

CHARACTERIZATION OF Mg-SAPONITES SYNTHESIZED FROM GELS CONTAINING AMOUNTS OF Na⁺, K⁺, Rb⁺, Ca²⁺, Ba²⁺, OR Ce⁴⁺ EQUIVALENT TO THE CEC OF THE SAPONITE*

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Abstract—Saponites were hydrothermally grown in the presence of amounts of NH₄⁺, Na⁺, K⁺, Rb⁺, Ca²⁺, Ba²⁺, and Ce⁴⁺ equivalent with the CEC of the saponite (155 meq/100 g), with or without F⁻, at a temperature of 200°C for 72 hr. XRD and CEC data revealed the formation of a two-water-layer saponite with mainly Mg²⁺ as interlayer cation. Dehydration occurred between 25° and 450°C and dehydroxylation occurred in two steps between 450° and 790°C and between 790° and 890°C. The relatively small length of the b-axis between 9.151 and 9.180 Å is explained by considerable octahedral Al substitution (between 0.28 and 0.70 per three sites) and minor tetrahedral Al substitution (between 0.28 and 0.58 per four sites). Under the synthesis conditions applied in this study, less than 13% of the interlayer sites are occupied by Na⁺, K⁺, and Rb⁺; between 13.3% and 21% by Ca²⁺ and Ba²⁺; while NH₄⁺ gives the highest value at 34%. The remaining sites are mainly filled by Mg²⁺. Ce⁴⁺ is not found in the saponite structure due to the formation of cerianite, CeO₂. The presence of F⁻ had little influence on the saponite composition. The formation of Mg-saponites is explained by a model in which an increased bayerite formation resulting in a higher octahedral Al³⁺ substitution and more Mg²⁺ in solution. Mg²⁺ is preferentially incorporated compared with the other interlayer cations due to its smallest ionic radius in combination with its 2+ charge.

Key Words—Cation exchange capacity, Saponite, Synthesis, Thermal analysis, X-ray powder diffraction.

INTRODUCTION

The research of synthetic saponites has mainly focused on Na-saponites (Koizumi and Roy, 1959; Suquet *et al.*, 1977; Iwasaki *et al.*, 1989) and on their saturation with various other cations in the interlayer region (Suquet *et al.*, 1977; 1981a, 1981b, 1982, 1987). Recently, Klopogge (1992) reported on the direct synthesis of ammonium-saponite, which is interesting as a potential acid catalyst after conversion of the NH₄⁺ to H⁺. This synthesis diminishes the catalyst preparation route by one step, the ammonium cation exchange. A major drawback of this synthesis was that the intercalation of Al³⁺ in the interlayer could not be controlled, resulting in non-swelling saponites with only low amounts of NH₄⁺ and, thus, low catalytic activity.

Saponite is a trioctahedral 2:1 smectite with an ideal composition given by M_xMg₃Al_xSi_{4-x}O₁₀(OH,F)₂,

where M represents one equivalent of the interlayer cation, e.g., Na⁺, K⁺, Rb⁺, NH₄⁺, or ½ Ca²⁺, ½ Ba²⁺, ½ Mg²⁺, or even ⅓ Al³⁺; and where x can range from approximately 0.3 to 0.6. A single 2:1 layer is normally organized with a central sheet of octahedrally coordinated Mg²⁺ with sheets of tetrahedrally coordinated Si⁴⁺ on both sides. The partial substitution of Si⁴⁺ by Al³⁺ causes the tetrahedral sheet to have an overall negative charge, which is compensated by interlayer cations. Actually, substitution of Al³⁺ also occurs at octahedral and interlayer sites. Substitution of Mg²⁺ at the interlayer sites may additionally proceed during the hydrothermal synthesis. Saponites with Na⁺, Ca²⁺, Mg²⁺, or Ba²⁺ as interlayer cations contain at a relative humidity of approximately 60% two water layers resulting in a basal spacing of approximately 15–16 Å, whereas saponites with interlayer cations such as K⁺ or NH₄⁺ have only one water layer, resulting in a basal spacing of approximately 12.5 Å (Suquet *et al.*, 1975).

The objective of this investigation was to identify the influence of various interlayer cations and F on the synthesis in order to prohibit the incorporation of Al³⁺ in the interlayer, as described for NH₄-saponite (Klopogge, 1992; Klopogge *et al.*, 1993). Therefore, this investigation reports the synthesis of saponites from stoichiometric gels containing Na⁺, K⁺, Rb⁺, Ca²⁺,

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Table 1. Experimental runs at 200°C for 72 hr.

