

## SYNTHESIS OF SMECTITE CLAY MINERALS: A CRITICAL REVIEW

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**Abstract**—Smectites are one of the most important groups of phyllosilicates found in soils and sediments, and certainly one of the most difficult to study. New information about the formation mechanisms, impact of structural features on surface properties, and long-term stability of smectites can best be gained from the systematic study of single-phase specimens. In most instances, these specimens can only be obtained through synthesis under controlled conditions. Syntheses of smectites have been attempted (1) at ambient pressure and low-temperature (<100°C), (2) under moderate hydrothermal conditions (100–1000°C, pressures to several kbars), (3) under extreme hydrothermal conditions (>1000°C or pressures >10 kbars), and (4) in the presence of fluoride. Of these approaches, syntheses performed under moderate hydrothermal conditions are the most numerous and the most successful in terms of smectite yield and phase-purity. Using hydrothermal techniques, high phase-purity can be obtained for beidellites and several transition-metal smectites. However, synthesis of montmorillonite in high purity remains difficult. Starting materials for hydrothermal syntheses include gels, glasses, and other aluminosilicate minerals. The presence of Mg<sup>2+</sup> seems to be essential for the formation of smectites, even for phases such as montmorillonite which contain low amounts of Mg. Highly crystalline smectites can be obtained when extreme temperatures or pressures are used, but other crystalline impurities are always present. Although the correlation between synthesis stability fields and thermodynamic stability fields is good in many instances, metastable phases are often formed. Few studies, however, include the additional experiments (approach from under- and over-saturation, reversal experiments) needed to ascertain the conditions for formation of thermodynamically stable phases. Thorough characterization of synthetic products by modern instrumental and molecular-scale techniques is also needed to better understand the processes leading to smectite formation.

**Key Words**—Beidellite, Fluoride, Hectorite, Hydrothermal, Montmorillonite, Nontronite, Phyllosilicate, Saponite, Sauconite, Stevensite.

### INTRODUCTION

Clay minerals form an important group of the phyllosilicate family of minerals, which are distinguished by layered structures composed of polymeric sheets of SiO<sub>4</sub> tetrahedra linked to sheets of (Al, Mg, Fe)(O,OH)<sub>6</sub> octahedra. The geochemical importance of clay minerals stems from their ubiquity in soils and sediments, high specific surfaces, and ion-exchange properties. Consequently, clay minerals tend to dominate the surface chemistry of soils and sediments. Furthermore, these properties have given rise to a wide range of industrial applications throughout history. Primitive peoples used clay minerals for ceramic figures and pottery as early as 25,000 years B.P. (Shaikh and Wik, 1986). Today, clay minerals are important materials with a great variety of applications in ceramics, nanocomposite materials, oil drilling, waste isolation, and the metal and paper industries. Chemical applications of clay minerals include their use as adsorbents, decolorizing agents, ion exchangers, and molecular-sieve catalysts (Fowden *et al.*, 1984; Murray, 1995).

Despite their importance, the clay minerals form a difficult group to study due to their small size, variable

structural composition, and relatively slow rate of formation and alteration. New information about the formation mechanisms, variation in surface properties with structure, composition, and solution composition, and the long-term stability of clay minerals in surficial and hydrothermal environments may be gained from studies of synthetic clay minerals. In particular, the rapid and reliable synthesis of single-phase end-member specimens for characterization and reference purposes will greatly accelerate progress in this area.

Smectites are one of the largest and most important classes of the phyllosilicate clay-mineral group. They are common in temperate soils and, because of their cation exchange capacities (CEC) and very high specific surfaces, tend to dominate the cationic adsorption chemistry of these soils. Their small particle size (typically <1 μm) and large aspect ratio also allow them to strongly influence the physical properties of soils and sediments. These chemical and physical properties explain the suitability of clays as catalysts and as pond liners for isolation of hazardous wastes. Small size and highly variable composition, however, have led to considerable uncertainty regarding the origin and thermodynamic stability of smectites. As reviewed by Borchardt (1989, p. 689–703), considerable evidence

suggests that they are of detrital origin (*i.e.*, a stage in the weathering of micas and chlorites to kaolinite and gibbsite) and not thermodynamically stable phases in soils and sediments, yet some evidence also exists suggesting that at least some of the end-member phases form authigenically in sediments under ambient conditions. Because natural specimens typically contain impurities, questions related to formation and stability are best answered by study of synthetic, fully characterized, single-phase specimens.

Although a number of clay minerals including kaolins and various smectites have been synthesized during the past 50 years, most of this synthetic work is empirical in nature (Güven, 1988). The most common synthetic approach is to treat starting materials (mostly solid phases such as other aluminosilicates, glasses, gels) having a composition close to the desired clay by heating in water or under hydrothermal conditions [*i.e.*, 100–1000°C, autogenous water pressure (the pressure reached when excess water is heated in a confined volume) or higher]. A major difficulty is that the reactions rarely go to completion unless hydrothermal conditions are employed and, even then, a mixture of products is typically obtained rather than a pure clay mineral.

The purpose of this review is to summarize and evaluate smectite synthesis techniques in terms of the crystallinity and phase-purity of the products obtained. Information about smectite (and clay-mineral) formation mechanisms that can be gleaned from the synthesis studies will also be presented. The review begins with a brief overview of the classification scheme of the smectite group. The main part of the review is divided into four sections that describe approaches to smectite synthesis under different sets of conditions (*i.e.*, low temperature and pressure, hydrothermal, very high temperature and pressure, and the presence of fluoride). These four sections are further divided into subsections that cover synthesis of individual smectite minerals. The review concludes with a critical discussion of the approaches to smectite synthesis and product characterization outlined in the previous four sections. Portions of this review were presented in Klopprogge (1998).

#### CLASSIFICATION OF SMECTITES

Smectites form a group in the class of minerals known as phyllosilicates or layer silicates. Other groups in this class include the micas, kaolins, vermiculites, chlorites, talc, and pyrophyllite. The phyllosilicate structure consists of layers in which planes of oxygen atoms coordinate to cations such as Si, Al, Mg, and Fe to form two-dimensional “sheets”. The coordination of cations in adjacent sheets typically alternates between tetrahedral and octahedral. Tetrahedral sheets, which commonly contain Si, Al, and Fe<sup>3+</sup>, consist of hexagonal or ditrigonal rings of oxygen tetrahedra linked by shared basal oxygens. The apical

oxygens of these tetrahedra help form the base of octahedral sheets having brucite-like or gibbsite-like structures and commonly containing Mg, Al, Li, Fe<sup>2+</sup>, and Fe<sup>3+</sup>. A regular repeating assemblage of sheets (*e.g.*, tetrahedral-octahedral or tetrahedral-octahedral-tetrahedral) is referred to as a layer.

Smectites, micas, vermiculites, talc, and pyrophyllite are characterized by a 2:1 layer structure in which two tetrahedral sheets form on either side of an octahedral sheet through sharing of apical oxygens. As the apical oxygens from the tetrahedral sheet form ditrigonal or hexagonal rings, one oxygen from the octahedral sheet is located in the center of each ring and is protonated to yield a structural hydroxyl. In 2:1 phyllosilicates, isomorphous substitution of cations having different valences can lead to charge imbalances within a sheet. These may be partly balanced by the opposite type of charge imbalance in the adjacent sheet (*e.g.*, a positively charged octahedral sheet may offset some of the negative charge associated with a tetrahedral sheet). The net charge imbalance on a 2:1 layer, if it occurs, is negative. This charge is referred to as the *layer charge* of the mineral and is balanced by larger cations (*e.g.*, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) that coordinate to the basal surfaces of the tetrahedral sheets from adjacent layers. Because these charge-balancing cations are located between adjacent 2:1 layers they are referred to as “interlayer cations”. The 2:1 phyllosilicates are distinguished chiefly on the basis of their layer charge.

Kaolins, on the other hand, form a 1:1 layer structure consisting of a single tetrahedral sheet linked to a single octahedral sheet through apical oxygens. As isomorphous substitution, if present, is very low in kaolins, adjacent 1:1 layers are linked by hydrogen bonding between the hydroxylated surface of the octahedral sheet and the basal oxygens of the tetrahedral sheet from the adjacent layer. No interlayer cations are present in the 1:1 structure.

The chlorite structure is in many ways a hybrid of the 2:1 and 1:1 structures. Although it includes a regular 2:1 layer, the layer charge is balanced by a positively charged sheet of hydroxylated cations in octahedral coordination (*i.e.*, a brucite-like or gibbsite-like sheet) thus simulating, in a gross sense, the alternating octahedral-tetrahedral structure of a 1:1 phyllosilicate. The bonding between the interlayer hydroxylated sheet and the 2:1 layer, however, is distinct from that of the 1:1 minerals in that the oxygen atoms in the hydroxylated sheet are not shared with the basal oxygen atoms of the tetrahedral sheets on the adjacent 2:1 layers.

A further designation among the phyllosilicates is made based on type and location of the cations in the oxygen framework. In half of a unit cell composed of ten oxygen atoms and two hydroxyl groups, there are four tetrahedral and three octahedral sites. A phyllosil-

Table 1. Classification of selected common hydroxylated phyllosilicates.

Layer type	Interlayer species	Layer charge	Octahedral-sheet type	Mineral name	Formula	
1:1	none or H <sub>2</sub> O only	≈0	dioctahedral	kaolinite	Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	
			trioctahedral	chrysotile	Mg <sub>6</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	
2:1	none	≈0	dioctahedral	pyrophyllite	Al <sub>4</sub> Si <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub>	
			trioctahedral	talc	Mg <sub>6</sub> Si <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub>	
	hydrated exchangeable cations	0.4–1.2	dioctahedral	montmorillonite	M <sub>x/n</sub> <sup>n+</sup> [Al <sub>4-x</sub> Mg <sub>x</sub> ][Si <sub>8</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O	
			dioctahedral	beidellite	M <sub>x/n</sub> <sup>n+</sup> [Al <sub>4</sub> ][Si <sub>8-x</sub> Al <sub>x</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O	
			dioctahedral	nontronite	M <sub>x/n</sub> <sup>n+</sup> [Fe <sub>4</sub> ][Si <sub>8-x</sub> Al <sub>x</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O	
			trioctahedral	saponite	M <sub>x/n</sub> <sup>n+</sup> [Mg <sub>6</sub> ][Si <sub>8-x</sub> Al <sub>x</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O	
			trioctahedral	(F-)hectorite	M <sub>x/n</sub> <sup>n+</sup> [Mg <sub>6-x</sub> Li <sub>x</sub> ][Si <sub>8</sub> ]O <sub>20</sub> (OH,F) <sub>4</sub> ·nH <sub>2</sub> O	
			trioctahedral	stevensite	M <sub>x/n</sub> <sup>n+</sup> [Mg <sub>6-x</sub> Vacancy <sub>x</sub> ][Si <sub>8</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O	
	non-hydrated cations	1.2–1.8	intermediate	vermiculite	[Mg,Ca] <sub>x/2</sub> <sup>2+</sup> [Al <sub>4-x</sub> Mg <sub>x</sub> ][Si <sub>8</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·8H <sub>2</sub> O	
			trioctahedral	vermiculite	[Mg,Ca] <sub>x/2</sub> <sup>2+</sup> [Mg <sub>6</sub> ][Si <sub>8-x</sub> Al <sub>x</sub> ]O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O	
hydroxyl sheet	0.4–2.0	trioctahedral	trioctahedral	paragonite	Na <sub>2</sub> [Al <sub>4</sub> ][Si <sub>6</sub> Al <sub>2</sub> ]O <sub>20</sub> (OH) <sub>4</sub>	
			trioctahedral	phlogopite	K <sub>2</sub> [Mg,Fe] <sub>6</sub> [Si <sub>6</sub> Al <sub>2</sub> ]O <sub>20</sub> (OH,F) <sub>4</sub>	
			trioctahedral	trioctahedral	clinochlore	[(Al,Mg <sub>6-x</sub> )(OH) <sub>6</sub> ][Mg <sub>6</sub> ][Si <sub>8-x</sub> Al <sub>x</sub> ]O <sub>20</sub> (OH) <sub>4</sub>
				trioctahedral	thuringite	[(Fe <sup>3+</sup> Fe <sup>2+</sup> <sub>6-x</sub> )(OH) <sub>6</sub> ][Fe <sup>2+</sup> <sub>6-y</sub> Mg <sub>y</sub> ][Si <sub>8-x</sub> Al <sub>x</sub> ]O <sub>20</sub> (OH) <sub>4</sub>

icate is dioctahedral if two of the octahedral sites are occupied by trivalent cations, and trioctahedral if all three octahedral sites are filled with divalent cations. Table 1 summarizes the most common smectites and their idealized structural formulae. For comparison, kaolinite (a dioctahedral 1:1 clay), chrysotile (a trioctahedral 1:1 clay), pyrophyllite, talc, vermiculite, the micas phlogopite (trioctahedral) and paragonite (dioctahedral), and the chlorites clinochlore (Mg-rich) and thuringite (Fe-rich), are included.

In talc and pyrophyllite, all tetrahedral sites are filled with Si<sup>4+</sup>. The octahedral sites of talc are completely filled with Mg<sup>2+</sup> (trioctahedral), whereas two-thirds of the octahedral sites in pyrophyllite are filled with Al<sup>3+</sup> and the remaining sites are vacant (dioctahedral). The electrically neutral sheets are linked by relatively weak dipolar and van der Waals forces (Giese, 1975). In contrast, the 2:1 layers of smectite have a net negative charge resulting from the isomorphous substitutions, viz., (1) Si<sup>4+</sup> by Al<sup>3+</sup> at tetrahedral sites, and (2) Al<sup>3+</sup> by Mg<sup>2+</sup>, or (3) Mg<sup>2+</sup> by Li<sup>+</sup> (or a vacancy) at octahedral sites. This layer charge is balanced by hydrated interlayer cations, such as, Na<sup>+</sup>, K<sup>+</sup>, or Ca<sup>2+</sup>.

The size of the layer charge of smectites is intermediate between that of vermiculites and that of pyrophyllite and talc. Differences in (1) the size of the layer charge, (2) its origin (*i.e.*, tetrahedral or octahedral sheet), and (3) the types of interlayer cations result in different physical and chemical properties, such as thermal stability, ion-exchange behavior, and swelling behavior. For example, the layer charge of an octahedrally-substituted smectite (such as montmorillonite) is distributed over the complete oxygen framework. Tetrahedral substitution (as in beidellite) leads to a more localized charge distribution at the surfaces of the layer and to higher three-dimensional order

(Brindley, 1980; Suquet *et al.*, 1975). Because the interlayer cations in pure smectites are completely exchangeable, the layer charge and CEC differ only slightly (as a result of the contribution of pH-dependent sites on the mineral edges). The two terms will be used interchangeably in this review.

#### SYNTHESIS AT LOW TEMPERATURE AND PRESSURE (<100°C AND 1 BAR)

##### *Hectorite and stevensite*

Hectorites and saponites are the most common authigenic clay minerals. They form at low temperatures and pressures by the alteration of oceanic and continental basalts and other basic volcanic rocks. Low-temperature synthesis will therefore yield fundamental data to aid in the understanding of these geological processes. Synthesis of saponite and hectorite at temperatures that are very low relative to the temperatures (>300°C) required for the synthesis of beidellite, is also important in the industrial application of these minerals as starting materials for pillared clays. Expensive equipment for hydrothermal synthesis is not involved.

