Handbook of Clay Science
Edited by F. Bergaya, B.K.G. Theng and G. Lagaly
Developments in Clay Science, Vol. 1

Chapter 4

SYNTHETIC CLAY MINERALS AND PURIFICATION OF NATURAL CLAYS

K.A. CARRADO[a], A. DECARREAU[b], S. PETIT[b], F. BERGAYA[c] AND G. LAGALY[d]

[a]*Chemistry Division, Argonne National Laboratory, Argonne, IL 60439-4837, USA*
[b]*UMR 6532, HydrASA, F-8602 Poitiers Cedex, France*
[c]*CRMD, CNRS-Université d'Orléans, F-45071 Orléans Cedex 2, France*
[d]*Institut für Anorganische Chemie, Universität Kiel, D-24118 Kiel, Germany*

Salient points on the synthesis of clay minerals are summarized in this chapter, focusing on specific clay mineral types. Further, methods of clay purification are described.

A subjective differentiation can be made between the formation of clay minerals in their natural, geologic environment such as in soils, and the synthesis of pure minerals in a controlled, laboratory environment. The former point would be of interest to the geochemist, soil scientist, or mineralogist, whereas the latter materials are prepared to exploit a clay mineral's unique structure and/or surface chemistry for some particular application. Among recent reviews on the geological aspects of clay mineral synthesis, that by Wilson (1999) makes the distinction between 'transformation' and 'neotransformation' in natural environments. The present review is concerned with the laboratory synthesis of clay minerals.

4.1. METHODOLOGY

More often than not, the main objective of producing synthetic clay minerals is to obtain pure samples in a short time and at the lowest possible temperature. These two parameters are important for geologists whose aim is to reproduce in the laboratory clay mineral formation under hydrothermal and diagenetic conditions (weathering, sedimentary neoformation) that prevail at the earth's surface. These parameters are equally important for chemists and physicists who aim to minimize the energy needed for clay synthesis.

Clay mineral synthesis can be viewed as a heterogeneous chemical reaction in an aqueous phase. The global kinetics of such a reaction are given by the classical

DOI: 10.1016/S1572-4352(05)01004-4

Arrhenius equation:

$$K_{(T)} = Ae^{-E_a/RT} \tag{1}$$

where $K_{(T)}$ is the rate constant of the reaction; A the pre-exponential factor; E_a the activation energy; R the gas constant; and T the absolute temperature.

The duration of clay mineral synthesis can therefore be minimized by an increase of T and/or a decrease of E_a. Many different varieties of clay minerals have been synthesized as described in the next section. Some general variables of clay mineral synthesis, with an emphasis on starting materials and hydrothermal conditions, are presented.

4.1.1. Synthesis from Very Dilute Solutions

This method, developed by Caillère et al. (1953, 1954) and used later by Harder (1972, 1978), is based on two assumptions: (i) that clay minerals are formed from dilute solutions in natural (weathering) processes (Millot, 1965) and (ii) that clay minerals can grow by silicification of $Mg(OH)_2$ (brucite-) or $Al(OH)_3$ (gibbsite-) like sheets (Caillère et al., 1956). The salt solutions used are very dilute (10–30 mg/L) and SiO_2 concentrations are less than 100 mg/L so as to prevent polymerization of silicic monomers. Since this method yields very small quantities of clay minerals that are difficult to characterize, it is no longer used.

4.1.2. Solid-State Reactions

In this process, three kinds of solids can be used as starting materials: minerals or rocks, glasses, and gels.

When minerals or rocks are used, they are of igneous origin such as feldspars, olivines, pyroxenes, basalts, and rhyolites (Fiore et al., 2001). This approach is interesting for geochemists because it involves hydrothermal alteration of primary minerals or rocks into clay minerals. However, the kinetics involved are generally slow as shown below, and clay minerals are often mixed with other phases. It is preferable, therefore, to use starting materials with a similar chemistry to that of clay minerals.

Glasses are easily obtained by the melting of salts (or oxides) mixed in the proper ratios. However, melting requires high temperatures (900 °C and above) and, if a salt flux is not added (such as Na_2CO_3), then demixing can occur (e.g., formation of hematite in the presence of Fe ions). For this reason, glasses also are not often used as starting materials.

The most commonly used starting materials are gels that can be prepared by one of the three methods: (i) using only organic salts tetraethoxysilane (TEOS), tri-isopropyl aluminate, iron acetylacetonate, etc. (De Kimpe et al., 1981); (ii) using TEOS and Mg^{2+}-, Al^{3+}-, or Fe^{3+}-nitrates, and heating the gels at 800 °C for complete dehydration (Roy and Tuttle, 1956; Kloprogge and Vogel, 1995); and (iii) using sodium metasilicate and Mg^{2+}-, Al^{3+}-, or Fe^{3+}-chlorides or sulphates (Decarreau, 1980). Applying all three methods, Iriarte-Lecumberri (2003) obtained 21 starting gels for the synthesis of smectites with variable ratios of Fe^{3+}, Al^{3+}, and Mg^{2+} ions. With the first method, the dissolution of magnesium ethylate is difficult, the dehydration of gels is long (480 h at 30 °C), and the gels are heterogeneous showing macroscopic segregation of elements. With the second method, the gels obtained are macroscopically homogeneous but the clay mineral compositions are significantly different from expectation, with an excess of Al^{3+}, Fe^{3+}, Mg^{2+}, and a deficit of Si^{4+}. At the TEM-AEM scale, the gels are heterogeneous with small dark nodules of high iron concentrations. Gels obtained by the third method are homogeneous at the TEM-AEM scale, and their compositions are close to expectation. These gels appear to form 2:1 clay minerals when they contain Mg^{2+}, and protoferrihydrite when they contain Fe^{3+} (Decarreau, 1980, 1981; Decarreau and Bonnin, 1986; Decarreau et al., 1987). Iriarte-Lecumberri (2003) concluded that gels obtained by this last method are more suitable for the synthesis of clay minerals having a complex chemistry, such as smectites. In all cases, the gels must be dried at a low temperature (30–60 °C) to prevent possible partial demixing and crystallization.

4.1.3. Hydrothermal Synthesis

Hydrothermal treatment can induce the germination and crystal growth of clay minerals. The important controlling parameters are temperature (T), duration of treatment (t) and solution chemistry, notably pH.

A. Germination Process

To ensure that germination of clay minerals occurs, the concentration of ions in solution (Si^{4+}, Al^{3+}, Mg^{2+}, Fe^{3+}, etc.) must be high enough to reach critical oversaturation (S^*). This condition is easily reached when the starting materials are gels or glasses because they are highly soluble and have compositions similar to those of the required clay minerals. S^* is more difficult to reach when the starting materials are minerals or rocks. For a given rate of nucleation (one seed per second per cm^3) the value of S^* is given by Eq. (2) (Stumm and Morgan, 1981):

$$\log S^* = \left[C\frac{\gamma^3}{T^3}\right]^{1/2} \tag{2}$$

where C includes the Boltzmann constant and parameters depending on the kind of clay mineral, T is the temperature, and γ is the clay/solution interface tension.

This simplified expression of S^* shows that elevated temperatures will act to decrease S^* values. Also, the value of γ is inversely related to the solubility product of the clay minerals (K_s). Trioctahedral clay minerals have high K_s values as compared with their dioctahedral counterparts with $\log K_s = 31.6$ for chrysolite and log

$K_s = 7.43$ for kaolinite (K_s values given for $T = 298\,\mathrm{K}$ and $P = 1\,\mathrm{b}$) (Fritz, 1981). Therefore, germination of trioctahedral clay minerals requires lower S^* values, and these minerals are easier to crystallize. In fact, explosive germination occurs for trioctahedral clay minerals after the co-precipitation reaction during gel preparation (Decarreau, 1980). This may explain the role of magnesium in the synthesis of dioctahedral aluminous clays since the presence of magnesium, even in low amounts, is essential for the formation of smectites (Kloprogge et al., 1999).

B. Crystal Growth

The rate of crystal growth (υ) at a given temperature (T) is given by Eq. (3) (Steefel and Van Capellen, 1990):

$$\upsilon = k_{(T)}S[(Q/K_s)^n - 1]^m \tag{3}$$

where $k_{(T)}$ is the rate constant of clay mineral precipitation; S is the external surface area of the mineral; K_s is the solubility product; (Q/K_s–1) is the index of S^* of the solution; m and n are experimental constants.

Role of temperature. The kinetics of clay mineral growth are strongly dependent on temperature, through $k_{(T)}$ and Eq. (1). Therefore, syntheses performed at low temperatures often do not succeed. For example, Rayner (1962) calculated a half-reaction time of 16×10^4 years for kaolinite synthesis at 20 °C. At $T > 500$ °C, other silicate or oxide phases become more stable than clay minerals. As a result, most clay mineral syntheses are performed in the range of 100–500 °C.

