

Chapter 7.2

THERMALLY MODIFIED CLAY MINERALS

L. HELLER-KALLAI

Institute of Earth Sciences, The Hebrew University of Jerusalem, IL-91904 Jerusalem, Israel

The structure and composition of clay minerals are modified by heating. The concomitant changes in properties can be exploited for practical purposes. The actual temperatures at which changes occur vary greatly from one clay mineral group to another, and even for different specimens within a given group. These temperatures also depend on the particle size and on the heating regime. Four principal temperature ranges in which significant changes occur in the structures of clay minerals may be distinguished.

- (1) Temperatures sufficiently low to cause partial freezing of clay suspensions or pastes (-5°C): in this temperature range some of the water is converted into ice. However, even at a temperature as low as -60°C a significant amount of water remains in a liquid or semi-liquid state, forming a film that separates the mineral surface from the ice.
- (2) Temperatures above dehydration but below dehydroxylation: when the temperature is raised from ambient to that of the onset of dehydroxylation, clays lose adsorbed and hydration water. As a result, the interlayer spaces collapse, while pore space is changed, and the acidity of the clay mineral surfaces and interlayers is substantially altered.
- (3) Temperatures above dehydroxylation, but below those leading to complete destruction of the structure: the changes occurring in this temperature range vary for different clay mineral groups. Dehydroxylation destroys the layer structure of trioctahedral, 2:1 type (T-O-T) minerals, whereas that of their dioctahedral counterparts is preserved. Kaolinite group minerals become amorphous to X-rays although some features of the structural framework are preserved.
- (4) Temperatures at which new phases crystallise: dehydroxylated clays that do not turn amorphous to X-rays may become so on further heating, before high-temperature phases crystallise. With trioctahedral clay minerals and palygorskite the interval between stages (3) and (4) is very short. Thus, intermediate phases, if formed, may escape detection. When new phases crystallise, clay minerals lose

their original identity although the crystallographic orientation of the products is frequently related to that of the starting material.

Clay minerals can be heated in different forms: (i) without any admixtures or pretreatment; (ii) mixed with various reagents before heating; (iii) after pretreatment such as acid-activation; and (iv) after preheating and pretreatment, for example, by acid-activation, and subsequent reheating.

In view of the great variety of starting materials and the many variables involved in the heating regime, a range of options is available for the thermal modification of clays. The ubiquitous impurities in natural clays may also play a part. The pre-activation temperatures required to develop desirable properties, or prevent undesirable properties from developing, vary with different clay minerals. Some minerals are preferably used in the dehydrated, others in the dehydroxylated form. The following discussion is concerned with some properties of clay minerals that are changed or modified by thermal treatment.

7.2.1. FREEZING OF CLAY MINERALS

Freezing affects pore water and water adsorbed on clay mineral surfaces, in the interlayer spaces, and in channels. Not all the water is converted into ice. Some remains in a mobile semi-liquid or liquid state, coating the surfaces (Anderson and Tice, 1971).

A. Effect of Freeze-Drying on the Texture of Clay Minerals

On freeze-drying, water is expelled from the frozen mineral (under vacuum) by evaporation of liquid water and sublimation of ice. This affects the texture of the clay mineral. Freeze-drying tends to promote edge-to-face association resulting in the formation of aggregates with more macropores than in air-dried samples (Lagaly, 1987) (Fig. 7.2.1). Freeze-drying may either increase or decrease the BET surface area, depending on the original clay mineral (de Carvalho et al., 1996).

B. Changes in Acidity

The effect of freezing on the acidity of smectite interlayers is similar to that of drying. As some of the hydration water is removed the interlayer spaces become more acidic (see Section 7.2.2.C). The proportion of water that is frozen depends upon the temperature. Changes in acidity in the interlayer spaces are clearly demonstrated by the colour of a benzidine–montmorillonite assemblage, which depends upon the H^+ ion concentration. On cooling from -5 to -15 °C and below, the colour changes from the original blue of the monovalent semiquinone to green or bluish-green. The green colour is produced by a mixture of the blue monomer and the yellow dimer that is formed at low pH (Lahav and Anderson, 1973).

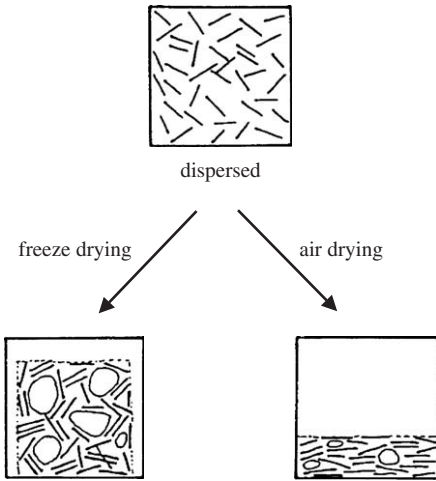


Fig. 7.2.1. Effect of freeze-drying on the aggregation of clay mineral particles (Lagaly, 1987).

C. Changes in Mechanical and Rheological Properties

Freezing of water in pores and fissures causes expansion, which leads to cracking and changes in the mechanical properties of the clay mineral. Repeated freezing–thawing cycles exacerbate this condition. The effect of freezing on clay mineral properties is of considerable importance to the behaviour of soils in cold climates.

Freezing and thawing has long-lasting effects on the rheological properties of 2:1 type clay minerals. Schwinka and Mortel (1999), for example, have found that the viscosity and plasticity of illite suspensions are increased by freezing and thawing. The effects are enhanced by the addition of small amounts of Na_2SiO_3 , but reduced by addition of divalent cations. Freezing and thawing also increase weight loss on dehydration. These phenomena are attributed to the formation of water layers bound to the clay mineral surface but are not observed with kaolins. The effects of freezing–thawing cycles on the illite slurries are persistent. They extend up to the sintering process and even influence the texture and mechanical strength of the ceramic material obtained from the slurries.

7.2.2. DEHYDRATION OF CLAY MINERALS

On heating, all clay minerals pass through a temperature range in which they are dehydrated to various degrees. In the upper region of this temperature range dehydration and dehydroxylation may overlap. Dehydration causes changes that can be controlled and utilised. Loss of adsorbed water alters the macro- and microporosity of the clay mineral as well as its plasticity. Interlayer spaces collapse and CEC

is reduced. Partial loss of adsorbed and hydration water increases hydrophilicity and surface acidity. The actual and potential applications of these modifications of clay mineral properties at relatively low temperatures have been investigated.

A. Changes in Porosity

Porous materials, and especially those that are thermally stable, are in great demand as adsorbents, catalysts, and catalyst supports. Clay mineral systems have macro-, meso-, and micropores. Macro- and mesopores arise from particle-to-particle interactions, while micropores occur in the interlayer spaces of pillared phyllosilicates, in channels of sepiolite or palygorskite, and also between interconnected fibres or layers of clay minerals.

The porosity of clay mineral aggregates is closely linked to their water content. On heating, water is driven off and the porosity changes. Acid treatment also increases the porosity. This property can therefore be manipulated by a combination of acid attack and heat treatment.

The porosity of smectites has mostly been investigated for acid-treated or pillared samples (see Chapters 7.1 and 7.5). Complex changes in surface properties occur when untreated smectites are heated. This is because different hydration states co-exist at any particular vapour pressure. Mesoporosity in Na^+ -montmorillonite is attributed to interparticle associations, while microporosity is due to irregular stacking of layers of different lateral dimensions within a particle. On dehydration, water is first lost from external surfaces and meso-pores. As the vapour pressure decreases, the hydration state of the interlayer spaces changes stepwise from a three- to a two- and then a one-layer structure, with some overlap. At a relative vapour pressure of 0.05 the interlayer spaces are completely collapsed. Na^+ -montmorillonite shows a strong hysteresis effect of surface properties on de- and re-hydration (Cases et al., 1992). Exchange of the interlayer cations affects the texture of smectites both before and after heating.

