

# CRYSTALLOGRAPHIC ASPECTS OF HIGH TEMPERATURE TRANSFORMATIONS OF CLAY MINERALS

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## EXTENDED ABSTRACT

THIS paper deals with the dehydroxylation reactions of clay minerals and allied substances such as lamellar hydroxides, serpentine minerals, and amphiboles. Probably in all cases, these reactions occur topotaxially, that is, there is a three-dimensional similarity between the crystal structures of starting material and product, as a result of which each crystal of the starting material is changed into something approaching a single crystal of the product. Many investigators have studied the orientation relationships between starting materials and products, and their results have provided the main experimental foundation for hypotheses about the reaction mechanisms. These hypotheses have, however, rested also on assumptions, of which until recently three have usually been made. These are (i) loss of water occurs more or less uniformly from all parts of the crystal; (ii) the Si-O parts of the structure are more stable than the metal-oxygen parts; and (iii) the silica-rich material often presumed to be formed as a subsidiary product is pure  $\text{SiO}_2$ . Recent work suggests, however, that none of these assumptions is securely based, and the purpose of this paper is to suggest an alternative approach to the problem.

The high temperature reactions of clay minerals are perhaps best understood by treating the latter as assemblies of close packed, or nearly close packed, oxygen ions with cations in the interstices. From this point of view, one might expect that the relatively small cations, such as  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and especially  $\text{H}^+$  would move more easily than the oxide ions. One would not expect the oxygen atoms that are lost as water to be necessarily those present initially as  $\text{OH}^-$  groups; they are more likely to be those that can most easily escape from the structure, e.g. from near external surfaces or grain boundaries. On this hypothesis, a typical dehydroxylation reaction involves three types of process:

(i). *Loss of oxide ions from exposed or "donor" regions*, and their combination with  $\text{H}^+$  ions from all regions, to form water. The donor regions are changed into pores.

(ii). *Cation migrations*. These may be of two kinds. Firstly, all cations other than  $\text{H}^+$  migrate from the donor regions into the remaining or "acceptor" regions, and  $\text{H}^+$  ions migrate in the opposite direction. Secondly, within the acceptor regions themselves, further migrations may cause differentiation into Si-rich and Si-poor parts to occur.

(iii). *Changes in the type of oxygen packing in the acceptor regions*, to complete the formation of the crystalline products. These last changes may occur throughout the acceptor regions, or only in certain parts of them.

### *Brucite*

This approach can be illustrated by reference to brucite ( $\text{Mg}(\text{OH})_2$ ). The sequence of layers in this mineral is  $-\text{OH}-\text{Mg}-\text{OH}-\text{Mg}-\text{OH}-$ . On the old hypothesis, dehydroxylation occurs by the loss of the elements of water from all parts of the crystal; a pair of

## 10 TWELFTH NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS

adjacent sheets of hydroxyl is replaced by a single sheet of oxide ions. This may be called a "homogeneous" mechanism. On the new hypothesis, the conversion of  $\text{Mg}(\text{OH})_2$  into  $\text{MgO}$  occurs not by loss of oxygen, but by gain of  $\text{Mg}^{2+}$  ions. Some parts of the crystal (donor regions) are destroyed and provide all the oxygen for the water that is formed. Counter migrations of  $\text{H}^+$  and  $\text{Mg}^{2+}$  occur between donor and acceptor regions. To convert the latter into  $\text{MgO}$ , a further change is necessary; the type of oxygen packing must change from hexagonal to cubic. There is, however, no appreciable change in the density of oxygen packing within the acceptor regions.

This type of mechanism may be termed "inhomogeneous". Experimental support for it is provided by its ability to explain the formation of an intermediate, spinel-like phase, and also by its ability to account for the differing behaviour of  $\text{Ca}(\text{OH})_2$ .

### *Serpentine*

Dehydroxylation of serpentine minerals in air below about  $1000^\circ\text{C}$  normally gives forsterite as the only detectable crystalline product. The orientation relationship is such as to give the best possible fit between the octahedral parts of the initial and final structures. It is suggested that the initial stage in the process is similar to that suggested for brucite;  $\text{H}^+$  ions migrate into donor regions, which are destroyed, and  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$  ions migrate into acceptor regions. Further cation movements within the acceptor regions then lead to the development of Mg-rich and Si-rich parts. In the Mg-rich parts a change in the type of oxygen packing can occur, giving forsterite. The Si-rich parts remain partly disordered until over  $1000^\circ\text{C}$ , when  $\text{MgSiO}_3$  is formed. The product formed below  $1000^\circ\text{C}$  is thus not a two-phase mixture of forsterite and amorphous silica, but something less definite; the forsterite and the Si-rich regions probably merge into each other without structural discontinuity, and there may well be a considerable proportion of material in which the Mg:Si ratio is not very different from that of the initial serpentine. There is no reason to suppose that the Si-rich regions are pure  $\text{SiO}_2$ .

When serpentine is dehydroxylated under certain hydrothermal conditions, forsterite is formed in different orientations from those obtained on heating in air. This can be explained in terms of the inhomogeneous mechanism described above.

Similar mechanisms can be postulated for the dehydroxylations of talc, and also of tremolite and other amphiboles.

### *Calcium Silicate Hydrates*

If the mechanisms of dehydroxylation reactions depend on the ionic radii of the cations present, one would expect minerals containing predominantly larger cations to behave differently from clay minerals. That this is indeed the case is shown by the behaviour of calcium minerals such as xonotlite ( $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ ). The products and orientation relationships in these cases suggest that the dominant tendency is for the Ca-O parts of the structure to remain undisturbed. Migrations occur among the  $\text{Si}^{4+}$  ions and those oxygen atoms not directly linked to calcium, and the mechanisms are homogeneous.

### *Al-containing Clay Minerals*

With Mg-rich clay minerals, loss of water is followed closely by recrystallization to new products; with their Al-rich analogues, there is a considerable temperature interval over which metaphases are formed. The difference can probably be attributed to the difference in cationic charge, since amphiboles rich in  $\text{Fe}^{3+}$  behave like the Mg-minerals, while those containing  $\text{Fe}^{3+}$  form metaphases.

There is little direct evidence as to whether Al-rich clay minerals dehydroxylate by homogeneous or inhomogeneous mechanisms; knowledge of the crystal structures of the better crystallized metaphases, such as pyrophyllite anhydride, would provide valuable data, but is at present lacking. If inhomogeneous mechanisms are assumed, the difference in behaviour from the Mg-minerals can most reasonably be attributed to a greater resistance to change in the type of oxygen packing in the case of the Al-rich minerals.