Geosciences

COMPARATIVE STUDY OF THE EFFECTS OF THERMAL AND MECHANICAL TREATMENTS ON THE STRUCTURES OF CLAY MINERALS*

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Abstract

Controlled heating (in air) of clay minerals leads to transformations into disordered structures and recrystallization into new phases at high temperatures. These phase transformations are of topotactic nature. On the other hand, prolonged dry-grinding treatments of the same silicates causes structural amorphization with no recrystallization into new phases. The mechanical energy relaxation mechanism, invoked to explain these differences, accounts for the particle size changes and the large growth of dislocations. The latters affect sensibly the reactivity of the materials submitted to such solid-state treatments.

These processes are monitored mostly by XRD, DTA and IR spectroscopy. The latter method allows to study in some silicates submitted to progressive grinding the location and nature of OH groups and water molecules.

Keywords: clay minerals, grinding and thermal treatments, reactivity, structural changes

Introduction

The effects of heating on solid materials have been studied for many decades. Thermal treatments deal with controlled heating in the oven in different atmospheres, covering a wide range of temperatures. Grinding treatments of these solids, in mortar and percussive mills, have been as well developed. Thermal or mechanical treatments of some crystalline solids lead to changes of the structure and of the physico-chemical properties of the solid, which may result in the formation of materials with interesting applications. Such physicochemical changes, involving

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particle size reduction (often as a result of mechanical activation) and structural transformations, allow the control of reactivity and formation of metastable phases in solid state reactions. The structural transformations giving rise to new phases may be topotactic, which means that there must be some three-dimensional correspondence between the structures and morphologies of the resulting product and its host (starting material). As we shall see along this contribution, gradual heating and on the other hand prolonged grinding of the same crystalline mineral do not lead, usually, to the same transformation products.

Earlier publications have dealt with the comparison of thermal and mechanical treatments of inorganic solids, mostly metal oxides [1, 2]. The scope of this contribution is to compare the effects of gradual heating and grinding treatments on the structures of clay minerals. We shall refer to thermal and mechanical processes carried out in air.

X-ray powder diffraction (XRD), infrared spectroscopy (IR), and differential thermal analysis (DTA) are the most common instrumental methods employed to study the comparative structural transformations.

Clay minerals

Clay minerals are mostly crystalline aluminosilicates and include also some accesory minerals. Clays are quite abundant in nature, being thus an important source of raw materials. It must be remembered that oxygen, silicon and aluminum – the main elements forming the aluminosilicates structure – are present in the earth crust, approximatively as 50, 26 and 7%, respectively. The thermal properties of clay minerals are largely determined by the crystal structure and chemical composition of their essential constituents, and by the nature and amount of accessory, associated minerals. The mineralogical characteristics of such materials and therefore their ceramic properties are subject to wide variation among different occurrences or even within the same occurrence, depending on the geological environment in which the mineral deposit was formed as well as the physical and chemical modifications that have taken place during subsequent geological history.

Typical clay minerals also known as phyllosilicates have a layered structure and are formed by the condensation of sheets of six-membered rings of silica tetrahedra (T) with sheets of alumina or magnesia octahedra (O_c), as in gibbsite, $Al(OH)_3$ or brucite $Mg(OH)_2$. The silica tetrahedra are arranged to form a hexagonal network which is repeated indefinitely. The major types are designated 1:1 or TO_c and 2:1 or TO_cT, depending on the ratio of tetrahedral to octahedral sheets in one repetitive unit (Fig. 1). Apart from the phyllosilicates, some other silicates will be considered like, palygorskite and sepiolite minerals. Their structure is also based on TO_cT units, but these are infinite in one direction only, so that a chain-like structure with channels results.