Role of pH. Data from numerous studies, described in the next section, show that the type of synthetic clay mineral produced depends on the pH of solutions at the end of hydrothermal treatment ($\mathrm{pH_f}$). Especially for systems containing Al^{3+} and/or Fe^{3+}, low $\mathrm{pH_f}$ (2–6) favours the formation of 1:1 clay minerals such as kaolinite, more or less mixed with oxides. Medium $\mathrm{pH_f}$ (7–10 for Al^{3+}, up to 12 for Fe^{3+}) favours 2:1 clay minerals such as smectites and micas. High $\mathrm{pH_f}$ favours zeolite (with Al^{3+}) or aegerine (with Fe^{3+}) minerals (Frank-Kamenetskii et al., 1973; Kloprogge et al., 1990; Huertas et al., 1999, 2000; Nagase et al., 1999; Decarreau et al., 2004). Fig. 4.1, from Grauby et al. (1993), demonstrates these phenomena. One of the major reasons for the higher dependence on $\mathrm{pH_f}$ than the Si/Al ratio is probably related to the thermodynamic stability fields of clay minerals (Bowers et al., 1984). Frank-Kamenetskii et al. (1973) have also suggested that the synthesis of tetrahedrally substituted (Si^{4+}–M^{3+}) 2:1 clay minerals is favoured at alkaline $\mathrm{pH_f}$.

Since the type of synthetic clay is dependent on $\mathrm{pH_f}$, it is necessary to follow the evolution of pH during synthesis. Appropriate starting gels have their own buffering power; although a drop of several pH units can occur after only a few minutes, this process may extend up to a few days at 25°C. The decrease in pH is most likely due to surface reactions between the solution and the oxo- or hydroxo-complexes present

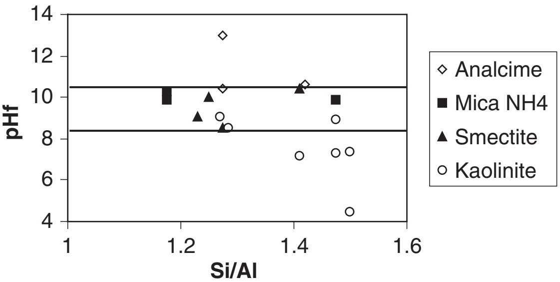

Fig. 4.1. Synthesized clay minerals in the system Si/Al/Na/H_2O at 200 °C. pH_f = final pH (end of synthesis), Si/Al = atomic ratio. 2:1 clay minerals are synthesized at pH_f values between 8.2 and 10.3.

at gel/solution interfaces (Decarreau, 1980; Huertas et al., 1999). Therefore, in constraining the pH_f for a given clay mineral synthesis the initial pH must be adjusted so that the buffering power of the gel does not contribute (Iriarte-Lecumberri, 2003).

Role of time: crystallization versus crystallinity. With increasing synthesis time the amount of starting material that is transformed into clay minerals increases. Thermal gravimetric analysis (TGA) is the method most often used to quantify the crystallization rate. Dehydroxylation of clay minerals occurs at relatively well-defined temperatures (Mackenzie, 1970; Smykatz-Kloss and Warne, 1991; Drits et al., 1995; Emmerich and Kahr, 2001). For poorly crystallized clay minerals, dehydroxylation occurs at lower temperatures. For example, in synthetic kaolinites the temperature shifts from 550 to 420 °C (Petit and Decarreau, 1990). For all types of clay minerals, the experimental rate of crystallization follows a similar pattern given by the relation:

$$\%\text{clay} = 1 - e^{-kt}$$

The value of k is dependent on experimental conditions, notably temperature (Huertas et al., 1999, 2000). Depending on the nature of the synthetic clay mineral, and for temperatures in the range 150–300 °C, crystallization reaches a plateau after a few days to a few months. These results can be explained by the kinetic law of Eq. (3). At the beginning, large amounts of starting materials dissolve and concentrations of ions in solution are high. At this point, $Q/K_s \gg 1$ and the rate of crystal growth is fast. Gradually $Q \approx K_s$ with time (t), and the kinetics of crystal growth tend to be very slow. At this point, additional time has no effect on crystallization.

As synthesis time increases, the crystallinity of clay minerals generally increases. Traditionally, 'crystallinity' is quantified by measuring the width of reflections in XRD patterns (mean crystal size coherency obtained using the Scherrer equation), or specific measurements such as the Hinckley (1963) index for kaolinites (Aparicio and Galan, 1999) (see Chapter 2). Crystallinity enhancement in the layer planes of clay minerals was measured for synthesized smectites and chrysotile using the width of

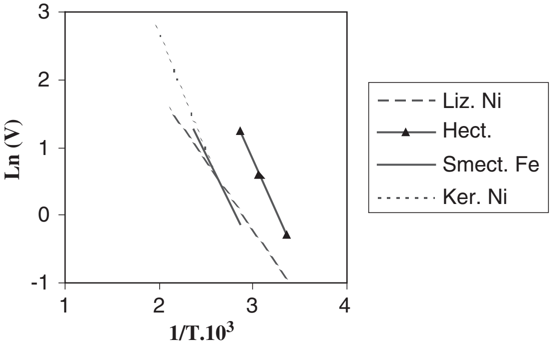

Fig. 4.2. Arrhenius scheme for the crystal growth of clay minerals synthesized from co-precipitated gels at neutral to alkaline pH_f. V = linear speed of domain size increase in the plane of layers (Ångstroms/day) where Liz.Ni = Ni-lizardite; Hect. = hectorite; Smect.Fe = iron smectite; Ker.Ni = Ni-kerolite.

(060,330) reflections in the XRD patterns. It appears that an increase in 'crystallinity' is strongly dependent on temperature, pH, and is similar for all kinds of clay minerals as will be seen in the following section (Fig. 4.2).

C. Intermediate phases. Intermediate phases commonly appear during synthesis. Most of these are hydroxides or pseudo-hydroxides such as the pseudo-boehmite observed during the synthesis of kaolinite (Fialips et al., 2000). These phases are generally of low crystallinity and/or are non-stoichiometric (siliceous hematite is an example) and are difficult to identify using classical techniques such as XRD, DTA-TGA, and FTIR.

The occurrence of these phases suggests that clay mineral synthesis is a complex heterogeneous reaction. Numerous authors suggest that the key step in smectite synthesis is the formation of pseudo-hydroxides of the octahedral cations, to which silica species are attached forming clay mineral nuclei (Kloprogge et al., 1999; Huertas et al., 2000). In a more complex system, the clay mineral itself can act as an intermediate phase. Grauby et al. (1993) have synthesized a metastable di-trioctahedral smectite that evolves by demixing (with increasing time and temperature) into extended dioctahedral (with Al^{3+}) and trioctahedral (with Mg^{2+}) domains in 2:1 layers. Huertas et al. (2000) have shown that smectites appear as intermediate phases during kaolinite synthesis. In summary, clay minerals may occur as metastable phases during synthesis. Therefore, one has to be certain that the reactions have been completed.

4.1.4. *Characterization of Synthetic Clay Minerals*

The characterization of synthetic clay minerals is often not adequate. For example, Nagase et al. (1999) have synthesized a smectite from a gel with a $Si^{4+}/Fe^{3+}/Mg^{2+}$

ratio of 4/1.7/0.3 at 200 °C. On the basis of XRD data alone, they concluded that the synthesized smectite was a Fe^{3+}-montmorillonite. However, Grauby et al. (1994) using similar synthesis conditions concluded from XRD before and after the Hofmann–Klemen test, FTIR, and TEM-AEM that the product was actually an Fe-beidellite.

The following set of characterization techniques should at least be used: (i) XRD of both powder and oriented samples, including all the classical tests for swelling. The Rietveld approach is useful for quantifying the amount of mixed phases and the occurrence of disordered phases; (ii) TEM-AEM for a precise measurement of clay mineral particle morphologies; and (iii) appropriate spectroscopic techniques such as EXAFS, NMR, Mössbauer, FTIR, ESR, for obtaining independent crystal-chemical data. These data are essential to characterize clay minerals with tetrahedral and/or octahedral substitutions. In particular, FTIR can readily provide much information on the structural composition, crystal chemistry, and crystallinity of the product (Farmer, 1974; Petit et al., 1998, 1999; Petit, 2004).

4.2. SYNTHESIS OF SPECIFIC CLAY MINERALS

4.2.1. Micas

The literature concerning micas, including their synthesis, is so vast that only some points will be highlighted here. For further information the reader is referred to the recent monograph by Mottana et al. (2002). The vast majority of mica minerals are assumed to be 'inherited' i.e., derived from pre-existing parent rock or weathered materials. This occurs under pressure and temperature conditions different from those that exist at the earth's surface (Fanning et al., 1989; Wilson, 1999). The few cases of apparently neoformed micas have been discussed recently. An iron-rich sample with perfect platy hexagonal morphology is an example (Norrish and Pickering, 1983). The low-grade metamorphism (or transformation) of phyllosilicates to micas has been reviewed by Arkai (2002). Weathering processes that form the rare trioctahedral micas have been summarized by Wilson (1999).

Laboratory syntheses of micas from as early as 1887 up to 1955 have been summarized by Cipriani (2002). He also points out that after this time micas have continued to be synthesized for one of two reasons: (i) verification of the geological conditions of formation with the goal of using micas as geothermometer or geobarometer indicators (mineral-petrogenic goal) or (ii) investigation of compositional variations including rare elements such as Ge or Rb (a crystallo-chemical goal). Early reports on hydrothermal synthetic micas include paragonite obtained at 420 °C (Barrer and White, 1952), ammonium mica at 300 °C (Levinson and Day, 1968), and muscovite at 500–700 °C (Rosenberg, 1987). Robert et al. (1993) have examined the distribution of fluorine versus hydroxyl in a synthetic tetra-silicic magnesium mica series. These synthetic micas have been characterized by X-ray crystallography

(Toraya et al., 1978), ^{27}Al and ^{29}Si MAS NMR (Komarneni et al., 1999), and XANES (Mottana et al., 1997).

