Genesis and evolution of the kaolin-group minerals during the diagenesis and the beginning of metamorphism

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Introduction

The kaolin group minerals include four members: kaolinite, dickite, nacrite, and the hydrated analogous, halloysite. Kaolinite, dickite and nacrite show very uniform chemical composition: 46.54 wt.% SiO₂, 39.50 wt.% Al₂O₃ and 13.96 wt.% H₂O, corresponding to a formula Al₂Si₂O₅(OH)₄. The formula of halloysite is Al₂Si₂O₅(OH)₄.2H₂O.

Typical wet chemical analyses of kaolin minerals frequently include small amounts of Fe, Ti, K, and Mg (Deer et al., 1976), generally due to the presence of impurities such as Fe- and Tioxides and mica. Improvement in instrumentation, especially in electron microscopy associated to energy dispersive analyses (EDX) has shown that, in most cases, K present in kaolinite analyses is due to interlayering with other clay minerals (e.g. Lee et al., 1975), whereas some other cations, such as Fe, Ti or Cr frequently substitutes in minor amounts in the structure (e.g. Brookins, 1973; Herbillon et al. 1976; Maksinovic et al., 1981; Mestdag et al. 1980). Maxima amounts of ionic substitutions (Fe =0.44 apfu; Cr=0.56 apfu - atoms per formula unit for $O_5(OH)_4$) have been described in halloysites (Newman and Brown, 1987). It appears that the type of foreign cations present in the kaolinite structure mainly depends on the bulk-rock composition, whereas the amount of substitution appears to be controlled by the structure, the disordered varieties accepting higher amounts of substitutions (Brindley et al., 1986).

The physical and chemical conditions under which the kaolin minerals form are relatively low pressures and temperatures. These minerals are typical of three main environments: 1) weathering profiles; 2) hydrothermal alterations; and 3) sedimentary rocks. The most common parent minerals from which kaolin minerals develop are feldspars and muscovite. The transformation of potassium feldspar into kaolin minerals occurs according to the equation:

$$2 \text{ KAlSi}_{3}O_{8} + 3 \text{ H}_{2}O \rightarrow \text{Al}_{2}\text{Si}_{2}O_{5}(OH)_{4} + 4 \text{ Si}O_{2} + 2 \text{ K}(OH)$$

Solubilities of the several chemical species are pH dependent (Mason, 1952). The pH values of the natural waters normally lie between 4 and 9; alumina is not soluble in this range; silica solubility increases parallely to the pH and the alkalis and alkaline earth elements are soluble and mobile. Thus, kaolinite is easily formed and is widespread in soils developed under hot-wet, intertropical climates (Chamley, 1989). As a consequence, detrital kaolin minerals are important components of sedimentary rocks deposited near these areas. In addition, kaolin minerals frequently grow, from the same phases (feldspars and white mica), during the early diagenesis.

The evolution of these minerals during the burial- or tectonic diagenesis is the aim of this contribution. The accurate study of this evolution requires, however, the knowledge of the main methods of identification and differentiation among the several kaolin minerals.

Methods of study of kaolin minerals

X-ray diffraction and infrared spectroscopy

Structurally, kaolin minerals consist of a sheet of corner-sharing tetrahedra, sharing a plane of oxygens and hydroxyls (inner hydroxyls) with a sheet of edge-sharing octahedral with every third site vacant (dioctahedral). This T-O layer has no charge, and interlayer cations are unnecessary to form the crystal. The T-O layer has two different surfaces: A surface of oxygens and a surface of hydroxyls (external hydroxyls). This fact determines the nature of the interlayer bonding between the successive layers, hydrogen bonding, and the need of a relative shift between adjacent layers = a/3 (Figure 1). The thickness of this elemental layer+interlayer unit is ~7.1 Å (basal spacing), and permits a rapid and easy identification of this mineral group by X-ray diffraction, especially when other 7-Å phyllosilicates (serpentine and chlorite) are lacking.