Run LTSAP	pH Fluid	pH Wash	CEC meq/100 g			d_{001} (Å) 20°C	b (Å)
			M	Mg ²⁺	Total		
NA	4.46	4.53	8.4	134.0	142.4	14.1	9.163
K	4.41	4.48	10.5	140.0	150.5	15.3	9.180
CA	—	4.48	13.3	101.4	114.7	14.6	9.169
BA	4.47	4.58	21.2	77.4	98.6	14.7	9.173
CE	4.33	4.54	0.0	74.3	74.3	14.7	9.172
NHF	4.43	4.54	40.0	19.8	58.8	14.7	9.164
NAF	4.41	4.52	4.8	85.0	89.8	—	9.157
KF	4.42	4.50	13.5	74.4	87.9	—	9.152
RBF	4.62	4.70	16.0	76.1	92.1	15.1	9.173
CAF	4.32	4.52	13.4	75.5	88.9	14.0	9.151
BAF	4.43	4.56	21.2	88.0	109.2	—	9.160

Ba²⁺, or Ce⁴⁺ as interlayer cations that may be replaced during the synthesis by Mg²⁺ or even Al³⁺; the influence of F⁻ on the synthesis of saponite; and the influence of partial replacement of hydroxyl groups by F⁻ on the saponite characteristics. Incorporation of Mg²⁺ and Al³⁺ on the interlayer must be reflected by changes in the 2:1 layer octahedral and tetrahedral substitution due to the stoichiometric starting composition. The synthetic products were characterized by X-ray powder diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TGA), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The data will be compared with those reported by Suquet *et al.* (1975, 1981a, 1981b), who exchanged Na-saponite to saturation with the above cations.

EXPERIMENTAL METHODS

A homogeneous powder mixture of amorphous silica (SiO₂), aluminum triisopropylate (Al[OCH(CH₃)₂]₃), and magnesium acetate-tetrahydrate ([CH₃COO]₂Mg·4H₂O) (Kloprogge, 1992; Kloprogge *et al.*, 1993) was mixed with a solution containing the desired cation in the form of a hydroxide or fluoride salt. The resulting stoichiometric gel had the theoretical saponite composition of M_{0.6}Mg₃Al_{0.6}Si_{3.4}O₁₀(OH)₂, where M represents one equivalent of the interlayer cation, i.e., Na⁺, K⁺, Rb⁺, Ca²⁺, Ba²⁺, or Ce⁴⁺.

Approximately 125 g of the above gel was hydrothermally treated for 72 hr at 200°C under autogenous water pressure. Kloprogge *et al.* (1993) have shown that under these conditions a crystalline yield near 100% is reached. After cooling, the solids were separated from the coexisting hydrothermal fluid, washed twice with distilled water to remove possible free salts, centrifuged, and dried overnight at 120°C.

Characterization of the solid product was based on the fraction smaller than 64 μm (Kloprogge, 1992; Kloprogge *et al.*, 1993). The coexisting hydrothermal fluid was analyzed by ICP-AES. The pH of the coexisting hydrothermal fluid at room temperature, as well as the pH of the water after washing the solid for the first time, were measured with a Consort P514 pH meter. XRD patterns were recorded with a Philips PW 1050/25 diffractometer, using CuKα radiation. Heating stage XRD was carried out at 350°C using a HT Guinier CuKα1 (Enraf Nonius FR553) focusing powder camera. TGA was made with a du Pont 1090 Thermal Analyzer using a heating rate of 10°C/min under a N₂ flow of 50 ml/min. Elemental analyses of the solid products were obtained by XRF. The cation exchange capacity (CEC) was determined by exchanging the product with a solution of 1 N ammonium chloride brought to pH 7 by addition of ammonium hydroxide. The exchanged solution was analyzed with ICP-AES for the interlayer cations, including Mg²⁺ and Al³⁺.

RESULTS

The results of the different runs are summarized in Tables 1, 2, and 3. The runs are denoted, for example, by LTSAPNA, when the run was performed with Na⁺ as the ion considered to be taken up at the interlayer positions. When F⁻ ions were also present, the run is indicated by LTSAPNAF.