In clays, the sheets may show electric charge imbalance (due e.g. to Al^{+3} partially replaced by Mg^{2+}) in the octahedral sheet, which can be satisfied by cations or protons, both species being usually mobile. These hydrated cations may ex-
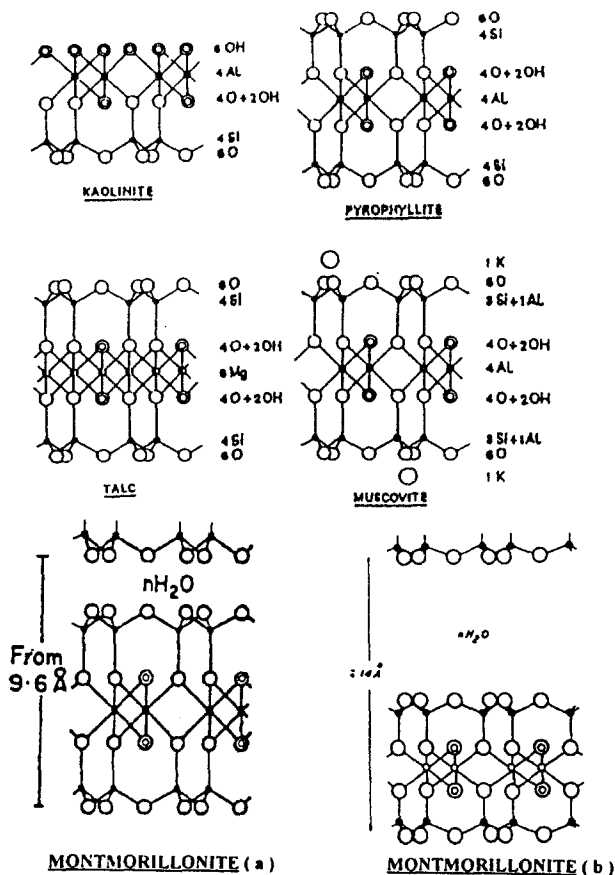
Fig. 1 Structures of main clay minerals (phyllosilicates)

change sites (positions) with solutions containing other suitable cations. This is known as the cation exchange capacity (CEC) in clays. The protons form hydroxyl groups OH, alternating with oxygens positions in the structure. Molecular water, H_2O, plays an important role in the structure and properties of some clay minerals. Origin, locations of H_2O and stability deserve a special consideration in clay minerals.

Thermal investigation of clays has been compiled by Mackenzie [3] and reviewed e.g. by Dent et al. [4], Bret et al. [5] and more recently by Brindley and Lemaitre [6]. The latters envisage many ranges of temperatures for the clays reactions:

1. Low temperature, below ~400°C involving dehydration.

2. Intermediate temperature (400–750°C) involving dehydroxylation.

3. High temperature reactions above 750°C, resulting mostly in recrystallization of new phases.

4. Oxidation reactions, important for minerals with variable valence cations.

Table 1 Summary of thermal reactions – dioctahedral minerals (Brindley and Lemaitre [6])

	Predehydroxylation state →	450–550°C	Metakaolin → 900°C	Spinel* type phase → 1000–1100°C	Mullite*
Kaolinite $Al_2Si_2O_5(OH)_4$ 1:1 type			$Al_2Si_2O_7$		$Al_6Si_2O_{13}$
Pyrophyllite $Al_2Si_4O_{10}(OH)_2$ 2:1 type		650°C	Pyrophyllite dehydroxylate → 950–1000°C $Al_2Si_4O_{11}$	⟶	Mullite* $Al_6Si_2O_{13}$
Montmorillonite** 2:1 type	→ 150–250°C Montmorillonite anhydride		→ 700°C Montmorillonite dehydroxylate 1000°C → Spynel-type phase	→ Spynel-type 1150°C phase	Mullite*
Muscovite 2:1 type		750°C	Muscovite dehydroxylate → 1050°C → Spynel-type phase 1250°C Sanidine		Corundum α-Al_2O_3 Mullite* other phases

*With separation of silica and/or other phases

**Ideal formula: $M^+_{0.33} nH_2O (Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$

Temperatures variable according to chemical composition, crystal size, conditions of heating.

Sharp lines of distinction cannot be drawn between these types of thermal reactions.

The thermal reactions of the main dioctahedral clays (those whose structure is based on aluminum atoms in the octahedral sheet) is given here in Table 1, partly reproduced from Brindley and Lemaitre [6].

Kaolinite and other TO_c (1:1) type silicates

The thermal transformations of kaolinite has been the subject of a large number of investigations. Some of them have been summarized by Grim [7] and more recently by Brindley and Lemaitre [6].