Changes in surface area and pore size distribution of sepiolite and palygorskite on heating were extensively investigated. Three temperature regions can be distinguished in which loss of hydration water and concomitant changes in porosity occur. In the first stage adsorbed and zeolitic water is lost, in the second two of the four molecules of coordination water are driven off, causing the structure to fold, and in the third the remaining two water molecules are eliminated (Nagata et al., 1974; Van Scoyoc et al., 1979). The actual temperature ranges in which these changes occur depend on the sample, the pretreatment, and the thermal regime. Sepiolite loses zeolitic water below 100 °C, two of the four water molecules coordinating Mg^{2+} in the channels below 300–380 °C, and the remaining coordination water below about 650 °C. Dehydroxylation occurs at higher temperatures. The corresponding temperature ranges for palygorskite are about 100 °C lower and dehydroxylation overlaps the final dehydration.

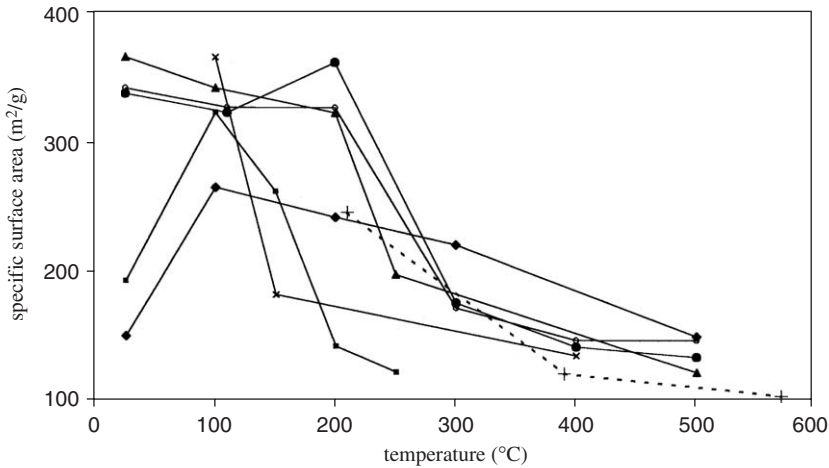


Fig. 7.2.2. Changes in the BET surface area (N_2) of sepiolite with temperature. Data from Dandy and Nadiye-Tabbiruka (1975) (\times); Fernandez Alvarez (1970, 1978) (\blacksquare); Jimenez-Lopez et al. (1978) (\bullet); Grillet et al. (1988) (\blacktriangle); Ruiz et al. (1996) (dotted line—few data points); Balci (1999) (\blacklozenge); and Caturla et al. (1999) (o).

Fig. 7.2.2 shows the effect of heating on total surface area (S_{total}), determined by N_2 adsorption, obtained in different studies. S_{total} comprises the total external surface area and the pore surfaces that are accessible to N_2 molecule. The graphs show some common features, but also significant differences. In the first stage of heating, below 100°C , an increase in S_{total} is observed in some instances, and a slight decrease in others. A drastic decrease occurs at higher temperatures when the structure folds (Serna et al., 1975) and pores are blocked. This reversible collapse commences at different temperatures in the various studies. On further heating, more water is expelled, and S_{total} of all the samples gradually decreases. In this temperature range the remaining coordination water is lost, the channels collapse irreversibly, sepiolite becomes hydrophobic, and sintering occurs.

The S_{total} of sepiolite can be increased, and its thermal stability improved, by acid pretreatment. In a systematic study of activation with HNO_3 of increasing acid strength and subsequent heating, the surface area of the sepiolite sample attained a maximum after pretreatment with 0.5 N HNO_3 and outgassing at 200°C . S_{total} decreased at higher temperatures, but the extent of reduction is less than for the untreated sample (Lopez-Gonzales et al., 1981)

Several investigations deal with changes in micro- and mesoporosity, as distinct from S_{total} . Because of the different definitions employed, however, it is difficult to compare the results. Micropores in the range of $0.015\text{--}1.0\ \mu\text{m}$ are preserved almost unchanged up to 900°C and in one, impure, sample even up to 1100°C (Goktas et al., 1997). Balci (1999) defines micropores as pores with diameter $<6.7\ \text{nm}$,

observing an initial increase in microporosity as zeolitic water is lost from the channels. Further heating leads to a progressive decrease in microporosity although about 60% of the original microporosity is retained up to 900 °C. [Fernandez Alvarez \(1978\)](#) restricts the size of micropores to pores with diameter <1.6–2 nm. These disappear after heating at 250 °C. [Grillet et al. \(1988\)](#) differentiate between structural micropores (cross-sectional area $1.34 \times 0.67 \text{ nm}^2$) and interfibre micropores (diameter 2–30 nm). After outgassing at 350 °C structural micropores disappear entirely, while interparticle microporosity is reduced from 0.031 to 0.026 cm³/g, but persists to 500 °C. [Molina-Sabio et al. \(2001\)](#) have derived the micropore volume and non-microporous surface area of a sepiolite from adsorption isotherms of various gases by application of the Dubinin–Radushkevich and BET equations. They define microporosity as the porosity that is lost between 110 and 500 °C. This amounts to ~0.11 cm³/g. Whereas this micropore volume is independent of the adsorbate used (N₂, CO₂, NH₃, or H₂O), the external surface area derived from the adsorption isotherms varies. The differences are attributed to the presence of specific adsorption sites on the surface.

Valid comparison of the results, obtained in investigations using different samples of sepiolite, would require similar pretreatment and identical thermal regimes. Even then, however, it would only be possible to establish general trends because the actual values of S_{total} and of the various porosities must be determined for individual samples.

Exfoliated vermiculite provides an extreme example of the changes in void volume that can occur when a clay mineral is heated. When the temperature is gradually raised, stepwise dehydration occurs. However, when vermiculite is flash-heated to temperatures of about 870–900 °C ([Justo et al., 1989](#)), or even up to 1500 °C ([Lagaly, 1993](#)) and then rapidly cooled, the mineral exfoliates in a direction approximately perpendicular to the layers. As a result, its volume increases to more than 20 times the original value, giving rise to a very porous, lightweight material with good absorptive and thermo-insulating properties. Exfoliation is attributed to the action of steam, which develops explosively between the layers, pushing them apart, while layer dehydroxylation (at the high prevailing temperatures) is restrained by rapid cooling. The degree of exfoliation depends upon the particle size. The smaller the particles, the easier it is for interlayer water to escape, and the less extensive is the exfoliation. [Justo et al. \(1989\)](#) reported that vermiculite samples containing mica or interstratified mica/vermiculite exfoliate more than pure vermiculite. They, therefore, consider that the sudden release of interlayer water is not the only factor controlling exfoliation. Impurities in, and the chemical composition or partial dehydroxylation of, the vermiculite may also play a part. No completely satisfactory explanation for the unique behaviour of vermiculite was yet offered. The phenomenon probably requires an appropriate balance between the amount of interlayer water and particle size. The latter controls the ease of diffusion of interlayer water and the stability of the T-O-T layers, as evidenced by the high dehydroxylation temperature. In view of the economic importance of exfoliated vermiculite, surprisingly few scientific papers

were published on this topic although many technical reports are available. This is an interesting challenge for further study.

B. De- and Re-Adsorption of Water

For the majority of clay minerals partial de- and re-hydration occurs very readily, but the temperatures required vary with clay mineral species.

