Journal of Thermal Analysis, Vol. 53 (1998) 375-381

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

SOME REMARKS ON THE METHODOLOGY OF THERMAL ANALYSIS OF CLAY MINERALS

S. Cebulak[1] *and A. Langier-Kuźniarowa*[2]

[1]Silesian University, Będzińska 60, 41–200 Sosnowiec
[2]Polish Geological Institute, Rakowiecka, 4, 00–975 Warsaw, Poland

Abstract

The influence of certain experimental conditions on the courses of the thermal curves (DTA and DTG) of selected clay minerals was studied. The thickness of the sample layer, the sample mass, the type of sample holder and the parameters of the air atmosphere were varied in thermal analyses of 13 samples of clay minerals. Comparison of the results obtained on different clay samples analysed under different experimental conditions may serve as the basis for the improvement of the thermal analysis methodology applied for the study of clay minerals.

Keywords: clay minerals, experimental conditions, oxyreactive thermal analysis

Introduction

A review of the literature dealing with the problem of thermal analysis applied for clay mineral investigations seems to confirm the opinion that the correct choice of the experimental conditions is one of the most important factors governing the results obtained.

We have studied the influence of the variation of different experimental conditions, such as the thickness of the sample layer, the sample mass, the type of sample holder and the parameters of the air atmosphere, on the results of thermal analysis. The investigations were carried out on 13 samples of clay minerals.

Experimental

The clay minerals used for the experiments were from the kaolinite group, smectites, sepiolite and vermiculite, as listed in Table 1. The majority of them originated from widely-known sources and have frequently been used as reference minerals for the study of clays. Most of the samples used were donated by late Dr. H. W. van der Marel.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The thermal analyses performed for the purposes of our studies involved the OTA (oxyreactive thermal analysis) technique described in detail in a previous paper [1] as an experimental procedure that is particularly suitable for the investigation of organic matter and clays containing organic matter.

Table 1 List of samples used

	Sample	Source	Dominant clay mineral
1	Kaolinite	Sedlec, Czech Republic	Well-ordered kaolinite
2	Fire clay	Cserszegtomaj, Hungary	Ordered kaolinite
3	Fire clay	Joliet, Ill., USA	Ordered kaolinite
4	Fire clay	Sayreville, N. Jersey, USA	Ordered kaolinite
5	Halloysite	Michalovce, Slovakia	Hydrated halloysite
6	Bentonite	Upton, Wyoming, USA	Na-montmorillonite
7	Bentonite	Minas de Gador, Almeria, Spain	Ca-montmorillonite
8	Bentonite	Milowice, Poland	Mixed layer illite/smectite
9	Nontronite	St. Andreasberg, Germany	Nontronite
10	Hectorite	Hector, California, USA	Hectorite
11	Laponite XLG	Laporte Absorbents	Synthetic hectorite
12	Sepiolite	Vallecas, Spain	Sepiolite
13	Vermiculite	Libby, Montana, USA	Vermiculite

In the investigations reported here, the Hungarian Derivatograph, a simultaneous TG/DTG/DTA instrument developed by Paulik, Paulik and Erdey [2], was used. The following experimental conditions were varied:

– the thickness of the sample layer,
– the type of sample holder: either a crucible or a multiplate one [2],
– the air atmosphere: either static or dynamic; a dynamic atmosphere was obtained by injection of air into the sample chamber at a rate of 1.0 l min^{-1}, and waste gases were extracted by suction at a rate of 1.9 l min^{-1}.

Three sets of experimental conditions were used, as follows:

– a routine procedure, using a crucible holder, a static air atmosphere, and a sample mass of 350 mg (slow emission of gaseous products of thermal reactions),
– the OTA [1] procedure, using a multiplate sample holder with 4 plates, a dynamic air atmosphere, and a sample mass of 280 mg (fast emission of gaseous products).
– a multiplate sample holder (4 plates), a static air atmosphere, and a sample mass of 280 mg (intermediate conditions of emission).

Results and discussion

The experimental conditions applied had the primary aim of a comparison of the thermal results obtained on selected clay samples under conditions usual in the thermal analysis of clays with those obtained with different sample holders and in a dynamic atmosphere. Figures 1–3 show thermal curves (DTG and DTA) obtained under routine conditions (crucibles and a static air atmosphere) or with the following modifications: 1) a multiplate sample holder and a static atmosphere, or 2) a multiplate sample holder and a dynamic atmosphere, as required in OTA [1]. The comparison of the results revealed the general similarity of the courses of the thermal reactions; the differences in the peak intensities were mainly due to the different sample masses.

