

INTERACTION OF KAOLINITE WITH CALCITE ON HEATING. I. INSTRUMENTAL AND PROCEDURAL FACTORS FOR ONE KAOLINITE IN AIR AND NITROGEN *

R.C. MACKENZIE and A.A. RAHMAN

Department of Chemistry, University of Aberdeen, Old Aberdeen (Gt. Britain)

(Received 16 October 1986; in final form 20 January 1987)

ABSTRACT

Possible reasons for distortion of the calcite endotherm on DTA curves for kaolinite–calcite mixtures were examined using one mixture in a nitrogen or air atmosphere. The complexity of the endotherm depends on the ease of egress of carbon dioxide, sample size (which may be related), intimacy of mixing, presence or absence of water vapour and particle size. These observations, which are inconsistent with a solid-state reaction mechanism, can be explained on the basis of adsorption and desorption of CO_2 by metakaolinite, although the validity of this explanation remains to be tested.

INTRODUCTION

Although kaolinite and calcite frequently coexist in the clay fractions of soils and sediments, the thermoanalytical characteristics of such mixtures have received scant attention. Indeed, the only direct study known to the authors is that of Grim et al. [1], who, in 1945, observed the calcite DTA peak to be modified by partial superposition of an exotherm due, according to X-ray diffraction evidence, to the formation of gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, by a solid-state reaction between metakaolinite and CaO . Since that time, a distorted calcite endotherm has generally been attributed to this reaction without further study.

In contrast, French and Warne [2] attributed distortion of the calcite peak on DTA curves for oil shales in a CO_2 atmosphere to interaction between calcite and organic matter, although kaolinite may well have been present. Other observations that may be relevant are those of MacIntire and Stansel

* To Professor W.W. Wendlandt in appreciation of his great efforts on behalf of thermal analysis and in celebration of his 60th birthday, the present paper is dedicated. Like the matter in this paper, Wesley's work is far from complete and we wish him many happy and fruitful years in the future.

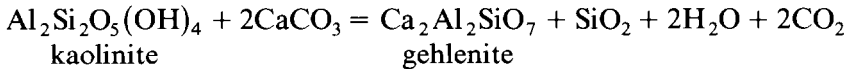
[3] on the catalytic effect of steam on calcite dissociation, of Brindley et al. [4] on the chemisorption of water by metakaolinite, of Heller-Kallai et al. [5] on what appears to be chemical transport of calcite by the water released during kaolinite dehydroxylation, and of Price et al. [6] on the effect of chemisorbed water on calcite dissociation in vacuo. Some time ago, it was also noted by one of the authors (R.C.M.) that the configuration of the calcite peak for artificial mixtures depended on sample packing and possibly on specimen-holder type (unpublished data).

The present investigation was, therefore, designed to assess the factors that influence the DTA curve of kaolinite–calcite mixtures and to determine the reasons for variability. As a first step and to minimize complexity, only one kaolinite sample was used and investigations were performed in a nitrogen or air atmosphere: the effect of varying the kaolinite and the atmosphere will be discussed in later papers of the series.

EXPERIMENTAL

Materials

As Grim et al. [1] had interpreted the curve in terms of gehlenite formation,



mixtures of kaolinite and calcite in the proportions 1.25 : 1, approximately the theoretical for gehlenite, were employed. The kaolinite used was “A1 BP Kaolin”, supplied by English China Clays, Ltd., which is a highly crystalline Cornish kaolinite with about 5% mica as the only impurity. Preliminary tests failed to distinguish between results obtained with a natural calcite and with AnalaR calcium carbonate: consequently, the latter, which was of a smaller particle size and required no grinding, was used throughout. Mixtures were prepared by thoroughly mixing the dry powders and rubbing gently (not grinding) in an agate mortar.

Equipment

The thermal analysis instruments used were:

(1) A Stone Model DTA-200 differential thermal analysis system, supplied by Columbia Scientific Industries, with an SH-8BE specimen holder which permits gas flow through the specimens during the determination and in which the specimens are placed between two porous ceramic discs in a metal block: the thermocouple junctions are in the centres of the specimens.

To prevent displacement of the top ceramic disc during gas flow, a light ceramic lid was placed on top of the whole assembly.