Distinction among the several members of the group requires, however, the detailed analysis of the non-basal reflections, which reflect the structural differences among the different members of the group (Table 1).Kaolinite and dickite structures are based on a similar sequence of layers, and would be identical if trioctahedral. In kaolinite, the vacant octahedral site is in the same place in all layers (B or C) (Figure 1). In dickite, the vacant octahedral site alternates between B and C in successive layers, leading to a 2-layer structure. Nacrite structure is based on a different stacking sequence; initially interpreted as a 6-layer structure, later was defined as a 2-layer structure in which the conventional X and Y axes are interchanged (Brindley and Brown, 1980).

The true nature of the halloysite structure is not well known (Giese, 1991). These structural differences are clearly reflected in the X-ray patterns, when one of the members is dominant. Identification is based on the presence of some diagnostic reflections; the more useful, grouped by zones, have been summarized in Table 2, and marked in Figure 2.

In addition, the different patterns of kaolinite vary considerably, showing in some cases sharp, narrow peaks and in other cases, bad-defined broad peaks, according to the degree of ordering. It is generally observed that the *hkl* reflections with k=3n are less influenced than those with $k\neq3n$. In extreme cases, these later peaks lose their identity and originate two-dimensional modulated bands, similarly to halloysite (Figure 2B).

Other structural differences among the several members of this group affect to the orientation of the inner and external hydroxyl groups. These differences can be only detected by spectroscopic methods. The more widely used has been the infrared spectroscopy (FTIR) although Raman spectroscopy supplies important information. The general features of the OH-



FIGURE 1. Left: [010] view of the elemental structure of the kaolin group minerals. Right: Types of octahedral positions.

	System	Space group	Cell parameters	References
Kaolinite	Triclinic	<i>C</i> 1	$a = 5.156 \text{ Å}$ $\alpha = 91.697^{\circ}$ $b = 8.945 \text{ Å}$ $\beta = 104.862$	Bish and Von Dreeh, 1988
Dickite	Monoclinic	Сс	$c = 7.05 \text{ Å} \qquad \gamma = 89.823^{\circ}$ $a = 5.138 \text{ Å} \qquad \beta = 96.74^{\circ}$ b = 8.918 Å	Joswig and Drits, 1986
Nacrite	Monoclinic	Сс	c = 14.389 Å $a = 8.908 \text{ Å}$ $\beta = 113.7^{\circ}$ b = 5.146 Å	Blount et al., 1969
Halloysite	Monoclinic	Сс	c = 15.697 A $a = 5.14 \text{ Å} \qquad \beta = 96^{\circ}$ b = 8.90 Å c = 14.70 Å	Chukhrov & Zvyagin, 1966

TABLE 1. Crystallographic data of the kaolin minerals.

stretching absorption bands are well established for kaolinite and dickite although some uncertainties remain concerning nacrite (Farmer, 1976; Russel and Fraser, 1994). A typical spectrum of kaolinite show four bands, at 3697, 3669, 3652 and 3620 cm⁻¹, whereas the spectra of dickite and nacrite present only three bands, at slightly different frequencies (Table 3 and Figure 3). The 3620 cm⁻¹ band has been ascribed to the inner hydroxyls, and the other three (or two) bands are generally ascribed to vibrations of the external hydroxyls.



FIGURE 2. XRD patterns obtained from unoriented samples. A: Ordered kaolinite from the Campo de Gibraltar area (Ruiz Cruz and Reyes, 1998, modified). B: Disordered kaolinite from Georgia (standard KGA-2). C: Ordered dickite from the Campo de Gibraltar area (Ruiz Cruz and Reyes, 1998, modified). D: Ordered nacrite from the Maláguide Complex (Ruiz Cruz, 1996, modified). In this later pattern the reflections of dolomite have been deleted.

Kaolinite	Ι	Dickite	Ι	Nacrite	Ι
4.180	50	4.260	8		
4.130	30	4.120	65	4.130	70
		3.954	10		
3.842	45	3.790	55		
				3.476	20
				3.413	20
		3.262	10		
2.558	60	2.558	35		
2.526	40				
2.491	80	2.505	50		
				2.432	60
2.338	90	2.412	20	2.404	40
2.288	80	2.386	15		
2.247	20	2.324	95	2.321	15

TABLE 2. Main diagnostic reflections (Å) and intensities (I) for kaolinite, dickite and nacrite.

