 l crystallographic planes parallel to the sample holder (glass slide for XRD, fluorite slide for FT-IR spectroscopy, carbon slide for electron microprobe and Ni grid for TEM-EELS).

The FT-IR spectra and X-ray powder patterns of the starting vermiculite and all the run products were taken at Laboratoire Environnement & Minéralurgie (LEM) and Ecole Nationale Supérieure de Géologie (ENSG) in Vandœuvre-lès-Nancy, France.

The FT-IR spectra were collected with a Bruker[®] IFS 55 Fourier transform spectrometer using two methods: (1) by transmission at various temperatures on clay deposits on CaF₂ slides with a Bruker microscope, which collects the IR beam with Cassegrain[®] objectives; (2) by diffuse reflectance on sample added to KBr powder under vacuum (<10⁻³ mbar). The spectral resolution was 4 cm⁻¹ and the recording time was 1 min. The Bruker microscope was equipped with a Linkam[®] microthermometric stage for analyses between -180°C/+600°C. By diffuse reflectance, band intensities at high wavenumbers are stronger than

by transmission. Each spectrum was processed using the OPUS program (©Bruker). Band areas were measured between 3800–3100 cm⁻¹ and 1700–1500 cm⁻¹, and assigned to OH and H₂O stretching vibrations and to H₂O-bending vibrations respectively. Bands located below 1200 cm⁻¹ were not taken into account in transmission mode because of MCT detector saturation in the region of the stretching Si–O bands and adsorption of the CaF₂ plate below 800 cm⁻¹.

The XRD patterns were recorded using a Bruker[®] D8 diffractometer, with diffracted-beam Co-K α radiation (35 kV, 45 mA) from 3° to 40°2 θ , with a step scan of 0.035°2 θ and time per step of 3 s.

Electron microprobe analyses and EELS at TEM were performed at the University Henri Poincaré (Nancy, France). Electron microprobe analyses were achieved on a Cameca[®] SX Electron Microprobe (analytical conditions: 10 kV, 6 nA, diameter of the investigated area 1 μ m, correction program – ZAF Cor2, and maximum analytical error – 3% of the total).

The EELS analyses were performed at 200 kV on a Philips[®] CM20 transmission microscope equipped with a Gatan collector. The resolution in energy loss was 1.3 eV.

Study of the valence state of Fe in vermiculite and run products obtained by EELS involved a special preparation of samples: (1) the samples were prepared by crushing under methanol, ultrasonic dispersion; (2) a drop of the suspension was then dried on a Ni grid; (3) a drop of MnBr₂ (diluted in methanol) was deposited onto the same grid to provide Mn²⁺ as an internal standard for the calibration of the spectra (Guillaume *et al.*, 2001). The valence state of Fe was measured using the chemical shift of Fe L₃ edge after calibration of the spectra with the Mn²⁺ L₃ edge.

The valence state of Fe was determined only for a few analyses on the starting vermiculite and the run samples. Thus, in order to compare the analytical results, all the structural formula are presented with Fe expressed as ferric iron (see Table 1).

STARTING MATERIAL AND EXPERIMENTAL PROCEDURE

The starting material was vermiculite from Santa Olalla in Spain. The origin and mineralogy of the Santa Olalla deposits have been studied extensively

TABLE 1. Mean half-structural formulae of vermiculite and run products calculated from microprobe analyses based on O₁₀ (OH)₂, assuming total Fe as Fe³⁺.

