

Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

SOLID-STATE TRANSFORMATION MECHANISMS OF ASSOCIATED MINERALS TO ALUMINOSILICATES

E. Mendelovici

Department of Materials Science, IVIC Apartado 21827, Caracas 1020A, Venezuela

Abstract

Thermochemical and mechanochemical transformation mechanisms of associated minerals in clay (quartz, calcite, Al and Fe oxyhydroxides) are comparatively examined. The phase transformation sequence resulting from heating and, on the other hand from dry grinding of each of the associated minerals, depends on the structure and physicochemical properties of the starting materials.

Grinding treatments may cause local heating and local pressure effects in some selective metal oxides and in calcite, respectively, accounting for their structural conversions.

Keywords: boehmite, calcite, gibbsite, grinding, (local) heating, local pressure effects, quartz

Introduction

Clays, are fine-grained inorganic aluminosilicates which are generally plastic at appropriate water contents and will harden when dried or fired. Associated minerals in clay may include materials that do not impart plasticity [1]. They comprise crystalline minerals such as quartz, calcite, aluminium and iron oxyhydroxides and hydroxides, and organic phases.

A comparison of the thermal and mechanical treatments of clays (layered structures) has been recently presented [2]. This broad study did not include the associated minerals in clay. The latter show distinctive transformation mechanisms especially when submitted to grinding treatments. In the present contribution we shall examine the mechanism of such solid-state treatments as heating and dry-grinding in individual associated minerals, mostly in Al hydroxylated oxides and quartz which are the most common crystalline minerals. Solid-state treatments of organic (crystalline or non-crystalline) phases associated to clay are a more complex matter and are not considered here.

Thermochemical and mechanochemical transformations of Al compounds vs. Fe counterparts

The Al compounds referred here are mostly gibbsite, $\text{Al}(\text{OH})_3$, diaspore, $\alpha\text{-AlOOH}$ and boehmite $\gamma\text{-AlOOH}$. We may call the latter alumina precursors, as

they lead ultimately to Al_2O_3 by solid-state treatments. Gibbsite, diaspore and boehmite are accessory minerals often associated to natural clay (mostly kaolin deposits).

The well known thermal transformations of these alumina precursors has been reviewed [3, 4]. Generally, these sort of transformations are topotactic, where the starting materials (gibbsite or boehmite) have a cubic close-packed oxygen structure vs. a hexagonal close-packed oxygen structure of the transformation products, i.e. $\alpha\text{-Al}_2\text{O}_3$. The comparison of the transformation sequence of boehmite ($\gamma\text{-AlOOH}$) and gibbsite, ($\text{Al}(\text{OH})_3$) to corundum, ($\alpha\text{-Al}_2\text{O}_3$) by heating and by ball milling has been recently described by Tonejc *et al.* [5]. By gradual heating up to 1000°C (in air), the transformation of boehmite and gibbsite to corundum occurs over a series of stable transition phases. On dry grinding, whether the starting powder was gibbsite or boehmite, the transformation sequence found was $\rightarrow \chi\text{Al}_2\text{O}_3 \rightarrow \kappa\text{Al}_2\text{O}_3 \rightarrow \alpha\text{Al}_2\text{O}_3$. These comparative thermal and mechanical transformations are compiled and summed up in Table 1.

Table 1 Thermal and mechanical transformations of common Al oxides

	Common names	Formulae	Alumina varieties
Hydroxides	Gibbsite or hydrargillite <0.2 μm	$\text{Al}(\text{OH})_3$	$\xrightarrow{150-300^\circ\text{C}} \chi \xrightarrow{970^\circ\text{C}} \kappa \xrightarrow{1200^\circ\text{C}} \alpha$
Oxyhydroxides	Boehmite	$\gamma\text{-AlOOH}$	$\xrightarrow{>430^\circ\text{C}} \gamma \xrightarrow{750^\circ\text{C}} \delta \xrightarrow{1000^\circ\text{C}} \theta \xrightarrow{1200^\circ\text{C}} \alpha$
	Diaspore	$\alpha\text{-AlOOH}$	$\xrightarrow{>450^\circ\text{C}} \alpha$
	Gibbsite or boehmite	Percussive dry-grinding	$\rightarrow \chi \rightarrow \kappa \rightarrow \alpha$

The table shows that during the heating process of boehmite, λ and δ were the transition phases and not χ and κ . Nevertheless Tonejc *et al.* [5] suggested that an equivalence exists between the high energy ball milling (using CW grinding devices) and the thermal processes. They also deal with another controversial aspect here, which is the role of local effective temperature on grinding. In the investigations of structural changes (by XRD and DSC) during ball milling of amorphous alloys (containing Fe, Co, Si, B and eventually Ni in different proportions), Trudeau *et al.* [6] claimed that there is no relation between the mechanical and thermal processes. In our opinion, the controversy of the former works on the analogy of ther-

mal and mechanical processes could be explained by the different nature and structure of the materials considered.