Electron microscopy study

Morphologies, as observed by scanning electron microscopy (SEM), can also be useful in identification of kaolin minerals. Halloysite shows generally tubular morphologies (Figure 4A) although spherical particles are also common. Formation of curved layers has been related to the higher tetrahedral Al for Si substitution, which would originate a mismatch between the octahedral and the tetrahedral sheets (Giese, 1991).

Kaolinite also shows a variety of morphologies, including platy, pseudohexagonal particles, booklets and vermicular stacks (Figure 4B). Dickite appears generally as larger blocky particles or stacks (Figure 4C). Available data for nacrite indicate that this mineral mainly form thin hexagonal particles (Figure 4D).

Data provided by synthetic kaolin minerals indicate, as previously suspected from natural occurrences, that morphologies are clearly related to the conditions (mainly fluid/rock ratio, pH and temperature) and mechanisms of formation. Experimental data indicate that a rapid precipitation leads to spherical morphologies, whereas slower recrystallization processes originate platy particles and stacks (Bentabol et al., 2006).



TABLE 3. OH-stretching bands for kaolin-group minerals

	υ_1	υ_2	υ_3	υ_4
Kaolinite	3697	3669	3652	3620
Dickite	3704		3654	3622
Nacrite	3703		3647	3629
Halloysite	3696		3620	

FIGURE 3. Typical FTIR spectra of kaolinite, dickite and nacrite. Provenance of samples as in Figure 1.



FIGURE 4. Scanning electron microscopic images showing the most common morphologies of kaolinminerals. A: Tubular halloysite in a sandstone from the Campo de Gibraltar area. B: Vermicular kaolinite from the Campo de Gibraltar area (Ruiz Cruz and Reyes, 1998, modified). C: Blocky dickite and stacks from Permo-Triassic sandstones of the Maláguide Complex. D: Thin platy particles of nacrite from Paleozoic greywackes from the Maláguide Complex (Ruiz Cruz, 1996, modified).

The study by transmission electron microscopy (TEM), the most useful technique for a precise identification at the nanometer scale, is hindered, in the case of the kaolin minerals, by the rapid damage of the crystals against the electron beam, which is especially evident in the case of kaolinite (Figure 5). The selected area electron diffraction patterns (SAED) permit, however, a rapid differentiation between 1-layer (kaolinite) and 2-layer (dickite or nacrite) structure (Figure 5, A and B, inset).

Evolution of kaolin minerals during the diagenesis

In contrast to the smectite-to-illite dioctahedral sequence, which has been extensively studied (Merriman and Peacor, 1999 and references therein), the other dioctahedral series, which evolved



FIGURE 5. Lattice-fringe images and SAED patterns of kaolinite from the Campo de Gibraltar area (A) and dickite from the Sierra Arana Triassic formations (B).

from kaolinite toward pyrophyllite, has been less studied. This is because, although kaolin minerals are common in pelitic sequences, they appear generally in very low amounts. Kaolin minerals are, however, abundant in two characteristic types of rocks: Fine-grained rocks with anomalous compositions (tonsteins) and coarse-grained rocks (sandstones and conglomerates).

The term tonstein strictly designates kaolinite-rich claystone beds interbedded with coalbearing strata. These sediments generally extend over large areas and are considered to have a major volcanic origin. Although kaolinite is the dominant mineral, it generally coexists with minor amounts of smectite and/or illite. Kaolinite from tonsteins is interpreted as formed during the early diagenetic alteration of tephra layers under acidic conditions.

We will focus this contribution on the diagenetic processes occurring in sandstones and associated shales, which have been summarized in Figure 6.

Metapelitic zone	Illite crystallinity (KI)	Temperature (°C)	%mica in I/S mixed-layers	Mean illite size (Å)	White mica polytype	Vitrinite reflectance Rr%	Kaol dic 1	Kaolinite- dickiteDickite- nacrite1234		د kaolin mineral- other phases		م kaolin mineral- pyrophyllite	
Early diagenetic zone	- 1.0	100	60-80 -		- 1Md	0.50	Kaolinite —	—Kaolinite — Dičkite —			-kaolin mineral-		- kaolin mineral-
Late diagenetic zone	0.42	200	90	220		0.75		Ī					
Low anchizone	0.12	200		220	2M1	2.50	Dickite		- Dickite		te		
High Anchizone	- 0.30		95	380		. 3.00					Muscovite + chlori		- Pyrophyllite
Epizone	0.25	300	>99	520		4.00							