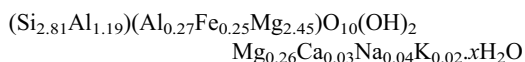
	Si	^{IV} Al	^{VI} Al	Fe ³⁺	^{VI} Mg	Ti	Mn	Ca	Na	K	Mg (IP)	I.C.
Vermiculite												
<i>n</i> = 17												
Mean	2.81	1.19	0.27	0.25	2.45	0.02	0.01	0.03	0.04	0.02	0.26	0.63
Standard deviation	0.05	0.05	0.06	0.05	0.06	0.01	0.01	0.02	0.02	0.01	0.03	0.09
150°C, 4 weeks												
<i>n</i> = 16												
Mean	2.85	1.15	0.23	0.23	2.50	0.02	0.01	0.04	0.24	0.04	0.15	0.65
Standard deviation	0.04	0.04	0.04	0.05	0.04	0.01	0.02	0.01	0.09	0.02	0.07	0.07
150°C, 12 weeks												
<i>n</i> = 25												
Mean	2.83	1.17	0.23	0.21	2.52	0.02	0.01	0.03	0.07	0.04	0.26	0.69
Standard deviation	0.04	0.04	0.03	0.03	0.03	0.01	0.01	0.02	0.03	0.02	0.04	0.05
150°C, 36 weeks												
<i>n</i> = 8												
Mean	2.71	1.29	0.17	0.27	2.53	0.02	0.01	0.02	0.07	0.00	0.35	0.81
Standard deviation	0.06	0.06	0.04	0.04	0.05	0.01	0.01	0.01	0.01	0.00	0.05	0.09
300°C, 4 weeks												
<i>n</i> = 15												
Mean	2.69	1.31	0.21	0.26	2.49	0.02	0.02	0.00	0.02	0.00	0.38	0.80
Standard deviation	0.12	0.12	0.09	0.06	0.08	0.01	0.02	0.01	0.02	0.00	0.10	0.17
300°C, 12 weeks												
<i>n</i> = 12												
Mean	2.72	1.28	0.22	0.22	2.54	0.01	0.01	0.02	0.04	0.00	0.37	0.82
Standard deviation	0.09	0.09	0.09	0.03	0.10	0.01	0.01	0.01	0.01	0.00	0.08	0.16

IP: interlayer position; I.C.: interlayer charge (2Mg(IP)+2Ca+Na+K)

n: number of analyses

(Velasco *et al.*, 1981; Justo, 1984; Luque *et al.*, 1985). Vermiculite occurs as lamellar flakes of variable size, up to 10 cm, showing perfect cleavage. It is formed from a mica identified as a phlogopite resulting from the alteration of pyroxenites. These micas are found in fractures and fissures and are the products of the alteration of the magnesian skarns of La Garrenchosa (Santa Olalla, Huelva, Spain). A complete review of its hydrated and cation-exchanged structure was published by De la Calle & Suquet (1988).

The chemical analyses of the vermiculite have been obtained by electron microprobe (Table 1). The mean formula, calculated on the basis of 10 structural oxygens and 2 OH and with Fe expressed as ferric iron, is:



The starting vermiculite shows a slight chemical heterogeneity (see standard deviations in Table 1). Magnesium is the main cation, both in octahedral and interlayer positions. The valence of Fe, determined by electron energy loss spectroscopy (Guillaume *et al.*, 2001) is 2.8 (20% Fe²⁺ and 80% Fe³⁺). This result is in good agreement with previous studies (De la Calle & Suquet, 1988; Pons *et al.*, 1989). Ca, K and Na are present as traces which could be attributed to impurities.

The experimental conditions are listed in Table 2. The temperature was fixed at 150 and 300°C (±2°C), liquid water pressure at 75 and 100 bars

TABLE 2. Experimental conditions.

Temperature (°C)	Pressure (bar)	Time (weeks)	Composition of the initial solution (mg/l)	Liquid/solid mass ratio
150	75	4	Na = 8470	10/1
		12	Ca = 111.7	
		36	K = 117	
300	100	4	Mg = 30.6	
		12	Cl = 13336	
			SO ₄ = 121	

(±5 bars) respectively, with the liquid/vermiculite mass ratio equal to 10/1. In each run, 50 mg of crushed vermiculite (grain-size <100 µm) were placed in a gold capsule with 500 µl of a solution containing Na (8470 mg/l), Ca (111.7 mg/l), K (117 mg/l), Mg (30.6 mg/l), Cl (13336 mg/l) and SO₄ (121 mg/l). The durations of the experiments were 4, 12 (150 and 300°C) and 36 weeks (at 150°C only).

The hydrothermal experiments were conducted using standard gold seal vessels in horizontal resistance furnaces equipped with temperature controllers. After treatment, the capsule was quenched at room conditions. Then, the solid samples were removed and washed until chloride- and sulphate-free. Because of their small amounts, the solutions were not recovered.