(2) A Stanton-Redcroft Model 673 DTA instrument with "dimpled" platinum specimen holders sitting on top of the thermocouple junctions in a ceramic block provided with a lid.

(3) A Stanton-Redcroft STA 780 simultaneous TG-DTG-DTA instrument with uncovered platinum specimen holders sitting on top of the thermocouples.

(4) A Du Pont Model 900 differential thermal analyser with a 1200°C furnace and uncovered platinum sleeve specimen holders situated on the thermocouple junctions.

(5) A Stanton-Redcroft DSC 1500 instrument with uncovered platinum specimen holders sitting on top of the thermocouples.

For conciseness, these instruments are referred to below as the Stone, 673, STA 780, Du Pont and DSC 1500 instruments, respectively.

Preliminary experiments with the Stone instrument showed that curves obtained with dry air flowing through the sample were indistinguishable from those with dry nitrogen at the same rate and that peak temperatures agreed to within a few degrees Celsius. Accordingly, air and nitrogen were used interchangeably.

Infrared spectra were recorded on a microcomputer-linked PE 580B spectrometer and scanning electron micrographs were obtained on a Cambridge Stereoscan S-4 instrument equipped with an electron probe microanalyser and a Links System energy-dispersive analyser. The starting materials were examined on a Philips 1130/90 X-ray diffractometer using Fe-filtered $\text{Co-K}\alpha$ radiation and X-ray diffraction data for heated samples were kindly provided by Prof. L. Heller-Kallai, The Hebrew University, Jerusalem.

RESULTS

Preliminary

DTA curves for the kaolinite and calcite used showed no anomalies. In the 673 instrument, for example, the kaolinite (Fig. 1, curves A and B) yielded the usual endotherm and exotherm and the calcite, whether alone or diluted with calcined kaolinite (Fig. 1, curves C-F), gave a simple endotherm. Changes in endothermic peak temperatures with changes in experimental conditions agreed with prediction in that removal of specimen holder lid, decrease in packing density and dilution of sample all decreased peak temperature. Changes in peak configuration were also what would have been expected. The kaolinite exotherm was not appreciably affected by experi-

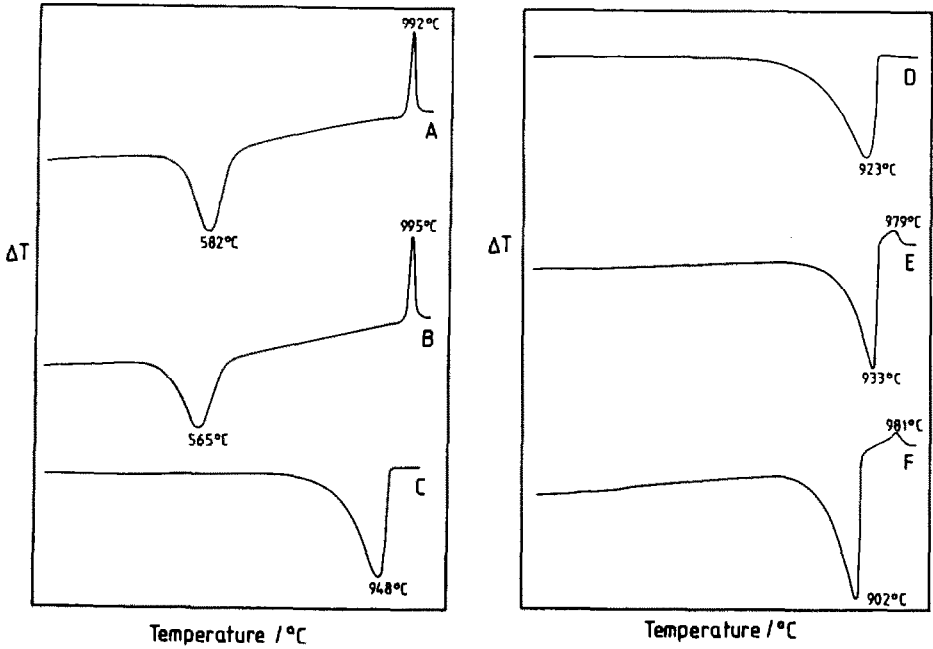


Fig. 1. DTA curves on the 673 instrument, at $10^{\circ}\text{C min}^{-1}$ with N_2 flowing over the sample, for: A, B – kaolinite, hard packed, lid on and lid off, respectively; C, D – AnalaR CaCO_3 , hard packed, lid on and lid off, respectively; E, F – 1.07:1 metakaolinite ($\sim 1000^{\circ}\text{C}$)/ CaCO_3 mixture, lid on, hard packed and loosely packed, respectively.