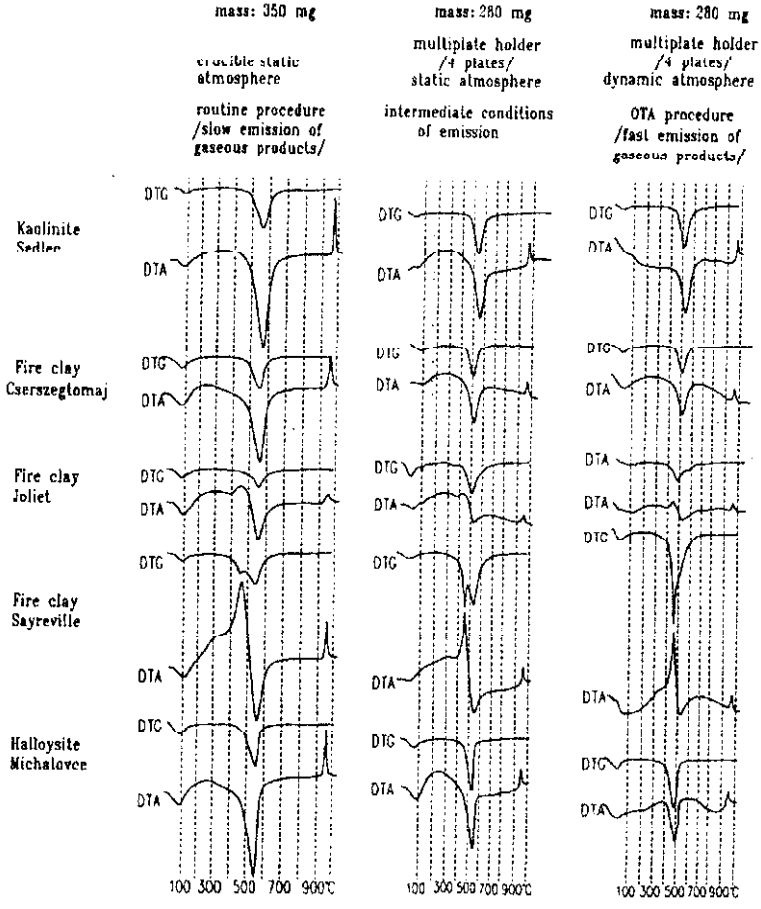

Fig. 1 DTA and DTG curves of clay minerals of kaolinite group – effects of modification of crucible, multiplate holder and atmosphere

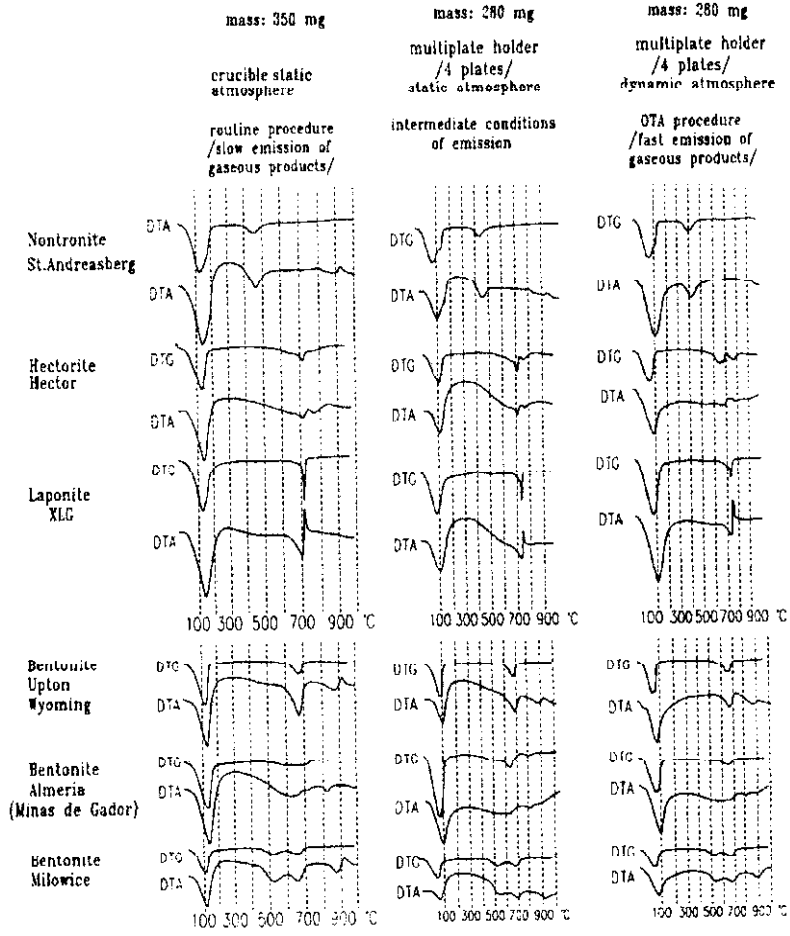

Fig. 2 DTA and DTG curves of clay minerals of smectite group: nontronite, hectorite, laponite XLG and bentonites – effects of modification of crucible, multiplate holder and atmosphere