Repeated wetting–drying cycles of K^+ -smectites cause ordering of layer stacking, accompanied by K^+ fixation (Gaultier and Mamy, 1979). These effects are more evident as the total layer charge of the smectite increases (Schultz, 1969; Eberl et al., 1986). Wetting–drying cycles in the presence of soluble salts cause some deprotonation, and effectively increase the layer charge (Heller-Kallai and Eberl, 1999).

Because dehydration is an endothermic and, conversely, re-hydration is an exothermic process, clay minerals can, in principle, be used for energy storage and as heat exchangers. Allophane and imogolite lose adsorbed water on mild heating. The total heat of re-hydration after preheating to 80–100 °C compares favourably with that of either Mg A-type zeolite or with B-type silica gel, which serve as standards (Suzuki et al., 2001a, 2001b). Montmorillonite requires higher temperatures for dehydration. Sadek and Mekhamer (2000, 2001) reported efficient energy storage with Na^+ - and Ca^{2+} -montmorillonites preheated at 200 and 250 °C, respectively, for extended periods. At these temperatures surface-adsorbed and interlayer water is lost, but is subsequently re-adsorbed exothermally on cooling in the presence of water vapour.

The reversibility of the dehydration process can also be exploited for humidity control. Attempts at using clays for this purpose have mostly focused on sepiolite. After prolonged outgassing at room temperature or heating up to 200 °C, when the micropores are still accessible and S_{total} is unchanged, sepiolite is very sensitive to changes in humidity. Even diurnal fluctuations can change the amount of water adsorbed, particularly at high relative humidities. These changes are attributed to differences in humidity rather than to variations in temperature (Caturla et al., 1999).

C. Changes in Surface Acidity on Dehydration

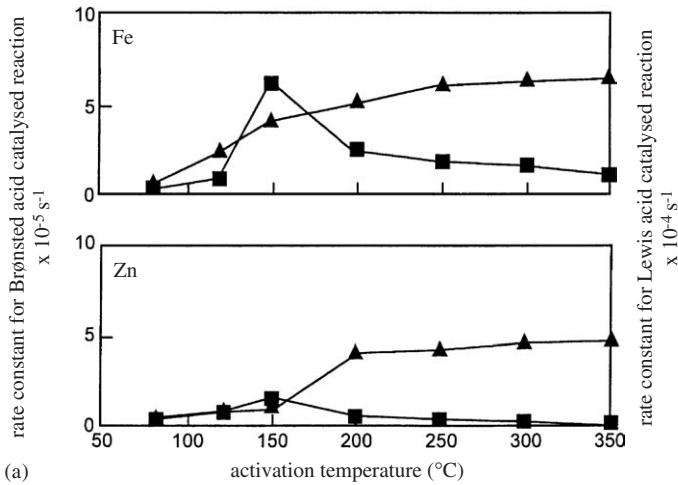
Clay mineral surfaces have both Brønsted and Lewis acid sites. The total acidity and the ratio of Brønsted to Lewis sites change with the hydration state of the mineral. Exposed Si^{4+} and tetrahedrally or octahedrally coordinated Al^{3+} and Fe^{3+} ions, when hydrated, are weak Brønsted acids. As in zeolites and silica–alumina catalysts, Si–OH–Al groups are much stronger Brønsted acids than either Si–OH–Si or Al–OH–Al groups. The acidity of Si–OH–Al groups may be greatly increased by drying, whereby these Brønsted sites are converted into Lewis acid sites. Incompletely coordinated Al^{3+} and Fe^{3+} ions, exposed at the edges, act as Lewis acids. Exposed Mg^{2+} ions, when hydrated, are basic (Yariv and Michaelian, 2002).

In smectites, strong Brønsted acidity derives from dissociation of water that is directly coordinated to interlayer cations. The acid strength increases with the polarising power of the cations, i.e. with decreasing size and increasing charge. The smaller the amount of hydration water present, the greater the polarisation of the remaining water molecules and hence their ability to donate protons. Dehydrated interlayer cations also act as Lewis acids. (For a review of methods of determining the surface acidity of smectites, see [Heller-Kallai, 2002](#).)

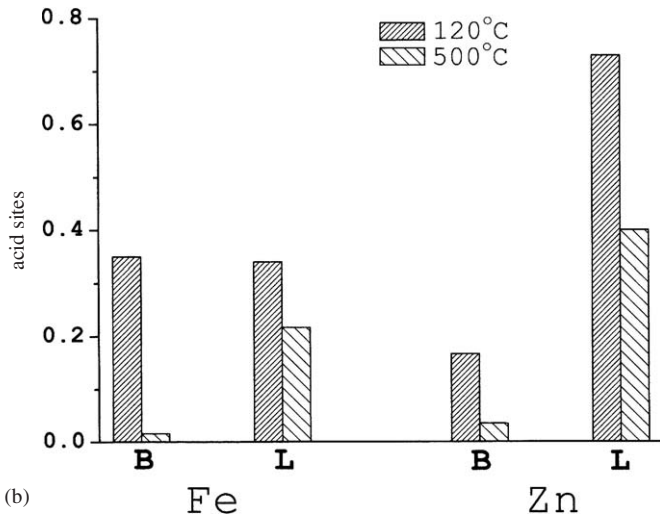
Quantitative measurements of changes in total surface acidity and in the ratio of Brønsted to Lewis acid sites, induced by heating, were mostly performed on acid-activated smectites because of their importance as catalysts for organic reactions. Using IR spectroscopy with pyridine as a molecular probe, [Cseri et al. \(1995\)](#) determined the Brønsted and Lewis acidity of a series of monoionic samples of K10 (a commercially available, acid-activated montmorillonite) after drying at 120 °C or calcining at 500 °C. Both Brønsted and Lewis acidity vary greatly with the nature of the interlayer cation. Brønsted acidity is much higher at 120 °C than at 500 °C. Lewis acidity is also reduced at the higher temperature, but not as much as Brønsted acidity. Similarly, [Brown and Rhodes \(1997\)](#) measured changes in surface acidity with preheating temperature of another commercially available acid-activated montmorillonite, Fulcat 40, by determining the rate constants of the Brønsted acid-catalyzed rearrangement of α -pinene to camphene, and of the Lewis acid-catalysed rearrangement of camphene hydrochloride to isobornyl chloride. IR studies using pyridine as a probe give results that are broadly consistent with those based on relative catalytic activities. Irrespective of the type of interlayer cation, maximum Brønsted activity is attained at about 150 °C and tends to zero on further heating. Maximum Lewis acidity is generated after thermal activation at 250–300 °C and does not change appreciably up to 500 °C.

The results for Fe^{2+} - and Zn^{2+} -saturated samples, used in the two studies, are shown in [Fig. 7.2.3](#). It is evident that there are significant differences between them. In both cases, Lewis sites predominate over Brønsted sites at high activation temperatures. However, the changes that occur in the number of Lewis sites with increasing temperatures are quite different. Whereas [Brown and Rhodes \(1997\)](#) measure higher Lewis acidity at higher temperatures, [Cseri et al. \(1995\)](#) report lower Lewis acidity after calcining at 500 °C than after drying at 120 °C. This applies to all nine monoionic samples examined. The ratio of Brønsted to Lewis acidity in the samples at any given temperature is also appreciably different in the two studies. It is difficult to determine the reasons for these discrepancies. Differences in thermal activation procedures (with [Cseri et al.](#) using a heating rate of 1 K/min in air, and [Brown and Rhodes](#) calcining for 1 h in dry air at the specified temperature) may account for some, but not all, of the differences. Other factors, such as specific features of the starting material, must also be considered. It would, therefore, appear that quantitative results obtained in any investigation are only valid for the particular system studied, and only overall trends can presently be generalised.