Accordingly, the dehydroxylation of kaolinites in normal atmospheres gives a mass loss of 14% which corresponds to the formula $Al_2Si_2O_5(OH)_4$. An endothermic DTA effect between 450 and 600°C (the exact position depending on the crystallinity and particle size) is characteristic of most kaolinites. The endothermic peak corresponds to a new disordered phase, metakaolin, $Al_2Si_2O_7$. The dehydroxylation process of kaolinite is preceded by a "predehydroxylation" state. Thus, below the dehydroxylation temperature, Fripiat and Toussaint [8] have conducted infrared investigations on kaolinite films, pointing to a degree of proton delocalization from OH groups in kaolinite, which further may lead to loss of hydroxyls as water molecules.

Between 900 and 1100°C, the appearence of crystalline phases (Table 1), like spinel (γ-Al_2O_3) and mullite ($Al_6Si_2O_{13}$), where silica is totally or partly segregated, is characterized by exothermic effects in DTA diagrams. The metakaolin mullite sequence via spinel phases, is of topotactic nature.

Controlled, grinding treatments of kaolinite have been conducted in percussive mills and in automatic mortars (see Ref.[9] and Refs. therein). We shall consider here mostly mortar-ground kaolinite, because in contrast to other grinding processes, mortar grinding minimizes samples contamination, which is advantageous for both research and industry.

Both, the morphology and crystalline structure of kaolinite are affected by dry grinding as shown by different instrumental methods. IR studies of progressively ground kaolinite permited to monitor its structural degradation [10]. An interesting effect called prototropy emerge from the former works on dry-ground kaolinites, represented by a weakening of some structural O–H bondings (located in the octahedral sheet) followed by migration and recombination of the split-proton. This reaction was carefully followed using mostly IR absorption spectroscopy which allowed to monitor in gradually ground kaolinite, a progressive gain of molecular water and its thermal stability [9]. That work indicated (Fig. 2) that from the first grinding steps the sharp OH–stretching bands of kaolinite at about 3690 and 3620 cm^{-1} gradually decreased in intensity with progressive grinding. Concomitantly, a broad band centered at about 3400 cm^{-1} was developed. Both these spectroscopic features tipify the prototropic effect, by the decrease of the peaks due to structural OH (also confirmed by mass losses at 600°C) and by the formation of OH groups of variable nature (represented by the wide band at ~3400 cm^{-1}) which result from the recombination of the split protons. We can see in Fig. 2, that the area of the 1640 cm^{-1} band (assigned to the bending vibration of molecular water)
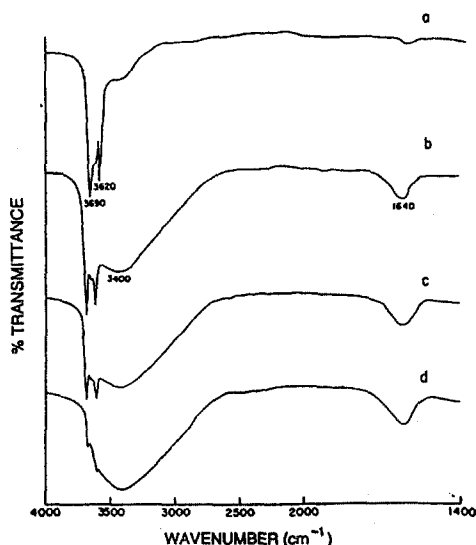
Fig. 2 Infrared spectra of kaolinite a) and of mortar-ground kaolinite for different times:
    b) 2h, c) 8h, d) 18h, [9], reproduced with permission of the Mineralogical Society of
    Great Britain and Ireland)

increases steadily with gradual grinding at room temperature. Table 2 shows that for any given grinding time, the areas of the 1640 cm^{-1} bands decrease about one third each, on heating from ambient temperature to 105°C. Further heating to 280°C strongly decreases the area of this band. The 1640 cm^{-1} peak is no longer detected after heating any of the ground kaolinites at 600°C. Thus, from the thermal point of view, we can distinguish between moisture or loosely held water (until 105°C) and firmly held water (until $\approx$600°C). The water gained by kaolinite on grinding may be formed by prototropy or/and adsorbed from the atmosphere.