The composition of the experimental solution was constrained by the consideration of interstitial water chemistry in Toarcian shales of the Paris basin (data provided by Agence Nationale pour la gestion des Déchets Radioactifs, France). These sediments contain kaolinite (40±5%), illite and

mixed-layer illite-smectite (30±5%), chlorite and detrital vermiculite, mostly in mixed-layer clays like vermiculite-chlorite, illite-vermiculite, or vermiculite-smectite (30%±5%). Other minor detrital minerals such as quartz, pyrite and organic matter (TOC = 3.54%) are present (Elie, 1994). As detrital vermiculite is mostly in mixed-layer minerals, it is difficult to determine its composition. Nevertheless, we judge that vermiculite in the equilibrium mineral assemblage for the natural interstitial water described above is probably Na-rich. So, the composition of the Santa Olalla vermiculite is slightly different from that of the detrital vermiculite of the shales. But, it has been chosen because of its extensive coverage in the literature.

RESULTS

FT-IR spectroscopy

Figure 1 presents three IR spectra obtained in transmission mode. The IR spectrum of the starting

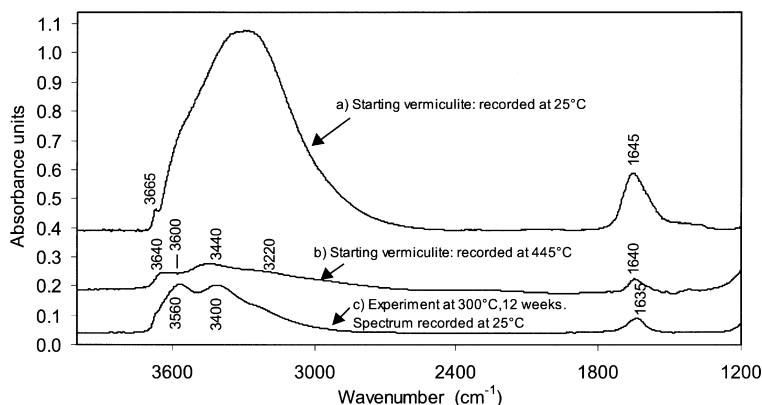


FIG. 1. IR spectra in transmission mode: starting vermiculite recorded at 25°C (a), 445°C (b) and run product obtained at 300°C (12 weeks' duration) (c).

vermiculite recorded at 25°C (a), the spectrum of the starting vermiculite heated for several minutes at 445°C and recorded at 445°C (b), and the spectrum of the run product, obtained after heating at 300°C over 12 weeks, recorded at 25°C (c), are compared. Spectra are normalized to the 3650 cm⁻¹ band contribution.

The spectrum b shows that in spite of the high-temperature treatment (445°C), the vermiculite from Santa Olalla is still hydrated. This is marked by the presence of 3440, 3220 and 1640 cm⁻¹ bands, assigned to liquid water (Van der Marel & Beutelspacher, 1976). The positions of these three bands are shifted slightly from the reference positions because of the high temperature of the recording. The third spectrum, c, for material from a long-period experiment at 300°C is very different from the others. It presents typical stretching bands of hydroxyl in a 'brucite type' environment (3560 cm⁻¹, 3400 cm⁻¹), shifted slightly from reference position given by some authors (Shirozu, 1980, 1985; Villiéras, 1993) because a significant amount of water is still present in the sample.

In spite of the difficulty of removing water from the starting sample, the strong differences between IR spectra b and c prove that a long-period experiment at 300°C of vermiculite in presence of a solution does not lead to a simple dehydration and more complex transformations are suspected.

In order to improve the removal of water in the different samples and the characterization of the run products, IR spectra were also recorded by diffuse reflectance under vacuum (<10⁻³ mbar). Figure 2

presents the diffuse reflectance spectra of the starting vermiculite, recorded at atmospheric pressure (a), under vacuum (b), of the run products after heating for 12 weeks at 150°C (c) and 300°C (d). The IR spectrum of the longest run at 150°C (36 weeks) was not presented because it is similar to the spectrum of the 12 week experiment. This result indicates that an equilibrium is reached quickly (<12 weeks), even at 150°C. Comparison of spectra a and b in Fig. 2 shows that the starting vermiculite is always partially hydrated in spite of the effect of vacuum.