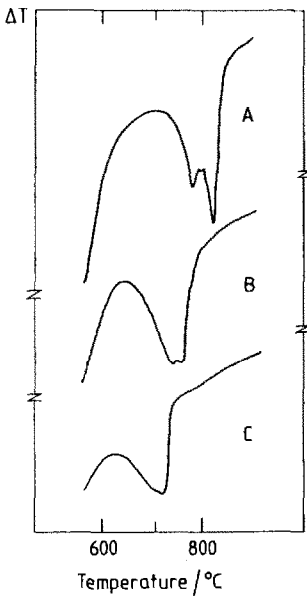


Fig. 2. Calcite region of DTA curves for a 4:1 kaolinite/calcite mixture in the Stone instrument at $14^{\circ}\text{C min}^{-1}$: A – in static air; B, C – with N_2 flowing through the sample at 17 and 35 ml min^{-1} , respectively.

mental conditions, the lower temperatures on curves E and F being mainly due to partial destruction of the exotherm during calcination of the kaolinite at about 1000°C.

As earlier observations of variability had been made with 5:1 or 4:1 mixtures of kaolinite with calcite (the maximum one would expect to find in most soil clays), some experiments were performed with a 4:1 mixture in the Stone instrument with air flowing through the sample at different rates. The strong dependence of the conformation of the calcite peak on rate of air flow (Fig. 2) suggests an association with extent of removal of CO₂ rather than with a solid-state reaction.

Effect of instrumental factors

Kaolinite/calcite 1.25:1 mixtures (the most likely to yield gehlenite) were examined in a variety of instruments under conditions that varied the ease of egress of volatiles. All the curves obtained (Figs. 3 and 4) showed either a two- or a three-peak system (assuming only endotherms are involved) in the calcite region, the latter being the more common. Relative sizes of the peak components varied markedly with apparatus and conditions. The Stone and STA 780 instruments yielded apparently discordant results in that the former produced a three-peak system with a hard-packed sample and a two-peak system with a loosely packed sample (Fig. 3, curves G and H), whereas the latter showed the reverse effect (Fig. 4, curves A and E): there was, however, a difference in experimental conditions in that the Stone curves were both in static air whereas one of the STA 780 was in flowing nitrogen.

The STA 780 curves show a dependence of the configuration of the calcite peak on both packing density and on rate of nitrogen flow (Fig. 4). However, the fact that the weight losses, as measured from the TG curve, were always consistent, within experimental error, with the amounts of H₂O and CO₂ expected indicated that no chemical transport [5] had occurred. Moreover, the exact agreement in shape between the DTA and DTG curves confirms that the effects observed are associated with loss of volatiles and not with solid-state reactions.

Other noteworthy features of the curves in Fig. 3 are the distinctive conformation of the Du Pont curves (curves E and F) and the similarity of curves B, C, D, H and I. Heating rate over a limited range (10–20°C min⁻¹) did not seem to affect the curves appreciably (curves H and I).

Effect of moisture

Two aspects were investigated, namely, the effect of moisture in the atmosphere in and around the sample [3] and the effect of moisture possibly chemisorbed on the metakaolinite [4].