Trioctahedral (Mg) smectites with octahedral layer charges caused by either Li substitution (hectorite) or vacancies (stevensite) are closely related. Often Li substitution and vacancies are present together in the same octahedral sheet. Hectorite suspensions display a high viscosity and transparency as well as other attractive rheologic properties, which render hectorite a very valuable clay mineral for industrial applications. A number of different procedures has been developed to synthesize hectorite in large volumes (Güven, 1988).

Strese and Hofmann (1941) were the first scientists to study the formation of hectorite at low temperatures.

They boiled  $\text{MgCl}_2$  and silicic acid in the presence of  $\text{CaOH}_2$ ,  $\text{NaOH}$ , or  $\text{KOH}$  for <20 h and obtained some poorly crystalline hectorite in an amorphous-gel matrix. Similar results were obtained whether the pH was 5–9, the concentration of structural ions was decreased, or the boiling period was increased. Hydrothermal treatment with  $\text{KOH}$  showed that the hectorite-like material was formed only at  $\text{KOH}$  concentrations of 0.1 and 0.3 N and temperatures of 200–250°C. Under other conditions with  $\text{KOH}$ , mica-like phyllosilicates were formed. In contrast, when  $\text{NaOH}$  was used, hectorite formed at all temperatures between 200–585°C.

Caillère *et al.* (1954) and Henin and Robichet (1954) obtained hectorite-like material when two very dilute solutions ( $\sim 10\text{--}20\text{ mg L}^{-1}$ ) containing the necessary constituents were slowly added to 2 L of water at various pH levels and this mixture was then boiled. Well-crystallized material was obtained at pH 8 and 9, whereas crystallinity was much poorer at lower pHs. They assumed a model in which brucite-like sheets formed first and served as a template for the attachment of a silicate sheet. Henin (1956) continued this approach by applying the method of “electrolytic attack” at temperatures as high as 100°C. This method involves the placement of a Pt electrode (anode) in a dilute silica solution together with a cathode made of the metal that furnishes the octahedral cation. With this approach, Henin succeeded in the formation of various smectites including stevensite, nontronite, saponite, and saunonite.

The low-temperature (3–60°C) syntheses of Harder (1972, 1977) were based on the coprecipitation of  $\text{SiO}_2$  and  $\text{Al}^{3+}\text{--Mg}^{2+}$  hydroxides. These  $\text{Al}^{3+}\text{--Mg}^{2+}$  hydroxides were expected to form two-dimensional sheets having the brucite  $[\text{Mg}(\text{OH})_2]$  or gibbsite  $[\text{Al}(\text{OH})_3]$  structure, which then were assumed to act as templates for the “condensation” of silica. The silica concentration had to be low, in the range of 10–100 mg  $\text{SiO}_2\text{ L}^{-1}$ , to prevent polymerization of the monomers in the silicic acid solution. The silica-to-metal-hydroxide ratio in the precipitate had to be similar to that of the desired smectite. Harder (1972) was unable to determine whether his reaction products contained single-phase smectites or mixtures of smectites and X-ray amorphous phases. He therefore could assess neither the exact composition nor the substitutions established in the smectite samples prepared. The main disadvantage of this procedure is the very low silica concentration required, which limits the yield to small quantities of smectites.

Decarreau (1980, 1985) developed another fairly simple procedure in which trioctahedral smectites (hectorite, stevensite, and saponite) were synthesized at low temperatures by mixing stoichiometric amounts of sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ) and metal salts (*e.g.*,  $\text{Mg}$ ,  $\text{Al}$ ,  $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Zn}$ ) into a solution of an appro-

priate acid. The resulting silicometallic precipitate contained small smectite nuclei, the crystallinity of which improved upon aging in the aqueous suspension at temperatures below 100°C. In contrast to the method of Harder (1972, 1977), this procedure allows better control of the homogeneity of the smectites, is easily reproducible, and can produce large quantities of material.

Granquist and Pollack (1960) synthesized hectorite by hydrothermal treatment of an aqueous slurry containing  $\sim 10\%$  freshly precipitated  $\text{Mg}(\text{OH})_2$ , silica gel, and various amounts of  $\text{NaOH}$ ,  $\text{LiOH}$ , and  $\text{LiF}$ . The synthesis conditions used ranged from reflux temperature and atmospheric pressure to 300°C and  $\sim 83$  bars. Use of  $\text{LiF}$  accelerated the crystallization of hectorite. The observations of Baird *et al.* (1971, 1973), based on the same synthesis procedures, suggested that the initial step in crystallization involves condensation of silica monomers onto previously formed brucite-like sheets, confirming the assumption of Harder (1972). The final step was postulated to involve an aging process whereby some of the initial nuclei redissolve and then recondense to form true hectorite nuclei.

Jacobs *et al.* (1997) studied the influence of organic molecules on the synthesis of hectorite and stevensite from  $\text{Mg}(\text{OH})_2$ , silica sol (Ludox),  $\text{LiF}$ , and tetraethylammonium (TEA) salt at 100°C under dynamic conditions for as long as 3 d. They observed that both the crystallization rate and the crystallinity of these materials was increased by the addition of  $\text{LiF}$ . The addition of TEA, on the other hand, had no effect on the rate of crystallization, but it did improve the stacking of the layers. This was explained by the immediate adsorption of the organic molecule upon formation of the 2:1 layer, leading to a hydrophobic, well-ordered structure.

Carrado (1992), Carrado *et al.* (1991, 1996, 1997a, 1997b), and Gregar *et al.* (1994) prepared synthetic hectorites intercalated with a variety of organic cations (*e.g.*, porphyrin rings, organic dyes, polyvinyl alcohols, transition-metal phenanthrolines) by refluxing ( $T = 100^\circ\text{C}$ ) a gel consisting of the organic cation,  $\text{LiF}$ , freshly precipitated  $\text{Mg}(\text{OH})_2$ , and silica sol (Ludox) for 48 h. This approach was unique in that the organic intercalate was present during synthesis rather than being added later by ion exchange. In general, the results, when compared with natural hectorites exchanged with the organic cations, showed the synthetic hectorite to have smaller particle sizes, smaller aspect ratios, and higher specific surfaces. However, when compared to synthesis in the absence of the organic cations, some of the cations [notably poly(dimethyl diallyl ammonium chloride) or PDDA] enhanced the particle size and aspect ratio. Experiments at room temperature (Carrado *et al.*, 1997b) showed very slow crystallization of hectorite in the absence of organics, and inhibition of crystallization when TEA was pres-

ent. All products of these syntheses contained large quantities of excess amorphous silica, although no other crystalline phases were identified.

### Saponite

The major problem encountered in saponite synthesis is that in addition to the tetrahedral substitution [*i.e.*,  $\text{Si}^{4+} \leftrightarrow \text{Al}^{3+}$ ], other substitutions, such as  $\text{Mg}^{2+} \leftrightarrow \text{Al}^{3+}$  at octahedral sites, can proceed, as well as incorporation of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  at the interlayer positions. The range of different sites for  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  prevents control of the composition and the layer charge of the composites during synthesis as demonstrated by Klopogge *et al.* (1993a, 1994a, 1994b) and Vogels *et al.* (1995).

Harder (1972) claimed to have synthesized trioctahedral smectite (*i.e.*, saponite) from Mg-containing  $\text{Al}(\text{OH})_3$ -silica precipitates at 20°C. However, no X-ray diffraction (XRD) data were presented to ascertain the crystallinity of the synthesized saponite.

Farmer *et al.* (1991, 1994) synthesized saponites and nontronites at temperatures below 100°C in a calcareous environment and in the presence of hydrazine. After incubation at 89°C for 8 wk, some saponite developed into rather well-formed crystallites. Diffraction patterns showed that both *hk*-ordered (*i.e.*, *a* and *b* axes in successive layers aligned or rotated by multiples of 60°) and turbostratic stacking occurred in the same samples. Small differences in the *b* cell parameters were observed among crystallites. Farmer *et al.* (1994) could not ascertain whether this difference was due to a difference in composition or in stacking.

Following a new approach, Vogels *et al.* (1995) synthesized saponites at 90°C from a Si-Al gel and a solution containing urea and an  $\text{M}^{2+}$ -nitrate [ $\text{M}^{2+} = \text{Zn}, \text{Mg}, \text{Ni}, \text{Co}$ ] in only a few (5–20) h. Precipitation from homogeneous solution was induced by the slow hydrolysis of the urea, which resulted in a homogeneous release of hydroxyl ions. The octahedral divalent metal had a large influence on the characteristics of the saponite product, such as stacking order, surface area, and pore volume. With Mg the nucleation and growth were rather slow compared to saponites containing Co or Zn. After 20 h with Mg some gel was still present and even after 2 d almost no stacking was observed by transmission electron microscopy (TEM) in agreement with the absence of the (001) reflection in the XRD pattern. The results with different divalent cations indicated that stacking increased in the order  $\text{Ni} = \text{Mg} < \text{Co} < \text{Zn}$ . Both the surface area and pore volume increased as  $\text{Zn} < \text{Co} < \text{Ni} < \text{Mg}$ . The Al distribution over the tetrahedral, octahedral, and interlayer sites was influenced by increasing the initial Si/Al ratio in the starting gel from 5.7 to 39. Adjusting both the octahedral-sheet and tetrahedral-sheet composition by the choice of divalent metals or combinations of met-

als and the Si/Al ratio offers the possibility to control properties like surface area, pore volume, and acidity.

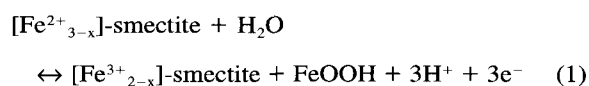
Brat and Rajan (1981) and Brat (1985) synthesized smectites in the stevensite-saponite group from the reaction of silica (65%  $\text{SiO}_2$ ) and alumina (70%  $\text{Al}_2\text{O}_3$ ) gels (prepared by the action of HCl on the Na salts) with Mg- or Na-acetate under boiling-reflux conditions for 45–50 d. Starting  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 2.1–7.9 were used and led to different degrees of octahedral and tetrahedral substitution.

### Nontronite and other ferric smectites

Caillère *et al.* (1953, 1955) obtained nontronite and iron-saponite by aging mixed dilute solutions of silica,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  chlorides, and salts of Mg and Al at 100°C and pHs of 8.5–9.5. In these clays, the octahedral sheet was partly occupied by either Mg or  $\text{Fe}^{2+}$ . Harder (1976, 1978), Decarreau and Bonnin (1986), and Decarreau *et al.* (1987) performed most of the low-temperature syntheses of iron-bearing smectites.

The nontronite synthesis under reducing conditions described by Harder (1976) is analogous to the procedure he used for other trioctahedral smectites (Harder, 1972, 1977) except that the brucite-like or gibbsite-like octahedral-sheet template is replaced by one consisting of  $\text{Fe}(\text{OH})_2$ . The addition of Na dithionite or hydrazinium dichloride established the reducing conditions. Ferrous iron was added as  $\text{FeSO}_4$  and precipitated as  $\text{Fe}(\text{OH})_2$ . A suspension containing 1% of the solid was aged  $\leq 15$  d at 3 or 20°C. The presence of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  was required for the formation of octahedral sheets containing Al and  $\text{Fe}^{3+}$ . At high Si/Fe ratios, nontronite and lebergite, the di- $\text{Fe}^{3+}$  and tri- $\text{Fe}^{2+}$  octahedral 2:1 phyllosilicates, formed. Lower Si/Fe ratios resulted in the formation of the 1:1 phyllosilicates greenalite and berthierine [Harder (1976) termed the latter phase chamosite, but Bailey (1980, p. 24) suggested that the proper name is berthierine].

Decarreau and Bonnin (1986) and Decarreau *et al.* (1987) synthesized ferric smectites using a procedure similar to that described for hectorite and stevensite (Decarreau, 1980). This procedure involves aging of freshly prepared coprecipitated gels of silica and  $\text{FeSO}_4$  under initially reducing conditions at 75°C for 15 d or 1 mo, at 100°C for 1 mo, or at 150°C for 12 d. Upon oxidation of the  $\text{Fe}^{2+}$ , the smectite crystallization is accelerated. Intermediate dissolution according to the reaction



does not proceed to a significant extent and, as a result, all the Fe remains in the octahedral sites of the sheets. Only very small amounts of cryptocrystalline Fe hydroxide or oxide were intergrown with the smectite at levels barely detectable by Möss-

bauer spectroscopy. A structural formula of  $\text{Na}_{0.05}\text{Fe}^{3+}_{1.95}\text{Si}_4\text{O}_{10}(\text{OH})_2$  was suggested. Under oxidizing conditions only, Decarreau *et al.* (1987) were able to synthesize a ferric smectite at 100 and 150°C with a composition of  $\text{Ca}_{0.26}\text{Fe}^{3+}_{1.83}\text{Si}_4\text{O}_{10}(\text{OH})_2$ . This smectite was considered to be a “defect” nontronite with the octahedral vacancies generating the layer charge.

Following the procedures of Kawano and Tomita (1992) and Kawano *et al.* (1993) to synthesize beidellite by hydrothermal alteration of volcanic glass, Tomita *et al.* (1993) synthesized  $\text{Fe}^{3+}$ -smectites at 90–100°C and ambient pressure by reaction of volcanic glass with NaOH. The ratio of glass to NaOH determined whether a smectite or a zeolite (P, E, or chabazite) formed, although a large overlap was observed.

Farmer *et al.* (1991, 1994) obtained poorly crystalline, Al-bearing layer silicates after precipitation in a calcareous environment, which also contained  $\text{Fe}^{2+}$ ,  $\text{Si}(\text{OH})_4$ , and hydrazine. After incubation at 89°C for 8 wk some well-formed aluminous nontronite crystallites, consisting of two to ten co-terminating parallel layers, were obtained. These parallel layers were assumed to be due to synchronous growth. The presence of Ca was essential for *hk*-ordered stacking to develop (ordered stacking was not seen when NaOH, KOH,  $\text{Na}_2\text{CO}_3$ , or  $\text{K}_2\text{CO}_3$  were used). Although no clear explanation was given by the authors, we surmise that the divalent nature of the Ca ions aided in the stacking of successive layers. Farmer (1997) repeated some of this work with a modified synthesis approach involving successive reduction and oxidation cycles (~15 d per cycle) for periods of 10–13 wk and stronger hydrazine solutions. He obtained nonexpanding hydroxy-interlayered ferruginous beidellites (similar to the chlorite structure but with incomplete interlayer hydroxyl sheets) that were of poorer crystallinity than the aluminous nontronites synthesized earlier.