For the run samples heated at 150 and 300°C, the intensities of the stretching and bending bands of water around interlayer Mg, in particular the band at 3220 cm⁻¹, decrease. Otherwise, a displacement of the bending band of water from 1645 cm⁻¹ and 1640 cm⁻¹ (on the spectra of the starting vermiculite) to 1633 cm⁻¹ on the spectra of run products is noticed.

An increase of the stretching bands at 3555 cm⁻¹ and 3420 cm⁻¹ assigned to hydroxyl in a brucite type environment and the refinement and a slight displacement of some bands (from 965 cm⁻¹ to 995 cm⁻¹) in the domain of Si-O-Si vibrations are also observed.

X-ray diffraction

The XRD patterns of air-dried vermiculite and air-dried run products obtained at 150°C (12 and 36 week experiments) are compared on Fig. 3 (XRD patterns of glycolated samples are not

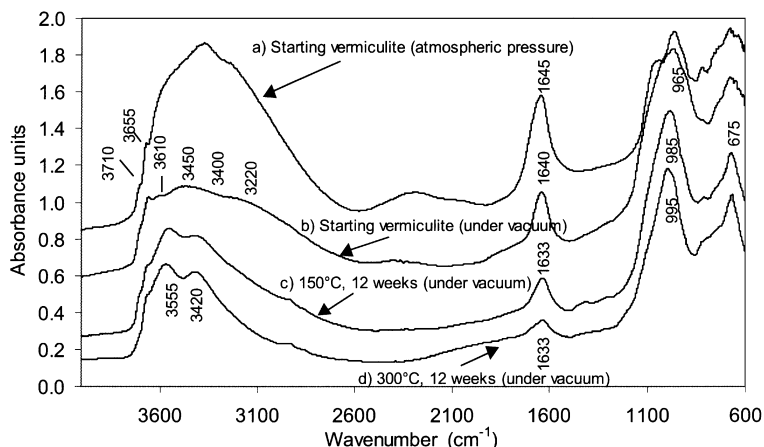


FIG. 2. IR spectra in diffuse reflectance mode: starting vermiculite, recorded at atmospheric pressure (a), under vacuum (b), and run products obtained after the 12 week experiments at 150°C (c) and 300°C (d).

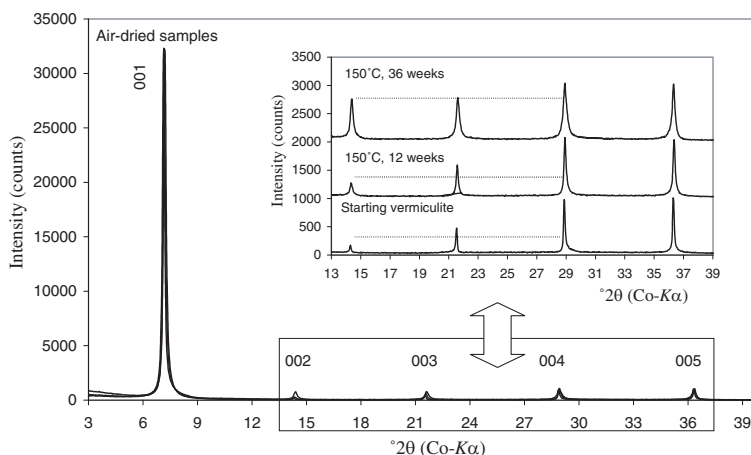


Fig. 3. XRD patterns of the air-dried starting vermiculite and run products obtained at 150°C.

presented as they are very similar). All XRD patterns are characterized by $00l$ reflections at constant position, but with changes in intensity when compared to the XRD pattern of the starting vermiculite. The intensities of the 002 and 003 reflections increase relative to the 004 and 005 reflections.

The XRD patterns of air-dried and glycolated run products obtained at 300°C show, in addition to the modification of the 001 intensities (Fig. 4a), shifts, broadenings or even 'splitting' of some reflections (Fig. 4b).