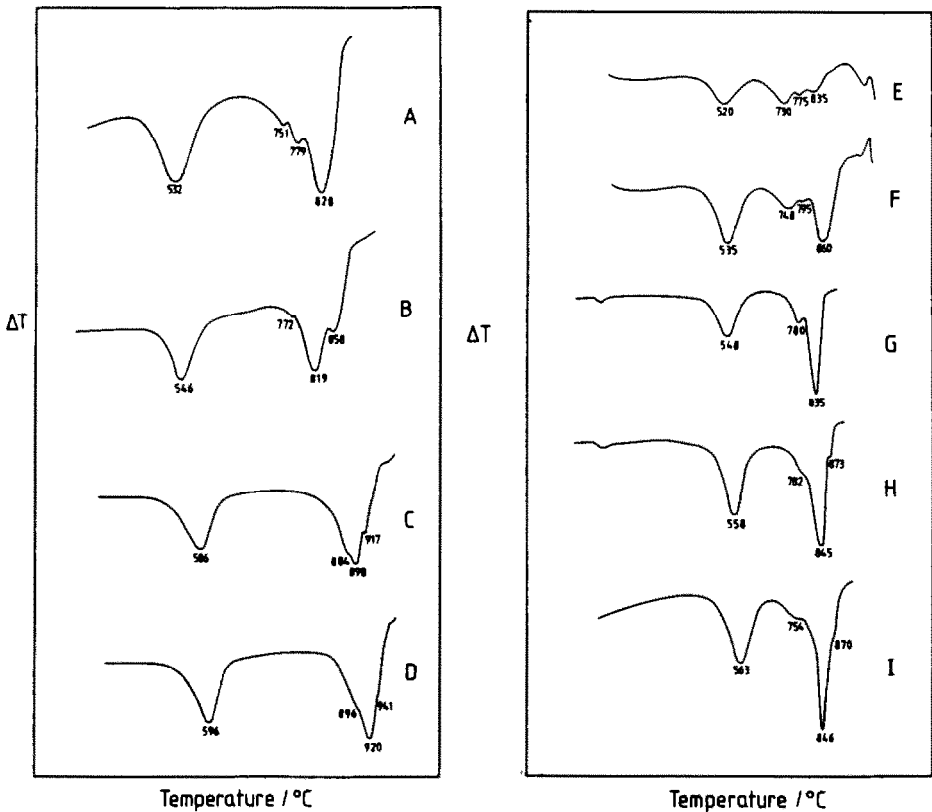


Fig. 3. DTA curves for a 1.25:1 kaolinite/calcite mixture: A, B, C, D – in the 673 instrument with N_2 flowing over sample, loosely packed without lid, loosely packed with lid, hard packed without lid, and hard packed with lid, respectively; E, F – in the Du Pont instrument with N_2 flowing over sample at 200 ml min^{-1} loosely packed and hard packed, respectively; G, H – in the Stone instrument in static air, loosely packed and hard packed, respectively; I – in the DSC 1500 instrument with N_2 flowing over sample, hard packed. Heating rate: A–H, $10^{\circ}\text{C min}^{-1}$; I, $20^{\circ}\text{C min}^{-1}$.

To assess the former, samples were examined in the Stone instrument (a) in static air, (b) with air dried by bubbling through concentrated H_2SO_4 flowing through the sample and (c) with air moistened by bubbling through water at room temperature flowing through the sample. Both dry and moist air through the sample converted the calcite two-peak system in static air into a three-peak system (Fig. 5) with a conformation not dissimilar to those in Fig. 3, curve A and Fig. 4, curve B. With moist air flowing through, the increase in size of the first endothermic component with respect to the others indicates a clear dependence on moisture.

The possible effect of moisture chemisorbed by metakaolinite was checked using samples prepared by heating kaolinite at 600 and 750°C for 30 min. Mixtures with calcite in the proportion 1.07:1 (corresponding to