#### Montmorillonite

Harder (1972) performed smectite syntheses at 3 and 20°C by precipitation of amorphous  $\text{Al}(\text{OH})_3$  with coprecipitation of  $\text{Mg}(\text{OH})_2$  and adsorbed silica. Depending on the initial solution composition he found (1) only amorphous material, (2)  $\text{Al}(\text{OH})_3$  or  $\text{Mg}(\text{OH})_2$ , or (3) various phyllosilicates (montmorillonite-, illite-, and chlorite-like). He concluded that to synthesize montmorillonite (1) the pH conditions must be basic to neutral, (2) a low silica concentration (undersaturated with respect to amorphous silica) is needed, (3) the composition of the initial precipitate has to be more or less stoichiometric, and (4) the Mg content must be at least 6%. These conditions agree quite well with the montmorillonite-forming conditions observed in nature. For example, volcanic material (ash, glass) can react with seawater, or with fresh water under basic conditions, to form smectite minerals. Tomita *et al.*

(1993) explored the formation of clay minerals and zeolites from volcanic glass (or obsidian) and pumice under basic conditions (NaOH) at temperatures of ~100°C. Smectites formed only at relatively low glass-to-NaOH ratios. X-ray and electron diffraction patterns showed the newly formed smectites to be expandable and to have *hk*-ordered stacking instead of the expected turbostratic stacking. Although they indicate that the formation of the octahedral sheet is important, they do not give a possible mechanism. This problem concerning dissolution and reprecipitation or *in situ* formation might have been partly solved if changes in the solution chemistry had been monitored during their experiments.

#### Sauconite and other transition-metal (Ni, Co, Zn, Cu) smectites

As quoted by Tiller and Pickering (1974), Esquevin (1960) reported the synthesis of sauconite at 100°C and 1 bar, although it is not clear if a single phase was obtained. Tiller and Pickering (1974) tried to synthesize trioctahedral zinc smectites (sauconite) under earth-surface conditions (20°C, 1 bar) from monomeric  $\text{H}_4\text{SiO}_4$ ,  $\text{ZnCl}_2$ , and, in some experiments,  $\text{AlO}_4^-$  solutions. In the Al-free experiments after one year of aging, XRD patterns showed broad peaks corresponding to a 2:1 phyllosilicate and to hydrozincite [ $2\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2$ ]. Aging for periods up to seven years did not increase crystallinity. Products containing Al showed an additional pattern interpreted as a 1:1 phyllosilicate.

Harder (1975) also synthesized a zinc hectorite under earth-surface conditions (~20°C, 1 bar) from dilute solutions of  $\text{Zn}(\text{OH})_2$  and  $\text{H}_4\text{SiO}_4$  at a pH of ~8. Hectorite was only formed when  $\text{H}_4\text{SiO}_4$  was present as monomers and within a small range of Zn/SiO<sub>2</sub> ratios. Otherwise  $\text{Zn}(\text{OH})_2$  plus quartz or amorphous material was formed. In addition to the montmorillonite-synthesis experiments (Harder, 1972), Harder (1977) synthesized smectites containing heavy metals such as Zn (sauconite), Ni, Cu, Cr, Mn, and Co under similar conditions. The main constraints were (1) that the cation size should be one that allows octahedral coordination by oxygen and the formation of a brucite-like sheet, and (2) that the precipitation rate must be slow.

Luca *et al.* (1991) described synthesis of fluorhectorite in which a small amount of Mg was replaced by Cu. They started with a mixture of tetraethylorthosilicate (TEOS),  $\text{CuCl}_2$ , and  $\text{MgCl}_2$  precipitated by NaOH. This precipitate was refluxed for 12 h together with LiF and NaF. The XRD pattern of the product was comparable to that of Laponite with no evidence of impurities. Total replacement of Mg by Cu in the fluorhectorite structure was also shown to be possible under these synthesis conditions.

Using the method of Decarreau (1980, 1985), Mosser *et al.* (1990) synthesized poorly crystallized Cu-

stevensites at 75°C where the atomic ratio Cu/Cu + Mg in the octahedra was <0.5. At higher Cu contents, chrysocolla crystallized. Differences in ionic radii were insufficient to explain the results. The results of an analysis of the local structure by extended X-ray absorption fine structure (EXAFS) spectroscopy could only be explained by a strong distortion of the Cu-octahedra due to the Jahn-Teller effect. This has two important consequences: (1) it is difficult to have many neighboring octahedra containing Cu in the clay structure (*i.e.*, Cu atoms are rather diluted in a Mg-matrix), and (2) the possible amount of Cu incorporation in an hydroxylated Mg octahedral sheet is limited.

The various procedures for synthesis under low-temperature and ambient-pressure conditions are summarized in Table 2.

#### HYDROTHERMAL SYNTHESIS (100–1000°C, P<sub>H<sub>2</sub>O</sub> OR HIGH PRESSURE)

Roy and Tuttle (1956) gave a good historical review of the various apparatus used for hydrothermal syntheses of minerals, most having changed only slightly today, and of the various mineral groups synthesized to that time. In an earlier publication on phase equilibria, Roy (1954) noted general criteria for hydrothermal synthesis, which are still useful. He suggested that the hydrothermal approach allows synthesis of clay minerals with controlled and definite amounts of substitutions and that syntheses at different compositions, temperatures, and pressures allow determination of the phase boundaries between various clay minerals. He also explained that high pH values, or basic conditions, are in nature mostly neutralized by common amphoteric oxides, and that the initial high pH values merely represent the presence of cations like Na<sup>+</sup>, K<sup>+</sup>, or Ca<sup>2+</sup> in the final product(s). We note that the metastable persistence of phases is always an important problem when examining clay-mineral synthesis results. A well-known example is the appearance of cristobalite as a secondary phase in clay synthesis or even cristobalite and quartz, where quartz is expected to be the stable phase (Kloprogge *et al.*, 1993b; Nakazawa *et al.*, 1991).

#### Compositional series

Early studies attempted to vary the layer charge of single-phase smectites prepared from gels in the montmorillonite-beidellite and saponite-beidellite compositional ranges by manipulating the synthesis pressure and temperature (Roy and Roy, 1952, 1955; Sand *et al.*, 1953, 1957; Roy and Sand, 1956). The results were inconclusive, perhaps because the phases obtained were not homogeneous or sufficiently crystalline. Koizumi and Roy (1959) then prepared two series of gels in the saponite and beidellite compositional region by mixing silica sol (Ludox) with a solution of

Al<sup>3+</sup>- or Mg<sup>2+</sup>-nitrate and NaOH, drying the resulting mixtures, and firing to 500°C. The gels resulting from the addition of water to the above solids were reacted at a water pressure of ~1 kbar and at temperatures of 200–850°C. Single-phase saponite (Figure 1) and beidellite (Figure 2), having layer-charge values that varied with the starting composition, were obtained at temperatures of 260–550°C (450°C for beidellite). These results and those of Roy and Sand (1956) suggested that the nature and extent of isomorphous substitution could be controlled. Harward and Brindley (1966), therefore, conducted experiments with gel compositions in the beidellite range to achieve tetrahedral substitution, and in the montmorillonite range to achieve octahedral substitution. Their results showed that isomorphous substitution is only possible within a relatively small compositional range, and that apparent differences in layer charge values may be attributed to the formation of other phases. The beidellite results are explained by the Al-O-Al avoidance rule (Loewenstein, 1954) and the theory concerning homogeneous dispersion of charges (Herrero *et al.*, 1985, 1987).

More recently, Decarreau *et al.* (1992) synthesized several series of tri- and dioctahedral smectites with different octahedral-cation compositions, by applying temperatures of 100–250°C and starting from gels or glasses with appropriate compositions. They rarely observed randomly mixed distributions of the octahedral cations, even for homovalent substitutions, thus suggesting that similar chemical properties are more important than similar ionic radii. They concluded that segregation of octahedral cations is common and leads either to clusters within the octahedral sheets or to an immiscibility of two different phases. Later, Grauby *et al.* (1993) showed that in the beidellite-saponite series three different interferential coherence domains occur: (1) dioctahedral, essentially aluminous, domains; (2) trioctahedral, essentially magnesian, domains, and (3) an intermediate mixed domain. In most instances, two kinds of domains were associated. The intermediate case was shown to be metastable and comprised of particles with stacked layers, each layer having a constant chemistry, and, thus, showing an apparent di-trioctahedral structure. In contrast, a true continuous solid solution was observed for the nontronite-saponite series (Grauby *et al.*, 1994) under the same experimental conditions. The absence of the chemical gap observed for natural smectites and other 2:1 phyllosilicates (Weaver and Pollard 1973; Foster, 1960) was related to the closed experimental systems of Grauby *et al.* (1994), in which Fe<sup>3+</sup> and Mg are continuously available and may react simultaneously with silica at higher temperatures than those typical of natural smectite formation.

Koizumi and Roy (1959) reported the formation of mixed-layer smectites from Na-rich compositions.

Table 2. Experimental results of low-temperature syntheses at atmospheric pressures.

Authors	Starting materials	Conditions	Phases obtained	Remarks
Strese and Hoffmann (1941)	silicic acid, MgCl <sub>2</sub> , Na-, K-, Ca-hydroxide	boiling 20 h	amorphous, hectorite	small amount of poorly crystalline hectorite
Caillère <i>et al.</i> (1953, 1954, 1955), Henin (1956), Henin and Robichet (1954)	SiO <sub>2</sub> , FeCl <sub>2</sub> , Mg-, Al-salts	100°C boiling	hectorite, Fe-saponite, nontronite	very dilute solutions
Harder (1972, 1977)	SiO <sub>2</sub> , Mg(OH) <sub>2</sub> , Al(OH) <sub>3</sub> (10–100 ppm)	3–60°C	amorphous, Mg, Al hydroxides, montmorillonite, illite, chlorite, saponite	not enough material to characterize due to dilute solutions
Decarreau (1980, 1985), Mosser <i>et al.</i> (1990)	Na <sub>2</sub> SiO <sub>3</sub> , metal salts, acid	<100°C	hectorite, stevensite, saponite	phases formed depend on starting composition
Granquist and Pollack (1960), Baird <i>et al.</i> (1971, 1973)	SiO <sub>2</sub> gel, Mg(OH) <sub>2</sub> , NaOH/LiOH, LiF	reflux and 300°C/83 bar	hectorite	Li accelerates crystallization
Jacobs <i>et al.</i> (1997)	Silica sol (Ludox) Mg(OH) <sub>2</sub> , TEA, LiF	100°C, ≤3 d	hectorite	TEA increased crystallinity and stacking
Carrado (1992), Carrado <i>et al.</i> (1991, 1996, 1997a, 1997b), Gregar <i>et al.</i> (1994)	Silica sol (Ludox), Mg(OH) <sub>2</sub> , organic cations, LiF	100°C reflux, 2 d	organo-hectorite	direct uniform intercalation, but crystallinity varied with ion
Farmer <i>et al.</i> (1991, 1994)	TEOS, AlCl <sub>3</sub> , FeCl <sub>2</sub> , Ca(OH) <sub>2</sub> , hydrazine	<100°C, ≤8 wk	saponite, nontronite	phases formed depend on starting composition
Vogels <i>et al.</i> (1995)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> gel, divalent metal nitrates, urea	90°C, <2 d from homogeneous solution	saponite	stacking order depends on divalent metal used
Brat and Rajan (1981), Brat (1985), Decarreau (1985)	gel from Na <sub>2</sub> SiO <sub>3</sub> , NaAlO <sub>2</sub> in HCl	boiling 45 d in Mg acetate	saponite	
Harder (1976, 1978)	SiO <sub>2</sub> , Fe(OH) <sub>2</sub> , dithionite or hydrazinium chloride, Fe(SO <sub>4</sub> ) <sub>2</sub>	3–20°C, 15 d	nontronite, lempbergite, greenalite, berthierine	lempbergite formed at high Si/Fe ratio, lower Si/Fe gave greenalite and berthierine
Decarreau and Bonnin (1986), Decarreau <i>et al.</i> (1987)	SiO <sub>2</sub> gel, Fe(SO <sub>4</sub> ) <sub>2</sub>	75°C (15 d and 1 mo) 100°C (1 mo) 150°C (12 d)	nontronite, Fe-smectite, trace Fe(OH) <sub>2</sub>	under oxidizing conditions Fe-smectite ("defect" nontronite)
Tomita <i>et al.</i> (1993)	volcanic glass or pumice, NaOH	90–100°C	Fe <sup>3+</sup> -smectite, zeolites	ratio glass/NaOH determines smectite or zeolite formation
Farmer (1997)	TEOS, AlCl <sub>3</sub> , FeCl <sub>2</sub> Ca(OH) <sub>2</sub> , hydrazine	95°C, 15-d redox cycles, 10–13 wk	hydroxy-interlayered Fe-beidellite	poorly crystalline
Tiller and Pickering (1974), Harder (1975)	silicic acid, ZnCl <sub>2</sub> or Zn(OH) <sub>2</sub> , Al(OH) <sub>4</sub> <sup>-</sup>	20°C, 1 y	2:1 phyllosilicates, hydrozincite, Zn(OH) <sub>2</sub> , quartz, amorphous	only when silicic acid present as monomer and in a small range of Zn/SiO <sub>2</sub> ratios
Luca <i>et al.</i> (1991)	TEOS, CuCl <sub>2</sub> , MgCl <sub>2</sub> NaOH, LiF, NaF	reflux, 12 h	Cu, Mg fluorhectorite	total replacement of Mg by Cu possible

Iiyama and Roy (1963a) attempted to systematize the preparation of mixed-layer phases and to obtain information on their stability. They used gels with compositions along the join talc-Na-saponite-Na-phlogopite. At 1 kbar and temperatures of 450–575°C, they found phases with random interstratification (Figure 1), whereas at higher pressure regularly interstratified mixed-layer, generally 1:1, phases were observed (data not shown).

The study on the maximum hydrothermal stability of montmorillonites by Ames and Sand (1958) showed that the highest stability is found where (1) all possible cation positions in the layer are occupied (*i.e.*, with trioctahedral smectites), (2) an optimum tetrahedral or octahedral substitution occurs, and (3) the resulting layer charge is compensated by exchangeable cations other than H<sup>+</sup>. They thus observed a maximum stability of ~420°C for beidellite and montmorillonite



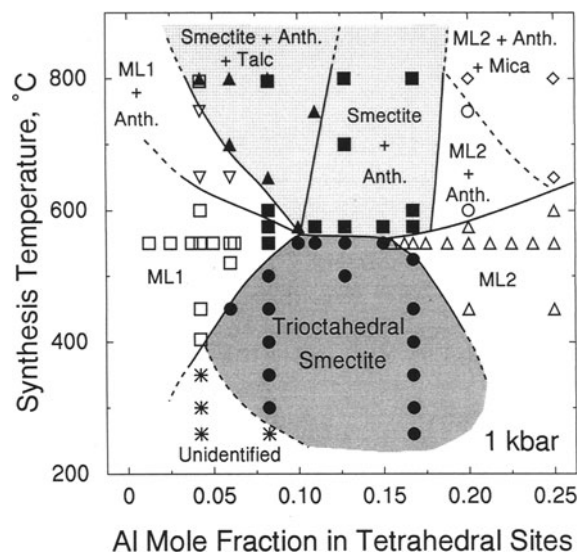


Figure 1. Synthesis fields of trioctahedral smectites prepared by hydrothermal techniques (1 kbar, 250–800°C) as a function of mole fraction of Al in the tetrahedral sites [data of Koizumi and Roy (1959) and Iiyama and Roy (1963b)]. ● Trioctahedral smectite, ■ Trioctahedral smectite + anthophyllite, ▲ Trioctahedral smectite + anthophyllite + talc, □ Mixed-layer phase #1, ▽ Mixed-layer phase #1 + anthophyllite, △ Mixed-layer phase #2, ○ Mixed-layer phase #2 + anthophyllite, ◇ Mixed-layer phase #2 + anthophyllite + mica, \* Unidentified phases.