Chemical data

Electron microprobe results obtained on samples heated at 150°C indicate discrete chemical evolution (Table 1, Fig. 5). Run products of the experiments at 150°C are characterized by: (1) a decrease of Si content and an increase of the interlayer cationic charge with time. The interlayer cationic charge is expressed as $2\text{Mg}+2\text{Ca}+\text{Na}+\text{K}$ in interlayer position. Mg is considered, in both the newly formed 'brucite sheet' and in the interlayer space between 2 TOT layers, to be balancing the TOT positive charge deficiency; (2) an introduction of Mg in the octahedral sheet, where it replaces Al and Fe (Table 1); and (3) for a short duration of experiment (4 weeks), a change in the interlayer occupancy, especially the exchange of Mg by cations from the solution (Na). For the longest durations, the cationic charge in interlayer position increases by incorporation of Mg (Fig. 5b).

For the samples heated at 300°C, more significant chemical changes are noticed (Table 1, Fig. 6a,b), especially after 4 weeks of experiment. The analytical points between the starting vermiculite and the run products are better discriminated than for run products issued from experiments at 150°C, even those from 36 weeks. No increase in Na is seen. The main compositional changes are: (1) a decrease of the Si content, and (2) an increase of the bulk Mg content, both in the octahedral sheet of the TOT layers and in interlayer positions (balancing the TOT charge deficiency and in the brucite sheet).

At 300°C, after 4 and 12 week experiments, there were no significant differences in the evolution of the run products' compositions.

The evolution of the Fe valency in the run products has also been determined by EELS. The results show that the experimental treatments at 150 and 300°C yield no significant changes in the Fe valence, which remains within the 2.78–2.81 range.

DISCUSSION

The IR results can be interpreted as (1) a partial dehydration of the vermiculite layers (from double sheets of interlayer water to single sheets of water molecules around the Mg interlayer position), and (2) the presence of 'chlorite-like layers'. They are in good agreement with the literature data.

Kawano & Tomita (1991) suggested that on heating Mg-vermiculite to high temperature (>500°C), the water is normally driven out

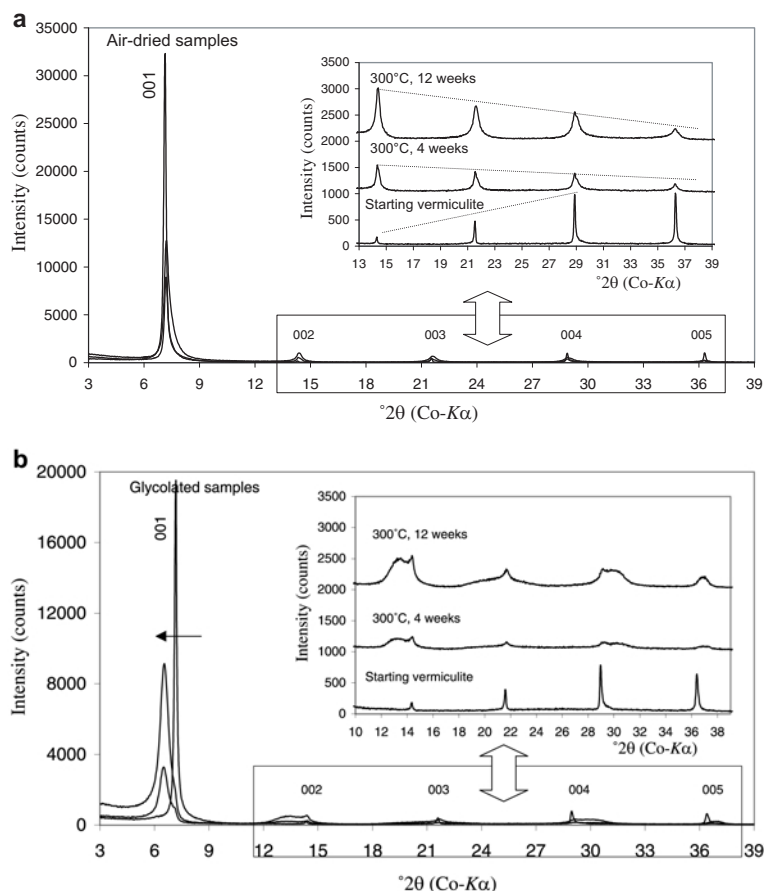


FIG. 4. (a) XRD patterns of the air-dried starting vermiculite and run products obtained at 300°C. (b) XRD patterns of the glycolated starting vermiculite and run products obtained at 300°C.