XRD of the synthesis products of all experiments revealed mainly (hkl) saponite reflections. The (001) reflections are very weak (LTSAPNA, -K, -CA, -BA, -CE, -NHF, -RBF, -CAF), or absent (LTSAPNAF, -KF, -BAF). Experiment LTSAPCE led to an X-ray pattern

Table 2. X-ray fluorescence analyses of the saponite bulk samples.

Run LTSAP	SiO ₂ wt. %	Al ₂ O ₃ wt. %	MgO wt. %	Na ₂ O wt. %	K ₂ O wt. %	Rb ₂ O wt. %	CaO wt. %	BaO wt. %	CeO ₂ wt. %	F wt. %
NA	51.77	9.16	24.71	bd						
K	52.63	9.47	24.71		0.57					
CA	54.13	9.01	23.55				0.31			
BA	54.34	9.35	21.23					2.04		
CE	55.84	9.64	19.40						2.10	
NHF	52.84	11.98	21.72							0.06
NAF	51.99	12.05	22.88	bd						0.06
KF	53.06	12.45	22.22		0.78					0.11
RBF	52.41	9.75	22.22			2.94				0.20
CAF	55.19	9.07	23.05				0.33			0.02
BAF	51.34	13.04	19.40					2.31		0.03

bd = below detection limit.

Table 3. Structural formulae of the Mg-saponites, based on XRF and CEC data.

Run LTSAP	Formula	Amorph
NA	$\text{Na}_{0.03}\text{Mg}_{0.27}(\text{Mg}_{2.58}\text{Al}_{0.28}\square_{0.14})(\text{Al}_{0.57}\text{Si}_{3.43})\text{O}_{10}(\text{OH})_2$	0.61 SiO ₂
K	$\text{K}_{0.04}\text{Mg}_{0.27}(\text{Mg}_{2.57}\text{Al}_{0.29}\square_{0.14})(\text{Al}_{0.58}\text{Si}_{3.42})\text{O}_{10}(\text{OH})_2$	0.64 SiO ₂
CA	$\text{Ca}_{0.03}\text{Mg}_{0.19}(\text{Mg}_{2.41}\text{Al}_{0.39}\square_{0.20})(\text{Al}_{0.41}\text{Si}_{3.59})\text{O}_{10}(\text{OH})_2$	0.42 SiO ₂
BA	$\text{Ba}_{0.04}\text{Mg}_{0.15}(\text{Mg}_{2.29}\text{Al}_{0.47}\square_{0.24})(\text{Al}_{0.38}\text{Si}_{3.62})\text{O}_{10}(\text{OH})_2$	0.57 SiO ₂
CE	$\text{Ce}_{0.00}\text{Mg}_{0.14}(\text{Mg}_{2.11}\text{Al}_{0.60}\square_{0.29})(\text{Al}_{0.28}\text{Si}_{3.72})\text{O}_{10}(\text{OH})_2$	0.62 SiO ₂
NHF	$(\text{NH}_4)_{0.15}\text{Mg}_{0.04}\text{Al}_{0.07}(\text{Mg}_{2.27}\text{Al}_{0.49}\square_{0.24})(\text{Al}_{0.45}\text{Si}_{3.55})\text{O}_{10}(\text{OH})_{1.99}\text{F}_{0.01}$	0.22 SiO ₂
NAF	$\text{Na}_{0.02}\text{Mg}_{0.16}\text{Al}_{0.04}(\text{Mg}_{2.24}\text{Al}_{0.30}\square_{0.26})(\text{Al}_{0.46}\text{Si}_{3.54})\text{O}_{10}(\text{OH})_{1.99}\text{F}_{0.01}$	0.12 SiO ₂
KF	$\text{K}_{0.05}\text{Mg}_{0.14}\text{Al}_{0.05}(\text{Mg}_{2.23}\text{Al}_{0.51}\square_{0.26})(\text{Al}_{0.49}\text{Si}_{3.51})\text{O}_{10}(\text{OH})_{1.98}\text{F}_{0.02}$	0.29 SiO ₂
RBF	$\text{Rb}_{0.06}\text{Mg}_{0.14}(\text{Mg}_{2.26}\text{Al}_{0.49}\square_{0.25})(\text{Al}_{0.34}\text{Si}_{3.66})\text{O}_{10}(\text{OH})_{1.96}\text{F}_{0.04}$	0.13 SiO ₂
CAF	$\text{Ca}_{0.03}\text{Mg}_{0.14}(\text{Mg}_{2.34}\text{Al}_{0.44}\square_{0.22})(\text{Al}_{0.34}\text{Si}_{3.66})\text{O}_{10}(\text{OH})_{1.99}\text{F}_{0.01}$	0.32 SiO ₂
BAF	$\text{Ba}_{0.04}\text{Mg}_{0.17}(\text{Mg}_{1.95}\text{Al}_{0.70}\square_{0.35})(\text{Al}_{0.42}\text{Si}_{3.58})\text{O}_{10}(\text{OH})_{1.99}\text{F}_{0.01}$	0.18 SiO ₂