(dioctahedral smectites, Figure 2), whereas saponite and hectorite (trioctahedral smectites, Figure 1) were stable to 800°C. A marked decrease in temperature of maximum stability was observed when the substitution deviated from the optimum level (e.g., ~0.1 Al mole fraction in the tetrahedral sites).

Eberl and Hower (1977) hydrothermally treated beidellite glasses, prepared by the Ludox sol-gel method (Luth and Ingamells, 1965) at temperatures below 300°C. After incubating samples for 92 and 259 d the authors obtained a reaction series containing products varying from 100% expandable Na-beidellite to randomly interstratified mixed-layer paragonite-beidellite plus kaolinite and quartz. Above 300°C, however, Na-beidellite reacted to form Na-rectorite, together with pyrophyllite and quartz or feldspar. Na-rectorite is a regularly interstratified paragonite-beidellite.

Starting from glasses, Yamada *et al.* (1991a) synthesized smectites in the compositional range montmorillonite-beidellite at 1 kbar. With initial Si/Al ratios between those corresponding to 100% montmorillonite and 78% montmorillonite/22% beidellite, they obtained single-phase montmorillonite at temperatures below 375°C. Lower initial Si/Al ratios (*i.e.*, Al contents corresponding to 22–100% beidellite) led to beidellite at temperatures below 400°C. An initial Si/Al ratio corresponding to 50% montmorillonite/50% beidellite, however, resulted in a mixed-layer phase of

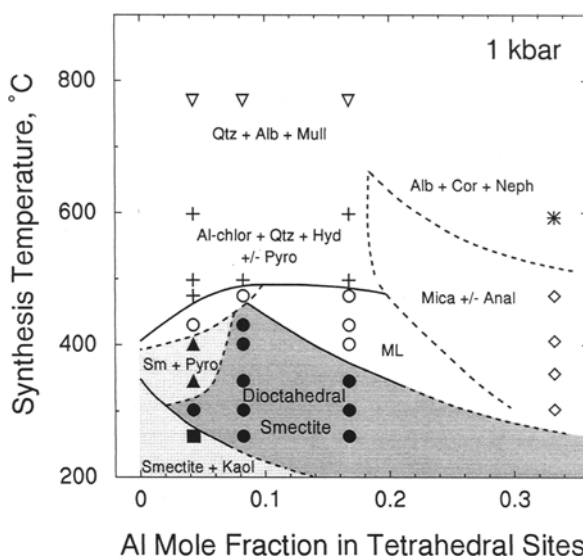


Figure 2. Synthesis fields of dioctahedral smectites prepared by hydrothermal techniques (1 kbar, 250–800°C) as a function of mole fraction of Al in the tetrahedral sites [data of Koizumi and Roy (1959) and Ames and Sand (1958)]. ● Dioctahedral smectite, ■ Dioctahedral smectite + kaolinite, ▲ Dioctahedral smectite + pyrophyllite, ○ Mixed-layer phases, + Al-chlorite + quartz + hydroxides ± pyrophyllite, ▽ Quartz + albite + mullite, \* Albite + corundum + nepheline, ◇ Mica ± analcime.

regularly interstratified montmorillonite-beidellite at temperatures below 400°C. Above 450°C they found Na-rectorite. Klopogge *et al.* (1993b) also observed this mixed-layer phase in their products synthesized at 2 kbar and higher. Additional experiments (Nakazawa *et al.*, 1992) showed that at 450°C cristobalite also formed, and at 475°C both cristobalite and quartz were present, in agreement with the data of Klopogge *et al.* (1993b).

Klopogge *et al.* (1993b) demonstrated that, starting from stoichiometric gels in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , the amount of Na determines whether, with increasing Na content, kaolinite + quartz (below 325°C) or pyrophyllite (above 325°C), beidellite, or paragonite + a  $\text{SiO}_2$  phase is formed. The synthesis field of the beidellite shows a minimum at a Na content of ~1.5 Na per  $\text{O}_{20}(\text{OH})_4$  unit. Based on their experiments, Nakazawa *et al.* (1991) suggested the following model: (1) two-dimensional fragments are formed by initial hydration of the glass, and (2) further hydration does not increase the dimensions of the fragments or the degree of interstratification, but does increase the number of poorly crystallized fragments.

#### Hectorite

A commercial synthetic hectorite from Laporte Industries Ltd., known by the trade name Laponite and used to control the rheological properties of paints and other aqueous solutions containing polar organic

compounds (Neumann, 1965; Taylor and Neumann, 1968; Neumann and Sansom, 1970), derives layer charge from a combination of vacancies and Li substitutions in the octahedral sheet. Neumann and Sampson (1970) reported a composition of  $\text{Na}_{0.30}(\text{Mg}_{2.55}\text{Li}_{0.30}\text{vac}_{0.15})\text{Si}_4\text{O}_{9.70}(\text{OH})_{2.30}$ , although substitution of F for structural OH is possible (Neumann and Sansom, 1976). The layer charge is apparently decreased by the presence of silanol (Si-OH) groups. The crystallinity of this material is rather poor, and, as noted by van Olphen and Fripiat (1979), the material reported as "pure" contains traces of carbonate. Green *et al.* (1970) investigated the thermal reactions of this synthetic hectorite. Most of the interlayer water was removed below 200°C, followed by a small but steady weight loss until dehydroxylation was completed at ~700°C. They stated that these results showed no anhydrous intermediate phase was formed prior to dehydroxylation. Three patents (Neumann, 1971, 1972; Neumann and Sansom, 1976) describe the synthesis, which involves the formation of an aqueous slurry from water-soluble Mg-salts,  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{CO}_3$  or NaOH, and LiF. This slurry is hydrothermally treated by boiling at reflux temperature under atmospheric pressure for 10–20 h. An improvement to the 1971 procedure (Neumann, 1972) involves hydrothermal treatment in an autoclave at 10–50 bars and 185–265°C for, at most, 8 h. Prolonged treatment results in further crystallization, which affects the rheological properties adversely.

Torii *et al.* (1983), Torii (1985), Torii and Iwasaki (1986, 1987), and Iwasaki *et al.* (1989) published a different method in which homogeneous slurries of the desired hectorite composition are utilized. The slurries were prepared by dissolving  $\text{MgCl}_2$  in a solution of  $\text{Na}_2\text{SiO}_3$  and  $\text{HNO}_3$ , followed by precipitation with  $\text{NH}_4\text{OH}$ , washing, and addition of NaOH and LiOH. The resulting slurries were hydrothermally treated at 125–300°C under autogenous water-vapor pressures for 1–24 h. They observed that the amount of octahedral Li increased with increasing temperature, but, at constant temperature, increasing the amounts of LiOH did not result in higher amounts of octahedral Li in the hectorite structure. This indicates that the layer charge of this type of synthetic hectorite was mainly due to octahedral vacancies, in contrast to natural hectorites where charge is derived from the substitution of Li for Mg in the octahedral sheet.

Orlemann (1972) used natural pure talc as a starting material, calcined together with  $\text{Li}_2\text{CO}_3$  at 760–980°C. The resulting solid was hydrothermally treated with an aqueous solution of Na silicate and carbonate for 8–16 h at 185°C and corresponding water-vapor pressure (11 bar). The main advantages of this procedure are the use of talc (a pure, relatively cheap, and readily available reactant material), and the simpler and shorter series of process steps.

In contrast to the general use of fluoride as a mineralizing agent in syntheses, several workers focused on the incorporation of fluoride into the structure of hectorite. Due to its easy formation and high-temperature stability, synthetic fluorhectorite has found use as a catalyst for organic reactions. Miller and Johnson (1962) described the formation of very small flakes of Li-fluorhectorite as a byproduct during the high-temperature synthesis of fluormica (taeniolite) under melt conditions (maximum temperature 1420°C, 2 h) from a mixture of  $\text{K}_2\text{SiF}_6$ , LiF,  $\text{Li}_2\text{CO}_3$ , MgO, and  $\text{SiO}_2$ .

Barrer and Jones (1970) synthesized Li-fluorhectorite in the solid state by 24-h treatments at 800°C and in melts by 2-h treatments at 850°C. As starting materials they used silica fused at 800°C and MgO, together with  $\text{MgF}_2$ , NaF, LiF,  $\text{Na}_2\text{CO}_3$ , and  $\text{Li}_2\text{CO}_3$ . At higher temperatures, only amphiboles formed due to the loss of F from sintering. At 800°C, a small excess of LiF was needed to form fluorhectorite as the major phase. Additional phases observed were quartz,  $\text{Li}_2\text{SiO}_3$ , and fluoramphiboles. The formation of quartz was shown to be a function of the oxygen to silicon ratio, whereas the amount of  $\text{Li}_2\text{SiO}_3$  was related to the amount of  $\text{Li}_2\text{CO}_3$ . In melts at 850°C, a larger excess of LiF was needed as a flux to form fluorhectorite. Small amounts of quartz,  $\text{Li}_2\text{SiO}_3$ , and some remaining LiF were also produced. The raw materials were consumed during the first 30 min, which were interpreted as a period of incipient crystallization of the fluorhectorite. Rapid crystalline growth followed during the final 90 min.

A similar route was used by Shabtai *et al.* (1984) to prepare fluorhectorites that were subsequently used as the starting material for the preparation of Al cross-linked smectites. In the <1- $\mu\text{m}$  fraction, the concentration of impurities was <5% and these consisted mainly of quartz, amphiboles, and, in some samples,  $\text{Li}_2\text{SiF}_6$ . The BET surface area of these fluorhectorites was shown to be <10  $\text{m}^2 \text{g}^{-1}$ .

Hertl and Bartholomew (1990) described the synthesis of fluorhectorite in a melt at 925°C from silica sand,  $\text{Na}_2\text{CO}_3$ , MgO, and  $\text{Na}_2\text{SiF}_6$ . No experiment time or characterization of this synthetic fluorhectorite was presented.

### Saponite

Iiyama and Roy (1963a) describe the synthesis of pure saponite and heteropolytypes (mixed-layer) of talc and saponite from gels prepared by mixing Al-, Mg-, and Na-nitrate solutions and colloidal-silica suspensions (Ludox AS). At temperatures to 575°C and 1 kbar, pure saponite could be formed although the composition range narrowed with increasing temperature (Figure 1). At lower Al and Na compositions, randomly interstratified mixed-layer talc-saponite was observed under the same pressure and temperature conditions. At higher pressures, regular interstratified

mixed-layer talc-saponite (generally 1:1) phases were formed. Additional experiments at 1 kbar and 600–850°C were conducted by Iiyama and Roy (1963b). They observed that the pure smectite field narrows with increasing temperature (Figure 1). The composition of this very stable saponitic smectite was approximately  $\text{Na}_{0.55}(\text{Mg}_{2.70}\text{Al}_{0.30})(\text{Si}_{3.15}\text{Al}_{0.85})\text{O}_{10}(\text{OH})_2$ . This material formed even at 900°C after short periods, but disappeared with longer periods indicating that it was unstable at this temperature. Depending on the temperature, additional materials such as talc, anthophyllite, and cordierite were obtained.

Hickson (1974, 1975) patented a procedure to synthesize a trioctahedral clay of the saponite type, which can be used as a component of a hydroconversion catalyst. The procedure comprises hydrothermal crystallization at pH ~9–10 and 300–350°C for ~4 h from aqueous slurries of hydrous silica sol,  $\text{Al}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$ , and either  $\text{NH}_4\text{OH}$  or  $\text{NH}_4\text{F}$ . X-ray diffraction patterns indicated the formation of a clay structure of the saponite type with a  $d(001)$ -value of 11.5–14 Å, which expanded to 18 Å upon treatment with glycol, and a  $d(060)$ -value of 1.52 Å.

A similar synthesis method is described in a patent by Granquist (1966) in which hydrous oxides of Si, Al, Mg, and Na are treated for several days under hydrothermal conditions to 350°C and autogenous water pressure. Kuchta and Fajnor (1988) describe the influence of temperature (100–355°C) and time (1–3 wk) at 133 bars on the phase(s) formed. They obtained  $\text{Mg}(\text{OH})_2$  and poorly crystalline saponite. At 200°C, saponite was formed only after 3 wk, with  $\text{Mg}(\text{OH})_2$  being formed in shorter periods. Saponite was formed in all experiments at higher temperature and the crystallinity was better than at 200°C.

Cohen *et al.* (1980) described the synthesis of saponite from naturally occurring igneous rocks of intermediate to ultrabasic composition. These rocks were treated with water at 350–450°C and pressures as high as 350 bars. Olivine and other ferromagnesian minerals along with cryptocrystalline and glassy material were believed to be the main reactive materials. As a result of this hydrothermal treatment, a number of chemical and physical changes occurred that resulted in a mineral mixture with saponite-like properties.

Almost simultaneously with Decarreau (1980), Brat and Rajan (1981) reported the synthesis of saponite using a similar gel prepared by dissolving  $\text{Na}_2\text{SiO}_3$  and  $\text{NaAlO}_4$  in HCl. In contrast to Decarreau, however, Brat and Rajan obtained saponite by boiling the gel in Mg-acetate for 45 d (thus not using hydrothermal conditions). Later, Decarreau (1985) also suggested the use of  $\text{NaAlO}_4$  as an Al source. The saponite obtained had a considerable adsorption capacity and could be effectively used in the disposal of radioactive liquid waste containing Cs or Sr.

Suquet *et al.* (1977) synthesized saponites using a method similar to that of Hamilton and Henderson (1968). Booij (1992) had considerable difficulties with this method, due to the formation of forsterite ( $\text{Mg}_2\text{SiO}_4$ ) during the calcination used to remove the nitrates from the gel. Suquet *et al.* (1977, 1981a), however, did not report the formation of forsterite, probably because their calcination procedure (600°C for 24 h) was not sufficiently severe to initiate crystallization. Suquet *et al.* (1981a, 1981b) varied the composition of the saponite and, subsequently, the extent of tetrahedral and octahedral Al substitutions. According to the general formula  $\text{Na}_x(\text{Mg}_{3-q}\text{Al}_q)(\text{Si}_{4-s}\text{Al}_s)\text{O}_{10}(\text{OH})_2$ , the layer charge  $x$ , being equal to  $s - q$ , ranged from 0.33 to 1.00, assuming a 1:1 substitution of  $\text{Mg}^{2+} \leftrightarrow \text{Al}^{3+}$ . This substitution results in a positively charged octahedral sheet, instead of the charge-neutral substitution of  $3\text{Mg}^{2+} \leftrightarrow 2\text{Al}^{3+} + 1$  vacancy, which is common in micas. Based on this substitution, for which no evidence was presented in their papers, Suquet *et al.* extensively studied the influence of layer charge, tetrahedral and octahedral substitution, and amount of interlayer water on crystallographic parameters such as the  $b$  axis and the  $d(001)$ -value (1981a, 1981b), and on the interaction with the interlayer cation (1982). Klopogge *et al.* (1993a, 1994b) have shown by means of mineral chemistry and especially  $^{27}\text{Al}$  and  $^{29}\text{Si}$  magic-angle-spinning nuclear-magnetic-resonance (MAS-NMR) spectroscopy that Al substitution cannot be controlled by gel composition only, and that  $\text{Mg}^{2+}$  and even  $\text{Al}^{3+}$  may be accommodated in the interlayer.