A high-charge sodium fluoro-phlogopite mica, called 'Na-4-mica', has been synthesized via sol–gel hydrothermal techniques (Paulus et al., 1992) as is a K-fluoro-phlogopite (Duldulao and Burlitch, 1991). This procedure has been simplified by using a solid-state method where the precursors in powder form are mixed and heated at high temperatures (Franklin and Lee, 1996; Komarneni et al., 1998; Kodama et al., 2000, 2001a). A 'Na-2-mica' has also been prepared by the latter method (Kodama et al., 2001b). An expandable fluorine-containing mica has been synthesized via solid-state method from talc and sodium fluorosilicate precursors (Tateyama et al., 1992).

Examples of micas synthesized with isomorphous layer substitutions include octahedral Ni^{2+}- and Ga^{3+}-phlogopite (Klingsberg and Roy, 1957), tetrahedral beta-phlogopite and muscovite (Stubican and Roy, 1962), Sr^{2+}-mica (Barrer and Marshall, 1964), Zn^{2+}-mica (Barrer and Sieber, 1977), and Rb^{+}-muscovite (Voncken et al., 1987). Some of these lead to partial layer substitution, while others containing rare elements form complete mica analogues. In other words, layer substitution can range from partial to full replacement of Si^{4+} or Al^{3+} by the rare element.

4.2.2. *Smectites*

The small particle size and highly variable composition of naturally occurring smectites led to considerable uncertainty regarding their origin and thermodynamic stability. Borchardt (1989) reviewed the natural formation of smectite minerals. He described the strong evidence for their detrital origin, a stage in the weathering of micas and chlorites to kaolinite and gibbsite. He also suggested that the phases are not thermodynamically stable, although at least some of the end-member phases may form authigenically in sediments under ambient conditions. Wilson (1999) also discussed the origin and formation of smectites in soils.

Because natural smectite-rich clays contain impurities and mixed phases, questions about their formation and stability are best addressed by studying synthetic, single-phase clay minerals that are more amenable to detailed structural characterization. Comprehensive reviews of smectite synthetic methods were provided by Kloprogge (1998) and Kloprogge et al. (1999). These include information on beidellite, hectorite, montmorillonite, nontronite, saponite, sauconite, and stevensite. In summary, synthetic conditions include (i) ambient pressure and temperature $<100\,^{\circ}C$; (ii) moderate hydrothermal conditions 100–1000 °C, pressures to several kbars; (iii) extreme hydrothermal conditions with $T > 1000\,^{\circ}C$ or pressures >10 kb; and iv) using fluoride ions as a flux. The mild hydrothermal approach is used most often because it yields the greatest amounts of high-purity smectites. This is especially true for beidellite and transition metal smectites. Montmorillonite remains the most difficult mineral to crystallize in high purity. This may be due, at least in part, to its low magnesium content.

Some additional studies regarding smectite synthesis have recently been published. One review (Manning, 2003), which is concerned with clay mineral occurrence and distribution in sedimentary rocks, discusses thermodynamic stability and reaction kinetics for kaolin, illite, smectite, and chlorite. It also includes the principles involved in experimental design of clay–mineral reactions. Another report concerns the synthesis of smectite from igneous rocks in NaOH at 100 °C, atmospheric pressure, and dilute suspensions (Tomita and Kawano, 2002). Huertas et al. (2000) have reported that kaolinite, formed from a gel by hydrothermal treatment, can transform through an intermediate phase to di- and trioctahedral smectites. Hectorite particles of approximately 0.3–0.5 μm have been obtained hydrothermally using TEOS, brucite, and LiF (Carrado et al., 2001). A high-temperature, high-pressure study has yielded large (> 10 μm) smectite 'crystals' with a homogenous charge distribution capable of stepwise hydration (Tamura et al., 2000).

Various metal-substituted smectites (e.g., Zn^{2+}, Co^{2+}, Ni^{2+}) have been synthesized by Shirai et al. (2001) and Higashi et al. (2002) and their catalytic activity has been investigated by Bhanage et al. (2002).

Of relatively new interest is the introduction of mesoporosity during the synthesis of smectite-based materials, including (i) hectorites derived from an excess of silica sol (Carrado et al., 2002) and (ii) Mg^{2+}- or Co^{2+}-based trioctahedral minerals that are talc-like (Shirai et al., 2000, 2002). These methods employ hydrothermal crystallization under mild conditions with catalytic applications in mind.

Another area of interest concerns the synthesis of hybrid smectite-organic nanocomposites. Some examples include (i) clay organic microspheres (talc-like) with either bubbled or entirely hollow interiors (Muthusamy et al., 2002); (ii) phenyl-grafted synthetic hectorite layers (Carrado et al., 2001); and (iii) alternating smectite-organo-siloxane layers where the talc-like layers are grafted with alkylammonium-derived molecules (Fujii et al., 2003).

4.2.3. Kaolinite

Wilson (1999) summarized the literature regarding the origin and formation of kaolin minerals in soils. Soil kaolinites are usually smaller in particle size, more disordered, more likely to be interstratified with smectites, and more likely to contain isomorphous Fe^{3+} than kaolinites in geological deposits.

Roy and Osborn (1954) were the first to investigate the initial phase equilibrium for kaolinite. Since then, numerous reports on laboratory-scale preparations of kaolin minerals have been published. Synthesis at low or room temperature requires low-to-neutral pH and six-fold coordinated Al (Harder, 1970; Linares and Huertas, 1971). La Iglesia and Van Oosterwyck-Gastuche (1978) and Van Oosterwyck-Gastuche and La Iglesia (1978) discussed the low-temperature (60 °C) synthesis of kaolinite including the thermodynamics and rates involved.

The use of aluminosilicate gels as starting materials is quite common, and the Si/Al ratio is important in hydrothermal systems. In some methods, gel precipitation is dependent on pH. The gels are then washed to eliminate excess ions. For example, kaolinite formed from amorphous gels (Si/Al <2) persists up to 405 °C. The formation of b-axis ordered kaolinite is favoured over the disordered form at lower Si/Al ratios and higher temperatures (Eberl and Hower, 1975). These authors also reported that contamination by alkali ions inhibits crystallization. However, De Vijnck (1973, 1975, 1976) published a series of papers on the formation of kaolinite from aluminosilicate sols containing Li^+ or K^+. Miyawaki et al. (1991) examined in detail the effects of solution chemistry by reacting Al_2O_3–SiO_2–H_2O gels at 220 °C and autogenous pressure for 5 days. They found that (i) the inhibitory effect of monovalent Li^+, Na^+, and K^+ ions is less than that of divalent Mg^{2+} and Ca^{2+} ions; (ii) trivalent Fe^{3+} and excess Al^{3+} significantly interfere with crystallization; (iii) chloride and nitrate salts are better than sulfate and acetate salts; and (iv) Li^+ ions give just a slight improvement in crystallinity, especially with respect to the 001 peak.

In other methods, gels are formed by hydrolysis of tetraethylorthosilicate and aluminium isopropoxide (De Vijnck, 1973; De Kimpe et al., 1981; De Kimpe and Kodama, 1984), sometimes followed by a thermal treatment (Tomura et al., 1983; Petit and Decarreau, 1990).

Tomura et al. (1985a, 1985b) produced kaolinites of spherical morphology through hydrothermal treatment of aluminosilicate gels. In ceramic technology, such materials improve some of the properties of the products. In addition, pure kaolinite of spherical morphology was synthesized at 150–200 °C, and platy kaolinite at 250 °C in hydrothermal experiments at autogenous pressure (Tomura et al., 1983). Solid-state ^{27}Al and ^{29}Si NMR investigations showed that the coordination number of aluminium in these minerals changes from a mixture of four- and six-fold to full six-fold coordination, and the spherical morphology is transformed to a platy one with time (Miyawaki et al., 1992). Satokawa et al. (1994) examined the importance of the silica-alumina gel structure. The spherical morphology develops when the gel, consisting of silica and alumina tetrahedra and some alumina octahedra, is precipitated at pH 9.6. The platy morphology with an allophane-like structure arises from a gel precipitated at pH 4.2. Using the co-hydrolysis method, Huertas et al. (1993a) reported a 65% yield of spherical kaolinite. Nearly perfect crystals are obtained from gels with Si/Al ratios lower than those of kaolinite.

The process of kaolinite formation via the co-hydrolysis method was studied by applying a two-stage kinetic model, with separate calculated rate constants and activation energies (Huertas et al., 1993b). The first step involves transformation of the amorphous gel into an intermediate product, with an activation energy of 86–118 kJ/mol depending on gel composition. The second step is the transformation of the intermediate phase to kaolinite, with an activation energy of 66 kJ/mol independent of gel composition.

Fialips et al. (2000) suggested that the hydrothermal formation of kaolinite from metakaolinite involves two processes that depend on pH and the type of metakaolinite. The kaolinite obtained is less ordered when the $pH = 4$–6 than when the

$pH = 1$. The first process involves dissolution of the metakaolinite followed by crystallization of either thin prismatic or dendritic kaolinite particles that curl due to surface tension. The second process involves the rapid formation of small, pseudo-hexagonal kaolinite particles that aggregate and coalesce to form larger particles.

Using seeds of dickite at 200–250 °C for 1–9 days, Tomura et al. (1990) obtained good yields of kaolinite. Petit and Decarreau (1990) obtained iron-rich kaolinites from glasses by hydrothermal synthesis at 200 °C. Some of these kaolinites show relatively good crystallinity as determined by IR spectroscopy.