FIGURE 6. Summary of the diagenetic-to-metamorphic parameters (modified from Merriman and Peacor, 1999) characterizing the transformations of kaolin-group minerals during the diagenesis and beginning of metamorphism. 1: Typical Triassic transition in the North See and in the Iberian and Betic ranges. 2. Transition observed in strongly deformed shales from El Campo de Gibraltar area (Ruiz Cruz and Reyes, 1998). 3. Transition observed by Shutov et al. (1970) and Ruiz Cruz (1996). 4. Other nacrite reports (Bühmann, 1988; Buatier et al., 1996). 5. After numerous sources (e.g. Eherenberg and Nadeau, 1989; Ruiz Cruz and Andreo, 1996a, b; Ruiz Cruz and Sanz de Galdeano, 2005; Ruiz Cruz et al., 2005). 6. Alter numerous sources (e.g., Merriman and Peacor, 1999).

Early diagenetic reactions

Sandstones are suitable rocks for the formation of secondary diagenetic minerals because their high porosity and permeability, which favour the migration of fluids. Most sandstones contain, in addition to quartz, some detrital feldspars and mica grains, which are favourable parent phases for kaolinite formation. It is difficult to distinguish unambiguously between detrital and authigenic clay minerals; nevertheless, detailed optical studies help to this distinction. Authigenic kaolin minerals generally are pore-lining, pore-filling, fracture-filling, and as pseudomorphs after previous phases, mainly white mica and feldspars, whereas detrital grains mainly occur as a dispersed matrix, flocculos and shale clasts.

Although halloysite can form in some sandstones, the most common kaolin mineral is kaolinite. In most cases its origin is clearly related to leaching of preexisting minerals, which is favoured at acidic conditions and in the presence of organic mater. During the pH rise subsequent to dissolution, kaolinite precipitates, since its solubility decreases rapidly as neutral pH values are reached. Formation of kaolinite through this process is enhanced in continental sandstones, such as those characteristic of the Permo-Triassic sequences, where kaolinite formed during an early diagenesis (Ruiz Cruz and Andreo, 1996a). Figure 7A shows the partial kaolintization of a detrital muscovite grain. In addition, in more altered sandstones, smaller kaolinite crystals fill the spaces between the grains (Figure 7B). Nevertheless, feldspar and mica dissolution also occur during the early diagenesis in marine sandstones, such as those deposited in turbiditic sequences from the Campo de Gibraltar area (Ruiz Cruz, 1994).

Late diagenetic reactions

The evolution of the kaolin minerals at increasing burial- or tectonic depth is different in pelitic and coarse-grained sequences. In pelitic sequences kaolinite frequently persists until thermal maturities of 1.9-2.1 %, equivalent to the beginning of the low anchizone (Kisch, 1983) (Figure 6). In contrast, in the matrix of sandstones, the transformation of kaolinite into dickite has been reported at approximately 120 °C, i.e., in the late diagenetic zone, in Triassic sandstones from the North Sea (Ehrenberg et al., 1993). Similar temperature intervals have been deduced in Permo-Triassic sandstones from the Betic Cordillera (Ruiz Cruz and Andreo, 1996a) and in Tertiary sandstones from the Campo de Gibraltar area (Ruiz Cruz, 1994). This different behaviour can be probably related with the notably higher permeability of sandstone-rich sequences, which favour the fluid circulation and the process of dissolution-precipitation responsible of this change.



FIGURE 7. Optical images showing two stages of kaolin-mineral formation in sandstones from the Maláguide Complex. A: Incipient muscovite-to-kaolinite transformation. B: Kaolinite and dickite pore-filling.

Although this is an unquestionable pattern, other data clearly indicate that the dickite formation is not only temperature-dependent, as proposed by Eherenberg et al. (1993). Thus, in Cretaceous shales from El Campo de Gibraltar area, where kaolinite and dickite fill small fractures in strongly deformed shales, the isotopic data indicate that the kaolinite- \rightarrow dickite transformation has occurred at lower temperatures (<100°C), near the transition between the early and the late diagenetic zones (Ruiz Cruz and Reyes, 1998). Indeed, in this area, dickite coexists with R₀ and R₁ illite/smectite mixed-layers. Strain-related dickite has also been described by Buatier et al. (1997) in Pyrenean thrust-fault zones, also suggesting that the kaolinite-to-dickite transition is favoured by strain.