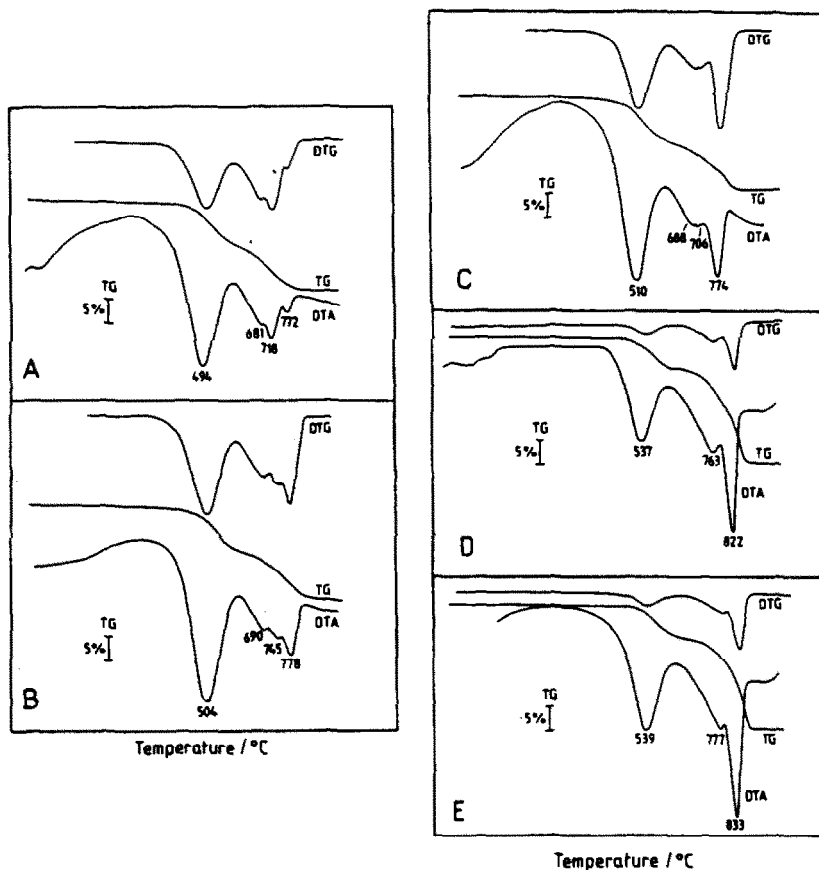


Fig. 4. TG, DTG and DTA curves on the STA 780 instrument at $10^{\circ}\text{C min}^{-1}$ for a 1.25:1 kaolinite/calcite mixture: A – loosely packed with N_2 flowing over sample at 40 ml min^{-1} ; B – lightly packed (under a 5 g weight) with N_2 flowing over sample at 40 ml min^{-1} ; C – hard packed with N_2 flowing over sample at 40 ml min^{-1} ; D – hard packed with N_2 flowing over sample at 12 ml min^{-1} ; E – hard packed in static air.

kaolinite/calcite 1.25:1) were then made up and examined in static air and with dry and moist air flowing through the sample. The mixture with the 600°C material gave a double peak in static air, flowing dry air and flowing moist air (Fig. 6, curves A–C), whereas the mixture with the 750°C material yielded only a simple calcite peak under all conditions tested (Fig. 6, curves D–F). As the 600°C material showed no trace of the kaolinite endotherm, dehydroxylation was complete, yet this material was, as shown by the appearance of the additional peak, to some extent “active” with respect to the calcite. The material calcined at 750°C , like that at 1000°C (Fig. 1), was, however, completely inactive, indicating that strongly adsorbed water, if that is the cause, must be absent from this material.

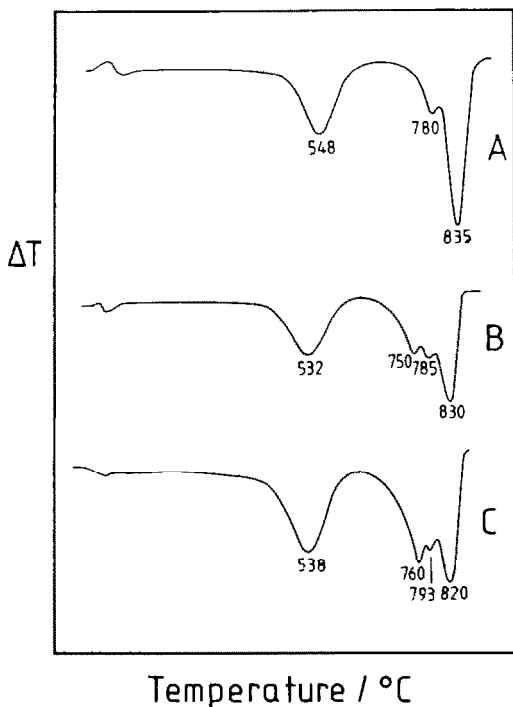


Fig. 5. DTA curves on the Stone instrument at $10^{\circ}\text{C min}^{-1}$ for a 1.25:1 kaolinite/calcite mixture: A – in static air; B – with dry air flowing through sample at 17 ml min^{-1} ; C – with moist air flowing through sample at 17 ml min^{-1} .