The synthesis of a mixed kaolinite–smectite mineral was reported by Środoń (1980). He obtained a mixed-layer mineral with 40–90% kaolinite layers, depending on the concentration of Al^{3+}, by reacting a Wyoming smectite in Al^{3+}/K^{+} or Al^{3+}/Ca^{2+} salt solutions at 150 °C for 4 months.

4.2.4. Sepiolite

Few references exist concerning the laboratory synthesis of sepiolite and palygorskite. This is because sepiolite is (i) unstable at hydrothermal conditions (>300 °C) (Frank-Kamenetskii et al., 1972; Otsuka et al., 1974; Güven and Carney, 1979; Komarneni, 1989); (ii) unstable in both acidic and alkaline solutions at elevated temperatures (Golden et al., 1985); and (iii) usually dominated by smectites that crystallize more readily from magnesium silicate gels at high pH. Although the synthesis of sepiolite was successful, the yields are low (Hast, 1956; Wiegmann and Horte, 1960; Siffert and Wey, 1962; Wollast et al., 1968; Nesterchuk and Makarova, 1973; Abtahi, 1985). Mizutani et al. (1991) successfully obtained sepiolite with the potential for greater yields by adding seed particles of sepiolite to a magnesium silicate gel at 150–200 °C, and subjecting the mixture to hydrothermal treatment. Under these conditions, the formation is determined primarily by the hydrothermal stability of sepiolite itself.

Recently, Birsoy (2002) calculated equilibrium activity diagrams for a seven-component system, pointing out that the most common formation mechanism of natural sepiolite–palygorskite minerals involves crystallization from solution. Some highlights from this detailed thermodynamic study are (i) the formation of these minerals is more favoured in the presence of amorphous silica than of quartz and (ii) the activity of aluminium affects the type of minerals formed.

4.3. PURIFICATION OF CLAYS

With the possible exception of vermiculites and micas, clay minerals are found mixed or associated with other minerals and/or amorphous materials. In many applications the clays, in particular bentonites, are used as mined from the deposit without separation or enrichment of the clay minerals. In the case of kaolins, a certain fractionation is required to enrich the kaolinite and to remove other unwanted clay minerals, especially montmorillonites (Jepson, 1984). However, the increased application of clay minerals in the manufacture of advanced materials raises the need for purification and enrichment.

Identification of clay minerals in a raw clay or soil always requires a purification step. This is because the presence of carbonates, iron oxides, or organic materials interferes with the identification procedure. Purification is also required for studying the properties of clay minerals. A common method for obtaining purified clay minerals is fractionation by sedimentation after removal of carbonates, (hydr)oxides,[1] and organic materials. However, complete (100%) enrichment of a clay mineral may only be achieved at the laboratory scale rather than at an industrial scale. Even then, no more than 90% enrichment is usually achievable.

Size fractionation of purified clays and identification of the clay minerals in different fractions often provide more precise information than could be obtained by analysis of the whole unfractionated purified clay. Size fractionation is especially recommended for soil clays because they usually contain different types and proportions of clay minerals (Tributh, 1976; Tributh and Lagaly, 1986b). Size fractions of several clay mineral standards differ in the type and amount of admixed phases, and in the structures of the clay minerals (Köster, 1996). For example, the finest fraction of kaolins contains montmorillonite, an unwanted phase in many ceramic applications (Jepson, 1984). Enrichment of clay minerals involves two steps (i) removal of unwanted materials by physical or chemical treatment and (ii) fractionation by sedimentation to facilitate the removal of the remaining larger than clay-size impurities (such as quartz) that could be trapped between the non-exfoliated aggregates.

4.3.1. Purification Procedures

These procedures consist of the decomposition of carbonates, the dissolution of (hydr)oxides and silica (Tributh and Lagaly, 1986a, 1986b), and the oxidation of organic materials.

Carbonates must be decomposed, especially when the purified clays are to be used in colloid chemical studies. This is because the calcium and magnesium ions in carbonates impede complete peptization of the clay minerals and the delamination of smectites.

Similarly, the presence of (hydr)oxides prevents optimal dispersion of the clay minerals and successful fractionation, because trivalent cations released by the (hydr)oxides cause strong coagulation. In addition, pH-dependent interactions of (hydr)oxides with clay minerals lead to aggregation. Such inorganic impurities also interfere with the X-ray identification of the clay minerals.

Likewise, organic materials must be removed because high amounts of humic materials, mainly associated with soil clays, can render X-ray identification difficult.

---

[1] The term (hydr)oxides indicates that the oxidic admixtures comprise oxides, hydroxides, and oxide hydroxides.

Organic materials, even in small amounts, can also exert a strong influence on the mechanical properties, stability, and flow behaviour of clay mineral dispersions.

Moreover, the presence of amorphous silica, acting as a cementing agent, impedes swelling and dispersion.

A. Decomposition of Carbonates

Carbonates are decomposed by the addition of dilute hydrochloric acid, taking care that the pH does not drop below 4.5 to avoid any attack on the clay mineral structure. Decomposition of high carbonate concentrations requires significant time (up to 2 days). A less drastic procedure is to treat the clay with acetate buffer (Tributh and Lagaly, 1986a) or complex the divalent cations with ethylenediamine tetraacetate (EDTA) (Köster et al., 1973; Köster, 1996, 1997). Treatment with EDTA solutions is also recommended when other Ca^{2+}- and Mg^{2+}-containing minerals (such as members of the apatite group) are present. Since EDTA adsorbs at clay mineral edges, the negative edge charge density increases. This influences the colloid chemical behaviour, and especially the rheological properties, of clay mineral dispersions. On the other hand, this effect can be of advantage in some other applications.

Recommended procedure. Disperse 10–15 g clay in 100 mL water, add 2 M HCl dropwise. The pH must not decrease below 4.5, control with a glass electrode is not always reliable because the electrode often does not indicate correct pH values in the presence of clays. Indicator strips are more reliable (Keller and Matlack, 1990). Recommended is an acetate buffer solution of pH = 4.8 (2 M sodium acetate + 2 M acetic acid) instead of hydrochloric acid. EDTA solutions can also be used to complex the divalent cations: either 0.1 mol/L Na_2H_2EDTA[2] solution of pH = 4.5, or 0.1 mol/L Na_3HEDTA solution of pH = 8. After the decomposition of carbonates the sample should be washed to remove the dissolved or complexed cations.

B. Dissolution of (Hydr)oxides

Iron (hydr)oxides (as also aluminium and manganese (hydr)oxides) are removed by complexing the multivalent cations with citrate. Fe(III) must be reduced with sodium dithionite to Fe(II) which forms a stable citrate complex (Mehra and Jackson, 1960; Holmgren, 1967). Stul and van Leemput (1982) have modified the procedure for bentonites to avoid the formation of (small amounts) of iron sulphides. The small amount of organic materials, commonly present in bentonites, is oxidized with H_2O_2 following reduction with dithionite.

The oxidation and reduction processes may change the layer charge. Although modest in the case of smectites, these changes are detectable (Rengasamy et al., 1976; Lagaly, 1981, 1994; Stul and van Leemput, 1982). Reduction of smectites increases the cation exchange capacity (CEC) in proportion to the Fe^{2+} content. Re-oxidation

---

[2] Both forms of EDTA are commercially available.

reduces the CEC which, however, remains somewhat higher than that of the starting material. This difference is dependent on the type of smectite (Stucki et al., 1984a, 1984b).

The CEC of high-charge clay minerals (vermiculites, micas) is distinctly enhanced by reduction (Roth et al., 1969). Subsequent oxidation does not reduce the CEC although the amounts of Fe(III) increase. The decrease in layer charge due to oxidation of Fe(II) is largely compensated by the dissociation of protons from structural OH groups. Ryan and Gschwend (1991) recommended extraction of iron and aluminium (hydr)oxides with the strongly reducing agent $TiCl_3$ in the presence of EDTA. These reagents remove the iron (hydr)oxides more effectively and more selectively than dithionite. Some TiO_2 particles are formed by hydrolysis of Ti^{4+}.

Iron and aluminium (hydr)oxides can also be removed by treating the clays with acidified sodium oxalate solution (1 M NaCl + 0.1 M $Na_2C_2O_4$ + 0.1 M HCl) for a few minutes, then washing several times with 1 M NaCl + 0.1 M $Na_2C_2O_4$ (Janek et al., 1997). As mentioned above, oxalate is adsorbed at the edges and changes the edge charge density. Calcium ions, when still present after the first treatment, are precipitated as CaC_2O_4[3], representing a permanent source of calcium ions.

Recommended procedure. Add 50 mL of 0.3 M sodium citrate solution and 10 mL of 1 M sodium hydrogen carbonate to the clay dispersion, heat to 75–80 °C. Add 3 g (solid) sodium dithionite. The colour should change from brown to blue; if not, add more dithionite. Hold at 75–80 °C for about 30 min and wash four times with 2 M NaCl. Washing with water is not possible because the clay begins to disperse. For bentonites, disperse 15 g of the clay in 250 mL water, and 200 mL buffer solution (a solution containing 0.3 M sodium citrate + 1 M sodium hydrogen carbonate + 1.2 M HCl), heat to 75 °C and add 4 g sodium dithionite (Stul and van Leemput, 1982). After about 30 min wash twice with 200 mL 0.05 M HCl. Repeat the reduction, wash with a mixture of 200 mL 0.5 M NaCl and 200 mL 0.5 M sodium acetate. Then oxidize the organic material by adding 1000 mL H_2O_2 solution (250 mL 30% H_2O_2 + 750 mL 0.5 M sodium acetate), holding for 30 min at 70 °C, washing twice with 200 mL of 0.5 M NaCl, and dialysing.