between the mica layers. Those authors also showed that the mineral is able to rehydrate quickly on exposure to moisture at room temperature, unlike Mg-saponite. Other literature data (Walker, 1956; Suquet *et al.*, 1984; De la Calle & Suquet, 1988), demonstrated that by increasing the temperature, the removal of water from vermiculite leads to the development of series of less hydrated phases, from double sheets of interlayer water to single sheets of water molecules, and from the one-layer hydrate to the anhydrous state. At high temperature, the dehydration is accompanied by structural changes such as the interlayer cations displacement and lateral displacement of the silicate layer.

Changes observed in XRD patterns, concerning intensity and broadening of some reflections, are assigned to a transition from vermiculite to chlorite and the presence of different types of layer. The

newly formed layers, which are able to expand when glycolated (shown by the shift of the 001 reflection to the weak angles, see arrow in Fig. 4b) and which are Mg-rich, could be attributed to smectite (saponite).

Interstratifications of high-charge saponite and octahedral vacancy-free chlorite (ordered corrensite phase) have already been described in the literature to interpret the formation of 'true' chlorite in caldera formations (Meunier *et al.*, 1991). Another hypothesis could be an interstratification with three different layer types (high-charge vermiculite, non-expandable; high-charge saponite, fully expandable; and chlorite, partly or non-expandable). Previous works have proposed interstratified clays with a minimum of three components (Drits *et al.*, 1997; Meunier *et al.*, 2000) in diagenetic transformation of smectite into illite.