Differences observed among the XRD patterns of several size-fractions of sandstones (2-20 μ m and <2 μ m) and between sandstones and interbedded shales, clearly indicate that the kaolinite-to-dickite transformation mechanism is different in coarse- and fine-grained rocks (Ruiz Cruz and Moreno Real, 1993). These authors interpreted these differences as due to the presence of randomly ordered kaolinite/dickite mixed-layers, which would be intermediate steps in the kaolinite to dickite transformation.

Whereas the kaolinite-to-dickite transition is widespread in sandstones, the transition dickite \rightarrow nacrite has been only rarely found. Shutov et al. (1970) recorded nacrite replacing dickite in deformed veins from Paleozoic and Riphean rocks. Ruiz Cruz (1996) described nacrite in Paleozoic greywackes underlying dickite-bearing Permo-Triassic rocks. Nacrite grew in small veins associated to dolomite (Figure 8). Although data from diagenetic terrains are scarce, the transition kaolinite \rightarrow dickite \rightarrow nacrite, at increasing temperatures has been well documented in hydrothermal deposits, using isotopic data (Katsumi, 1989).

Nevertheless, thermodynamic determinations clearly indicate that the relative stability of the several members of the kaolin group does not change significantly with pressure and temperature over their range of occurrence, kaolinite being the stable phase (de Ligny and Navrotsky, 1999). Thus, dickite and nacrite are metastable phases, and the described patterns must be interpreted in terms of kinetics rather than as resulting from changes in the thermodynamically stable assemblage.

Recent reports of nacrite as well as experimental results agree with this later interpretation. Thus, at the Lodève basin, nacrite occurs in dolomite cavities associated to barite deposits of hydrothermal origin (Buatier et al., 1996). Study of the fluid inclusions indicated the presence of



FIGURE 8. Optical microscopic image showing nacrite associated with dolomite in a Paleozoic greywacke from the Malaguide Complex (Ruiz Cruz, 1996, modified).



FIGURE 9. Optical microscopic image showing the beginning of the illitization process in a Permo-Triassic sandstone (Ruiz Cruz and Andreo, 1996a, modified).

high-salinity brines, and heating runs indicated temperatures of formation between 80 and 100 °C. In addition, Bühmann (1988) described authigenic nacrite, which forms a thin layer coating a carbonaceous shale, originated at ambient temperature. Precipitation from saturated pore solutions was suggested as the factor determining the precipitation. Our experimental results (unpublished data) indicate that nacrite formation is favoured by the presence of saturated solutions, and a rapid precipitation process. At these conditions, nacrite originates metastable spherical particles similar to those observed in synthetic kaolinite and halloysite, which rapidly evolves toward platy particles and kaolinite stacks through a slower dissolution-precipitation process.

All these data indicate that nacrite is not a valid kaolin-mineral indicator of high temperature, as previously assumed (Hanson et al., 1981). On the contrary, nacrite genesis is temperature–independent and is more clearly related to the presence of saturated solutions.

Very low-grade metamorphic reactions

rich rocks, and Al-rich microdomains.

The transition kaolin mineral \rightarrow pyrophyllite approximately marks the transition diagenesismetamorphism (Figure 6). This reaction is known many years ago, and has been extensively studied in natural and experimental systems (Frey, 1987; Bucher and Frey, 1994). Nevertheless, this reaction only occur in very Al-rich rocks, since, in the presence of K , Mg or Fe, the kaolin minerals evolve towards other minerals before the temperature necessary for the pyrophyllite formation was reached. Illitization of kaolin minerals has been frequently described and the estimated temperatures are in the order of 140 °C (Ehrenberg and Nadeau, 1989). Thus, in Permo-Triassic rocks from the Betic and the Iberian ranges, a complete evolution from dickite to illite can be observed, which is not strictly related to the depth but to the bulk-rock composition. Although illitization is the dominant process (Figure 9), formation of chlorite and of illite+chlorite stacks from dickite is also frequently observed (Ruiz Cruz and Andreo, 1996a). Bulk-rock composition also appears to control other less-known transformations of kaolin minerals. Thus, in Triassic rocks of the Betic Cordillera, dickite evolves toward sudoite (Ruiz Cruz and Sanz de Galdeano, 2005), whereas in Carboniferous rocks, dickite and nacrite appear locally transformed into tosudite (Ruiz Cruz and Andreo, 1996b) (Figure 10). Whereas sudoite is

widespread in rocks with variable grain-size and lithologies, tosudite formation is limited to Al-