[Brown and Rhodes \(1997\)](#) also remarked that when heated, Na^+ -exchanged clay minerals have very low acid activity, concluding that both Brønsted and Lewis



(a)



(b)

Fig. 7.2.3. Changes in acidity with temperature of Fe and Zn saturated acid-activated montmorillonite. (a) Activity in the Brønsted acid-catalysed rearrangement of α -pinene (■) and the Lewis acid-catalysed rearrangement of camphene hydrochloride (▲). Adapted from Brown and Rhodes (1997). (b) Brønsted (B) and Lewis (L) acid sites determined by pyridine adsorption at 120 and 500 °C. Data from Cseri et al. (1995).

acidity derive mostly from the interlayer cations. Acid sites known to be present elsewhere on the mineral may be too weak to be effective in the reactions studied.

Thermally activated acid-treated smectites are widely used as catalysts in organic syntheses (Balogh and Laszlo, 1993).

D. The Hofmann–Klemen Effect

This effect refers to the reduction in negative layer charge, CEC and expansibility of octahedrally charged smectites saturated with small cations (e.g. Li^+ , Mg^{2+} , Cu^{2+}) following thermal treatment (Hofmann and Klemen, 1950; Quirk and Theng, 1960; Russell and Farmer, 1964; McBride and Mortland, 1974; Emmerich et al., 1999; Stackhouse and Coveney, 2002; Komadel et al., 2003). The common explanation of this effect is that heating induces the small cations to migrate from their interlayer positions into the layer structure where they become essentially non-exchangeable. In the case of Li^+ -montmorillonite, heating induces the Li^+ ions to migrate from the interlayer space into the vacant octahedral sites (Hofmann and Klemen, 1950), or into the hexagonal holes of the tetrahedral sheets (Tettenhorst, 1962; Theng et al., 1997), or both. The appearance of an AlMgLiOH stretching band near 3670 cm^{-1} in the IR spectrum of montmorillonites and some features of the near-IR region are indicative of the presence of Li^+ in the octahedral sheets (Madejová et al., 2000a, 2000b). The amount of 'fixed' Li^+ increases as the temperature is increased, up to about $250\text{ }^\circ\text{C}$. A series of reduced-charge smectites can thus be prepared from the same parent mineral. A high Mg^{2+} for Al^{3+} substitution and a high ratio of octahedral to tetrahedral charge are conducive to extensive negative-charge reduction. Low Li^+ fixation is observed for heated minerals with a relatively high fraction of tetrahedral charge (Madejová et al., 2000a; Hrobáriková and Komadel, 2002).

Li^+ fixation decreases the layer charge density, CEC, the amount of water and ethylene glycol monoethyl ether sorbed, as well as swelling (in water) of the smectite. Since the layer charge density controls the distribution of cations in the interlayer spaces, the interlayer spacing of alkylammonium–montmorillonite complexes is affected (Bujdák et al., 1992). Likewise, layer charge reduction affects the distance separating adsorbed dye cations (e.g. methylene blue). As a result, the colour of the clay mineral–dye complexes is modified because colour is determined by the type and extent of molecular aggregation (Bujdák et al., 2001). The presence of non-expanding layers in reduced-charge montmorillonite reduces its solubility in HCl (Komadel et al., 1996).

Heating in the presence of proton acceptors leads to partial deprotonation of structural hydroxyl groups, thus facilitating penetration of small divalent cations into the octahedral sheets (Heller-Kallai, 2001).

7.2.3. DEHYDROXYLATED PHASES

A. Kaolinite Group

When kaolinite is heated beyond the temperature of the dehydroxylation endotherm, metakaolinite is formed. Between 500 and $900\text{ }^\circ\text{C}$, this is the main product obtained. The exact temperature range depends on the starting kaolinite and on the heating regime. At higher temperatures a spinel-type phase is formed together with

amorphous silica, after which mullite and cristobalite appear. Nacrite and halloysite resemble kaolinite in their dehydroxylation reactions. Dickite forms a 1.4 nm superstructure before complete dehydroxylation occurs (Brindley and Lemaitre, 1987).

Brindley and Nakahira (1959) pioneered the study of the kaolinite-to-mullite reaction sequence. Since then numerous publications on this topic appeared, and only the salient points will be mentioned here.

As metakaolinite is amorphous to X-rays, alternative methods were used for structure determination, including IR spectroscopy (Stubican and Roy, 1961; Pampuch, 1966), X-ray fluorescence (XRF) spectrometry (Gastuche et al., 1963), radial distribution function (RDF) (Gualtieri and Bellotto, 1998), NMR spectroscopy (Komarneni et al., 1985; Watanabe et al., 1987; Sanz et al., 1988; Lambert et al., 1989; Rocha and Klinowski, 1990; Lussier, 1991; Massiot et al., 1995), and conductometry (Murat and Driouche, 1988). The results indicate that in metakaolinite the SiO_4 sheets persist but in a distorted form, while the octahedral sheets are profoundly altered although some short-range order is preserved. A TEM study (Bergaya et al., 1996), which includes selected area diffraction and lattice imaging, shows that metakaolinite has a layer structure, composed of very distorted SiO_4 sheets and Al-polyhedra. The particles are a few layers thick. Metakaolinite can be completely rehydroxylated, restoring the kaolinite particles with edges parallel to those of the original material (Rocha and Klinowski, 1991).

The structure of metakaolinite changes on heating. Solid-state NMR spectroscopy (Massiot et al., 1995) showed that, as the temperature is increased, the coordination number of Al atoms is reduced from 6 to 5 and 4, with Al^{V} and Al^{IV} developing simultaneously. At high temperatures, when new phases begin to crystallise, Al^{VI} reappears, some Al^{IV} persists, but Al^{V} disappears. The reactivity of metakaolinite is at a maximum when the content of Al^{VI} is at a minimum. This is illustrated in Fig. 7.2.4, which compares changes in Al coordination (determined by NMR, for a kaolinite calcined in air for 1 h in the range 400–1000 °C at 50 °C intervals) with the changes in some properties of kaolinites. Although these properties are assessed by different investigators, using different samples of kaolinite and under different thermal regimes, the trend of increasing reactivity of metakaolinite with decreasing content of 6-coordinated Al is common to all.

The chemical properties of metakaolinite differ greatly from those of the parent material. Whereas kaolinite is fairly stable towards acids, metakaolinite is easily attacked. Better ordered kaolinite is transformed into less-reactive metakaolinite (Kakali et al., 2001). A decrease in Al-coordination number renders the Al sheets prone to acid extraction, leaving a very porous material. Metakaolinite with the highest content of 5-coordinated Al is also the most acid-reactive (Lussier, 1991). The tetrahedral sheets of the microporous products retain some structural features of kaolinite and do not resemble the structure of silica gel (Okada et al., 1998).

Kaolinite and metakaolinite have globular pores with a mean diameter of 10.5 nm. Dealumination of metakaolinite by acid attack enhances the globular pore volume and also creates slit-shaped pores (Vollet et al., 1994). The total surface area

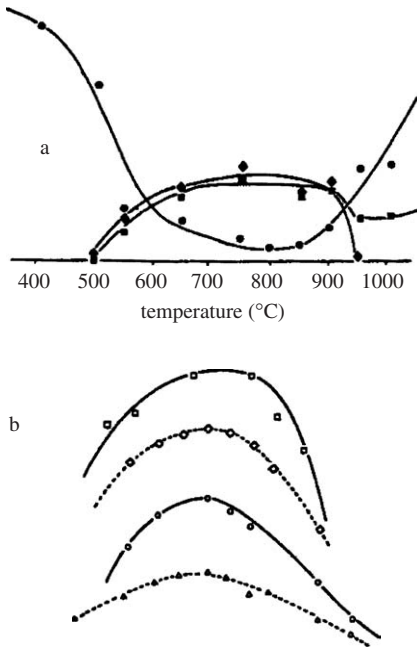


Fig. 7.2.4. Changes in kaolinite heated at different temperatures: (a) population of 6-(●), 5-(◆), and 4-(■) coordinated Al; (b) compressive strength of mixture of metakaolinite and Ca(OH)₂ (Δ); IR-disorder index of the 460–470/cm band (○); dissolution enthalpy in HF (◇); and yield of zeolite X synthesis (□). Adapted from Rocha and Klinowski (1990).

and the microporosity of kaolinite increase with calcination temperature, up to a maximum of about 850–875 °C. Above that temperature non-microporous solids are obtained (Duarte et al., 1995).