A structurally different Al oxyhydroxide, diaspore, α -Al(OOH) is directly and topotactically transformed to corundum by heating at $>450^{\circ}\text{C}$ (Table 1). No such a transformation was detected by prolonged, mortar dry-grinding of this hard material although other properties were affected [7]. Similar conclusions were reported in a later work on ball milling of diaspore [8].

Iron oxides and oxyhydroxides (hematite, goethite and lepidocrocite) are also accessory minerals associated to clays. Goethite, α -FeOOH is directly transformed to hematite, α -Fe₂O₃, either by heating or by grinding. Other polymorphic FeOOH structures do not show the same properties. In this respect it is relevant to quote the investigation of Mendelovici *et al.* [9] on the mechanochemical transformation of lepidocrocite, γ -FeOOH, which led to the development of hematite, α -Fe₂O₃ with no intermediary phases. In contrast, maghemite, γ -Fe₂O₃ is an intermediary phase in the well known thermochemical transformation of γ -FeOOH into α -Fe₂O₃. The observed absence of the intermediate maghemite (or any other metastable forms) in the mechanochemical sequence – in contrast to its thermochemical counterpart – brings to mind the well known resemblance of the topotactic reactions in iron and aluminium oxyhydroxide and oxide systems. In aluminium-based systems, the series of intermediate metastable aluminas known to form during thermochemical transformation from the starting phase (γ -AlOOH) to the end product (α -Al₂O₃) are probably due to pseudomorphism; the latter cannot exist in mechanochemical reactions because the grinding treatment excludes pseudomorphism, hence the formation of metastable phases [10].

Thermal and grinding treatments of quartz

Quartz is often an abundant accompanying mineral of clay formations. A well documented chapter on the thermal conversion of quartz (the room temperature stable form of silica) to polymorphic phases has been written [11]. The distorted structure of quartz at low temperature is derived to a symmetrical form at high temperature (573°C) by a displacive mechanism. This distortion occurs by the correlated shifting of ions in the structure of quartz. Smykatz Kloss and Klinke [12] proposed to use the high-low inversion of quartz crystals for petrogenetical purposes.

DTA of quartz reveals a sharp endothermic peak at 573°C corresponding to the low-high inversion. The percussive grinding of quartz (or of other accessory minerals) affects the mineral's particle size, thermal diffusivity, density and reactivity. Moore and Rose [13] observed that if quartz is subjected to prolonged percussive grinding, the inversion-peak size decreased and eventually vanished in the DTA diagram run at $10^{\circ}\text{C min}^{-1}$. This was attributed to the formation of amorphous silica (about 25%). The sample was found, however, to have the X-ray structure of crystalline, low quartz (~75%) which changed to high quartz when heated at 573°C . In addition, the powdered, ground quartz samples contained about 4% firmly held water (until 800°C) sorbed from the atmosphere. Other silicate minerals like kaolinite, as well produced thermally resistant water molecules on dry grinding [14]. When the DTA of ground quartz was carried out at about $18^{\circ}\text{C min}^{-1}$, the

'lost' 573 °C peak became again quite pronounced, possibly because the dispersion of the inversion over a small range of temperature becomes less and a greater fluctuation of differential temperature is produced. When DTA is carried out at low rates of heating, each fragment of quartz inverts at its own individual inversion temperature, and more time is available for heat to be conducted to the sample as a whole, giving rise to a smaller inversion peak [13].

Local heating and pressure effects on grinding

In contrast to the mechanochemical transformations of some metal oxides, a local heating effect is improbable in the grinding of quartz, as the low temperature form is not converted to high quartz during the grinding process. Again, a local heating effect on grinding depends on the structure of the starting material and on its physicochemical properties. Clay minerals (phyllosilicates) as well, do not show, generally, a local temperature increase when submitted to mechanical treatments [2]. Otherwise, metals or some finely powdered metal oxides like e.g. binary cobaltite spinels [15] show the magma-plasma or local heating effect on grinding, which means a local increase in temperature and melting in the microcontact region (up to 10^3 K), the mean temperature of the ground sample remaining unchanged. Generally these mechanochemical transformations imply plastic deformation and a change in the relaxation mechanism.

A local pressure increase can also be developed in the microcontact region of some ground products. This is the case of calcite (CaCO_3) – an accessory mineral to clay – which is transformed to its polymorphic form, aragonite by mortar-grinding at room temperature [16]. Otherwise, on heating, the calcite \rightarrow aragonite transformation must be carried out at $>400^\circ\text{C}$. Structural factors and hydrostatic pressure developed in the mortar-grinding process must be accounted for the mechanochemical transformation of this accessory mineral.

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