C. Oxidation of Organic Materials

The organic materials can be oxidized with hydrogen peroxide, sodium hypochlorite (Anderson, 1963), bromine in water (Pérez-Rodriguez and Wilson, 1969; Mitchell and Smith, 1974), and peroxodisulphate in the presence of a buffer such as sodium hydrogen carbonate, sodium tetraborate, or sodium hydrogen phosphate (Meier and Menegatti, 1997; Menegatti et al., 1999). Sodium hypochlorite is more effective than H_2O_2 while bromine and peroxodisulphate are even more effective (van Langeveld et al., 1978; Meier and Menegatti, 1997). Oxidation of organic materials to CO_2 using hydrogen peroxide is seldom complete (Theng et al., 1999) and several low

---

[3] Calcium oxalate is insoluble in solutions acidified with acetic acid but is dissolved with stronger acids.

molecular weight compounds, especially oxalate, are formed (Pérez-Rodriguez and Wilson, 1969). Since some of this oxalate are adsorbed at clay mineral edges by complexing to aluminium ions in the structure (Siffert and Espinasse, 1980; Permien and Lagaly, 1994), only a portion can be removed by washing (Farmer and Mitchell, 1963). Oxidation with peroxodisulphate (in great excess, about 40 g $Na_2S_2O_8$ per g sample), with $NaHCO_3$ as buffer, is performed at about 80 °C. The procedure does not appear to cause any significant damage to clay mineral, such as kaolinite, montmorillonite, and illite.

Recommended procedure. Following removal of carbonates, add small amounts of 10% H_2O_2 to the wet sediment. The reaction can be vehement when large amounts of organic materials are present. Heat to 60–70 °C and add further amounts of about 50 mL H_2O_2 as long as any reaction (foaming) is observed. To avoid vigorous reactions, wash the sediment with water. If some clay is dispersed, add small volumes of 2 M NaCl solution (never $CaCl_2$) to coagulate the dispersion.

D. Dissolution of Silica

Amorphous silica is dissolved in a boiling solution of 5% (w/w) sodium carbonate. Because this reaction makes the dissolution of the metal (hydr)oxides more difficult, it should be used when all the above treatments have been completed (Stul and van Leemput, 1982). Allophanes are rapidly dissolved in boiling 0.5 M NaOH or KOH (Hashimoto and Jackson, 1960; Alexiades and Jackson, 1966). However, this method is not recommended because it attacks other clay minerals. The preferred method is treatment with acid oxalate solution at pH 3.5 in the dark (Parfitt, 1989).

4.3.2. Removal of Remaining Salt by Dialysis and Fractionation

The clay dispersions obtained after the treatments described above contain considerable amounts of salts, mainly NaCl. Excess salts are normally removed by washing with large amounts of water. However, repeated washing with water causes peptization of the clay mineral particles. In terms of separating the solids, filtration is impractical because of the formation of very thin but almost impermeable filter cakes, while centrifugation requires strong centrifugal fields and long running times. In practice, excess salt is removed by dialysis. This process takes several days but it should not be unnecessarily prolonged because this can lead to coagulation of the clay mineral particles, especially when the pH decreases below 7. Removal of Na^+ and Cl^- promotes edge(+)/face(−) coagulation.

Because clay mineral particles begin to coagulate below pH of about 6, the pH of the water outside of the dialysis bags must be held at pH = 7.5–8 by adding small amounts of dilute sodium hydroxide. Dialysis is complete when no traces of chloride are detected by a test with silver nitrate or when the conductivity of the water outside the dialysis bags is $\leqslant 30\,\mu S/cm$. Optimal dispersion is obtained after removal of the salts. The dispersion may be dried in several ways. However, drying in air produces a hard mass that is difficult to re-disperse. Similarly, spray-drying gives rise to materials that are not completely re-dispersible. Thus, freeze-drying is normally recommended. A certain amount of water may be removed beforehand in a rotary evaporator.

4.3.3. A Simplified 'Gentle' Purification Method

Raw clays from identified geological deposits may be purified without applying the treatments to remove carbonates, hydr(oxides), and organic material. This classical 'gentle' purification method (van Olphen, 1963) consists of replacing the exchangeable cations with Na^+ followed by washing with water. Washing removes excess salts as described before and also enables fine impurities to be separated (Annabi-Bergaya, 1978; Benna et al., 1999).

A. Na^+-exchange
The raw clay is carefully dispersed in 1 M NaCl solution by shaking for about 12 h, and separated by centrifugation. This procedure is repeated several times (at least 5 times for Ca^{2+}-saturated clays).

B. Washing
The sediment of the Na^+-exchanged clay mineral is washed with water. As long as the clay minerals can be separated by centrifugation, the 'visually' clear supernatant is decanted. After each centrifugation, the fine fraction on the top of the sediment is collected with a spatula and separated from the coarse fractions. The procedure may be repeated until the clay mineral forms a stable colloidal dispersion. Then the dispersion and the re-dispersed fine fractions of the sediments are dialysed until free of chloride. The very dilute dispersion (1%) is then allowed to stand and the $<2\,\mu m$ fraction is collected according to Stokes law. The bulk of the water is removed by oven drying at 60 °C, while the remaining purified clay mineral slurry is freeze-dried.

Recommended procedure. The raw clay (180 g) is placed in 6 centrifuge bottles (6×30 g) and 400 mL of 1 M NaCl is added to each bottle. The bottles are shaken in a rotary shaker overnight and then centrifuged at 3000 rpm for 2 h. This cycle of agitation/centrifugation is repeated 6 times to achieve close to 99% exchange. The washing procedure is the same as that for the Na^+-exchange (3–4 agitation/centrifugation cycles) but more drastic centrifugation (7000 rpm for 3 h) is used because the stability of the colloidal dispersion has increased. The final 'washing' is performed by dialysis (about 7 days). After evaporating the bulk of the water in an oven at 60 °C (1 day), the concentrated purified slurry is freeze-dried (2 weeks). The amount of clay mineral recovered is about one third of the initial weight. This method is also suitable for clay mineral identification but it is time-consuming and yields are low. However, a highly purified clay mineral can be obtained without damage to the initial structure and fabric.

4.3.4. A Pilot Purification Technique

To save time and increase yield, a pilot-scale purification technique was developed. Here the Na^+-exchange step is carried out by continuous circulation of 1 M NaCl through the clay mineral suspension (180 g in about 10 L) in a multi-channel membrane. The exchange takes 3 h to complete. The Na^+-exchanged clay is then washed by passing water continuously through a series of dialysis columns for about 12 h to reach the conductivity of deionized water. The technique is user-friendly, largely automatic, and easy to extend to an industrial scale. At the same time, a two-fold increase in yield is achieved within a fraction of the time required in the conventional method (2 days versus 1 month).

4.3.5. Conclusions

A complete purification cycle is time-consuming. However, not all the purification steps described above are always necessary. Which steps can be omitted depend on the purpose of the investigation. In contrast to soil clays, clays from geological deposits (such as bentonites, kaolins) commonly contain only small amounts of organic materials. As such, oxidation with H_2O_2 or peroxodisulphate may not be required and the simplified ('gentle') procedure may be satisfactory. Similarly, silica does not always act as a cementing agent, and can be removed without chemical treatment.

It should be stressed, however, that even small amounts of carbonates, (hydr)oxides, and organic materials can strongly influence the colloidal and rheological properties of clay pastes, slips, and dispersions. The chemical reactions involved in clay mineral purification may also cause changes to the clay mineral structure. In selecting a given purification procedure, the effect of different reactions must be duly considered.

REFERENCES

Abtahi, A., 1985. Synthesis of sepiolite at room temperature from silica and magnesium chloride solution. Clay Minerals 20, 521–523.

Alexiades, C.A., Jackson, M.L., 1966. Quantitative clay mineralogical analysis of soils and sediments. Clays and Clay Minerals 164, 35–52.

Anderson, J.U., 1963. An improved treatment for mineralogical analysis of samples containing organic matter. Clays and Clay Minerals 10, 380–388.

Annabi-Bergaya, F., 1978. Adsorption du Méthanol par la Montmorillonite. Ph.D. thesis. University of Orléans, France.

Aparicio, P., Galan, E., 1999. Mineralogical interference on kaolinite crystallinity index measurements. Clays and Clay Minerals 47, 12–27.

Arkai, P., 2002. Phyllosilicates in very low-grade metamorphism: transformation to micas. In: Mottana, A., Sassi, F.P., Thompson, J.B., Guggenheim, S. (Eds.), Micas: Crystal

Chemistry and Metamorphic Petrology. Reviews in Mineralogy & Geochemistry, vol. 46. Mineralogical Society of America, Washington, DC, pp. 463–478.

Barrer, R.M., Marshall, D.J., 1964. Hydrothermal chemistry of silicates. Part XII. Synthetic strontium aluminosilicates. Journal of the Chemical Society, 485–497.

Barrer, R.M., Sieber, W., 1977. Evidence for the replacement of silicon by a divalent cation: synthesis of a novel zinc mica, $K_2H_2Zn_5[ZnSi_7O_{20}](OH)_4$. Journal of the Chemical Society, Chemical Communications, 905.