Dealuminated metakaolinite has both Lewis and Brønsted acid sites. The total number of sites, the ratio of Lewis to Brønsted sites, and their relative strengths depend on the calcination temperature, the acid used, the severity of acid treatment, and the washing procedure. A judicious choice of porosity and acidity can produce efficient, selective catalysts (Macedo and Duarte, 1995; Perissinotto et al., 1997; Sabu et al., 1999; Breen et al., 2002). Indeed, Macedo et al. (1994) claimed that calcined, partially dealuminated metakaolinites may act as superacids, capable of catalysing cumene cracking. This was attributed to synergism between Brønsted and Lewis acidity, associated with 4- and 5-coordinated Al, respectively.

Acid-activated metakaolinite has a higher CEC than the parent clay mineral, and can be used to scavenge hazardous metal ions, such as Cd²⁺ and Cu²⁺ (Suraj et al., 1998).

Metakaolinite combines rapidly with lime at ambient temperatures to develop cementing properties. Ever since its incorporation into the Jupia Dam, Brazil in 1962, metakaolinite has been used to supplement or replace cement in mortar or

concrete. The extensive literature on the pozzolanic properties of metakaolinite has recently been reviewed by Sabir et al. (2001). At the high pH prevalent in cement, some Al is dissolved from metakaolinite and forms an Al-rich calcium silicate hydrate gel (C–S–A–H). In the presence of water, crystalline calcium aluminate hydrates and calcium silicate aluminate hydrates develop, the composition of which depends on the AS_2/CH ratio and the thermal regime. Gypsum enhances the pozzolanic reactivity of metakaolinite (Kurdowski and Pomadovski, 2001). Partial replacement of cement by metakaolinite in cement pastes reduces the pore volume and shifts the distribution towards smaller values. A good correlation is obtained between porosity and degree of hydration of the pastes (Frias and Cabrera, 2000). Use of less porous metakaolinite-blended cements in mortar or concrete increases their strength and durability as well as their resistance to aggressive solutions, such as sulphate (Vu et al., 2001) or chloride (Gruber et al., 2001).

Metakaolinite was long used as a starting material for zeolite synthesis. In recent years the ever-increasing demand for zeolites provided a new impetus for further research, giving rise to an extensive literature. Zeolites are formed when metakaolinite is hydrothermally reacted with NaOH or KOH solutions. The synthesis occurs most readily when the content of 4- and 5-coordinated Al is at a maximum, while the population of 6-coordinated Al is at a minimum (Madani et al., 1990; Rocha et al., 1991).

When kaolinite is heated in the presence of salts of alkali metals, alkali ions are incorporated into the structure during the course of dehydroxylation. The greater the solubility of the salt in hot water, the further the reaction proceeds under given experimental conditions (Heller-Kallai, 1978; Heller-Kallai and Frenkel, 1979). X-ray amorphous products with an $SiAlO_4$ tetrahedral framework are formed when kaolinite– K_2CO_3 mixtures are calcined at about 500 °C. This amorphous phase, with a composition of $KAlSiO_4$, is converted into crystalline kaliophilite at about 700 °C, far below the temperature at which metakaolinite is transformed to high-temperature phases. Attempts at synthesising zeolite from the amorphous phase gave promising results (Heller-Kallai and Lapides, 2003).

B. Serpentine

With serpentines, the trioctahedral analogues of kaolinite, the interval between dehydroxylation and crystallisation of new phases is small. Several reaction mechanisms were proposed for the dehydroxylation of chrysotile (Ball and Taylor, 1963; MacKenzie and Meinhold, 1994a). Solid-state NMR spectroscopy provided evidence for the existence of two dehydroxylates. Dehydroxylate I appears at the onset of dehydroxylation, at about 650–700 °C, when some of the original chrysotile is still present. Dehydroxylate I is a Mg-rich, X-ray amorphous phase with Mg^{2+} in octahedral coordination. It transforms to forsterite on further heating. Simultaneously, at about 800 °C, the remaining chrysotile forms dehydroxylate II. This phase contains less Mg^{2+} than dehydroxylate I, and transforms to enstatite at higher

temperatures. The two reaction pathways may be ascribed to the presence of different amounts of water in the outer and inner regions of the chrysotile fibrils. Water diffuses readily from the outer regions, whereas quasi-hydrothermal conditions prevail on the inside, where dehydroxylate II is formed. If this interpretation is correct, the particle size and heating regime would be expected to have a drastic effect on the relative amounts of the two dehydroxylates formed. This point needs to be checked.

C. T-O-T Minerals

Dehydroxylation disrupts the structure of trioctahedral minerals, such as talc (Ball and Taylor, 1963) and hectorite (MacKenzie and Meinhold, 1994b). On the other hand, the layer structure of pyrophyllite and other dioctahedral T-O-T minerals is preserved on dehydroxylation. However, the interlayer spaces collapse, the CEC approaches zero, and the surface area and porosity decrease. The XRD patterns of these dehydroxylates are diffuse but distinct.

The differential thermal analysis (DTA) curves of dioctahedral smectites and of finely divided micas show that dehydroxylation occurs at different temperatures, giving rise to single peaks at either $\sim 700^\circ\text{C}$ or at $\sim 500^\circ\text{C}$, or to a doublet between 500 and 700°C . Beidellites, nontronites, and volkhonskoites dehydroxylate at about 500°C (Greene-Kelly, 1957).

Drits et al. (1995) were able to relate the dehydroxylation temperature to the structure of the octahedral sheets of the phyllosilicates. In dioctahedral structures, octahedral cations occupy either two *cis* sites (*tv*), or one *cis* and one *trans* site (*cv*) (see Chapter 2). On dehydroxylation, cations that originally occupy *cis* sites become 5-coordinated, while those occupying *trans* positions become 6-coordinated. Structures with Al^{3+} in distorted hexagonal sites are unstable and these ions migrate to vacant 5-coordinated sites. Thus, the dehydroxylates derived from samples that are originally of the *cv* type are similar to those obtained from the *tv* type, with all former *cis* sites occupied. Dehydroxylation of *cv* structures is a two-stage process, which is completed at higher temperatures than dehydroxylation of *tv* structures.

Al-rich dioctahedral clay minerals rehydroxylate readily (Grim and Bradley, 1948; Heller et al., 1962) and *cv* montmorillonite even spontaneously (Emmerich, 2000). The rehydroxylates are of the *tv* type, whatever the cation distribution is in the original structure. In contrast, dehydroxylation of glauconite and celadonite is accompanied by migration of cations from *cis* to formerly vacant *trans* sites. They hydroxylate to predominantly *cv* structures (Muller et al., 2000).

7.2.4. HIGH-TEMPERATURE PHASES

When clay minerals are heated to sufficiently high temperatures, new phases crystallise. These are of great industrial importance, and play a significant role in natural processes.