However, a detailed comparison of the thermal curves demonstrated essential differences in the courses of the thermal reactions of clay minerals, e.g. dehydration, dehydroxylation and phase transformation. Dehydration occurring under OTA conditions furnished a reaction maximum at markedly lower temperature; although the difference was variable, this phenomenon was observed for all clay samples investigated. It may be explained as due to the effect of the higher rate of evolution of the volatile reaction products under OTA conditions (a multiplate holder and a dynamic atmosphere). The largest difference (40°C) was observed for hectorite, Almeria bentonite and laponite. The difference varied with the clay mineral studied, and may reflect different water adsorption properties.

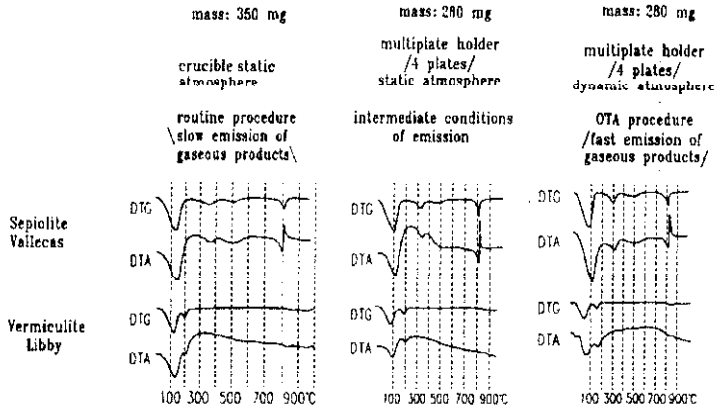

Fig. 3 DTA and DTG curves of clay minerals: sepiolite and vermiculite – effects of modification of crucible, multiplate holder and atmosphere

Under OTA conditions the dehydroxylation peaks shifted towards lower temperatures only for the kaolinite group minerals and for nontronite, with a difference of 40–50°C. None of the bentonite samples, consisting of smectite or mixed layer illite/smectite, displayed a difference in dehydroxylation peak temperature under OTA and routine conditions.

The three endothermic DTA peaks of sepiolite in the temperature range 300–800°C behave variously. Two low-temperature endothermic peaks correspond to the evolution of bound water. Under OTA conditions, the first undergoes a peak temperature lowering of more than 40°C. The second, slow reaction, in the temperature range 430–600°C, with maximum at about 500°C, exhibits no shift due to the experimental conditions employed. The third DTA peak, in the temperature range 300–800°C, resulting from the liberation of OH groups from metasepiolite, shifts towards higher temperature under OTA conditions in comparison with the temperature observed when the routine experimental procedure is used, but this change is somewhat smaller (about 20°C). The maximum for the clinoenstatite formation reaction also occurs at a higer temperature under OTA conditions.

The problem of bound water evolution from sepiolite has been studied by many authors, using different experimental methods, such as X-ray, IR spectroscopy, electron microscopy and thermal analysis (e.g. [3–7]). The IR results revealed that the process of crystallization water removal from the sepiolite structure is very complicated and occurs in several stages, resulting in different structural transformations, accompanied by rotation and distortion, leading to metasepiolite formation. This phase still contains OH groups inside the structure channels. This differentiated course of the DTA and DTG curves corresponding to particular reactions for sepiolite, as the response in the OTA procedure in com-

parison with the routine experimental conditions, may be used for the interpretation of these processes. Only a single DTA and DTG effect displayed by Fe-containing sepiolites in the temperature range 300–600°C [10] may suggest the occurrence of different processes of thermal transformation leading to metasepiolite formation.

The dehydroxylation and phase transformation reactions of hectorite exhibit other differences in the thermal curves obtained under routine and OTA conditions. Under routine conditions, dehydroxylation proceeds in two stages, with peaks at 710 and 775°C, the first of them accompanying a greater loss in mass. The phase transformation appears here as a weak DTA effect with maximum at 850°C. With the OTA procedure, three peaks of dehydroxylation are obtained, at 665, 690 and 780°C, whereas the phase transformation reaction (clinoenstatite formation) is almost unobservable in the DTA curve. Further, the first and third stages of dehydroxylation correspond to a greater mass loss than that for the second one. The probable reason for such differences is the presence of F besides OH groups in the octahedral sheet of hectorite. The three stages of volatile component liberation mentioned above prove the differentiated bonding in the clay mineral structure. This may result from the occurrence of another element besides Mg in the octahedral sheet.