Barrer, R.M., White, E.A.D., 1952. The hydrothermal chemistry of silicates. Part II. Synthetic crystalline sodium aluminosilicates. Journal of the Chemical Society, 1561–1571.

Benna, M., Kbir-Ariguib, N., Magnin, A., Bergaya, F., 1999. Effect of pH on rheological properties of purified sodium bentonite suspensions. Journal of Colloid and Interface Science 218, 442–455.

Bhanage, B.M., Fujita, S., He, Y., Ikushima, Y., Shirai, M., Torii, K., Arai, M., 2002. Concurrent synthesis of dimethyl carbonate and ethylene glycol via transesterification of ethylene carbonate and methanol using smectite catalysts containing Mg and/or Ni. Catalysis Letters 83, 137–141.

Birsoy, R., 2002. Formation of sepiolite–palygorskite and related minerals from solution. Clays and Clay Minerals 50, 736–745.

Borchardt, G., 1989. Smectites. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. Soil Science Society of America, Madison, WI, pp. 675–727.

Bowers, T.S., Jackson, K.J., Helgeson, H.C., 1984. Equilibrium Activity Diagrams: for Coexisting Minerals and Aqueous Solutions at Temperature and Pressures up to 5 Kb and 600 °C. Springer, Berlin.

Caillère, S., Hénin, S., Esquevin, J., 1953. Synthèses à basse température de phyllites ferrifères. Comptes Rendus de l'Académie des Sciences, Paris 237, 1724–1726.

Caillère, S., Hénin, S., Esquevin, J., 1956. Etude expérimentale du mécanisme de la formation des antigorites nickellifères. Bulletin de Société Française de Minéralogie et Cristallographie 79, 408–421.

Caillère, S., Oberlin, A., Hènin, S., 1954. Etude au microscope électronique de quelques silicates phylliteux obtenus par synthèses à basse température. Clay Minerals Bulletin 2, 146–156.

Carrado, K.A., Csencsits, R., Thiyagarajan, P., Seifert, S., Macha, S.M., Harwood, J.S., 2002. Crystallization and textural porosity of synthetic clay minerals. Journal of Materials Chemistry 12, 3228–3237.

Carrado, K.A., Xu, L., Csencsits, R., Muntean, J.V., 2001. The use of organo- and alkoxysilanes in the synthesis of grafted and pristine clays. Chemistry of Materials 13, 3766–3773.

Cipriani, C., 2002. Micas: historical perspective. In: Mottana, A., Sassi, F.P., Thompson, J.B., Guggenheim, S. (Eds.), Micas: Crystal Chemistry & Metamorphic Petrology. Reviews in Mineralogy, vol. 46. Mineralogical Society of America, Washington, DC, pp. 479–499.

Decarreau, A., 1980. Cristallogenèse expérimentale des smectites magnésiennes: hectotite, stévensite. Bulletin de Minéralogie 103, 579–590.

Decarreau, A., 1981. Cristallogenèse à basse tempèrature de smectites trioctaèdriques par viellissement de coprécipités sillicométalliques. Comptes Rendus de l'Académie des Sciences, Paris 292, 61–64.

Decarreau, A., Bonnin, D., 1986. Synthesis and crystallogenesis at low temperature of Fe^{3+} smectites by evolution of coprecipitated gels: experiments in partly reducing conditions. Clay Minerals 21, 861–877.

Decarreau, A., Bonnin, D., Badaut-Trauth, D., Couty, R., Kaiser, P., 1987. Synthesis and crystallogenesis of ferric smectite by evolution of Si–Fe coprecipitates in oxidizing conditions. Clay Minerals 22, 207–223.

Decarreau, A., Petit, S., Viellard, Ph., Dabert, N., 2004. Hydrothermal synthesis of aegirine at 200 °C. European Journal of Mineralogy 16, 85–90.

De Kimpe, C.R., Kodama, H., 1984. Transformation of aluminosilicate gels into pre-kaolinitic and pre-zeolitic structure: effects of the solution media. Clay Minerals 19, 237–242.

De Kimpe, C.R., Kodama, H., Rivard, R., 1981. Hydrothermal formation of a kaolinite-like product from noncrystalline aluminosilicate gels. Clays and Clay Minerals 29, 446–450.

De Vijnck, Y.A., 1973. Etude des phases cristallines appartenant au système Al_2O_3-SiO_2-H_2O formées par traitement hydrothermal de gels obtenus par coprécipitation d'$Al(OH)_3$ et de $Si(OH)_4$. Silicates Industriels 38, 193–209.

De Vijnck, Y.A., 1975. Action des ions alcalins sur la transformation hydrothermale de gels silico-alumineux. I. Influence de l'ion Li^+. Silicates Industriels 40, 259–272.

De Vijnck, Y.A., 1976. Action des ions alcalins sur la transformation hydrothermale de gels silico-alumineux. II. Influence de l'ion K^+. Silicates Industriels 41, 67–81.

Drits, V.A., Besson, G., Muller, F., 1995. An improved model for structural transformations of heat-treated aluminous dioctahedral 2:1 layer silicates. Clays and Clay Minerals 43, 718–731.

Duldulao, F.D., Burlitch, J.M., 1991. Multistep sol-gel synthesis of a layered silicate, potassium fluorophlogopite. Chemistry of Materials 3, 772–775.

Eberl, D., Hower, J., 1975. Kaolinite synthesis. The role of the silicon-aluminum ratio and alkali-hydrogen ion ratio in hydrothermal systems. Clays and Clay Minerals 23, 301–309.

Emmerich, K., Kahr, G., 2001. The cis- and trans-vacant variety of a montmorillonite: an attempt to create a model smectite. Applied Clay Science 20, 119–127.

Fanning, D.S., Keramidas, V.Z., El-Desoky, M.A., 1989. Micas. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. Soil Science Society of America, Madison, WI, pp. 551–634.

Farmer, V.C., 1974. The layer silicates. In: Farmer, V.C. (Ed.), The Infrared Spectra of Minerals. Mineralogical Society, London, pp. 331–365.

Farmer, V.C., Mitchell, B.D., 1963. Occurrence of oxalates in soil clays following hydrogen peroxide treatment. Soil Science 96, 221–229.

Fialips, C.-I., Petit, S., Decarreau, A., 2000. Hydrothermal formation of kaolinite from various metakaolins. Clay Minerals 35, 559–572.

Fiore, S., Huertas, F.J., Huertas, F., Linares, J., 2001. Smectite formation in rhyolitic obsidian as inferred by microscopic (SEM-TEM-AEM) investigations. Clay Minerals 36, 489–500.

Frank-Kamenetskii, V.A., Kotov, N.V., Klochkova, G.N., 1972. Phase and structural changes in sepiolite and palygorskite under hydrothermal conditions in the presence of KCl and NaCl. Geokhimiya 10, 1227–1235.

Frank-Kamenetskii, V.A., Kotov, N.V., Tomashenko, A.N., 1973. Role of Al(IV) and Al(VI) in transformation and synthesis of layer silicates. Kristall und Technik 8, 425–435.

Franklin, K.R., Lee, E., 1996. Synthesis and ion-exchange properties of Na-4-mica. Journal of Materials Chemistry 6, 109–115.

Fritz, B., 1981. Etudes Thermodynamiques et Modélisation des Réactions Hydrothermales et Diagénétiques. Sciences Géologiques, Mémoire 65, 197.

Fujii, K., Hayashi, S., Kodama, H., 2003. Synthesis of an alkylammonium/magnesium phyllosilicate hybrid nanocomposite consisting of a smectite-like layer and organosiloxane layers. Chemistry of Materials 15, 1189–1197.

Golden, D.C., Dixon, J.B., Shadfan, H., Kippenberger, L.A., 1985. Palygorskite and sepiolite alteration to smectite under alkaline conditions. Clays and Clay Minerals 33, 44–50.

Grauby, O., Petit, S., Decarreau, A., Baronnet, A., 1993. The beidellite–saponite solid-solution: an experimental approach. European Journal of Mineralogy 5, 623–635.

Grauby, O., Petit, S., Decarreau, A., Baronnet, A., 1994. The nontronite–saponite series: an experimental approach. European Journal of Mineralogy 6, 99–112.

Güven, N., Carney, L.L., 1979. The hydrothermal transformation of sepiolite to stevensite and the effect of added chlorides and hydroxides. Clays and Clay Minerals 27, 253–260.

Harder, H., 1970. Kaolinit-Synthese bei niedrigen Temperaturen. Naturwissenschaften 4, 193.

Harder, H., 1972. The role of magnesium in the formation of smectite minerals. Chemical Geology 10, 31–39.

Harder, H., 1978. Synthesis of iron layer silicate minerals under natural conditions. Clays and Clay Minerals 26, 65–72.

Hashimoto, J., Jackson, M.L., 1960. Rapid dissolution of allophane and kaolinite–halloysite after dehydration. Clays and Clay Minerals 7, 102–113.

Hast, N., 1956. A reaction between silica and some magnesium compounds at room temperature and at +37 °C. Arkiv för Kemi 9, 343–360.

Higashi, S., Miki, K., Komarneni, S., 2002. Hydrothermal synthesis of Zn-smectite. Clays and Clay Minerals 50, 299–305.