FIGURE 10. Left: TEM image of sudoite formed from dickite in Triassic sandstones from the Sierra Arana area (Ruiz Cruz and Sanz de Galdeano, 2005). Right: SEM image showing the transformation of nacrite into Tosudite (Ruiz Cruz and Andreo, 1996b, modified).



FIGURE 11. XRD patterns (oriented samples) of the <2µm size-fractions of two samples from the Sierra Arana sector. Ms: Muscovite/Illite. Prl: Pyrophyllite. Dk: Dickite. Qtz: Quartz.



FIGURE 12. Optical microscopic image showing the dickite to pyrophyllite transformation in a Triassic sandstone from Sierra Arana (Ruiz Cruz et al., 2005, modified).

In some Al-richer protolites, the kaolin minerals persist at higher temperatures and originate pyrophyllite (Figure 12). Generally, temperature controls the dickite/pyrophyllite ratio, and the Al_2O_3 content determines the illite/pyrophyllite ratio. In these rocks, dickite, pyrophyllite and illite coexist in a short temperature interval (Figure 9). The transformation of dickite into mica is assumed that occurred at high diagenetic conditions. On the contrary, pyrophyllitization of dickite is assumed to have occurred at incipient metamorphic conditions.

Conclusions and future research

- 1. The kaolinite \rightarrow dickite \rightarrow nacrite transition is well documented in natural environments and occurs at increasing temperatures.
- 2. Thermodynamic and experimental data indicate, however, that the stable phase, at the common P-T conditions, is kaolinite. Thus, the described transformations are not only controlled by temperature.
- 3. Strain and solutions composition appear to be important factors controlling the dickite and nacrite formation.
- 4. Futures researches must be focused in natural fluid characterization by means of stable isotopic and fluid inclusions studies. Parallel synthesis in well-controlled chemical systems must supply additional information.

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References

Bailey, S.W. (1984). Structures of layer silicates. Pp. 1-123 in: Crystal Structures of Clay Minerals and their X-ray Identification (G.W. Brindley and G. Brown editors). Mineralogical Society, London.

Bentabol, M., Ruiz Cruz, M.D., Huertas, F.J., Linares, J. (2006). Clays Clay Miner., 54, 667-677. Bish, D.L. and Von Dreele, R. (1988). Annual Meeting of the Clay Minerals Society, Michigan.

Blount, A.M., Threadgold, I.M., Bailey, S.W. (1969). Clays Clay Miner., 17, 185-194.

Brindley, G.W., Chih-Chun Kao, Harrison, J.L., Lipsicas, M., Raythatha, R. (1986). Clays Clay Miner., 34, 239-249.

Brookins, D.G. (1973). Clays Clay Miner., 21, 421-422.