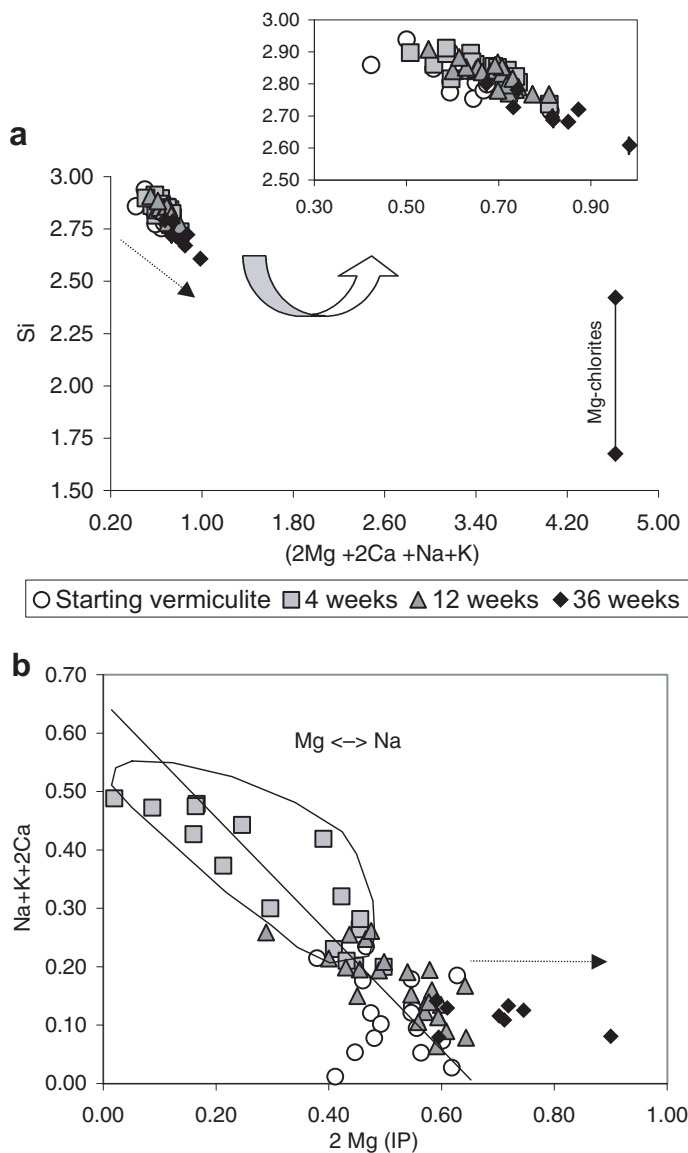


FIG. 5. Evolution of the composition of the run products obtained at 150°C: (a) Si vs. cationic charge in interlayer position (I.C. (interlayer charge) = 2Mg (both in newly formed brucite sheets and in interlayer positions between two TOT layers) + $2\text{Ca} + \text{Na} + \text{K}$), Mg-chlorites (calculated on the basis of 11 oxygens); (b) $\text{Na} + \text{K} + 2\text{Ca}$ vs. 2Mg in interlayer position (IP).

Older works (Stephen & MacEwan, 1950a,b; Honeyborn, 1951) described 14 Å minerals from the Keuper marl in central England as imperfect structures in which the brucite sheet is discontinuous and can be viewed as 'islands' between the silicate layers. The islands would prevent the collapse of the minerals on heating but would be

insufficient to prevent expansion during glycolation. These 14 Å minerals with discontinuous brucite layers were referred to as 'swelling chlorite' in the past. However, these minerals have recently been recognized as corrensite-chlorite mixed-layer phases (Buatier *et al.*, 1995).

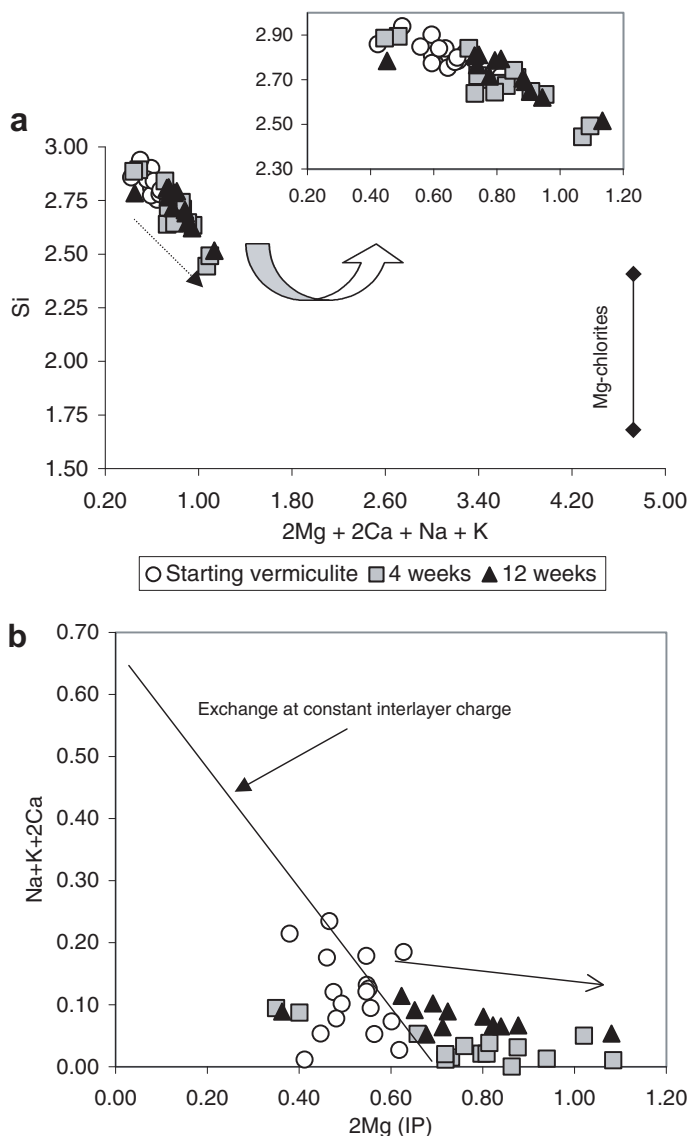


FIG. 6. Evolution of the composition of the run products obtained at 300°C: (a) Si vs. cationic charge in interlayer position (I.C. (interlayer charge) = $2Mg$ (both in brucite sheets and in interlayer positions) + $2Ca + Na + K$), Mg-chlorites (calculated on the basis of 11 oxygens); (b) $Na + K + 2Ca$ vs. $2Mg$ in interlayer position (IP).