showing additionally 2 wt. % (calculated from the amount of Ce in gel) cerianite, CeO₂ (Figure 1). The presence of corundum ($\leq 3\%$, Klopprogge *et al.*, 1993), which was mainly observed in the patterns of the experiments where fluorine ions were present, was caused by contamination from the corundum mortar during grinding of the starting compounds (Klopprogge, 1992; Klopprogge *et al.*, 1993). This corundum does not react in the synthesis and is not significant with regard to the saponite composition.

As shown in Table 1, at a relative humidity of approximately 60%, the basal spacings of the saponites vary between 14.0 Å and 15.3 Å independently of the various interlayer cations present during the synthesis. During dehydration at 350°C, the basal spacing slightly decreased to a rather uniform value between 14.0 Å and 14.5 Å, which indicates the presence of Mg²⁺ as main interlayer cation.

The length of the b-axis based on the (060) reflection is relatively small compared with the values reported in various articles (e.g., Suquet *et al.*, 1981a, 1981b), and varies between 9.151 Å and 9.184 Å. The mean values of the b-axes of the F-containing saponites are 0.1% smaller than those containing only hydroxyl groups with the same interlayer cation. After dehydration at 350°C, the b-axis became 9.150 Å for all of the saponites.

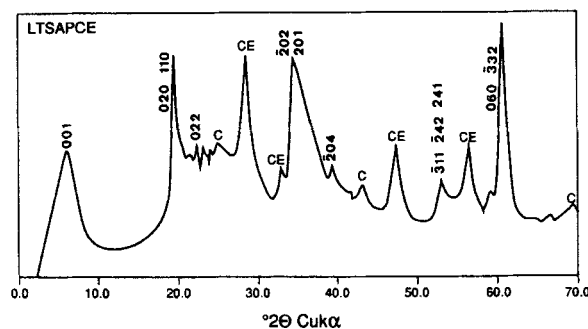


Figure 1. X-ray powder diffraction pattern of Mg-saponite synthesized in the presence of Ce⁴⁺ as competitive cation. CE = cerianite.

Cation exchange determinations (hereafter denoted as CEC although based on exchange from total crystalline product) on the possible interlayer cations (NH₄⁺, Na⁺, K⁺, Rb⁺, Ca²⁺, Ba²⁺, Ce⁴⁺) yielded values between 4.8 and 21.2 meq/100 g, except for LTSAPNHF with an extreme of 40 meq/100 g (Table 1). These values were extremely low with respect to the theoretical saponite composition (155 meq/100 g). ICP analyses of the exchanged CEC-fluids revealed high concentrations of Mg that corresponds to CEC values of about 74.3 to 140 meq/100 g. No Al was measured in these fluids. The totals approach the 155 meq/100 g for Na and K, while the others give lower values. This may indicate a somewhat lower crystallinity or a different amount of substitution.

The XRF data on the bulk synthetic product (Table 2) exhibited relatively high Al, intermediate Si, and low Mg contents in comparison with the intended theoretical saponite composition, M_{0.6}Mg₃Al_{0.6}Si_{3.4}O₁₀(OH)₂. With M = NH₄⁺, the SiO₂, Al₂O₃, and MgO theoretical wt. %s are 52.5, 15.7, and 31.1, respectively (Klopprogge *et al.*, 1993).

Analyses of the coexisting hydrothermal fluids yielded very low concentrations of Si and Al, whereas the Mg concentrations were too high for congruent solution. No clear relationship was observed between the Si, Al, and Mg content of the fluid and the interlayer cation or F⁻. The concentration of the alternative interlayer cation in the fluid of runs with F⁻ was 4%–20% higher than those without F⁻. The Ce concentration was extremely low due to the precipitation of crystalline cerianite.

The pH of the coexisting hydrothermal fluid was rather constant (4.33 to 4.62) and independent of the presence or absence of F⁻. The pH of the water after the first washing was consequently slightly higher (Table 1).