Diocahedral clay minerals generally show a temperature interval between the breakdown of the dehydroxylated phase (whether this be crystalline or amorphous to X-rays) and the crystallisation of new phases. In the case of trioctahedral clay minerals, on the other hand, the breakdown of the dehydroxylate and the crystallisation of high-temperature phases tend to coincide.

The compositions of the high-temperature products frequently differ from those of the dehydroxylates, although they are necessarily limited by the chemical composition of the starting clay mineral. The Al-rich members of the kaolinite group, as well as allophane, pyrophyllite, and montmorillonites of the Wyoming-type ultimately produce mullite and cristobalite. Talc forms enstatite and cristobalite. Apart from having minor amounts of an Al-containing phase, the high-temperature products of saponite are similar to those of talc. The high-temperature reactions of serpentines, in particular those of chrysotile fibres, were studied in considerable detail (see MacKenzie and Meinhold, 1994a and references therein). Mixtures of forsterite, enstatite, and silica are first obtained. On further heating, forsterite reacts with silica to form more enstatite.

The chemical composition of the starting materials is not the only factor that determines the nature of the high-temperature products. Thus, montmorillonites of the Cheto-type, which contain more Mg^{2+} in octahedral positions than montmorillonites of the Wyoming-type, form cordierite, instead of mullite, at high temperatures. However, addition of Mg^{2+} to the Wyoming-type montmorillonite does not inhibit mullite formation, nor does leaching of Mg^{2+} from the octahedral sheets of the Cheto-type montmorillonite promote its formation (Grim and Kulbicki, 1961).

In many instances, the crystalline products that form at high temperatures are topotactically related to the starting clay. This was long regarded as an indication of structural inheritance in solid-state reactions. It is possible, however, that the original structures do break down, and that nucleation of the products occurs in orientations that reduce the misfit between old and new phases (Brindley and Lemaitre, 1987). The two mechanisms may not be mutually exclusive but perhaps operate either separately or simultaneously in different systems.

REFERENCES

- Anderson, D.M., Tice, A.T., 1971. Low-temperature phases of interfacial water in clay-water systems. *Soil Science Society of America Proceedings* 35, 47–54.
- Balci, S., 1999. Effect of heating and acid pre-treatment on pore size distribution of sepiolite. *Clay Minerals* 34, 647–655.
- Ball, M.C., Taylor, H.F.W., 1963. The dehydroxylation of chrysotile in air and under hydrothermal conditions. *Mineralogical Magazine* 33, 467–482.
- Balogh, M., Laszlo, P., 1993. *Organic Chemistry Using Clay*. Springer, Berlin.
- Bergaya, F., Dion, P., Alcover, J.F., Clinard, C., Tchoubar, D., 1996. TEM study of kaolinite thermal decomposition by controlled-rate thermal analysis. *Journal of Materials Science* 31, 5069–5075.

- Breen, C., Taylor, S., Burguin, E., Centeno, M., 2002. Preparation and characterization of dealuminated metakaolin and its use in the transformation of waste plastics to aromatic hydrocarbons. *Journal of Colloid and Interface Science* 247, 246–250.
- Brindley, G., Lemaitre, J., 1987. Thermal, oxidation and reduction reactions of clay minerals. In: Newman, A.C.D. (Ed.), *Chemistry of Clays and Clay Minerals*, Monograph No. 6. Mineralogical Society, London, pp. 319–370.
- Brindley, G.W., Nakahira, M., 1959. The kaolinite–mullite reaction series: I. Survey of outstanding problems. II. Metakaolin. III. The high-temperature phases. *Journal of the American Ceramic Society* 42, 311–324.
- Brown, D.R., Rhodes, C.N., 1997. Brønsted and Lewis acid catalysis with ion-exchanged clays. *Catalysis Letters* 45, 35–40.
- Bujdák, J., Janek, M., Madejová, J., Komadel, P., 2001. Methylene blue interactions with reduced charge smectites. *Clays and Clay Minerals* 49, 244–254.
- Bujdák, J., Slosiariková, H., Čičel, B., 1992. Interaction of long chain alkylammonium cations with reduced charge montmorillonite. *Journal of Inclusion Phenomena and Molecular Recognition* 13, 321–327.
- Cases, J.M., Berend, I., Besson, G., François, M., Uriot, J.P., Thomas, F., Poirier, J.E., 1992. Mechanism of adsorption and desorption of water-vapor by homoionic montmorillonite. 1. The sodium-exchanged form. *Langmuir* 8, 2730–2739.
- Caturla, F., Molina-Sabio, M., Rodriguez-Reinoso, F., 1999. Adsorption-desorption of water vapor by natural and heat-treated sepiolite in ambient air. *Applied Clay Science* 15, 367–380.
- Cseri, T., Bekassy, S., Figueras, F., Rizner, S., 1995. Benzoylation of aromatics on ion-exchanged clays. *Journal of Molecular Catalysis A: Chemical* 98, 101–107.
- Dandy, A.J., Nadiye-Tabbiruka, M.S., 1975. The effect of heating in vacuo on the microporosity of sepiolite. *Clays and Clay Minerals* 23, 428–430.
- de Carvalho, M.B., Pires, J., Carvalho, A.P., 1996. Characterisation of clays and aluminium pillared clays by adsorption of probe molecules. *Microporous Materials* 6, 65–77.
- 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.
- Duarte, M.A.I., Macedo, J.C.D., Alves, D.B., 1995. Generation of pores in metakaolin by acid dealumination. In: Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. (Eds.), *Clays: Controlling the Environment. Proceedings of the 10th International Clay Conference*, Adelaide, Australia, 1993. CSIRO, pp. 112–115.
- Eberl, D.D., Šrodoň, J., Northrop, H.R., 1986. Potassium fixation in smectites by wetting and drying. In: Davis, A., Hayes, K.F. (Eds.), *Geochemical Processes at Mineral Surfaces*, ACS Symposium Series 323. American Chemical Society, Washington, DC, pp. 296–326.
- Emmerich, K., 2000. Spontaneous rehydroxylation of a dehydroxylated cis-vacant montmorillonite. *Clays and Clay Minerals* 48, 405–408.
- Emmerich, K., Madsen, F.T., Kahr, G., 1999. Dehydroxylation behaviour of heat-treated and steam-treated homoionic cis-vacant montmorillonite. *Clays and Clay Minerals* 47, 591–604.
- Fernandez Alvarez, T., 1970. Superficie específica y estructura de poro de la sepiolita calentada a diferentes temperaturas. In: Serratos, J.M. (Ed.), *Reunion Hispano-Belga de Minerales de la Arcilla*, Madrid. Consejo Superior de Investigaciones Científicas, Madrid, pp. 202–209.