Based on the same method described above for hectorite, Torii *et al.* (1983) and Iwasaki *et al.* (1989) also prepared synthetic saponites. The particles were described as foliated aggregates having maximum diameters of ~1 µm. The addition of  $\text{F}^-$  seemed to increase the average particle size.

Klopogge *et al.* (1993a, 1994a, 1994b) and Vogels *et al.* (1997) synthesized saponites following a procedure originally described by Breukelaar *et al.* (1989, 1990). This procedure involved treating a gel containing  $\text{SiO}_2$ ,  $\text{Al}(\text{isopropoxide})_3$ ,  $\text{Mg}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{NH}_4^+$  at 125–300°C for 1–72 h. The crystallites obtained were similar to those of Farmer *et al.* (1991, 1994) prepared at 89°C and ambient pressure. The work of these groups supports a conceptual crystallization model based on the nucleation and lateral growth of individual layers which later stack together to form quasicrystals.

Li *et al.* (1993) synthesized saponites from a homogeneous gel at 290°C for 12 h in a closed system. The gel was prepared by the sequential addition of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$  solutions to a solution containing NaOH and waterglass (*i.e.*,  $\text{Na}_2\text{SiO}_3$ ). They found by  $^{27}\text{Al}$  MAS-NMR spectroscopy that almost all Al in the saponite structure was in tetrahedral coordination (strong signal at 63 ppm) and only a very small

amount was in octahedral coordination (very weak and broad signal at 8 to  $-3$  ppm). The XRD and MAS-NMR results seem to indicate that no other phases, including amorphous ones, were present, although other analytical techniques, such as TEM, were not used for confirmation. No information was given on crystallinity or stacking sequences.

Golden *et al.* (1985), Golden and Dixon (1990), and Komarneni (1989) studied the hydrothermal alteration of palygorskite and sepiolite to smectite. They observed that, at 80–160°C under autogenous water pressure, smectites are easily formed within 24 h. The XRD data revealed the trioctahedral nature of the smectite and that the negative charge was located in the tetrahedral sheet, suggesting that the newly formed smectite was saponite. Analysis by  $^{27}\text{Al}$  MAS-NMR revealed the change of the Al coordination from mainly octahedral in palygorskite to tetrahedral in the saponite (Komarneni, 1989). Chemical analyses of the supernatants of the treated palygorskite indicated that substantial Si and Al went into solution, whereas little Mg was solubilized (Golden and Dixon, 1990). The limited solubility of  $\text{Mg}^{2+}$  at high pH explains why only small amounts of saponite were formed after treatment in NaOH solutions. The addition of  $\text{MgCO}_3$  strongly increased the amount of  $\text{Mg}^{2+}$  in solution and, consequently, favored the formation of saponite. Based on the XRD and NMR results, both Komarneni (1989) and Golden and Dixon (1990) concluded that a dissolution and reprecipitation mechanism was responsible for the saponite formation. Images obtained by TEM revealed that the newly formed saponite had a lath-like morphology similar to that of palygorskite. Komarneni (1989) suggested a nucleation and epitaxial-growth mechanism for saponite on the surface of the palygorskite remnants. Hydrothermal experiments with sepiolite at 300°C and 300 bars in the presence of  $\text{CsCl}$ ,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$  (Komarneni, 1989) revealed a similar dissolution and reprecipitation mechanism, but the nucleation and epitaxial-growth mechanism was absent; no explanation was given for this absence.

#### *Nontronite and other ferric smectites*

High-temperature nontronite syntheses were reported by Ewell and Insley (1935), who kept mixtures of silica gel and  $\text{Fe}_2\text{O}_3$  at 340–350°C and 167 bars for 6 d. A mixture of nontronite, hematite, and an unknown phase was formed as indicated by XRD, dissolution experiments in hot 6 N HCl, and examination by optical microscopy. Hamilton and Furtwängler (1951) kept dilute solutions of  $\text{Na}_2\text{SiO}_3$  in  $\text{FeCl}_3$  at high temperatures to obtain nontronite.

Mizutani *et al.* (1991) prepared Fe-rich 1:1 and 2:1 phyllosilicates by hydrothermal treatment (100–200°C, 50 h) of a reaction mixture of silicic acid,  $\text{FeSO}_4$ , and NaOH. The Fe/Si ratio determined whether the 1:1 or

2:1 phyllosilicate was formed. Ratios of 0.75 and 1.5 resulted in the formation of the nontronite-like material. Mössbauer spectroscopy ( $^{57}\text{Fe}$ ) revealed that 97% of the Fe in the nontronite was  $\text{Fe}^{3+}$  with only  $\sim 3\%$  present as octahedral  $\text{Fe}^{2+}$ . Both the octahedra and tetrahedra seem to be more distorted than in natural nontronite. The authors attributed this distortion to the relatively rapid crystallization when compared to natural formation. Even the addition of 1 wt. % Na-dithionite did not prevent the oxidation of  $\text{Fe}^{2+}$  during the synthesis. Temperatures  $> 150^\circ\text{C}$  resulted in the additional formation of an Fe-oxide impurity. Analyses by TEM and XRD showed the absence of an amorphous phase. The electron-diffraction pattern indicated a turbostratic stacking of small crystallites.

#### *Montmorillonite*

Noll (1936) recognized early that the formation of montmorillonite from natural minerals was hampered by the low reactivity of silicates such as feldspars. Therefore, he chose an artificial simplified hydrothermal system (300°C, autogenous water pressure  $\pm 87$  bar, 15–24 h) containing the required chemical composition, including “tonerde” (a natural clay material), silicic acid, and several hydroxides. In the presence of  $\text{Ca}(\text{OH})_2$ , KOH, and NaOH he found that montmorillonite formed across a limited hydroxide concentration range equivalent to a molar ratio of  $\text{M}^{2+}\text{O}:\text{Al}_2\text{O}_3$  (or  $\text{M}_2\text{O}:\text{Al}_2\text{O}_3$ ) of 0.2:1. Magnesium hydroxide was also shown effective although the optimum concentration was higher than the other hydroxides. Lowering of the hydroxide concentrations resulted in the additional formation of kaolinite. Replacing the hydroxides by other soluble salts, such as chlorides or sulfates, resulted in mixtures of kaolinite and montmorillonite. The reaction temperature of 300°C agrees well with the results of Sand *et al.* (1953), who observed that the maximum temperature for the synthesis of montmorillonite was 250–450°C, although at a higher pressure of  $\sim 1$  kbar.

Roy and Sand (1956) obtained well-defined crystals approaching lath-like habit by treating Na-aluminosilicate gels at 400°C and 1 kbar for 2 wk. Although this phase was reported to be a montmorillonite, it was more likely a beidellite based on the starting composition.

In a comparison between the hydrothermal treatment at 1 kbar of Wyoming bentonite and a gel of identical composition, Sand and Crowley (1956) showed that the montmorillonite single-phase upper stability limit is  $\sim 380^\circ\text{C}$ , whereas at higher temperatures additional phases such as cristobalite, mullite, and mica are formed. Sand *et al.* (1957) studied the phase-equilibria of paragonite and montmorillonite in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  using gels from solutions of metal-organic compounds. At temperatures above 250°C, paragonite and montmorillonite coexist, and, to 400°C, they may be joined by either kaolinite

or albite. Although they could not confirm that montmorillonite was formed under the conditions of stable equilibrium, they concluded that montmorillonite could be formed. The influence of pressure on the equilibrium temperatures was found to be minimal, in agreement with the general concept explained by Roy (1954). The equilibrium temperatures changed only by  $\sim 25^\circ\text{C}$  when the pressure was increased from 345 to 2068 bars.

In other early work, Otsubo and Kato (1954) synthesized a montmorillonite containing Zn in the octahedral sheet by mixing the appropriate oxides and heating in an autoclave at  $150\text{--}300^\circ\text{C}$  for 5–20 h. X-ray diffraction patterns indicated a dioctahedral structure and chemical analysis substantiated the presence of Zn in the structure, the amounts of which corresponded to the layer charge of the mineral.

Karšulin and Stubičan (1954) and Stubičan (1959) studied the synthesis of montmorillonite in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  and  $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{H}_2\text{O}$  at  $312^\circ\text{C}$  and 100 bars. They proved a direct relation between the amount of isomorphous substitution and the base-exchange capacity. Low  $\text{Mg}^{2+}$  or  $\text{Na}^+$  concentrations resulted in the additional formation of kaolinite. At higher  $\text{Na}^+$  concentrations, analcime formed in addition to montmorillonite and, at the highest concentration, was the only phase. Syntheses at lower temperatures and pressures yielded amorphous silica in the product in addition to the crystalline phases.

Based on the work of Koizumi and Roy (1959), Harward and Brindley (1966) synthesized smectites with various compositional substitutions at  $300\text{--}350^\circ\text{C}$  and 1 kbar. In addition to the formation of beidellite or montmorillonite, they also found various other components, including kaolinite, saponite, paragonite, and amorphous material in their products. Due to the formation of these mixtures, layer-charge measurements always yielded lower values than anticipated from the gel composition. Increasing the amount of Mg and subsequently decreasing the amount of Al resulted in the formation of two phases, one with a trioctahedral and the other with a dioctahedral nature.

Levinson and Vian (1966) and Levinson and Day (1968) studied the hydrothermal formation of montmorillonite from natural minerals at  $175$  and  $300^\circ\text{C}$  at autogenous water pressure for 4 or 5 d. They found that the reaction dolomite + kaolinite + quartz + water easily proceeded to montmorillonite + calcite +  $\text{CO}_2$ . Replacement of the dolomite by other carbonates, such as magnesite, calcite, smithsonite, or siderite, significantly slowed the reaction to montmorillonite. The addition of  $\text{NH}_4^+$  to the system, however, resulted in the formation of an  $\text{NH}_4$ -mica and  $\text{NH}_4$ -analcime. These results were supported by Tsunashima *et al.* (1975), who were able to synthesize amino acid-montmorillonite (glycine and lysine) under hydrothermal conditions of  $200\text{--}250^\circ\text{C}$ . At lower temperatures,

no clay minerals were formed. At higher temperatures, however, the amino acids degraded to  $\text{NH}_4^+$ , and  $\text{NH}_4$ -micas were formed instead.

Nakazawa *et al.* (1991) synthesized montmorillonites by hydration of Na, Mg-aluminosilicate glass under hydrothermal pressure of 1 kbar with varying water/solid ratios. At  $250\text{--}400^\circ\text{C}$ , poorly crystallized montmorillonite was formed as the only crystalline product. Higher temperatures resulted in the additional formation of cristobalite or cristobalite and quartz. At low temperatures, some amorphous material may have been present also, but its presence was not adequately proven by the authors. Based on peak-width data from the XRD patterns, they suggested a growth mechanism in which two-dimensional fragments were formed by an initial hydration of the glass. Further hydration did not result in growth of these fragments, but rather in the formation of more poorly crystallized fragments. Smectites in the montmorillonite (M)-beidellite(B) series were also synthesized from glass at  $250\text{--}500^\circ\text{C}$  and 1 kbar. Montmorillonite was obtained as a single phase below  $375^\circ\text{C}$  in the composition range  $\text{M}_{100}\text{B}_0$  to  $\text{M}_{78}\text{B}_{22}$ .

#### Beidellite

Among the first to synthesize beidellite were Ewell and Insley (1935) by hydrothermal treatment of aluminosilicate glasses or gels (silica and boehmite) at temperatures of  $350$  and  $390^\circ\text{C}$  and autogenous water pressure for 9–12 d. Although the starting materials were prepared from Na-bearing silicon compounds, no information is given on the amount of Na present for the synthesis or in the final products. In additional experiments, Ewell and Insley (1935) showed that the reaction to beidellite proceeds by dissolution of the silica and transport of the silica through the gaseous or liquid phase followed by reaction with the solid alumina.

Norton (1939, 1941) extensively studied the reactions of various magmatic minerals under hydrothermal conditions in  $\text{CO}_2$ -percolated water. From the minerals studied, only albite and anorthite were thought to yield beidellite or montmorillonite, in the low-temperature and  $\text{CO}_2$ -pressure range, accompanied by quartz. Unfortunately, no glycol- or glycerol-expansion and heat-treatment tests were performed to distinguish between these two clay minerals using XRD. In general, he found that smectites were only formed at  $250\text{--}350^\circ\text{C}$  and  $\text{CO}_2$  pressures around 35 bars.

Harward and Brindley (1966) synthesized beidellites at  $300\text{--}350^\circ\text{C}$  and 1 kbar from gels. However, single-phase products were not obtained.

Granquist and Pollack (1967) and Granquist *et al.* (1972) describe the synthesis of a randomly interstratified dioctahedral 2:1 smectite with Al as the only octahedral cation and partial substitution of Al for Si (*i.e.*, beidellite) under hydrothermal conditions of

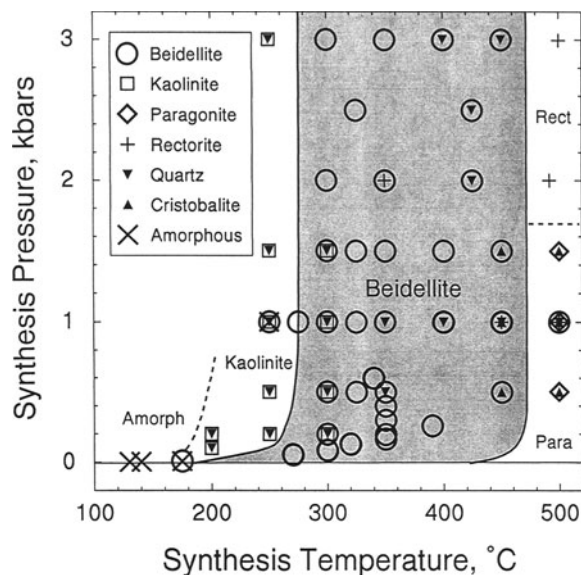


Figure 3. Pressure-temperature data for synthesis of Na-beidellite. Most of the data are from Klopprogge *et al.* (1990a, 1990b, 1993b) for a starting gel composition of 62.7% SiO<sub>2</sub>, 34.2% Al<sub>2</sub>O<sub>3</sub>, and 3.1% Na<sub>2</sub>O ( $p = .7$ ), with additional data from Ewell and Insley (1935), Granquist *et al.* (1972), De Kimpe (1976), Eberl (1978), Plee *et al.* (1987), Schutz *et al.* (1987), and Yamada *et al.* (1991a, 1991b). Formation of kaolinite occurs at 300°C only when slow heating rates (*i.e.*, <30°C min<sup>-1</sup>) are used (unpublished data of Klopprogge).