The TGA plots of all experimental products exhibited the same profile (see example in Figure 2). Below 125°C, up to 9.0 wt. % physically adsorbed water was lost. The profile in the temperature range 125°–790°C can be divided in two parts. In the range between 125°C and approximately 450°C, 3.7 to 4.9 wt. % water pres-

ent within the interlayer was lost. The weight loss of approximately 1.6%–2.2% in the range from 500°–790°C was attributed to the start of dehydroxylation. Between 790° and 890°C, the dehydroxylation reached a maximum and the sample lost an additional 1.8–2.3 wt. %. The lowest values were observed for the F-containing samples.

DISCUSSION

The synthesis of saponite was successful in all experiments as demonstrated by the XRD spectra and the drop in pH of the coexisting fluid to relatively low values due to the release of acetate ions (Kloprogge, 1992; Kloprogge *et al.*, 1993).

The very low intensity of the basal spacings indicates that the stacking of the saponite sheets is very low. The basal spacings measured for the saponites prepared in the presence of sufficient Na⁺, Ca²⁺, Ba²⁺, and Ce⁴⁺ should be within a range of approximately 14–16 Å at 25°C, as reported for saponites with two water layers (Suquet *et al.*, 1975). Saponite synthesized in the presence of K (LTSAPK) yielded a similar basal spacing of 15.29 Å; yet K-saponite, like NH₄-saponite (Kloprogge, 1992), normally should have only one water layer leading to a basal spacing of approximately 12.6 Å.

Upon partial dehydration, all basal spacings decreased to 14–15 Å. After dehydration, Suquet *et al.* (1975) observed basal spacings of 12.4 Å for Na-, 10.0 Å for K-, 12.0 Å for Ca-, 12.2 Å for Ba-, and 14.3 Å for Mg-saponites. The uniform 14–15 Å basal spacings of our samples and the CEC results (Table 1) point to Mg²⁺ as the main interlayer cation with the whole set of saponites synthesized, which is confirmed by the CEC data. Due to the stoichiometry of the starting gel, the intercalation of Mg²⁺ has to be accompanied by a considerable substitution in the 2:1 layer. Based on the initial gel composition, Al³⁺ may also be taken up at interlayer positions. Kloprogge (1992) and Kloprogge *et al.* (1993) have shown that saponites with Al³⁺ as interlayer cation exhibit behavior corresponding to one water layer within the interlayer and, thus, a basal spacing of 12.4 Å. Therefore, the presence of Al³⁺ as major interlayer cation was excluded by the analyses of the exchanged CEC-fluid and the basal spacing.

The length of the b-axis correlates 1) with the interlayer cation and its ionic radius, when the saponite was in the dehydrated state, and 2) with the Al substitution on tetrahedral and octahedral sites (Suquet *et al.*, 1981a, 1981b). For two water layer saponites (Li, Mg, Ca, Ba, and Na) in the hydrated state with a negligible influence of the interlayer cation, the relation between b-axis and Al substitution is expressed as (Suquet *et al.*, 1981a):

$$b = 9.178 + 0.076x \pm 0.01 \text{ \AA}, \quad (1)$$

where x is the layer charge and is considered to be equal to the difference between Al^{IV} and Al^{VI}. The Al^{IV}-

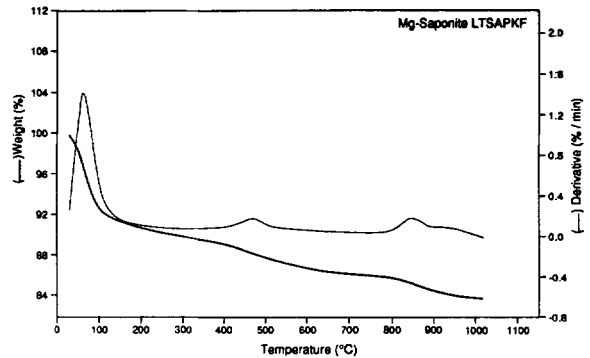


Figure 2. Thermogravimetric analysis (heating rate 10°C/min) of Mg-saponite. The thick solid line represents the weight loss (left y-axis) and the thin solid line the derivative (right y-axis).