Table 2 1640 cm^{-1} peak area* after heating kaolinite at different temperatures as a function of grinding time (data from Mendelovici *et al.* [9], reproduced with the permission of the Mineralogical Society of Great Britain and Ireland)

Grinding time/h	Ambient temperature/°C	105°C	280°C	600°C
0	0.40	n.m.	n.m.	–
2	2.15	1.40	0.75	–
5	3.10	2.10	0.65	–
8	3.70	2.75	0.60	–
14	4.40	2.95	0.50	–
18	4.80	3.25	0.30	–

*peak area (in cm^2) measured with a planimeter from corresponding spectra (Fig. 2)
    n.m. = non measurable.

Serpentine, $Mg_3Si_2O_5(OH)_4$ is the trioctahedral analogue of kaolinite, where octahedral sites are filled principally by Mg instead of Al. This may cause a strain and bending in the structure, resulting in a fibrous and tubular morphology, as in the case of chrysotile (asbestos). An amorphous phase is formed on heating chrysotile at about 600°C. Then, forsterite, Mg_2SiO_4 recrystallizes slowly between 600 and 800°C accompanied by enstatite, $MgSiO_3$ after further heating at ~1100°C.

In constrast to the dry-grinding results of kaolinite and other clay minerals, Papirer and Roland [11] reported that ball-milling of chrysotile produced no morphologic changes. With progressive grinding time, the specific area of chrysotile increased, but at a lower rate than that of grinding chrysotile in presence of liquids. The authors invoke a specific energy dissipative process that consumes energy and preserves the integrity of the fiber bundle.

TO_cT or 2:1 type clays aluminosilicates

Here we will consider solid-state treatments of two kinds of 2:1 type silicates : thermally, non collapsable and collapsable clays. Among the first kind we have e.g. pyrophillite, talc and muscovite (mica), whereas montmorillonite, is a representative of the thermally collapsable clays.

Pyrophyllite, $Al_2Si_4O_{10}(OH)_2$ is topotactilly transformed at 650°C into a dehydroxylated meta-phase, $Al_2Si_4O_{11}$, and then into mullite, $Al_6Si_2O_{13}$, after heating between 950 and 1100°C. Both, pyrophillite and kaolinite give qualitatively the same transformation products on heating at >1000°C.

Ball-milling of pyrophyllite causes some delamination in the first stages of grinding followed by structural degradation on prolonged grinding. XRD results of the last grinding stages indicated that some residual order persists [12] as occurs with other silicates. As well, the surface area (BET) which initially increased, reversed its trend due to particles aggregation, as observed e.g. with kaolinite minerals. Grinding causes a decrease in bond energy of OH structural groups. Thus, as shown also by other clays, there is a lowering in the position of the endothermic (dehydroxylation) effect in the DTA curves of gradually ground products, which is also related to the changes in particle size with grinding [13].

Talc, $Mg_3Si_4O_{10}(OH)_2$, which is the trioctahedral analogue of pyrophyllite, is easily transformed to a new structure on dehydroxylation, giving enstatite, $MgSiO_3$ after heating at 900–1000°C. On grinding, talc losses its crystallinity and undergoes morphological and particle size changes.

Muscovite, $KAl_4Si_8O_{20}(OH)_4$ is the major dioctahedral mica mineral. Partial substitution of Si^{4+} by Al^{3+} in the tetrahedral sheet giving a negative charge is compensated by K^+ placed in interlayer positions. Typically, muscovite yields a DTA pattern showing two endothermic effects at about 800°C and 1200°C. The first represents dehydroxylation with some structural rearrangement [3]. Corundum is the major phase detected after heating at ~1200°C. Dehydroxylation of muscovite appear to be a diffusion-controlled process of water molecules formed by condensation of 2 hydroxyls. Proton jump between oxygens (belonging to hydroxylated species) is an alternative mechanism proposed by Rouxhet [14] to explain the dehydroxylation of muscovite.