Effect of intimacy of mixing

In view of the results obtained by Heller-Kallai et al. [5] with the pyroprobe, where the kaolinite and calcite were physically separated, experiments were performed with the “sandwich-packing” arrangements depicted schematically in Fig. 7. Alumina (Al), the reference material, was used as the inert separating material, the thermocouple junction (TC) also being embedded in this layer. In experiments with static air, the gas entry line to the base of the sample was closed off to prevent gas flow by convection. The variation in the relative sizes of the kaolinite and calcite peaks in Fig. 7 arose from difficulties encountered in replicating the amounts of the three components in every experiment, but the main features are clear. With kaolinite (Ka) at the foot of the sample well and calcite (Ca) at the top, the curve in static air (curve A) shows a calcite peak with what appears to be, from their sharpness, two exotherms (at 848 and 855 $^{\circ}\text{C}$) superposed, a configuration quite distinct from any of the previous three-peak systems. This curve was perfectly reproducible. With dry air flowing through the sample, an additive curve (curve B) with two simple endotherms was

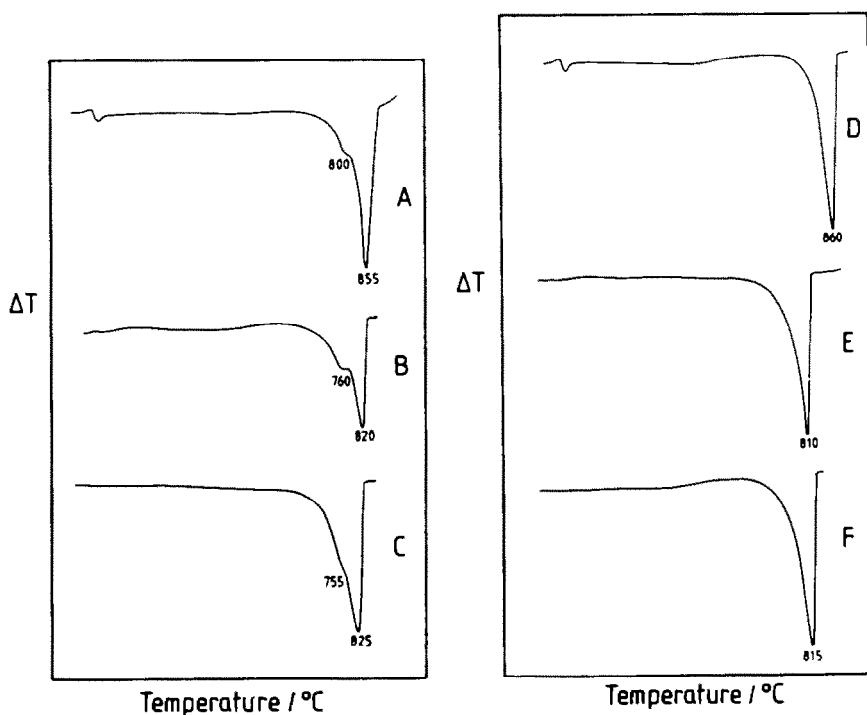


Fig. 6. DTA curves on the Stone instrument at $10^{\circ}\text{C min}^{-1}$ for: A, B, C – 1.07:1 metakaolinite (600°C)/calcite mixture, in static air, with dry air flowing through sample at 12 ml min^{-1} , and with moist air flowing through sample at 15 ml min^{-1} , respectively; D, E, F – 1.07:1 metakaolinite (750°C)/calcite mixture, in static air, with dry air flowing through sample at 15 ml min^{-1} , and with moist air flowing through sample at 17 ml min^{-1} , respectively.

obtained, but with moist air the calcite peak was broadened to lower temperatures (curve C), perhaps by the catalytic effect of moisture [3], although no definite shoulder could be pinpointed. With calcite at the foot of the well and kaolinite on top, no complexity would be expected and this was so for both dry and moist air flowing through the sample (curves E and F). However, the similarity of the curve obtained in static air with that from the previous arrangement with moist air flowing through (curve C) suggests that, in static air, water vapour from the kaolinite dehydroxylation might have diffused down into the calcite to give the broadening effect once the calcite started to dissociate.