- Fernandez Alvarez, T., 1978. Efecto de la deshidratación sobre las propiedades adsorbentes de la palygorskita y sepiolita. *Clay Minerals* 13, 325–335.
- Frias, M., Cabrera, J., 2000. Pore size distribution and degree of hydration of metakaolin-cement pastes. *Cement and Concrete Research* 30, 561–569.
- Gastuche, M.C., Toussaint, F., Fripiat, J.J., Touilleaux, R., van Meersche, M., 1963. Study of intermediate stages in the kaolin–metakaolin transformation. *Clay Minerals Bulletin* 5, 227–236.
- Gaultier, J.P., Mamy, J., 1979. Evolution of exchange properties and crystallographic characteristics of bionic K–Ca montmorillonite submitted to alternate wetting and drying. In: Mortland, M.M., Farmer, V.C. (Eds.), *International Clay Conference 1978*. Elsevier, Amsterdam, pp. 167–175.
- Goktas, A.A., Misirli, Z., Baykara, T., 1997. Sintering behaviour of sepiolite. *Ceramics International* 23, 305–311.
- Greene-Kelly, R., 1957. The montmorillonite minerals (smectites). In: Mackenzie, R.C. (Ed.), *The Differential Thermal Investigations of Clays*. Mineralogical Society, London, pp. 140–164.
- Grillet, Y., Cases, J.M., François, M., Rouquérol, J., Poirier, J.E., 1988. Modification of the porous structure and surface area of sepiolite under vacuum thermal treatment. *Clays and Clay Minerals* 36, 233–242.
- Grim, R.E., Bradley, W.F., 1948. Rehydration and dehydration of the clay minerals. *American Mineralogist* 33, 50–59.
- Grim, R.E., Kulbicki, G., 1961. Montmorillonite: high temperature reactions and classification. *American Mineralogist* 46, 1329–1369.
- Gruber, K.A., Ramlochan, T., Boddy, A., Hooton, R.D., Thomas, M.D.A., 2001. Increasing concrete durability with high-reactivity metakaolin. *Cement and Concrete Composites* 23, 479–484.
- Gualtieri, A., Bellotto, M., 1998. Modelling the structure of the metastable phases in the reaction sequence kaolinite–mullite by X-ray scattering experiments. *Physics and Chemistry of Minerals* 25, 442–452.
- Heller, L., Farmer, V.C., Mackenzie, R.C., Mitchell, B.D., Taylor, H.F.W., 1962. The dehydroxylation and rehydroxylation of triphormic dioctahedral clay minerals. *Clay Minerals Bulletin* 5, 56–72.
- Heller-Kallai, L., 1978. Reactions of salts with kaolinite at elevated temperatures. 1. *Clay Minerals* 13, 221–235.
- Heller-Kallai, L., 2001. Protonation–deprotonation of dioctahedral smectites. *Applied Clay Science* 20, 27–38.
- Heller-Kallai, L., 2002. Clay catalysis in reactions of organic matter. In: Yariv, S., Cross, H. (Eds.), *Organo-Clay Complexes and Interactions*. Marcel Dekker, New York, pp. 567–613.
- Heller-Kallai, L., Eberl, D.D., 1999. Potassium fixation by smectites in wetting–drying cycles with different anions. In: Kodama, H., Mermut, A.R., Torrance, J.K. (Eds.), *Clays for our Future. Proceedings of the 11th International Clay Conference, Ottawa, Canada. ICC97 Organizing Committee, Ottawa*, pp. 561–567.
- Heller-Kallai, L., Frenkel, M., 1979. Reactions of salts with kaolinite at elevated temperatures—Part 2. In: Mortland, M.M., Farmer, V.C. (Eds.), *International Clay Conference 1978*. Elsevier, Amsterdam, pp. 629–637.
- Heller-Kallai, L., Lapidés, I., 2003. Thermal reactions of kaolinite with potassium carbonate. *Journal of Thermal Analysis and Calorimetry* 71, 689–698.

- Hofmann, U., Klemen, R., 1950. Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung. *Zeitschrift für anorganische und allgemeine Chemie* 262, 95–99.
- Hrobáriková, J., Komadel, P., 2002. Sorption properties of reduced-charge montmorillonites. *Geologica Carpathica* 53, 93–98.
- Jimenez-Lopez, A., Lopez-Gonzales, J.D., Ramirez-Saenz, A., Rodriguez-Reinoso, F., Valenzuela-Calahorro, C., Zurita-Herrera, L., 1978. Evolution of surface area in a sepiolite as a function of acid and heat treatments. *Clay Minerals* 13, 375–385.
- Justo, A., Maqueda, C., Perez-Rodriguez, J.L., Morillo, E., 1989. Expansibility of some vermiculites. *Applied Clay Science* 4, 509–519.
- Kakali, G., Perraki, T., Tsivilis, S., Badogiannis, E., 2001. Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. *Applied Clay Science* 20, 73–80.
- Komadel, P., Bujdák, J., Madejová, J., Šucha, V., Elsass, F., 1996. Effect of non-swelling layers on the dissolution of reduced-charge montmorillonite in hydrochloric acid. *Clay Minerals* 31, 333–345.
- Komadel, P., Madejová, J., Hrobáriková, J., Janek, M., Bujdák, J., 2003. Fixation of Li⁺ cations in montmorillonite upon heating. *Solid State Phenomena* 90/91, 497–502.
- Komarneni, S., Fyfe, C.A., Kennedy, G.J., 1985. Order–disorder in 1:1 type clay minerals by solid-state ²⁷Al and ²⁹Si magic-angle-spinning NMR spectroscopy. *Clay Minerals* 20, 327–334.
- Kurdowski, W., Pomadovski, H., 2001. Influence of Portland cement composition on pozzolanic reactivity of metakaolin. *Silicates Industriels* 66, 85–90.
- Lagaly, G., 1987. Surface chemistry and catalysis. The 6th Meeting of the European Clay Groups, Seville, Spain, pp. 97–115.
- Lagaly, G., 1993. Praktische Verwendung und Einsatzmöglichkeiten von Tonen. In: Jasmund, K., Lagaly, G. (Eds.), *Tonminerale und Tone*. Steinkopff Verlag, Darmstadt, pp. 358–427.
- Lahav, N., Anderson, D.M., 1973. Montmorillonite–benzidine reactions in the frozen and dry states. *Clays and Clay Minerals* 21, 137–139.
- Lambert, J.F., Millman, W.S., Fripiat, J.J., 1989. Revisiting kaolinite dehydroxylation: a ²⁹Si and ²⁷Al MAS NMR study. *Journal of the American Chemical Society* 111, 3517–3522.
- Lopez-Gonzales, J.deD., Ramirez-Saenz, A., Rodriguez-Reinoso, F., Valenzuela-Calahorro, C., Zurita-Herrera, L., 1981. Activation de una sepiolita con disoluciones diluidas de NO₃H y posteriores tratamientos termicos: I Estudio de la superficie especifica. *Clay Minerals* 16, 103–113.
- Lussier, R.J., 1991. A novel clay-based catalytic material—preparation and properties. *Journal of Catalysis* 129, 225–237.
- Macedo, J.C.D., Duarte, M., 1995. Alternative methods for synthesis of catalyst matrices. 1. Silica–alumina from metakaolinite. *Quimica Nova* 18, 26–29.
- Macedo, J.C.D., Mota, C.J.A., de Menezes, S.M.C., Camorim, V., 1994. NMR and acidity studies of dealuminated metakaolin and their correlation with cumene cracking. *Applied Clay Science* 8, 321–330.
- MacKenzie, K.J.D., Meinhold, R.H., 1994a. Thermal reactions of chrysotile revisited: a ²⁹Si and ²⁵Mg MAS NMR study. *American Mineralogist* 79, 43–50.
- Mackenzie, K.J.D., Meinhold, R.H., 1994b. The thermal reactions of synthetic hectorite studied by 29-Si, 25-Mg and 7-Li magic angle spinning nuclear magnetic resonance. *Thermochimica Acta* 232, 85–94.