300°C and 86 bars. Starting materials were prepared from ion-exchanged Na-silicate solution and gibbsite. Sodium and NH<sub>4</sub><sup>+</sup> were used as interlayer cations. Rapid crystallization was observed with NH<sub>4</sub><sup>+</sup>. The slower reaction with Na<sup>+</sup> was attributed to its ability to promote the conversion of gibbsite to the less-reactive boehmite under hydrothermal conditions. Partial replacement of OH<sup>-</sup> by F<sup>-</sup> had a positive effect on the crystallization of beidellite. This effect of the F/OH ratio was explained as due to either (1) the control of the solubilities of Al<sup>3+</sup> and Si<sup>4+</sup> by pH adjustment and F<sup>-</sup> complexation, or (2) the easier entry of F<sup>-</sup> into the site in the clay structure relative to OH<sup>-</sup>. The latter option stems from the anisotropic shape and charge distribution of OH<sup>-</sup>, which make its orientation vis-à-vis the octahedral sheet an additional entropic barrier that must be overcome to enter the clay structure. Klopprogge *et al.* (1990a) observed the same effect of F<sup>-</sup> and favored the entropic explanation given by Granquist *et al.* (1972). In a continuous preparation, some unreacted material in the form of boehmite (formed by dehydration of the gibbsite) was found in addition to the beidellite.

Roy and Sand (1956) synthesized well-defined crystals of beidellite using a mixture of Na<sub>2</sub>O:6 Al<sub>2</sub>O<sub>3</sub>:24 SiO<sub>2</sub> at 400°C and 1 kbar for 2 h. Although they described the product as montmorillonite, it is in fact beidellite. Koizumi and Roy (1959), using gels of sil-

ica sol (Ludox) and metal nitrates (pH adjusted with NaOH), conducted ~40 experiments at 260–770°C and 1 kbar. Their results showed that beidellites of variable exchange capacity could be synthesized at 300–425°C.

Frank-Kamenetskii *et al.* (1973a, 1973b) demonstrated the importance of not only pressure, temperature, and composition, but also the role of Al coordination in the starting material. They showed that the degree of beidellite crystallization depended on both the character of the Al coordination in the starting material and the pH of the surrounding fluid. Gels with less Al than needed for stoichiometric beidellite yielded more tetrahedrally coordinated Al in the newly formed crystalline material at higher pH values, which favor formation of the tetrahedral AlO<sub>4</sub><sup>-</sup> ion and thus promote the formation of beidellite. The influence of higher pH values on the crystallization of beidellite, although in this case from stoichiometric gels, was confirmed by Klopprogge *et al.* (1990b), who found optimal crystallization at pH 7.5–10.

Eberl (1978) explored relationships among dioctahedral smectites through the evolution of reaction series. The experiments were similar to those described by Eberl and Hower (1977), but at higher pressures and temperatures (*i.e.*, 2 kbar and 300–500°C) using gels of K- or Na-beidellite composition [prepared according to the method of Luth and Ingamells (1965)]. With increasing time, the series gel → K-beidellite → illite-smectite (random) → K-rectorite → illite was observed. With the Na-beidellite gel, however, Na-rectorite was formed together with quartz and kaolinite (350°C) or pyrophyllite (492°C, Figure 3). This Na reaction series was described earlier in more detail by Eberl and Hower (1977). In general, the reaction series proceeds towards the development of a collapsed structure with increasing time and temperature. The exact trend depends on the interlayer cation and on the concentration of its salt in solution.

Low-temperature hydrothermal experiments using silica-alumina gels and NaOH solutions were performed by De Kimpe (1976) at 130–175°C, 2.7–8.8 bars, and incubation periods of several days. An aluminous smectite, *i.e.* beidellite, was only formed at 175°C and a pH of 7–9 (900 mg gel in 100 mL solution, Figure 3). In other experiments at 175°C this product was accompanied by either kaolinite (high gel/solution ratio) or zeolites such as chabazite and phillipsite (lowest gel/solution ratio). At temperatures below 175°C, mainly amorphous material, kaolinite, or zeolites (at lowest gel/solution ratio) were formed (Figure 3). These results represent the lowest pressure and temperature conditions under which beidellite formation has been reported and differ from those of other authors, such as Klopprogge *et al.* (1993b), who found a minimum temperature of 200°C to yield beidellite + amorphous material.

Several patents (Granquist, 1966; Capell and Granquist, 1966; Jaffe, 1974) describe synthesis procedures for 2:1 layer silicates having the beidellite structure and substitution of Al and Si by metal cations, such as Cr, Mn, Co, Ga, Rh, Sc, Ni, Cu, Zn, and Ge, to improve catalytic characteristics. Although these materials do not contain any montmorillonite and have the beidellite structure, they are known as synthetic mica-montmorillonite (SMM). The reason for this designation is that the materials were thought to be randomly interstratified phases containing alternating expandable montmorillonitic layers and nonexpandable micaceous layers. Based on an improvement of the procedure of Granquist (1966), Gaaf *et al.* (1983), Röbschläger *et al.* (1984), and van Santen *et al.* (1985) synthesized pure beidellite and Ni-substituted beidellite, which they claimed was identical to SMM. Heirnerman (1985) patented the improved procedure, involving the use of commercial amorphous silica-alumina as starting material and minimum quantities of water.

Komarneni and Roy (1983) and Komarneni and Breval (1985) studied the formation mechanism of smectite using the zeolites phillipsite and erionite as starting materials. They reported the formation of an unidentified smectite by the hydrothermal treatment of these zeolites in a Mg-rich brine at 300°C and 300 bars for 4 wk. These smectites were thoroughly characterized and identified subsequently as beidellites (Komarneni and Breval, 1985). This synthetic approach yielded nearly pure smectite with only minor amounts of albite and mica. Although mica was already present as a trace impurity in the starting zeolite sample, the albite seemed to form during the transformation. The additional presence of amorphous SiO<sub>2</sub> or Mg(OH)<sub>2</sub> could not be excluded. Detailed XRD, layer charge, and TEM analyses revealed the beidellitic nature of the smectite formed with Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> as exchangeable cations. Komarneni and Breval (1985) proposed a mechanism in which acidic conditions are formed by the hydrolysis of Mg<sup>2+</sup> from the brine. Proton saturation of the zeolites resulted in their decomposition and recrystallization to beidellite. This study differs significantly from most other studies in this section in that the beidellite is formed in an acidic environment. Apparently, acidic conditions are needed to decompose the zeolite, but are unnecessary where a gel is the starting material.

Plee *et al.* (1984, 1987) and Schutz *et al.* (1985, 1987) prepared a synthetic Na-beidellite having a composition near Na<sub>0.7</sub>Al<sub>4.7</sub>Si<sub>7.3</sub>O<sub>20</sub>(OH)<sub>4</sub>·nH<sub>2</sub>O. Because this mineral only shows tetrahedral substitution, they used it to prepare an Al-pillared beidellite having a more ordered pillar distribution and a much stronger acidity than a pillared montmorillonite prepared under similar conditions. Plee *et al.* (1987) prepared a gel according to the method of Luth and Ingamells (1965).

The gel was placed in a gold capsule together with a 0.01 N NaOH solution and hydrothermally treated for 10 d at 340°C and 600 bars, resulting in single-phase beidellite with a layer charge of 1000 meq kg<sup>-1</sup>. Schutz *et al.* (1987) treated 200 mg of the gel plus 640 mL of 0.1 M NaOH in a 1-L autoclave for 5 d at 320°C and 130 bars, yielding >90% beidellite. The layer charge was determined to be 940 meq kg<sup>-1</sup>. These layer-charge values are higher than the 700 meq kg<sup>-1</sup> obtained by Klopogge *et al.* (1990a, 1990b) for beidellites synthesized from gels consisting of TEOS and Al(NO<sub>3</sub>)<sub>3</sub> using the method of Hamilton and Henderson (1968). The lower value obtained by the latter approach was attributed to the collapse of portions of the interlayer space (Plee *et al.*, 1987). Yanagisawa *et al.* (1995) showed that the formation of beidellite from a gel, which was prepared from a mixture of silica sol (Ludox), Al(NO<sub>3</sub>)<sub>3</sub>, and NaNO<sub>3</sub> at 350°C under basic conditions, follows a dissolution and precipitation process at the surface of the starting gel particles. During the synthesis, the pH drops to near neutral (6.8). Addition of NaOH to the solution accelerated the formation of beidellite, probably due to the high solubility of silica in these basic solutions.

Since water is an essential constituent of smectites, Yamada *et al.* (1991a, 1991b) investigated the role of water on the formation of beidellite by varying the water/solid (glass Na<sub>0.66</sub>Al<sub>4.66</sub>Si<sub>7.34</sub>O<sub>22</sub>) ratio at synthesis temperatures of 250–450°C at 1 kbar for 7 d. At 300–400°C they observed only beidellite as a crystalline phase, whereas at 250°C beidellite was accompanied by kaolinite and amorphous material (Figure 3). At 450°C, a dioctahedral smectite with octahedral charge, cristobalite, and quartz, were observed in addition to beidellite. At higher water/solid ratios Na-rectorite, a mixed-layer paragonite-beidellite phase, was formed instead of beidellite.

Klopogge *et al.* (1993b) investigated the paragenesis of beidellite with respect to temperature, pressure, and composition. The effects of temperature and pressure deviated slightly from the results presented above. For example, Klopogge *et al.* (1993b) observed kaolinite + quartz + beidellite at 300°C instead of 250°C and, above 500°C, they found paragonite at low pressure (≤2 kbar) instead of a dioctahedral smectite (Figure 3). These differences may be related to the amount of water present. Klopogge and Vogels (1995) described their efforts to hydrothermally synthesize NH<sub>4</sub>-beidellite at 250 and 350°C and 1 kbar for 7 d applying various NH<sub>4</sub><sup>+</sup> sources. At 250°C, and in the presence of urea and (NH<sub>4</sub>)<sub>3</sub>AlF<sub>6</sub>, only the H<sup>+</sup>-saturated form of beidellite was formed along with amorphous material and NH<sub>4</sub>-analcime. The syntheses at 350°C were more successful. In the presence of urea, NH<sub>4</sub>OH, and (NH<sub>4</sub>)<sub>3</sub>AlF<sub>6</sub>, a mixture of H<sup>+</sup>-beidellite and NH<sub>4</sub>-beidellite was formed. In the presence of glycine, only NH<sub>4</sub>-beidellite was formed. Apparently, the slightly

acidic conditions of the experiment inhibited the formation of analcime.

Kawano and Tomita (1992) and Kawano *et al.* (1993) studied the formation of beidellite and allophane (a very poorly crystalline aluminosilicate) during hydrothermal treatment of obsidian (volcanic glass). They observed the formation of allophane as the first alteration product after treatment of the glass in distilled water at 150–200°C. Within the allophane particles, straight fibrous material formed, which transformed into circular-shaped smectite particles with a beidellitic composition. The low-temperature formation of beidellite seems to agree with the experiments of Klopprogge *et al.* (1993b), who were able to synthesize Na-rich beidellite at 200°C (and 1 kbar) from a gel.

Huve *et al.* (1992, 1997) prepared well-crystallized and virtually pure beidellite by treating an aluminosilicate hydrogel with F<sup>-</sup> at pH 3–7, ~220°C, and autogenous water pressure for several hours to days. The general formula of the beidellites they obtained was  $M_x(\text{Al}_2)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_{2-y}\text{F}_y$  with  $x = 0.4\text{--}0.7$  and  $y = 0.25\text{--}0.6$ . In neutral to acid media, F<sup>-</sup> was shown to act as a mineralizing agent (probably through the formation of Si- and Al-fluoride complexes), and, thus plays a role similar to that of OH<sup>-</sup> ion in alkaline solution. The thermal stability of the product increased in proportion to the degree of substitution of F for OH groups in the beidellite structure. A similar synthesis method using a wide range of starting materials was described in a patent by Holmgren (1995). She indicated that the preferred conditions for the formation of fluoride-containing beidellites were (1) pH 4–7, (2) 150–200°C, and (3) treatment periods of 1–20 d.

#### *Sauconite and other (Ni, Co, Zn, Cu) smectites*

Franzen and van Eyk van Voorthuisen (1950) prepared a hectorite-type clay in which Ni is the divalent metal instead of Mg. The starting material, formed by addition of boiling Ni(NO<sub>3</sub>)<sub>2</sub> solution to a Na<sub>2</sub>SiO<sub>3</sub> solution (NiO:SiO<sub>2</sub>:Na<sub>2</sub>O ratios of 3:4:0.5–1.5), was hydrothermally treated at 250°C at unknown pressure for an unknown period. The resulting clay had a basal spacing of 9.6 Å, which expanded to 14–18 Å after treatment with glycerol, confirming the smectitic nature of the Ni hydrosilicate.

Synthesis of hectorites with partial substitution of Mg by Ni is described by Yamada *et al.* (1994a). The starting gel, prepared from TEOS and varying amounts of MgCl<sub>2</sub>, NiCl<sub>2</sub>, LiOH, and NaOH, was hydrothermally treated at 200°C and autogenous water pressure for 7 d. After radiolytic reduction of the Ni<sup>2+</sup> to Ni<sup>+</sup>, two sites with different reactivity towards water and methanol were identified in the hectorite structure using electron-paramagnetic resonance (EPR) spectroscopy. The reactive site was thought to be an edge site of the octahedral sheet, whereas the nonre-

active site was probably an interior site in the octahedral sheet of the hectorite.

Urabe *et al.* (1989) showed that the use of Ni as an octahedral cation instead of Mg results in a saponite that is an efficient catalyst for the selective dimerization of ethene. They hydrothermally treated an aqueous Na-Ni-Si-Al gel having a Ni:Si:Al ratio of 8.13:9.36:1 (which leads to a small excess of Ni as compared to the stoichiometric composition) at 280°C and saturated water vapor pressure (~65 bar) for 2 h.

As mentioned above, van Santen *et al.* (1985) synthesized a Ni-SMM of composition (Si<sub>5.26</sub>Al<sub>2.74</sub>)-(Al<sub>1.32</sub>Ni<sub>4.02</sub>)O<sub>20</sub>(OH)<sub>2.5</sub>F<sub>1.5</sub> by hydrothermal treatment for 16 h at 300°C. In this beidellite-like clay, the Ni<sup>2+</sup> cations occupy the octahedral positions, two Al ions being replaced by three Ni<sup>2+</sup> ions [one Ni<sup>2+</sup> ion fills the octahedral vacancy present in the beidellite structure].