An interesting paper of Mackenzie and Milne [15] deals with mortar-grinding of muscovite and other clays. The gradual grinding of muscovite as followed by X-ray photographs, showed a weakening of the characteristic reflections of muscovite in the first steps of grinding but on further grinding it was observed a reappearence of the original XRD pattern. However, the latter was different from that of original muscovite as the diagnostic lines had different intensities and two new lines became visible, not present in the muscovite pattern but which are given by many hydrous micas. In the thermoanalytical curve, a moisture peak at ~100°C was developed on gradual grinding, indicating the progressive hygroscopicity of muscovite as a result of dry grinding. Thus, a possible explanation is that some K^+ from muscovite is replaced by H_3O^+ generated in the grinding process, leading to hydrous mica structures.

Montmorillonite, $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O$ is a member of the smectite group of clays, with swelling properties derived from the presence of variable amounts of interlayer water (or other species). In such a hydrated, swollen state, the main X-ray basal spacing of montmorillonite is expanded from about 10 to 14 Å or more (Fig. 1a, b), the expansion depending also on the nature of the interlayer (hydrated) cations. On heating montmorillonite at low temperatures, interlayer water is driven off accompanied by a contraction of the basal spacings. To prevent this contraction, pillaring of the structure has been developed. The pillaring agents are thermally stable, robust inorganic or organic (including organo-metallic) species which act as pillars to keep the silicate layers separated in the absence of a swelling solvent. This causes an increase in the surface area and pore size of montmorillonite, which has applications e.g. on catalysis.

Brown et al. [16] published a comprehensive study on the thermal reactions of montmorillonite by diverse methods including solid–state ^{29}Si and ^{27}Al nuclear magnetic resonance. Accordingly, montmorillonite reversibly loses its interlayer water when heated below ~450°C. This water loss is accompanied by a collapse of the basal spacing from 15 to ~10 Å and by a change of ~2 ppm in the ^{29}Si NMR signal. As dedydroxylation proceeds at >450°C, OH groups of montmorillonite are not regained on standing and the ^{27}Al spectra suggest a partial change of the normal hexacoordination of aluminum in the octahedral sheet, mostly to 5-coordinated aluminum. Heating at >850°C results in an X-ray amorphous phase which contains silicon in a wide range of environments, but NMR indicates that the Al-containing regions retain elements of the dehydroxylate structure. The recrystallization products which appear at higher temperatures reflect the chemical constitution of the starting material.

The percussive grinding process of montmorillonite studied by XRD, IR and DTA was described as a series of simultaneous changes proceeding at different rates [17]. Accordingly, the fastest reaction, namely a change in status of the exchangeable cations was explained by the different hydration states of exchangeable Ca-ions. Then followed a change in the status of OH groups, where upon partial dehydroxylation remaining OH groups are randomly bound at unsaturated broken bounds, or in the form of water molecules. The water content in initial unground montmorillonite (~17%) remained unchanged in the product of final grinding. Finally, comes the slowest process, degradation of the montmorillonite structure with separation of the octahedral and tetrahedral sheets in the final stages of grinding. It

was inferred that the structural degradation proceeds by delamination of particles, breaking and crushing of layers and other rearrangements including proton transfer within the structure. No structural recrystallization was reported on prolonged grinding. The discrepancy in detecting the same effects at quite different grinding times, was attributed to the different sensitivities of the instrumental methods [17].

Palygorskite, also known as attapulgite, has a structural arrangement of inversed silica tetrahedra allowing the formation of channels, which contain water molecules randomly distributed (so-called zeolitic water) attached to the silica unit. At the edges, exposed OH are neutralized by protons, forming more resistant H_2O, bound (coordinated) to the octahedral elements. Four molecules of each kind of water is present in its respective positions in the structure of palygorskite, whose ideal formula is: $Si_8(M^{VI}_5)O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$, where the octahedral unit, (M^{VI})– continuous in only one direction – usually contain Al and Mg in variable solid solution. Energetically different hydrogen bondings may associate the OH and water molecules in palygorskite. The loss of zeolitic (hydration) water around 100°C occurs with almost no structural change. Bound or crystal water molecules are evolved in two stages on heating (from ~200 to ~600°C), the exact temperature depending on the experimental conditions. First, $2H_2O$ are lost and the structure collapses ("folding"). In the second stage, when the remaining water is lost, some dehydroxylation also occurs. At higher temperatures (~800°C), further dehydroxylation and recrystallization mostly into enstatite takes place [6].