Compositional changes in the run products, observed at 150 and 300°C, in particular the Mg enrichment and the decrease of Si content are consistent with the formation of chlorite and/or saponite.

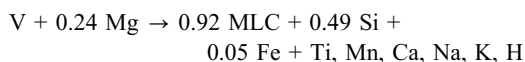
The cation exchange of vermiculite, which is rapid and enhanced by temperature (Le Dred *et al.*, 1978; Saehr *et al.*, 1982; Inoue, 1984; Martin de Vidales *et*

al., 1990, 1991) can explain the interlayer substitution (Mg for Na) observed for the short experiment run product obtained at 150°C. The increase of temperature should have accelerated the reaction.

The stability of the Fe valence indicates that the redox conditions remain constant during experiments or are compatible with this oxidation state of Fe in clays.

From the analytical data and using the following considerations: (1) the structural formulae of the starting vermiculite:

$(\text{Si}_{2.81}\text{Al}_{1.19})(\text{Al}_{0.27}\text{Fe}_{0.25}^{\text{III}}\text{Mg}_{2.45}\text{Ti}_{0.02}\text{Mn}_{0.01})\text{O}_{10}(\text{OH})_2\text{Mg}_{0.26}\text{Ca}_{0.03}\text{Na}_{0.04}\text{K}_{0.02}\cdot x\text{H}_2\text{O}$; (2) the structural formulae of a run product obtained at 300°C, calculated from one of the 12 chemical analysis (Table 1): $(\text{Si}_{2.52}\text{Al}_{1.48})(\text{Al}_{0.13}\text{Fe}_{0.21}^{\text{III}}\text{Mg}_{2.66}\text{Ti}_{0.01})\text{O}_{10}(\text{OH})_2\text{Mg}_{0.54}\text{Ca}_{0.01}\text{Na}_{0.02}\cdot x\text{H}_2\text{O}$; (3) a density of 2.5 for vermiculite in a dehydrated state (V), and 2.6 for the newly formed mixed-layer clay (MLC) which is a minimal value for a chlorite (Caillère *et al.*, 1982); (4) a constant Al content in the system (no Al is added), it is possible to write the reaction as follows:



One mole of vermiculite + ~0.25 mole Mg (from dissolution of vermiculite layers) react to form ~0.9 mole of a mixed-layer clay (MLC) and 0.5 mole of Si, which could precipitate as quartz (not observed with TEM), and traces of Fe and other cations (Ti, Mn, Ca, Na, K). This calculation must be considered with caution because of the rough valuation of the clay minerals' densities and the variability of the run product compositions (see standard deviations in Table 1). Nevertheless, the mass transfers inferred in the above reaction and the evidence of an important dehydration at 300°C, could cause a decrease of the total solid volume.

CONCLUSION

The Mg-vermiculite from Santa Olalla is unstable since it reacts at 150°C in hydrothermal solutions and transforms into new clay phases. The main changes observed in the run products concern the dehydration of the interlayer Mg cation, the formation of a 'brucite' sheet, the formation of mixed-layer minerals composed of two (saponite/chlorite) or three (vermiculite/saponite/chlorite) components.

The evidence of saponite formation is revealed by the expandable capacity of glycolated run products, observed by XRD. The main chemical changes are an increase in Mg content and a decrease in Si content and are consistent with the formation of chlorite and/or saponite. The temperature increases the reaction rate of the transformation of the vermiculite, which stops abruptly at 300°C (before 4 weeks), probably related to the availability of Mg in the system.

This study shows that saponite is probably a transition phase in the vermiculite–chlorite transformation. The complementary use of additional analytical techniques (IR, electron microprobe) to XRD in the understanding of the chloritization process is also demonstrated.

ACKNOWLEDGMENTS

We thank H. Suquet for providing the samples and the Agence Nationale pour la Gestion des Déchets Radioactifs (ANDRA) which supported this work.

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