Hinckley, D.N., 1963. Variability in "crystallinity" values among the kaolin deposits of the coastal plain of Georgia and South Carolina. Clays and Clay Minerals 11, 229–235.

Holmgren, G.G.S., 1967. A rapid citrate–dithionite extractable iron procedure. Soil Science Society of America Proceedings 31, 210–211.

Huertas, F.J., Cuadros, J., Huertas, F., Linares, J., 2000. Experimental study of the hydrothermal formation of smectite in the beidellite–saponite series. American Journal of Science 300, 504–527.

Huertas, F.J., Fiore, S., Huertas, F., Linares, J., 1999. Experimental study of the hydrothermal formation of kaolinite.. Chemical Geology 156, 171–190.

Huertas, F.J., Huertas, F., Linares, J., 1993a. Hydrothermal synthesis of kaolinite: method and characterization of synthetic materials. Applied Clay Science 7, 345–356.

Huertas, F.J., Huertas, F., Linares, J., 1993b. A new approach to kinetics of kaolinite synthesis. In: Cuney, M., Cathelineau, M. (Eds.), Proceedings of the 4th International Symposium on Hydrothermal Reactions. Nancy, France, pp. 87–90.

Iriarte-Lecumberri, I., 2003. Synthèse de minéraux argileux dans le système SiO_2–Al_2O_3–-Fe_2O_3–Na_2O–H_2O. Ph.D. thesis. Universities of Poitiers, France and Granada, Spain, p. 2.

Janek, M., Komadel, P., Lagaly, G., 1997. Effect of autotransformation on the layer charge of smectites determined by the alkylammonium method. Clay Minerals 32, 623–632.

Jepson, W.B., 1984. Kaolins: their properties and uses. Philosophical Transactions of the Royal Society, London, A 311, 411–432.

Keller, W.D., Matlack, K., 1990. The pH of clay suspensions in the field and laboratory, and methods of measurement of their pH. Applied Clay Science 5, 123–133.

Klingsberg, C., Roy, R., 1957. Synthesis, stability and polytypism of nickel and gallium phlogopite. American Mineralogist 42, 629–634.

Kloprogge, J.T., 1998. Synthesis of smectites and porous pillared clay catalysts: a review. Journal of Porous Materials 5, 5–41.

Kloprogge, J.T., Jansen, J.B., Geus, J.W., 1990. Characterization of synthetic Na-beidellite. Clays and Clay Minerals 38, 409–414.

Kloprogge, J.T., Komarneni, S., Amonette, J.E., 1999. Synthesis of smectite clay minerals: a critical review. Clays and Clay Minerals 47, 529–554.

Kloprogge, J.T., Vogels, R.J., 1995. Hydrothermal synthesis of ammonium-beidellite. Clays and Clay Minerals 43, 135–137.

Kodama, T., Harada, Y., Ueda, M., Shimizu, K., Shuto, K., Komarneni, S., Hoffbauer, W., Schneider, H., 2001a. Crystal-size control and characterization of Na-4-mica prepared from kaolinite. Journal of Materials Chemistry 11, 1222–1227.

Kodama, T., Higuchi, T., Shimizu, T., Shimizu, K., Komarneni, S., Hoffbauer, W., Schneider, H., 2001b. Synthesis of Na-2-mica from metakaolin and its cation exchange properties. Journal of Materials Chemistry 11, 2072–2077.

Kodama, T., Komarneni, S., Hoffbauer, W., Schneider, H., 2000. Na-4-mica: simplified synthesis from kaolinite, characterization and Zn, Cd, Pb, Cu and Ba uptake kinetics. Journal of Materials Chemistry 10, 1649–1653.

Komarneni, S., 1989. Mechanisms of palygorskite and sepiolite alteration as deduced from solid-state 27Al and 29Si NMR. Clays and Clay Minerals 37, 469–473.

Komarneni, S., Pidugu, R., Amonette, J.E., 1998. Synthesis of Na-4-mica from metakaolinite and MgO: characterization and Sr^{2+} uptake kinetics. Journal of Materials Chemistry 8, 205–208.

Komarneni, S., Pidugu, R., Hoffbauer, W., Schneider, H., 1999. A synthetic Na-rich mica: synthesis and characterization by ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy. Clays and Clay Minerals 47, 410–416.

Köster, H.M., 1996. Mineralogical and chemical heterogeneity of three standard clay mineral samples. Clay Minerals 31, 417–422.

Köster, H.M., 1997. Methoden und kritische Anmerkungen zur Aufbereitung von Karbonatgesteinen und zur Analyse der schwerlöslichen Gesteinsbestandteile und der Carbonate. Zentralblatt für Geologie und Paläontologie I 1033–1043.

Köster, H.M., Kohler, E.E., Krahl, J., Kröger, J., Vogt, K., 1973. Veränderungen am Montmorillonit durch Einwirkung von 0,1 m AeDTE-Lösungen, 1 n NaCl-Lösung und 0,1 n Salzsäure. Neues Jahrbuch für Mineralogie. Abhandlungen 119, 8–100.

La Iglesia, A., Van Oosterwyck-Gastuche, M.C., 1978. Kaolinite synthesis. I. Crystallization conditions at low temperatures and calculation of thermodynamic equilibriums. Applications to laboratory and field observations. Clays and Clay Minerals 26, 397–408.

Lagaly, G., 1981. Characterization of clays by organic compounds. Clay Minerals 16, 1–21.

Lagaly, G., 1994. Layer charge determination by alkylammonium ions. In: Mermut, A. (Ed.), Charge Characteristics of 2:1 Clay Minerals. CMS Workshop Lectures, vol. 6. The Clay Minerals Society, Boulder, CO, pp. 1–46.

Levinson, A.A., Day, J.J., 1968. Low-temperature hydrothermal synthesis of montmorillonite, ammonium-micas, and ammonium-zeolites. Earth and Planetary Science Letters 5, 52–54.

Linares, J., Huertas, F., 1971. Kaolinite: synthesis at room temperature. Science 171, 896–897.

Mackenzie, R. C. (Ed.), 1970. Differential Thermal Analysis. In: Fundamental Aspects, vol. 1. Academic Press, London.

Manning, D.A.C., 2003. Experimental studies of clay mineral occurrence. In: Worden, R., Morad, S. (Eds.), Clay Mineral Cements in Sandstones. Special Publication of the International Association of Sedimentologists 34. Blackwell Science, Oxford, pp. 177–190.

Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays and Clay Minerals 7, 317–327.

Meier, L.P., Menegatti, A.P., 1997. A new, efficient, one-step method for the removal of organic matter from clay-containing sediments. Clay Minerals 32, 557–563.

Menegatti, A.P., Früh-Green, G.L., Stille, P., 1999. Removal of organic matter by disodium peroxodisulphate: effects on mineral structure, chemical composition, and physicochemical properties of some clay minerals. Clay Minerals 34, 247–257.

Millot, G., 1965. Géologie des Argiles. Masson, Paris (Section C).

Mitchell, B.D., Smith, B.F.L., 1974. The removal of organic matter from soil extracts by bromine oxidation. Journal of Soil Science 25, 239–241.

Miyawaki, R., Tomura, S., Inukai, K., Shibasaki, Y., Okazaki, M., Samejima, S., Satokawa, S., 1992. Formation process of kaolinite from the amorphous mixture of silica and alumina. Clay Science 8, 273–284.

Miyawaki, R., Tomura, S., Samejima, S., Okazaki, M., Mizuta, H., Maruyama, S.-I., Shibasaki, Y., 1991. Effects of solution chemistry on the hydrothermal synthesis of kaolinite. Clays and Clay Minerals 39, 498–508.

Mizutani, T., Fukushima, Y., Okada, A., Kamigaito, O., 1991. Hydrothermal synthesis of sepiolite. Clay Minerals 26, 441–445.

Mottana, A., Robert, J.-L., Marcelli, A., Giuli, G., Della Ventura, G., Paris, E., Wu, Z., 1997. Octahedral vs tetrahedral coordination of Al in synthetic micas determined by XANES. American Mineralogist 82, 497–502.

Mottana, A., Sassi, F. P., Thompson, J. B., Guggenheim, S. (Eds.), 2002. Micas: Crystal Chemistry and Metamorphic Petrology. In: Reviews in Mineralogy & Geochemistry, vol. 46. Mineralogical Society of America, Washington, DC.

Muthusamy, E., Walsh, D., Mann, S., 2002. Morphosynthesis of organoclay microspheres with sponge-like or hollow interiors. Advanced Materials 14, 969–972.

Nagase, T., Iwasaki, T., Ebina, T., Hayashi, H., Onodera, Y., Dutta, N.C., 1999. Hydrothermal synthesis of Fe-montmorillonite in Si-Fe-Mg system. Chemistry Letters 28, 303–304.

Nesterchuk, N.I., Makarova, T.A., 1973. Hydrothermal synthesis of sepiolite. Zapisky Vsesoyuznogo Mineralogicheskogo Obshchestva 102, 232–242.

Norrish, K., Pickering, J.G., 1983. Clay minerals. In: Soils: an Australian Viewpoint. CSIRO, Melbourne/Academic Press, London, pp. 281–308.

Otsuka, R., Sakamoto, T., Hara, Y., 1974. Phase transformations of sepiolite under hydrothermal conditions. Journal of the Clay Science Society of Japan 14, 8–19.

Parfitt, R.L., 1989. Optimum conditions for extraction of Al, Fe and Si from soils with acid oxalate. Communications in Soil Science and Plant Analysis 20, 801–806.