Grinding experiments carried out in our laboratory employing mortar and percussive processes, showed that a harsh treatment was necessary to attack the cross-
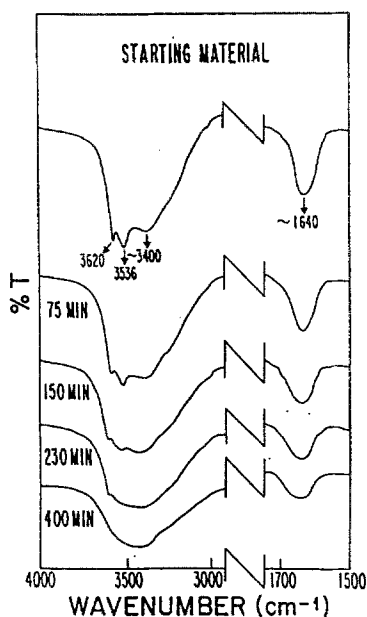

Fig. 3 Infrared spectra of palygorskite and of ground palygorskite (0.50% KBr disks) for the times shown

linked, ribbon structure of palygorskite. Thus, prolonged percussive mill treatments (400 min), using tungsten carbide grinding devices, were necessary to cause significant structural alterations in this silicate [18]. This gradual grinding process can be monitored by the IR spectra exhibited in Fig. 3. Infrared spectroscopy allows to follow the changes in the lattice vibrations as well as the changes in the water and OH bands of palygorskite. The latter simultaneous changes can be seen in the spectral region covering 1500 to 4000 cm^{-1} (Fig. 3). The large band at ~1640 cm^{-1}, arising from the H–O–H bending vibration in palygorskite is ascribed to molecular water. The planimetred area of this absorption band decreases progressively after 75 min grinding, reaching a 40% decrease in the last stages of grinding (400 min).

The prototropic effect (proton split from OH groups followed by migration and recombination to form OH associations in different structural positions) was well typified in the dry grinding processes of kaolinite clays [9, 19] and later explained as a mechanochemical reaction in kaolinite [10]. The prototropic effect was observed from the first stages of grinding by IR spectroscopy. The 1640 cm^{-1} band of kaolinite gradually increased with progressive grinding, matched by a pronounced broadening at the band around 3400 cm^{-1}, both bands arising from molecular water vibrations (Fig. 2). The increase of these bands was interpreted as a gain of additional water molecules, originated either from split-protons of structural OH groups in kaolinite and/or from atmospheric water. In palygorskite, however, we see that the IR band of molecular water at 1640 cm^{-1} decreases on grinding, and it is matched only by a decrease of the peak at 3536 cm^{-1}, but not matched by the 3400 cm^{-1} band development. This agrees with our former IR study on thermal deuteration of palygorskite [20] showing that the 1640 and 3536 cm^{-1} bands arise from the same source.

Thus, the development in the IR bands due to HOH vibrations is different from that observed in kaolinite. Besides, in contrast to kaolinite, the prototropic effect in palygorskite doesn't take place from the first stage of grinding (we detected it only after 75 min). Therefore an alternative mechanism must be invoked in order to explain a prototropic effect in ground palygorskite. It is our opinion that the increase of the 3400 cm^{-1} band in palygorskite on grinding (Fig. 3) is related to the decrease of both peaks at 3536 and 3620 cm^{-1} (the latter assigned to a νOH vibration), meaning that the split-protons recombine to give differently located associations of OH bonds and contribute to the development of the ~3400 cm^{-1} band. This is the reason why we have singled out the 1640 cm^{-1} band, which appears in a OH–free spectral region, to study the evolution of molecular water in ground silicates.

IR spectroscopy and XRD results (not shown here) indicate that the crystalline structure of palygorskite is destroyed with progressive grinding, leading to an amorphous phase with some residual order after >230 min grinding. In this case, no recrystallization was detected after prolonged grinding.