Bruce *et al.* (1986) synthesized a range of Co hydrosilicates from reaction mixtures of Co(NO<sub>3</sub>)<sub>2</sub>, colloidal silica, and a metal hydroxide that were hydrothermally treated at 250°C for 16 h under an initial P(H<sub>2</sub>) of 34 bars at ambient temperature. The H<sub>2</sub> atmosphere was used to minimize oxidation of Co<sup>2+</sup> to Co<sup>3+</sup> by the NO<sub>3</sub><sup>-</sup> counterion. When NaOH was used as the metal hydroxide, a low layer-charge, blue, smectite-like material with composition Na<sub>0.06</sub>Co<sub>3.07</sub>Si<sub>3.95</sub>O<sub>10</sub>(OH)<sub>2</sub> was obtained. The XRD patterns for this material showed a basal spacing of 12.4 Å that easily expanded to 15.2 Å upon hydration and to 16.9 and 17.3 Å upon treatment with ethylene glycol and glycerol, respectively. The *d*-value for the 060 reflection was 1.557 Å, which, although slightly larger than that normally observed for hectorite and stevensite, clearly showed the trioctahedral nature of this clay. Bruce *et al.* (1986) suggested that the large *d*(060)-value was at least partly due to the larger ionic radius of high-spin, octahedral Co<sup>2+</sup> compared to Mg<sup>2+</sup>. The diffuse-reflectance, ultraviolet-visible spectra indicated the presence of some tetrahedrally coordinated Co (IVCo) in addition to the large fraction of Co in octahedral coordination. Four possible positions for IVCo in the material were suggested: (1) substituted for Si<sup>4+</sup> in the tetrahedral sheet, (2) adsorbed as a hydroxy species on edges or faces of the clay particles, (3) present in the interlayer as an hydroxy species, and (4) present in the hexagonal holes of the silicate sheets. Bruce *et al.* (1986) were unable to discriminate among these possibilities, nor could they explain why a smectite-like material formed only in the presence of Na and not in the presence of other alkali metals such as K, Cs, or Li, or in the presence of tetraalkylammonium.

Xiang and Villemure (1996) also synthesized a trioctahedral Co<sup>2+</sup>-smectite using a reaction mixture described by Mizutani *et al.* (1991) for Fe-smectites and hydrothermal treatments similar to that of Bruce *et al.* (1986). The pink color of the clay suggested the



absence of  $^{14}\text{Co}$ . The clays were subsequently studied for their electrochemical properties.

Roy and Mumpton (1956) studied the synthesis and stability relations of silicates in the  $\text{ZnO-SiO}_2$  system using gels incubated at 130–730°C and 35–276 bars. Sauconite was formed with difficulty under these conditions and pure sauconite was stable only to 210°C. Two other phases, willemite and hemimorphite, were more stable than sauconite.

Usui *et al.* (1985) described the synthesis of sauconite from “active” silicic acid and either  $\text{ZnO}$ ,  $\text{Zn(OH)}_2$ , or a Zn salt that can form the oxide or hydroxide. The active silicic acid was prepared by acid treatment of clay minerals mainly from the smectite or kaolinite groups. The  $\text{ZnO/SiO}_2$  ratio must be near 0.75, which results in the stoichiometric amounts needed to form sauconite. Relatively low temperatures of 130–170°C at autogenous water pressure were reported as favorable for sauconite formation.

Luca *et al.* (1992) synthesized Zn-fluorhectorites from a starting material containing TEOS,  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ , LiF, and NaF, at 225–250°C for 48 h in a Parr bomb. In some materials, minor amounts of noncrystalline impurities formed that were removed easily by reaction with 0.05 M HCl. Increasing the amount of Zn, as well as the OH/F ratio, apparently increased the catalytic activity (Friedel-Crafts alkylation of benzene by benzyl chloride) of these Zn-hectorites, presumably by increasing the strength of the surface Lewis-acid sites as measured by pyridine adsorption. In later work, Luca *et al.* (1995) prepared (Zn,Ti)-substituted fluorhectorites. In this synthesis, the  $\text{MgCl}_2$  was replaced by  $\text{ZnCl}_2$ , and  $\text{Ti}^{4+}$  was added in the form of Ti isopropoxide. The resulting starting gel was hydrothermally treated at 230°C for 66 h with occasional stirring. Spectroscopic analyses of the resulting fluorhectorite by X-ray absorption near-edge structure and EPR spectroscopies suggested that  $\text{Ti}^{4+}$  substituted primarily into the octahedral sites in the structure.

The various methods for moderate hydrothermal synthesis of smectites are summarized in Table 3.

#### SYNTHESIS ABOVE 1000°C AND AT VERY HIGH PRESSURE

Synthesis of montmorillonite single crystals at very high temperatures and pressures was reported by Nakazawa *et al.* (1992) and Yamada *et al.* (1994b, 1994c). The starting material was a glass, as described earlier for the hydrothermal synthesis of montmorillonite (Nakazawa *et al.*, 1991; Yamada *et al.* 1991a, 1991b). The glass was treated in the presence of water for 10–50 min at  $\leq 5.5$  GPa and 700–1600°C. This approach yielded smectite accompanied by coesite, jadeite, kyanite, a small amount of an unidentified phase (possibly a mica), and some remaining glass. Under these conditions, the amount of montmorillonite generally increased with increasing temperature. Above 1400°C,

montmorillonite and coesite were the dominant phases, and kyanite and jadeite were minor phases. At temperatures below 1000°C and the same high pressures, no smectite formed, but clinopyroxene, chlorite, and an unknown phase were found in addition to coesite, jadeite, and kyanite.

Images of these montmorillonite crystals obtained by TEM showed them as extremely thin ribbons, laths, and plates having partly hexagonal edges. Diffraction yielded a very sharp (001) reflection when compared to natural montmorillonite indicating high crystallinity (three-dimensional periodicity). *In situ* XRD with increasing relative humidity (RH) showed that the hydration state of the montmorillonite was a clear function of RH (Yamada *et al.*, 1994b). The  $d(001)$ -value increased with distinct steps from 10.0 to 12.4 and 15.2 Å corresponding to 0-, 1-, and 2-layer hydration states, respectively. In contrast to natural montmorillonite, only the 2-layer hydration state was reached at 100% RH instead of the 3-layer hydration state. Apparently, the high crystallinity promoted a stronger interaction force between the silicate layer and interlayer cations. In addition, the transitions between the various hydration states occurred at higher levels of RH than for natural montmorillonite.

Bai *et al.* (1993) noted that “back reactions” during quenching of high-temperature and pressure syntheses in the presence of  $\text{H}_2\text{O}$  vapor promoted larger grain sizes in chlorite and vermiculite specimens and suggested that a similar process might have accounted for the highly crystalline smectites produced by Nakazawa *et al.* (1992).

Yamada and Nakazawa (1995) reported syntheses in the montmorillonite-beidellite pseudo-binary system using starting glasses having a range of chemical compositions. Glasses with compositions ranging from pure montmorillonite to 25% montmorillonite–75% beidellite resulted in the formation of a mineral assemblage comparable to those described above for the pure montmorillonite synthesis. When a pure beidellite glass was used, however, no smectite formed and the product consisted of coesite, kyanite, jadeite, and a small amount of an amorphous phase. This result shows the importance of Mg to the formation of smectites and supports the hypothesis described earlier for the hydrothermal formation of montmorillonite (*i.e.*, the early formation of brucite-like sheets followed by the attachment of silicate sheets).

#### DISCUSSION

##### *Synthetic approaches*

Under the conditions found near the earth's surface, the mechanisms leading to formation of complex phases such as clay minerals in aqueous solutions are not obvious. Even in monometallic systems (*e.g.*, Fe) a wide range of hydroxide, oxide, or oxyhydroxide

Table 3. Experimental results of hydrothermal syntheses.

Authors	Starting materials	Conditions	Phases obtained	Remarks
Neumann (1971, 1972), Neumann and Sansom (1976)	Mg salts, Na <sub>2</sub> SiO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> or NaOH Li salt, HF or LiF	1 bar, boiling or reflux 10–20 h; 185– 265°C at 10–50 bar, ≤8 h	hectorite	commercially available as Laponite
Torii <i>et al.</i> (1983), Torii (1985), Torii and Iwa- saki (1986, 1987), Iwasaki <i>et al.</i> (1989)	MgCl <sub>2</sub> , Na <sub>2</sub> SiO <sub>3</sub> , HNO <sub>3</sub> NH <sub>4</sub> OH, NaOH, LiOH	125–300°C, P <sub>H<sub>2</sub>O</sub> , 1–24 h	hectorite, saponite	less structural Li with increasing T, layer charge due to octa- hedral vacancies
Orlemann (1972)	talc, Li <sub>2</sub> CO <sub>3</sub> (calcined at 760–980°C), Na <sub>2</sub> SiO <sub>3</sub> Na <sub>2</sub> CO <sub>3</sub>	185°C, P <sub>H<sub>2</sub>O</sub>	hectorite-like material	talc is relatively cheap and readily avail- able source
Miller and Johnson (1962)	K <sub>2</sub> SiF <sub>6</sub> , LiF, Li <sub>2</sub> CO <sub>3</sub> , MgO, SiO <sub>2</sub>	1420°C, 2 h	Li-fluorhectorite, tae- niolite	very small flakes as byproduct
Barrer and Jones (1970), Shabtai <i>et al.</i> (1984)	silica (fused at 800°C) MgO, MgF <sub>2</sub> , NaF, LiF Na <sub>2</sub> CO <sub>3</sub> , Li <sub>2</sub> CO <sub>3</sub>	800°C, 24 h; 850°C, 2 h	Li-fluorhectorite, quartz, Li <sub>2</sub> SiO <sub>3</sub> , fluoramphiboles fluorhectorite	excess LiF needed to form fluorhectorite
Hertl and Bartholomew (1990)	silica sand, MgO, Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> SiF <sub>6</sub>	925°C	fluorhectorite	
Iiyama and Roy (1963a, 1963b)	Mg-, Al-, Na-nitrates, Sil- ica sol (Ludox)	mostly ≤575°C and 1 kbar, some synthe- ses at 600–900°C or >1 kbar	saponite	at lower Na, Al com- positions randomly stacked mixed-layer talc/saponite, at higher P regular stacked mixed-layer talc/saponite
Hickson (1974, 1975)	hydrous silica sol, Al(OH) <sub>3</sub> , Mg(OH) <sub>2</sub> NH <sub>4</sub> OH or NH <sub>4</sub> F	pH 9–10, 300–350°C, 4 h	saponite	
Granquist (1966), Kuchta and Fajnor (1988)	hydrous oxides of Si, Al, Mg, and Na	100–355°C, P <sub>H<sub>2</sub>O</sub> , 133 bars, 1–3 wk	saponite, brucite	poor crystallinity at ≤200°C
Cohen <i>et al.</i> (1980)	igneous rocks	350–450°C, ≤350 bars	saponite-like material	likely a mixture of various smectites
Suquet <i>et al.</i> (1977, 1981a, 1981b), Hamil- ton and Henderson (1968), Booij (1992)	TEOS, Mg-, Al-nitrate Na <sub>2</sub> CO <sub>3</sub> , HNO <sub>3</sub> , NH <sub>4</sub> OH	450°C, 1.5 kbar, 15 d	saponite	no forsterite formation during gel prepara- tion
Breukelaar <i>et al.</i> (1989, 1990), Klopprogge <i>et al.</i> (1993a, 1994a, 1994b), Vogels <i>et al.</i> (1997)	SiO <sub>2</sub> , Al isopropoxide, Mg acetate, NH <sub>4</sub> OH	125–300°C, P <sub>H<sub>2</sub>O</sub> , 1–72 h	saponite, amorphous	amount of amorphous material obtained depends on time and amount of NH <sub>4</sub> OH
Li <i>et al.</i> (1993)	Na <sub>2</sub> SiO <sub>3</sub> , NaOH, Mg-, Al- sulfate	290°C, P <sub>H<sub>2</sub>O</sub> , 12 h	saponite, amorphous?	most Al seems to be in tetrahedral coord- ination
Golden <i>et al.</i> (1985), Golden and Dixon (1990), Komarneni (1989)	palygorskite, sepiolite, NaOH, MgCO <sub>3</sub>	80–160°C, P <sub>H<sub>2</sub>O</sub> , 24 h	saponite	addition of Mg im- proves the forma- tion of saponite
Ewell and Insley (1935)	silica gel, Fe <sub>2</sub> O <sub>3</sub> + AlOOH	340–350°C, 167 bars, 6 d 350, 390°C, 9–12 d, high temperature	nontronite, hematite, unknown beidellite	
Hamilton and Furtwäng- ler (1951)	Na <sub>2</sub> SiO <sub>3</sub> , FeCl <sub>3</sub>		nontronite	dilute solutions
Mizutani <i>et al.</i> (1991)	H <sub>4</sub> SiO <sub>4</sub> , FeSO <sub>4</sub> , dithionite, NaOH	100–200°C, 50 h	1:1 and 2:1 Fe-smec- tites	Fe/Si ratios of 0.75 and 1.5 gave non- tronite-like material
Noll (1936)	kaolin, H <sub>4</sub> SiO <sub>4</sub> , Na-, K-, Ca-hydroxides	300°C, P <sub>H<sub>2</sub>O</sub> , 15–24 h	montmorillonite, amorphous	low pH yielded kao- linite
Sand <i>et al.</i> (1953, 1957), Sand and Crowley (1956)	gels from metal organic compounds	25–450°C, 1 kbar	montmorillonite, para- gonite, kaolinite, mullite, cristobalite, mica, albite	accompanying miner- als depend mainly on P and T condi- tions
Otsubo and Kato (1954)	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , ZnO	150–300°C, P <sub>H<sub>2</sub>O</sub> , 5–20 h	montmorillonite	layer charge equaled Zn substitution

Table 3. Continued.