Paulus, W.J., Komarneni, S., Roy, R., 1992. Bulk synthesis and selective exchange of strontium ions in $Na_4Mg_6Al_4Si_4O_{20}F_4$ mica. Nature 357, 571–573.

Pérez-Rodriguez, J.L., Wilson, M.J., 1969. Effects of pretreatment on a 14 Å swelling mineral from Gartly, Aberdeenshire. Clay Minerals 8, 39–45.

Permien, T., Lagaly, G., 1994. The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds. IV. Sodium montmorillonites and acids. Applied Clay Science 9, 251–263.

Petit, S., 2004. Crystal-chemistry of talcs: a NIR and MIR spectroscopic approach. In: Kloprogge, J.T. (Ed.), Vibrational Spectroscopies. CMS Workshop Lectures. vol. 13. The Clay Minerals Society, Aurora, CO., in press.

Petit, S., Decarreau, A., 1990. Hydrothermal (200 °C) synthesis and crystal chemistry of iron-rich kaolinites. Clay Minerals 25, 181–196.

Petit, S., Righi, D., Madejova, I., Decarreau, A., 1998. Layer charge estimation of smectites using infrared spectroscopy. Clay Minerals 33, 579–591.

Petit, S., Righi, D., Madejova, I., Decarreau, A., 1999. Interpretation of the infrared NH_4^+. spectrum of the NH_4^+-clays: application to the evaluation of the layer charge. Clay Minerals 34, 543–549.

Rengasamy, P., van Assche, J.B., Uytterhoeven, J.B., 1976. Particle size of Wyoming bentonite and its relation to the cation exchange capacity and the homogeneity of the charge density. Journal of the Chemical Society, Faraday Transactions I 72, 376–381.

Rayner, J.H., 1962. An examination of the rate of formation of kaolinite from a co-precipitated silica gel. Colloques Internationaux du CNRS, 105, Genese et Synthèse des Argiles, pp. 124–127.

Robert, J.-L., Beny, J.-M., Della Ventura, G., Hardy, M., 1993. Fluorine in micas: crystal-chemical control of the OH–F distribution between trioctahedral and dioctahedral sites. European Journal of Mineralogy 5, 7–18.

Rosenberg, P.E., 1987. Synthetic muscovite solid solutions in the system K_2O–Al_2O_3–SiO_2–-H_2O. American Mineralogist 72, 716–723.

Roth, C.B., Jackson, M.L., Syers, J.K., 1969. Deferration effect on structural ferrous–ferric iron ratio and cec of vermiculites and soils. Clays and Clay Minerals 17, 2.

Roy, R., Osborn, E.F., 1954. The system Al_2O_3–SiO_2–H_2O. American Mineralogist 39, 853–885.

Roy, R., Tuttle, O.F., 1956. Investigations under hydrothermal conditions. Physics and Chemistry of the Earth 1, 138–180.

Ryan, J.N., Gschwend, P.M., 1991. Extraction of iron oxides from sediments using reductive dissolution by titanium(III). Clays and Clay Minerals 39, 509–518.

Satokawa, S., Osaki, Y., Samejima, S., Miyawaki, R., Tomura, S., Shibasaki, Y., Sugahara, Y., 1994. Effects of the structure of silica-alumina gel on the hydrothermal synthesis of kaolinite. Clays and Clay Minerals 42, 288–297.

Shirai, M., Aoki, K., Arai, M., 2002. Control of mesopore structure of smectite-type materials synthesized with a hydrothermal method. Studies in Surface Science and Catalysis 141, 281–288.

Shirai, M., Aoki, K., Torii, K., Arai, M., 2001. In situ EXAFS study on the formation of smectite-type clays containing cobalt cations in lattice. Journal of Synchrotron Radiation 8, 743–745.

Shirai, M., Torii, K., Arai, M., 2000. Synthesis and size-selective application of palladium metal particles intercalated in mesopore-size controlled smectite. Molecular Crystals and Liquid Crystals 341, 1125–1130.

Siffert, B., Espinasse, P., 1980. Adsorption of organic diacids and sodium polyacrylate onto montmorillonite. Clays and Clay Minerals 28, 381–387.

Siffert, B., Wey, R., 1962. Synthese d'une sepiolite a temperature ordinaire. Comptes Rendus de l'Académie des Sciences 254, 1460–1464.

Smykatz-Kloss, W., Warne, S. St. J., 1991. Thermal analysis in the geosciences. Lecture Notes in Earth Sciences, vol. 38. Springer, Berlin.

Srodon, J., 1980. Synthesis of mixed-layer kaolinite/smectite. Clays and Clay Minerals 28, 419–424.

Steefel, C.I., Van Capellen, P., 1990. A new kinetic approach to modeling the water-rock interaction: the role of nucleation, precursors and Ostwald ripening. Geochimica et Cosmochimica Acta 54, 2657–2677.

Stubican, V., Roy, R., 1962. Boron substitution in synthetic micas and clays. American Mineralogist 47, 1166–1173.

Stucki, J.W., Golden, D.C., Roth, C.B., 1984a. Effects of reduction and reoxidation of structural iron on the surface charge and dissolution of dioctahedral smectites. Clays and Clay Minerals 32, 350–356.

Stucki, J.W., Low, P., Roth, C.B., Golden, D.C., 1984b. Effects of oxidation state of octahedral iron on clay swelling. Clays and Clay Minerals 32, 357–362.

Stul, M.S., van Leemput, L., 1982. Particle-size distribution, cation exchange capacity and charge density of deferrated montmorillonites. Clay Minerals 17, 209–215.

Stumm, W., Morgan, J.J., 1981. Aquatic Chemistry, 2nd edition. Wiley, New York.

Tamura, K., Yamada, H., Nakazawa, H., 2000. Stepwise hydration of high-quality synthetic smectite with various cations. Clays and Clay Minerals 48, 400–404.

Tateyama, H., Hishimura, S., Tsunematsu, K., Jinnai, K., Adachi, Y., Kimura, M., 1992. Synthesis of expandable fluorine mica from talc. Clays and Clay Minerals 40, 180–185.

Theng, B.K.G., Ristori, G.G., Santi, C.A., Percival, H.J., 1999. An improved method for determining the specific surface areas of topsoils with varied organic matter content, texture and clay mineral composition. European Journal of Soil Science 50, 309–316.

Tomita, K., Kawano, M., 2002. Synthesis of smectite from igneous rocks at atmospheric pressure. Clay Science 11, 585–599.

Tomura, S., Shibasaki, Y., Mizuta, H., Kitamura, M., 1983. Spherical kaolinite: synthesis and mineralogical properties. Clays and Clay Minerals 31, 413–421.

Tomura, S., Shibasaki, Y., Mizuta, H., Kitamura, M., 1985a. Growth conditions and genesis of spherical and play kaolinite. Clays and Clay Minerals 33, 200–206.

Tomura, S., Shibasaki, Y., Mizuta, H., Sunagawa, I., 1985b. Origin of morphology of spherical kaolinite. Clay Science 6, 159–166.

Tomura, S., Shibasaki, Y., Miyawaki, R., Mizuta, H., Yamashita, Y., 1990. Synthesis of kaolinite with dickite seed: a study by the experimental design method. Clay Science 7, 315–323.

Toraya, H., Iwai, S., Marumo, F., Hishikawa, T., Hirao, M., 1978. The crystal structure of synthetic mica, $KMg_2.75Si_3.5AlO.5O_{10}F_2$. Mineralogical Journal 9, 210–220.

Tributh, H., 1976. Die Umwandlung der glimmerartigen Schichtsilikate zu aufweitbaren Dreischicht-Tonmineralen. Zeitschrift für Pflanzenernährung und Bodenkunde 1, 7–25.

Tributh, H., Lagaly, G., 1986a. Aufbereitung und Identifizierung von Boden- und Lagerstättentonen. I. Aufbereitung der Proben um Labor. GIT-Fachzeitschrift für das Laboratorium 30, 524–529.

Tributh, H., Lagaly, G., 1986b. Aufbereitung und Identifizierung von Boden- und Lagerstättentonen. II. Korngrössenanalyse und Gewinnung von Tonsubfraktionen. GIT-Fachzeitschrift für das Laboratorium 30, 771–776.

van Langeveld, A.D., van der Gaast, S.J., Eisma, D., 1978. A comparison of the effectiveness of eight methods for the removal of organic matter from clay. Clays Clay Minerals 26, 361–364.

van Olphen, H., 1963. An Introduction to Clay Colloid Chemistry, 2nd edition. Wiley, New York.

Van Oosterwyck-Gastuche, M.C., La Iglesia, A., 1978. Kaolinite synthesis. II. A review and discussion of the factors influencing the rate process. Clays and Clay Minerals 26, 409–417.

Voncken, J.H.L., van der Eerden, M.J., Jansen, J.B.H., 1987. Synthesis of a Rb analogue of 2M1 muscovite. American Mineralogist 72, 551–554.

Wiegmann, J., Horte, C.H., 1960. Eigenschaften und thermische Reaktionen gefallter Magnesiumsilikate. Silikattechnik 11, 380–384.

Wilson, M.J., 1999. The origin and formation of clay minerals in soils: past, present and future perspectives. Clay Minerals 34, 7–25.

Wollast, R., Mackenzie, F.T., Bricker, O.P., 1968. Experimental precipitation and genesis of sepiolite at earth-surface conditions. American Mineralogist 53, 1645–1662.