- Brown, G. and Brindley, G.W. (1980). X-ray Diffraction Procedures for Clay Mineral Identification. Pp. 305-360 in: Crystal Structures of Clay Minerals and their X-ray Identification. (G.W. Brindley and G. Brown, editors). Mineralogical Society, London.
- Buatier, M.D., Deneele, D., Dubois, M., Ptdevin, J-L., Lopez, M. (1996). Eur. J. Mineral., 8, 847-852.
- Buatier, M.D., Travé, A., Labaume, P., Potdevin, J.L. (1997). Eur. J. Mineral., 9, 875-888.
- Bühmann, D. (1988) Clays Clay Miner., 36, 137-140.
- Bucher, K. and Frey, M. (1987). Petrogenesis of metamorphic rocks. Springer-Verlag, Berlin, 318 p.
- Chamley, H. (1989). Clay sedimentology. Springer-Verlag, Berlin, 623 p.
- Chukhorv, F.V. and Zvyagin, B.B. (1966). Proc. Int. Clay Conf. Jerusalen, 11-25.
- Deer, W.A., Howie, R.A., Zussman, M.A. (1976) Sheet Silicates. Rock Forming Minerals, vol. 3, 270 p.
- Eherenberg, S.N. and Nadeau, P.H. (1989). Clay Miner., 24, 233-253.
- Ehrenberg, S.N., Aagaard, P., Wilson, M.J., Fraser, A.R., Duthie, D.M.L. (1993). Clay Miner., 28, 325-352.
- Farmer, V.C. (1974). The layer silicates. Pp. 331-365 in: The Infrared Spectra of Minerals (V.C. Farmer editor) Mineralogical Society, London.
- Frey, M. (1987). Very low-grade metamorphism of clastic sedimentary rocks. Pp. 9-58 in: Low-temperature metamorphism (M. Frey ed.) Blackie, Glasgow, U.K.
- Giese, R.F. (1991). Kaolin minerals: structures and stabilities. Rev. Mineral., 19, 29-66.
- Hanson, R.F., Zamora, R., Keller, W.D. (1981). Clays Clay Miner., 29, 451-453.
- Herbillon, A.J., Mestdagh, M.M., Vielvoye, L., Derouane, E. (1976). Clay Miner., 11, 201-220.
- Joswig, W. and Drits, V.A. (1986). N. Jb. Mineral. Mh., 19-22.
- Katsumi, M. (1989). Geochim. Cosmochim. Acta, 53, 2915-2924.
- Kisch, H.J. (1983). Mineralogy and petrology of burial diagenesis (burial metamorphism) and incipient metamorphism in clastic rocks. Pp. 289-493 in: Diagenesis in Sediments and Sedimentary Rocks (G. Larsen and G.V. Chilingar eds). Elsevier, New York.
- Lee, S.Y., Jackson, M.L., Brown, J.L. (1975). Clays Clay Miner., 23, 125-129.
- Ligny, D. and Navrotski, A. (1999). Am. Mineral., 84, 506-516.
- Maksimovic, Z., White, J.L., Logar, M. (1981). Clays Clay Miner., 29, 213-218.
- Mason, B. (1952). Principles of Geochemistry. John Wiley and Sons, New York, 274 p.
- Merriman R.J. and Peacor D.R. (1999). Very low-grade metapelites: mineralogy, microfabrics and measuring reaction progress. Pp. 10-60 In: Low-grade metamorphism (M. Frey and D. Robinson eds.) Blackwell Science, Oxford, U.K.
- Mestdagh, M.M., Vielvoye, L., Herbillon, A.J. (1980) Clay Miner., 15, 1-13.
- Newman, A.C.D. and Brown, G. (1987) The Chemical Constitution of Clays. Pp. 1-128 in: Chemistry of Clays and Clay Minerals. Mineralogical Society, London.
- Ruiz Cruz, M.D. (1994). Clay Miner., 29, 93-104.
- Ruiz Cruz, M.D. (1996). Clays Clay Miner., 44, 357-369.
- Ruiz Cruz, M.D. and Moreno Real, L. (1993). Clays Clay Miner., 41, 570-579.
- Ruiz Cruz, M.D. and Andreo, B. (1996a). Clay Miner., 31, 133-152.
- Ruiz Cruz, M.D. and Andreo, B. (1996b). Eur. J. Mineral., 8, 1391-1399.
- Ruiz Cruz, M.D. and Reyes, E. (1998). Geochem., 13, 95-104.
- Ruiz Cruz, M.D., Sanz de Galdeano, C., Lázaro, C. (2005). Eur. J. Mineral., 17, 81-91.
- Ruiz Cruz, M.D. and Sanz de Galdeano, C. (2005). Clays Clay Miner., 53, 639-652.
- Russell, J.D. and Fraser, A.R. (1994). Infrared methods. Pp. 11-67 in: Clay Mineralogy: Spectroscopic and chemical determinative methods (M.J. Wilson editor) Chapman and Hall, London.

Shing, B. and Gilkes, R.J. (1991). Clays Clay Miner., 39, 571-579. Shutov, V.D., Aleksandrove, A.V., Losievskaya, S.A. (1970). Sedimentology, 15, 69-82.