Laponite XLG shows thermal effects of dehydroxylation and phase transformation similar to those observed for sepiolite, in spite of its having a structure of hectorite type, but the reactions given by laponite and hectorite both occur at lower temperatures (by almost 100°C) than those for sepiolite.

For laponite XLG, similarly as sepiolite, the DTA endo- and exothermic reactions in the temperature range 700–740°C, and the DTG effect at about 710°C, occur at slightly higher temperatures under OTA conditions than when the routine procedure is applied. In the DTA curve of laponite XLG obtained with the OTA procedure, a certain duality of the dehydroxylation effect can be observed. This may result from the presence of a small amount of Li besides Mg in the octahedral sheet. This does not influence the shape of the very intensive DTA exothermic reaction corresponding to the phase transformation, i.e. clinoenstatite formation.

The differences in the courses of the thermal reactions, depending on the experimental conditions applied, which result in easier or more difficult and slower volatile product emission, have been relatively well recognized for certain minerals, and especially for carbonates, for which the course of the thermal dissociation reaction is very strongly connected with the parameters of evolution of CO_2. However, for clay minerals these dependences between the evolution of the volatile thermal decomposition products (bound water and OH groups) and the experimental conditions are weaker and of an unlike character. It should be mentioned that, as long ago as 1961, Cole and Rowland [8] noted the effects of different heating conditions on montmorillonite and vermiculite dehydroxylation and

on the peak temperatures of these reactions. Stoch [9] too reported the dependence of the resolution of the DTA peaks of kaolinite and dickite dehydroxylation on the thickness of the sample layer in the sample holder.

The thermal analysis results obtained by the present authors on sepiolite, hectorite and laponite under variable experimental conditions allow the recommmendation of this mode of investigations for recognition of the details of OH and OH_2 bondings. The example of the fire clay from Sayreville (Fig. 1) indicates that the OTA procedure may be useful for the investigation of clay samples containing organic matter admixtures. The heating of samples spread in thin layers on the plates of the multiplate sample holder under a dynamic air atmosphere permits dissociation of the organic compounds, evolution of their products and their oxidation in the thin layers of the sample. It also allows the oxidation reaction to be recorded with markedly higher sensitivity and resolution than when the routine procedure is used.

Conclusions

1. The results of the study indicate that use of the OTA method (i.e. the analysis of thin sample layers on multiplate holders in a dynamic atmosphere) greatly increases the applicability of TA for clay mineral analysis.

This effect was obtained in clay mineral testing, despite the fact that this method was originally designed for the analysis of organic matter dispersed in rocks (DOM).

2. It has been established that the methodology of thermal analysis employed can be applied for the recognition of certain structural details of clay minerals, which routine thermal analysis does not allow.

3. Many of the structural details of clay minerals that are revealed when OTA methodology is used correspond with differences in composition of these minerals.

4. The OTA methodology, originally designed for the analysis of organic matter dispersed in rocks, proved to be very useful for the investigation of organic matter contained in clays.

References

1 S. Cebulak and A. Langier-Kuzniarowa, J. Thermal Anal., 50 (1997) 175.
2 F. Paulik, Special Trends in Thermal Analysis, John Wiley & Sons 1995.
3 C. Serna, M. Rautureau, R. Prost, C. Tchoubar and J. M. Serratosa, Bull. Groupe franç. Argiles, 26 (1974) 153.
4 H. Nagata, S. Shimoda and T. Sudo, Clays and Clay Min., 22 (1974) 285.
5 C. Serna, J. L. Ahlrichs and J. M.Serratosa, Clays and Clay Min., 23 (1975) 452.
6 M. Rautureau and C. Tchoubar, Clays and Clay Min., 24 (1976) 43.
7 A. Preisinger, Tenth Natl. Conf. Clays and Clay Min., 12 (A. Swineford, ed.) (1963) 365.
8 W. F. Cole and N. M. Rowland, Amer. Miner., 46 (1961) 304.
9 L. Stoch, Bull. Acad. Pol. Sci. Ser. Sci. Geol. Geogr., 12 (1964) 173.
10 A. Lewandowska, Mineralogia Polonica, 27 (1996) 9.