- Madani, A., Aznar, A., Sanz, J., Serratos, J.M., 1990. ^{29}Si and ^{27}Al NMR study of zeolite formation from alkali-leached kaolinites. Influence of thermal preactivation. *Journal of Physical Chemistry* 94, 760–765.
- Madejová, J., Bujdák, J., Petit, S., Komadel, P., 2000a. Effect of chemical composition and temperature of heating on the infrared spectra of Li-saturated dioctahedral smectites. (I) Mid-infrared region. *Clay Minerals* 35, 739–751.
- Madejová, J., Bujdák, J., Petit, S., Komadel, P., 2000b. Effect of chemical composition and temperature of heating on the infrared spectra of Li-saturated dioctahedral smectites. (II) Near-infrared region. *Clay Minerals* 35, 753–761.
- Massiot, D., Dion, P., Alcover, J.F., Bergaya, F., 1995. Al-27 and Si-29 MAS NMR-study of kaolinite thermal decomposition by controlled rate thermal-analysis. *Journal of the American Ceramic Society* 78, 2940–2944.
- McBride, M.B., Mortland, M.M., 1974. Copper(II) interactions with montmorillonite: evidence from physical methods. *Soil Science Society of America Proceedings* 38, 408–415.
- Molina-Sabio, M., Caturla, F., Rodriguez-Reinoso, F., Kharitonova, G.V., 2001. Porous structure of a sepiolite as deduced from the adsorption of N_2 , CO_2 , NH_3 and H_2O . *Microporous and Mesoporous Materials* 47, 389–396.
- Muller, F., Drits, V., Plançon, A., Robert, J.-L., 2000. Structural transformation of 2:1 dioctahedral layer silicates during dehydroxylation–rehydroxylation reactions. *Clays and Clay Minerals* 48, 572–585.
- Murat, M., Driouche, M., 1988. Conductometric investigations on the dissolution of metakaolinite in dilute hydrofluoric acid. Structural implications. *Clay Minerals* 23, 55–67.
- Nagata, H., Shimoda, S., Sudo, T., 1974. On dehydration of bound water of sepiolite. *Clays and Clay Minerals* 22, 285–293.
- Okada, K., Shimai, A., Takei, T., Hayashi, S., Yasumori, A., MacKenzie, K.J.D., 1998. Preparation of microporous silica from metakaolinite by selective leaching method. *Microporous and Mesoporous Materials* 21, 289–296.
- Pampuch, R., 1966. Infrared study of thermal transformations of kaolinite and the structure of metakaolin (in Polish). *Polska Akademia Nauk, Prace Mineralogiczne* 6, 53–70.
- Perissinotto, M., Lenarda, M., Storaro, L., Ganzerla, R., 1997. Solid acid catalysts from clays: acid-leached metakaolin as isopropanol dehydration and 1-butene isomerization catalyst. *Journal of Molecular Catalysis A-Chemical* 121, 103–109.
- Quirk, J.P., Theng, B.K.G., 1960. Effect of surface density of charge on the physical swelling of lithium montmorillonite. *Nature* 187, 967–968.
- Rocha, J., Klinowski, J., 1990. Solid-state NMR studies of the structure and reactivity of metakaolinite. *Angewandte Chemie International Edition (in English)* 29, 553–554.
- Rocha, J., Klinowski, J., 1991. The rehydration of metakaolinite to kaolinite. *Journal of the Chemical Society—Chemical Communications* 8, 582–584.
- Rocha, J., Klinowski, J., Adams, J.M., 1991. Synthesis of zeolite Na-A from metakaolinite revisited. *Journal of the Chemical Society, Faraday Transactions* 87, 3091–3097.
- Ruiz, R., del Moral, J.C., Pesquera, C., Benito, I., Gonzalez, F., 1996. Reversible folding in sepiolite: study by thermal and textural analysis. *Thermochemica Acta* 279, 103–110.
- Russell, J.D., Farmer, V.C., 1964. Infrared spectroscopic study of the dehydration of montmorillonite and saponite. *Clay Minerals Bulletin* 5, 443–464.
- Sabir, B.B., Wild, S., Bai, J., 2001. Metakaolin and calcined clays as pozzolans for concrete: a review. *Cement and Concrete Composites* 23, 441–454.

- Sabu, K.R., Sukumar, R., Rekha, R., Lalithambika, M., 1999. A comparative study on H_2SO_4 , HNO_3 and HClO_4 treated metakaolinite of a natural kaolinite as Friedel-Crafts alkylation catalyst. *Catalysis Today* 49, 321–326.
- Sadek, O.M., Mekhamer, W.K., 2000. Ca-montmorillonite clay as thermal energy storage material. *Thermochimica Acta* 363, 47–54.
- Sadek, O.M., Mekhamer, W.K., 2001. Na-montmorillonite clay as thermal energy storage material. *Thermochimica Acta* 370, 57–63.
- Sanz, J., Madani, A., Serratos, J.M., Moya, J.S., Aza, S., 1988. Aluminum-27 and silicon-29 magic angle spinning nuclear magnetic resonance study of the kaolinite–mullite transformation. *Journal of the American Ceramic Society* 71, C418–C421.
- Schultz, L.G., 1969. Lithium and potassium absorption, dehydroxylation temperature and structural water content of aluminous smectites. *Clays and Clay Minerals* 17, 115–149.
- Schwinka, V., Mortel, H., 1999. Physico-chemical properties of illite suspensions after cycles of freezing and thawing. *Clays and Clay Minerals* 47, 718–725.
- Serna, C., Ahlrichs, J.L., Serratos, J.M., 1975. Folding in sepiolite crystals. *Clays and Clay Minerals* 23, 452–457.
- Stackhouse, S., Coveney, P.V., 2002. Study of thermally treated lithium montmorillonite by Ab Initio methods. *Journal of Physical Chemistry B* 106, 12470–12477.
- Stubican, V., Roy, R., 1961. Proton retention in heated 1:1 clays studied by infrared spectroscopy, weight loss and deuterium uptake. *Journal of Physical Chemistry* 65, 1348–1351.
- Suraj, G., Iyer, C.S.P., Lalithambika, M., 1998. Adsorption of cadmium and copper by modified kaolinite. *Applied Clay Science* 13, 293–306.
- Suzuki, M., Ohashi, F., Inukai, K., Maeda, M., Tomura, S., Mizota, T., 2001a. Hydration enthalpy measurement and evaluation as heat exchangers of allophane and imogolite (in Japanese). *Journal of the Ceramic Society of Japan* 109, 681–685 (abstract ISI Web of Science).
- Suzuki, M., Suzuki, S., Maeda, M., Tomura, S., Mizota, T., 2001b. Hydration rate of allophane and imogolite by hydration heat measurement—using as heat exchange absorbents for lower temperature heat source and speedy drying desiccant (in Japanese). *Journal of the Ceramic Society of Japan* 109, 874–881 (abstract ISI Web of Science).
- Tettenhorst, R., 1962. Cation migration in montmorillonites. *American Mineralogist* 47, 769–773.
- Theng, B.K.G., Hayashi, S., Soma, M., Seyama, H., 1997. Nuclear magnetic resonance and X-ray photoelectron spectroscopic investigation of lithium migration in montmorillonite. *Clays and Clay Minerals* 45, 718–723.
- Van Scoyoc, G.E., Serna, C.J., Ahlrichs, J.L., 1979. Structural changes in palygorskite during dehydration and dehydroxylation. *American Mineralogist* 64, 215–223.
- Vollet, D.R., Macedo, J.C.D., Mascarenhas, Y.P., 1994. Pore structure characterization of kaolin, metakaolin, and their acid treated products using small-angle X-ray scattering. *Applied Clay Science* 8, 397–404.
- Vu, D.D., Stroeven, P., Bui, V.B., 2001. Strength and durability aspects of calcined kaolin-blended Portland cement mortar and concrete. *Cement and Concrete Composites* 23, 471–478.
- Watanabe, T., Shimizu, H., Nagasawa, K., Masuda, A., Saito, H., 1987. ^{29}Si and ^{27}Al -MAS/NMR study of the thermal transformations of kaolinite. *Clay Minerals* 22, 37–48.
- Yariv, S., Michaelian, K.H., 2002. Structure and surface acidity of clay minerals. In: Yariv, S., Cross, H. (Eds.), *Organo-Clay Complexes and Interactions*. Marcel Dekker, New York, pp. 1–38.