General discussion

Thermal treatments of clay minerals (phyllosilicates) result generally in metastable phases at intermediate temperatures (~400–750°C), when dehydroxylation

takes place. Then, follows at high temperatures (~800–1200°C) recrystallization in new structures with partial or total separation of silica. The magnesium minerals (trioctahedral clays) decompose at higher temperatures than their dioctahedral aluminum analogues but recrystallize almost inmediately, whereas the aluminum minerals recrystallize after further heating [5]. The decomposition reactions, especially those of the magnesium silicates show good and simple topotactic relations, i.e. the main products have important and usually simple crystallographic relations to the parent material. According to Brindley and Lemaitre [6] the topotactic behaviour is consistent with the classical concepts of nucleation and phase growth. The strain energy due to misfits between the new and old phases is likely to be minimized by the particular, preferentially developed orientations. The activation energy for phase growth also may be minimized when structural reorganization is small. The phases formed are not always those expected from equilibrium diagrams and metastable situations can develop.

The rebuilding of the metastable amorphous phases into crystalline phases at high temperatures involucrates diffusional migration of cations from the octahedral layers. Transport of structural elements in solids, which may include coordination polyhedra like silicates, also depend on the structural composition and anisotropy [21]. In the case of some Mg minerals, like sepiolite, $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$ which has a keen structure to palygorskite, the recrystallization into the chain structure of enstatite, $MgSiO_3$ with a release of SiO_2 excess, may follow inmediately after dehydroxylation. The structural rearrangements of sepiolite on heating, have been described as a multi-stage process [22].

Kinetic studies on the dehydroxylation of clay minerals are not conclusive, partly because the reactions of clay grade materials involve considerations which are not present in single crystal studies [6]. Later experiments using micro-balances and thin layers of material tended to confirm diffusion-controlled kinetics, although there is not complete agreement on this question. However, beside surface and particle size factors, temperatures and vapour pressure dependences for the reaction rates have been established.

Thermal dehydration of clays take place at low temperatures, usually below 400°C, and the process is generally reversible under specific conditions. Protons and water molecules are the main actors to be considered in the dehydration as well as dehydroxylation processes. Since protons can diffuse more easily than water molecules a so-called heterogeneous mechanism has been applied to silicate dehydroxylation reactions [6]. Accordingly, free protons H^+ produced by dissociation of OH structural groups migrate to sites where water molecules are formed at the expense of such protons. A counter-migration of cations (Al^{3+}, Mg^{2+}, etc.) will maintain electrical neutrality. Diffusion-controlled kinetics may then be related to the escape of water molecules (via pores or other defects) or to the counter-migration of cations or to both processes.

Some other differences and transformation mechanisms are further discussed: unlike in the high-temperature treatments of clay silicates, prolonged grinding leads, with a few exceptions, to the irreversible formation of amorphous phases with no recrystallization in new structures. It is possible to assume that the

mechanochemical transformation is energetically more effective than the thermal one since, in the case of thermal transformation all the atoms of the crystal should be excited to the same extent, whereas only a small number of atoms are necessary to activate for triggering the mechanochemical nucleation [24]. The mobility and kind of displacements of excited atoms will decide if nucleation is favored over crystal amorphization.

The mechanochemical reactions which occur during comminution are the consequence of a relaxation process, i.e. release of accumulated activation energy in the material. It is thus associated with a "reaction-triggering dimensionality" (RTD) and depends largely on the nature of the relaxation mechanism and on the characteristics of the material. Topotactic transformations and syntheses have relatively higher RTD, otherwise microcrystallinity (XRD-detected "amorphization") is observed. Another factor favouring higher RTD is a low shear rigidity in certain crystallographic planes [23]. Topotaxy is more frequently observed in the thermochemical conversions of clays which are pseudomorphic in character, than in counterpart mechanochemical transformations.

The size of particles and an increase in structural defects are the main factors governing reactivity of solids, both factors involucrated in the relaxation mechanism. The nature and mechanical properties of the material must be accounted for these considerations. Particles that are larger than certain limit undergo breakage if subjected to enough stress, while the smaller ones undergo plastic deformation [25]. These changes lead to a substantial growth in structural defects identified with phase transformations, when an increased reactivity of the material is observed.

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