Si substitution results in a negative charge, which is partially compensated by the positive charge due to the one-to-one Al^{VI}-Mg substitution. These considerations lead to:

$$b = 9.174 + 0.079 \text{ Al}^{\text{IV}} - 0.07 \text{ Al}^{\text{VI}} \pm 0.01 \text{ \AA} \quad (2)$$

Kloprogge (1992) and Kloprogge *et al.* (1993) argued that the normal muscovite substitution $3\text{Mg}^{2+} = 2\text{Al}^{3+} + 1 \text{ vacancy}$ was more appropriate. This results in a neutral octahedral sheet and, therefore, a slightly higher layer charge in comparison with the one-to-one Al-Mg substitution. According to these relations, the small values of the b-axes displayed by our samples can be explained by a considerable octahedral Al substitution or by a minor tetrahedral Al substitution. Kloprogge *et al.* (1993) confirmed a substantial octahedral Al substitution based on ²⁷Al MAS-NMR, whereas the ²⁹Si MAS-NMR data indicated a tetrahedral Al substitution of approximately 0.6 Al per four tetrahedral sites in the clay structure. The substitution of Al at octahedral sites was also evident from the low CEC values of Table 1.

The presence of only 20–200 ppm F in the saponite structure, which replaced 0.5%–3% of the hydroxyl groups, had no noticeable effect on the basal spacing, although it is known that trioctahedral fluor-micas exhibit a smaller basal spacing due to increasing interlayer bond strength (Giese, 1984; Munoz, 1984). However, a small influence was found on the b-axis, which has become a little smaller as compared with the corresponding saponites without F. A comparable influence was found on the Mg²⁺ CEC, whereas the NH₄⁺ exchange remained unaltered.

Approximate structure formulae of the saponites can be calculated using the CEC data and XRF data assuming that 1) all of the exchangeable cations are at the interlayer sites of the saponite; 2) all Mg and Al measured with XRF are present in the saponite struc-

ture; and 3) the bulk consists of approximately 80–85 wt. % saponite and 15–20 wt. % amorphous SiO₂ (Kloprogge, 1992) (Table 3). Our XRD, XRF, and CEC data combined with earlier published NMR data indicate that the muscovite substitution of 3Mg²⁺ by 2Al³⁺ and one vacancy is more appropriate, leaving a zero charge on the octahedral sheet. The negative charge of the tetrahedral sheet is completely compensated by the interlayer cations, of which a considerable amount is Mg²⁺.

The two-step weight loss between 25°C and approximately 450°C shown in the TGA plots was due to bulk water sorbed at the surface and in the interlayers of the saponite. This agrees well with the decrease in basal spacing during dehydration exhibited within the same temperature range. Between 450°C and 790°C, the saponites dehydroxylated very slowly, followed by the main hydroxylation peak between 790°C and 890°C. The corresponding DTA plot revealed its main dehydroxylation peak between 800°C and 850°C and a very weak, subsidiary peak at approximately 600°C supporting the interpretation of the TGA plot. The weight loss of 3.7%–4.5%, with the lowest values for the F containing saponites, is in reasonable to good agreement with the theoretical value of approximately 4.5 to 5 wt. %, which depends on the exact saponite composition.

Kloprogge (1992) and Kloprogge *et al.* (1993) have proposed a crystallization model for NH₄-saponites consisting of the formation of separate tetrahedral sheets with Si and Al in a fixed ratio together with bayerite, followed by the incorporation of the bayerite as building unit and stacking of the sheets. The main differences in the synthesis conditions described in this study compared with theirs are found in the 2.5 times increased amount of water and the use of other interlayer cations in the starting gel instead of ammonium. The results of this study exhibit three marked differences between those of Kloprogge (1992) and Kloprogge *et al.* (1993). We found 1) the presence of interlayer Mg²⁺ and the absence of interlayer Al³⁺; 2) a much higher amount of octahedral Al; and 3) that synthesis experiments with fluorine do not result in incorporation of extensive F⁻ into the saponite structure replacing hydroxyl groups, nor in the formation of sellaite, MgF₂. The amounts of Mg²⁺ and F⁻ in the hydrothermal fluid largely exceeds the solubility product of sellaite, indicating possible complexation with the organic constituents in the fluid prohibiting sellaite crystallization. The formation of Mg-saponites may be explained by lower starting pH values due to the use of interlayer cations different from NH₄⁺ resulting in an increasing bayerite formation and, therefore, increasing the octahedral Al³⁺ substitution. As a result more Mg²⁺ remained in solution,

which will be preferentially incorporated in the interlayer due to its 2+ charge in combination with the smallest ionic radius compared with the other interlayer cations.

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