Authors	Starting materials	Conditions	Phases obtained	Remarks
Karšulin and Stubičan (1954), Stubičan (1959)	silica gel, Al-, Mg-hydroxides, NaOH	312°C, 100 bars	montmorillonite, kaolinite, analcime, amorphous silica	additional minerals depend on starting composition
Harward and Brindley (1966)	gel from metal salt solutions	300–350°C, 1 kbar	montmorillonite, saponite, kaolinite, paragonite, beidellite, amorphous	in all cases mixtures were observed, ratios depended on starting composition
Levinson and Vian (1966), Levinson and Day (1968)	dolomite, kaolinite, quartz, water	175°C, 300°C, P <sub>H<sub>2</sub>O</sub> , 4–5 d	montmorillonite, calcite	other carbonates gave worse results
Nakazawa <i>et al.</i> (1991)	Na, Mg, aluminosilicate glass	250–500°C, 1 kbar	montmorillonite, cristobalite, quartz, amorphous	Quartz and cristobalite present at T > 400°C
Norton (1939, 1941)	albite, anorthite	25–350°C, P <sub>CO<sub>2</sub></sub> , 34 bars	beidellite/montmorillonite	authors could not distinguish between these two
Granquist and Pollack (1967), Granquist <i>et al.</i> (1972)	Na <sub>2</sub> SiO <sub>3</sub> , gibbsite, NaOH, NH <sub>4</sub> OH, or partial NaF, NH <sub>4</sub> F	300°C, 86 bars	beidellite	better results with NH <sub>4</sub> and F
Roy and Sand (1956)	Na <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	400°C, 1 kbar, 2 wk	beidellite	described by authors as montmorillonite
Koizumi and Roy (1959)	Silica sol (Ludox), Al-, Mg-nitrates, NaOH	260–770°C, 1 kbar	beidellite, pyrophyllite, kaolinite	beidellite formed at 270–425°C
Eberl and Hower (1977), Eberl (1978)	Silica sol (Ludox), metal salts, NaOH	300–500°C, 2 kbar	K-beidellite, Na-rectorite, kaolinite, pyrophyllite, quartz	beidellite only with K-gel, Na-gel resulted in rectorite + quartz + kaolinite (350°C) or pyrophyllite (492°C)
De Kimpe (1976)	aluminosilica gel, NaOH	130–175°C, 2.7–8.8 bars, several d	beidellite, kaolinite, zeolites, amorphous	beidellite only formed at 175°C which is lower than reported by others
Granquist (1966), Capell and Granquist (1966), Jaffe (1974), Gaaf <i>et al.</i> (1983), Röbschläger <i>et al.</i> (1984), van Santen <i>et al.</i> (1985), Heinerman (1985)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , Al isopropoxide, NH <sub>4</sub> F	300°C, 16 h, P <sub>H<sub>2</sub>O</sub>	SMM (synthetic micromontmorillonite)	SMM is probably identical to beidellite, many metal substitutions are shown to be possible, for catalytic purposes
Komarneni and Roy (1983), Komarneni and Breval (1985)	phillipsite, erionite, Mg-rich brine	300°C, 300 bars, 4 wk	beidellite, SiO <sub>2</sub> , Mg(OH) <sub>2</sub> , mica, albite	impurities from starting zeolite tuff remain
Plee <i>et al.</i> (1984, 1987), Schutz <i>et al.</i> (1987), Yanagisawa <i>et al.</i> (1995)	Silica sol (Ludox) Al salt, NaOH	320–350°C, 600 bar/10 d, 130 bar/5 d	beidellite, amorphous	<10% amorphous
Yamada <i>et al.</i> (1991a, 1991b)	stoichiometric glass	250–500°C, 1 kbar, 7 d	beidellite, kaolinite, amorphous, paragonite, rectorite	beidellite at 300–400°C, other phases are function of P, T and water/solid ratio
Klopprogge <i>et al.</i> (1990a, 1990b, 1993b), Klopprogge and Vogels (1995)	TEOS, Al(NO <sub>3</sub> ) <sub>3</sub> , NaOH (NaF, NH <sub>4</sub> sources)	range from 100–500°C, 0.2–5 kbar, ≤10 d	beidellite, kaolinite, paragonite, quartz, cristobalite, amorphous, rectorite	other phases are function of P, T and composition, beidellite stable 275–475°C in whole P range
Kawano and Tomita (1992), Kawano <i>et al.</i> (1993)	volcanic glass, water	150–200°C, ≤30 d	allophane, beidellite	allophane was formed as first product, followed by beidellite
Huve <i>et al.</i> (1992, 1997)	aluminosilicate hydrogel, alkali F <sup>-</sup> salts	220°C, P <sub>H<sub>2</sub>O</sub> , pH 3–7, 6–8 d	fluorbeidellite	low pH decreases <sup>IV</sup> Al content
Holmgren (1995)	AlOOH, Silica sol (Ludox) or fumed silica, Na salt or organo-cation, HF or alkali F <sup>-</sup> salt	200°C, pH 4–7, 5–6 d	fluorbeidellite	Al-Si gel aged 6 h before hydrothermal treatment

Table 3. Continued.

Authors	Starting materials	Conditions	Phases obtained	Remarks
Franzen and van Eyk van Voorthuijsen (1950)	Na <sub>2</sub> SiO <sub>3</sub> , NiNO <sub>3</sub>	250°C	Ni hydrosilicate	thought to have a hectorite-like structure
Yamada <i>et al.</i> (1994a)	TEOS, Mg-, Ni-chloride NaOH, LiOH	200°C, P <sub>H<sub>2</sub>O</sub> , 7 d	Ni-hectorite	EPR showed Ni in the octahedral positions
Urabe <i>et al.</i> (1989)	Ni, Si, Al gel	280°C, P <sub>H<sub>2</sub>O</sub> , 2 h	Ni-saponite	effective catalyst for dimerization of ethene
Bruce <i>et al.</i> (1986)	colloidal SiO <sub>2</sub> , Co(NO <sub>3</sub> ) <sub>3</sub> NaOH	250°C, P <sub>H<sub>2</sub></sub> 34 bars, 16 h	Co-hectorite	exact structure and Co position not determined
Xiang and Villemure (1996)	CoCl <sub>2</sub> , H <sub>4</sub> SiO <sub>4</sub> , dithionite	250°C, P <sub>Ar</sub> 34 bars for 15 h, or 150°C, P <sub>H<sub>2</sub>O</sub> for 50 h	Co-hectorite	used for electrochemical studies
Roy and Mumpton (1956)	ZnO, SiO <sub>2</sub> gels	130–730°C, 35–276 bars	sauconite	stable phase only at ≤210°C
Usui <i>et al.</i> (1985)	acid-treated clay, Zn salt, hydroxide or oxide	130–170°C, P <sub>H<sub>2</sub>O</sub>	sauconite	ZnO/SiO <sub>2</sub> ratio ~0.75
Luca <i>et al.</i> (1992, 1995)	TEOS, Mg-, Zn-chloride LiF, NaF, Ti-isopropoxide	225–250°C, P <sub>H<sub>2</sub>O</sub> , 48–66 h	(Zn,Ti) fluorhectorite	minor amounts of noncrystalline impurities, active catalyst in Friedel-Crafts alkylation

phases can form, depending on solution parameters such as pH, temperature, concentrations, *etc.* For multicomponent aqueous systems, *e.g.*, with Si, Al, Fe, and the alkali and alkaline-earth metals, the number of possible phases is substantially larger and includes the complex clays and zeolites. Therefore, a thorough knowledge and understanding of the reactions occurring at low temperature and atmospheric pressure is of great importance. Early syntheses under these conditions (Strese and Hofmann, 1941; Harder, 1972, 1977) demonstrated the difficulties of obtaining single-phase smectites even after very long periods. An added problem is the necessity of using very dilute solutions, which result in small amounts of product (*e.g.*, 150 mg) and large volumes of solution (*e.g.*, several liters). Under these conditions, silica concentrations are maintained at sufficiently low levels to ensure that all silicic acid is present as the monomer.

Nevertheless, the early experimental work at low temperature shows that smectites will form, given sufficient time. The rate of formation seems to depend on the initial hydrolysis of the octahedral cations. Cations such as Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup> that hydrolyze at circumneutral pHs seem to form clay structures easily, whereas cations that hydrolyze at low pH (*e.g.*, Mg<sup>2+</sup>) form clay structures more slowly. The key step seems to be the initial formation of hydrolyzed species of octahedral cations onto which silicate anions condense to form nuclei. These nuclei then grow to yield smectite materials.

The major difficulties in smectite synthesis at low temperatures and atmospheric pressure are that (1) the reactions rarely go to completion, and (2) a mixture

of products, including both crystalline and amorphous phases, is usually obtained. From experimental evidence, hectorite, stevensite, and saponite can be formed as nearly single-phase materials at conditions below 100°C and 1 bar. However, for saponite, the distribution of Al among the octahedral, tetrahedral, and even interlayer, sites in the structure is difficult to control. One known exception is the reflux method described by Vogels *et al.* (1995), in which nearly all the Al incorporates into the tetrahedral sheet. Other smectites, such as montmorillonite and beidellite, are difficult or even impossible to synthesize under these conditions with current methods. Lastly, although both Fe<sup>2+</sup> and Fe<sup>3+</sup> play important roles in the structural chemistry of naturally occurring clay minerals, absolute control of the Fe oxidation state in the product is difficult under any synthesis conditions.

Several authors showed that better results are obtained in boiling gel-solution systems or under reflux conditions. For example, Vogels *et al.* (1995), Carrado *et al.* (1991), and Jacobs *et al.* (1997) synthesized single-phase saponite or hectorite in a few days. Tomita *et al.* (1993) explored the use of natural materials, (*i.e.*, volcanic glass and pumice) and the influence of pH on the formation of smectite (and zeolites) under reflux conditions. Single-phase smectite was obtained only with volcanic glass and dilute concentrations of NaOH.

Hydrothermal techniques are a logical extension of synthetic approaches involving gels under boiling or reflux conditions. Under hydrothermal conditions, most reactions go to completion and single-phase products are commonly obtained when the correct

temperatures and pressures are applied. To a large extent, the success of this approach stems from the much faster hydrolysis rates of the octahedral cations at high temperature, which favor nucleation and growth of the smectitic materials.

In the last 50 years, many phyllosilicates including kaolinite, various smectites, and micas have been synthesized hydrothermally, although most of this work has been empirical in nature. Several minerals that do not form readily at low temperatures and pressures can be synthesized in nearly pure form using the hydrothermal approach. In particular, nearly pure beidellite can be formed, accompanied only by a small amount (<5–10%) of amorphous material (Plee *et al.*, 1984, 1987; Schutz *et al.*, 1987; Kloprogge *et al.*, 1990a, 1990b, 1993b; Yanagisawa *et al.*, 1995). Pure montmorillonite phases, however, are still difficult to form under hydrothermal conditions and are usually accompanied by other phases such as kaolinite, paragonite, cristobalite, and quartz.

The most common approach has been to use a starting material, such as another aluminosilicate mineral, a gel, or a glass, having a composition more or less approaching that of the desired clay-mineral composition (*i.e.*, a stoichiometric starting composition). Luth and Ingamells (1965), Hamilton and Henderson (1968), and Biggar and O'Hara (1969) provide classic descriptions of methods for the preparation of gels and glasses.

Natural minerals often serve as starting materials for the hydrothermal synthesis of hectorite, saponite, beidellite, and montmorillonite. Orlemann (1972) used talc as an inexpensive starting material for the formation of hectorite. The disadvantage of this method, however, is that talc must first be calcined in the presence of  $\text{Li}_2\text{CO}_3$  at high temperatures before the remaining procedure is performed at 185°C. Komarneni (1989) and Golden and Dixon (1990) studied the formation of saponite from palygorskite and sepiolite and showed that the addition of Mg is essential for smectite formation. This was also shown by Levinson and Vian (1966) and Levinson and Day (1968), who studied the formation of montmorillonite from mixtures of several carbonates, kaolinite, and quartz. Only dolomite gave satisfactory results and the montmorillonite formed by this reaction was always accompanied by calcite. The results of these experiments suggest that, under natural conditions, either another Mg mineral or soluble  $\text{Mg}^{2+}$  must be present for smectite genesis.

Beidellite was formed by the repeated reaction of several zeolites with Mg-rich brines (Komarneni and Roy, 1983; Komarneni and Breval, 1985) and by reaction of volcanic glass with water (Kawano and Tomita, 1992; Kawano *et al.*, 1993). In the zeolite-brine reactions, other phases such as  $\text{SiO}_2$ ,  $\text{Mg}(\text{OH})_2$ , mica (from the starting material), and albite were present in small amounts. In the volcanic-glass experiments, al-

lophane formed initially and then transformed later to beidellite. Kawano and his coworkers were unable to synthesise pure beidellite even after 1 mo of reaction time, indicating the sluggish transformation from a structure with short-range order to one with long-range order. None of these investigators used seeding techniques to facilitate smectite formation.

The use of very high pressures and temperatures (comparable to those in the earth's mantle) to synthesize smectite (Nakazawa *et al.*, 1991, 1992; Yamada *et al.*, 1994b, 1994c) yields large single crystals that may prove useful for structure determinations. However, other minerals such as coesite, jadeite, and kyanite are always present in the product, and the approach is of limited importance in explaining the formation of smectites under natural conditions. Indeed, Bai *et al.* (1993) suggest that the products are the result of back reactions during the quench process, and thus, do not even represent synthesis at the stated conditions.

The formation of smectite minerals in the presence of  $\text{F}^-$  is important because  $\text{F}^-$  can substitute for some or all of the structural OH groups. Such replacement affects the expansive properties and the thermal stability of smectite. Under natural conditions,  $\text{F}^-$  is commonly found in the hydrothermal solutions that accompany the formation of pegmatites. Thus, the synthesis of clay minerals in  $\text{F}^-$  melts has little relation to the formation of smectites under natural earth-surface conditions. Currently, F-bearing smectites (mainly hectorite) are used primarily as heterogeneous catalysts because of the improved thermal stability. However, in the future, F-bearing smectites are expected to find major use in nanocomposite materials (organic-inorganic and inorganic-inorganic).

Lastly, we note that the conditions under which a smectite will form are not necessarily the conditions of thermodynamic equilibrium. Many synthetic products are metastable and form in lieu of the thermodynamically stable phase(s) because of favorable kinetics. An example of metastable-phase formation is given in Figure 3, where kaolinite forms in the beidellite stability field under one set of conditions (slow heating rates to "synthesis" temperatures of 300°C). When the samples are brought to the synthesis temperature at a faster rate, then no kaolinite is formed and the sole crystalline product is beidellite. For practical reasons, many, if not most, experimental syntheses do not allow sufficient time to ascertain that the synthesis products are also the thermodynamically stable phases. Reversal experiments, in which the final synthesis conditions are approached from higher pressures and temperatures, are too often neglected, thereby making rigorous assignment of thermodynamic stability fields difficult. The determination of stability fields is particularly difficult for the clays, which tend

to form at low temperatures and pressures where reaction rates are relatively slow.

### Characterization

Most papers concerning the synthesis of smectite minerals lack complete characterization of the products formed. In many cases, although the crystalline phases present were determined, the amounts of accompanying phases, both crystalline and amorphous, were not determined. Future research on the synthesis of smectites will require far more detail, both in the identification and in the quantification of the products. To accomplish this task, XRD alone is insufficient, and other techniques, such as analytical-electron microscopy (AEM), must also be used. Furthermore, far more details must be obtained on the formation mechanisms and surface chemistry of smectite minerals. Future research must include nucleation and growth mechanisms for sheets and layers, applying techniques (not available to early workers on the synthesis of smectites) that probe the nascent clay particles at the atomic level, the extended-structure level, and on to the macroscopic level. The atomic and molecular structure of nascent phases can be obtained by using high-resolution  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{17}\text{O}$ , or  $^{23}\text{Na}$  MAS-NMR techniques, EXAFS, vibrational spectroscopy (Fourier-transform infrared, Raman), AEM, and XRD. Additional information can be gained from chemical analysis, potentiometric titrations (zeta-potential determination, surface-charge characteristics), and new techniques such as atomic-force microscopy (AFM) and X-ray microscopy (XRM). For example, AFM enables observations of the nucleation and growth of clay layers on substrates *in situ* and in real time; see, for example, Hartman *et al.* (1990). X-ray microscopy may also offer the possibility of observing the growth of clay nuclei in solution at a resolution between that of optical and electron microscopy (Thieme and Niemeyer, 1995). Although heating was not demonstrated, it seems only a matter of time before XRM images for experiments at 100°C are obtained.

### ACKNOWLEDGMENTS

We thank M. Batchelder, and one anonymous reviewer for many constructive comments. Work supported in part by Laboratory-Directed Research and Development Funds, Pacific Northwest National Laboratory (PNNL), Richland, Washington. PNNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

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(Received 9 April 1998; accepted 25 October 1998; Ms. 98-049)