

STUDY OF THE DEHYDROXYLATION OF CLAY MINERALS USING CONTINUOUS  
SELECTIVE WATER DETECTOR

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ABSTRACT

The dehydroxylation of pyrophyllite, illite and muscovite has been investigated by various thermoanalytical methods. The water detector reveals much more complicated decomposition patterns than those of obtained by traditional methods (TG, DTG, DTA).

INTRODUCTION

The pyrophyllite, illite and muscovite minerals investigated are 2:1 type, three layered, dioctahedral layer silicates in which a dioctahedral Al, O(OH) sheet is sandwiched between two Si, O tetrahedral sheets. The formation of water in the 300-900°C range can be due to the OH-groups reacting locally to form O<sup>2-</sup> and H<sub>2</sub>O. The most characteristic feature of the dehydroxylated pyrophyllite structure is that the originally octahedrally coordinated layer shows a five-fold coordination (AlO<sub>5</sub>) through the formation of coordination polyhedra.

EXPERIMENTAL

High purity pyrophyllite, illite (mixed layered), and muscovite samples were investigated by simultaneous TG, DTG, DTA measurements (derivatograph), microprocessor controlled derivatograph (courtesy of Prof. J.Paulik), and continuous selective water detector [1]. Figs. 1-3 show the thermoanalytical curves of pyrophyllite, illite, and muscovite, respectively.

RESULTS AND DISCUSSION

The fact that the water detector reveals very closely overlapped decomposition stages indicates that five-fold coordination in the central layer is achieved gradually. Since the structures of the minerals investigated are very similar to that of pyrophyllite it is not surprising that

illite and muscovite show complex dehydroxylation patterns as well (5 decomposition stages can be observed for illite, while 4 stages can be recognized for muscovite). Two approaches to the complex dehydroxylation process have been considered:

- I. The environments of the  $\text{OH}^-$  ions are not identical;
- II. Intermediate structures are formed during dehydroxylation.

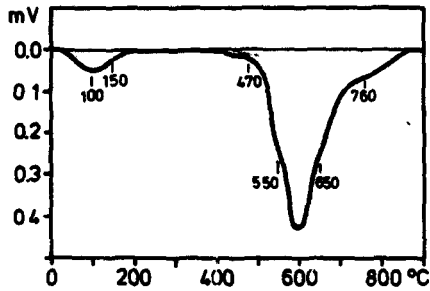


Figure 1

Dehydroxylation curve of pyrophyllite 1-Tc (water detector)

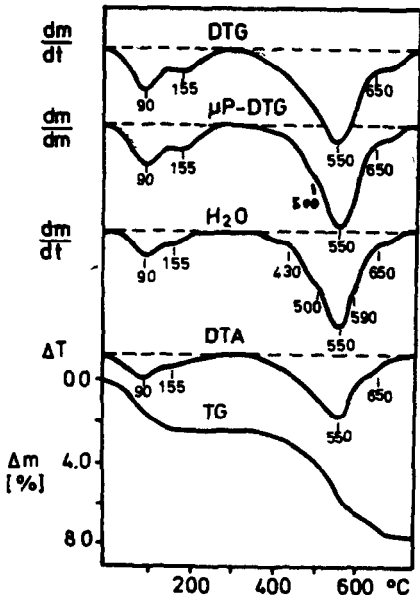


Figure 2

Thermoanalytical curves of illite

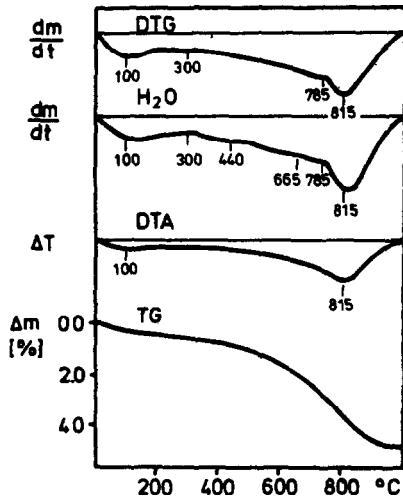


Figure 3

Thermoanalytical curves of muscovite

I. According to Wardle and Brindley [2] the  $\text{OH}^-$  groups have identical environments in the idealized pyrophyllite structure. The single crystal X-ray data of Lee and Guggenheim [3] agree closely with the above results. Environmental differences may, however, exist between  $\text{OH}^-$  ions located on the surface and inside of the particles, as well as between  $\text{OH}^-$  groups close to dislocations and vacancies, and those located apart from these. As for illite and muscovite, different environments may exist for  $\text{OH}^-$  ions located close to replaced sites of the tetrahedral and octahedral sheets as compared to those of  $\text{OH}^-$  ions situated in ideal dioctahedral sheets. Furthermore, in the case of illite there can be differences between the environments of  $\text{OH}^-$  ions situated inside the mica and montmorillonite layers, and at the connecting plane of these layers.

II. Incipient dehydroxylation may produce charge- and geometrical conditions in the vicinity of the dehydroxylated sites which, in a narrow temperature range, can stabilize the whole structure in which original and dehydroxylated areas are present simultaneously. The formation of such "intermediate structures" can explain the complex dehydroxylation process, even in the idealized pyrophyllite structure.

Incipient dehydroxylation itself creates differences among the coordination octahedra, even in idealized structures. In the real structure there can be  $\text{OH}^-$  ion positions which produce  $\text{H}_2\text{O}$  at a lower temperature than the rest of the  $\text{OH}^-$  ions of the structure. The structure of the remainder material and its dehydroxylation properties in the function of the temperature can be considered as determined by the initial and the intermediate structures together.

#### CONCLUSIONS

Due to the extreme low noise level of the water detector a more detailed study of the dehydroxylation of minerals is possible. Quantitation of the individual decomposition stages and a thorough X-ray diffraction study of the structure as a function of the temperature are necessary to find out the

causes of the complex decomposition pattern.

#### REFERENCES

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- 3 J.H. Lee and S. Guggenheim, American Mineralogist,  
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