A determination made with calcite on top of kaolinite without any separating alumina yielded a curve (Fig. 8, curve A) with a calcite peak that appeared to be a summation of that for the 1.25:1 mixture (Fig. 5, curve A) and that for the sandwich with the intervening alumina (Fig. 7, curve A), both in static air. The first effect may have been due to unavoidable mixing at the boundary (although it is remarkably strong if this be the sole reason) and the second clearly replicates the result with the intervening alumina.

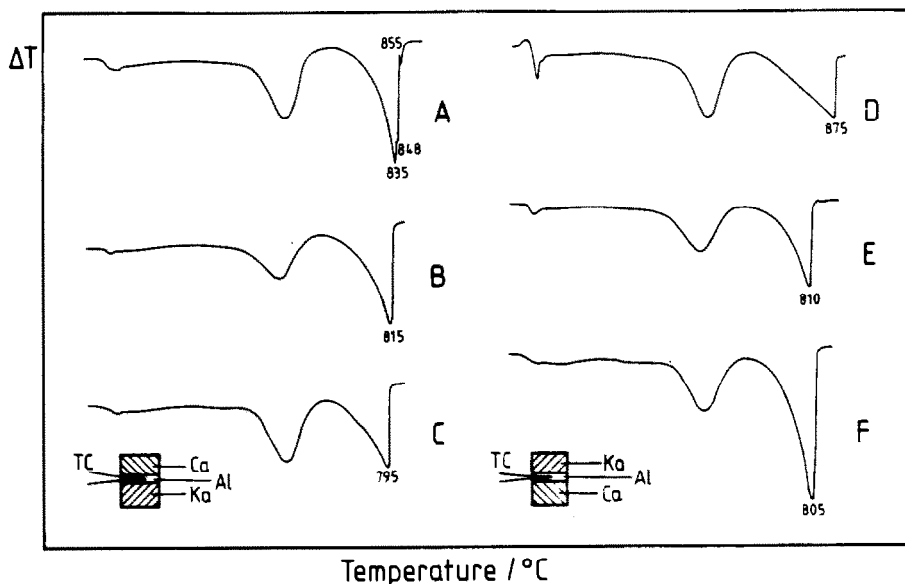


Fig. 7. DTA curves on the Stone instrument at $10^{\circ}\text{C min}^{-1}$ for sample arrangements shown (Ka, kaolinite; Al, alumina; Ca, calcite; TC, thermocouple junctions): A, D – in static air; B, E – with dry air flowing through sample at 15 ml min^{-1} ; C, F – with moist air flowing through sample at 17 ml min^{-1} .

This curve was also replicable. When alumina was used in place of kaolinite, no complexities were observed (Fig. 8, curve B). No reason can presently be advanced for the two apparent “exotherms”, as it was not possible to carry out an X-ray diffraction examination of the samples.

To go to the other extreme and increase the intimacy of mixing, a 1.25 : 1 kaolinite/calcite mixture was prepared by wet mixing. The curve obtained with dry nitrogen flowing through the sample (Fig. 8, curve C) was quite different from that obtained with the dry mix (Fig. 5, curve B) but resembled that for a hard-packed sample in static air (Fig. 3, curve H), suggesting that a closer association of the kaolinite and calcite particles had indeed been attained. However, the central component of the three-peak system had a very rough outline (replicates showed the same effect, although individual “spikes” could not be reproduced), the origin of which is uncertain. Passage of moist nitrogen through the sample gave a smooth curve (Fig. 8, curve D) with a double peak system unlike that on any previous except possibly that for the 4 : 1 mix with rapid gas flow through the sample (Fig. 2, curve C). It would appear again, however, that moisture has enhanced the first component.

From these results, it is clear that the type of curve obtained is dependent on the intimacy of association of kaolinite and calcite particles in the sample.

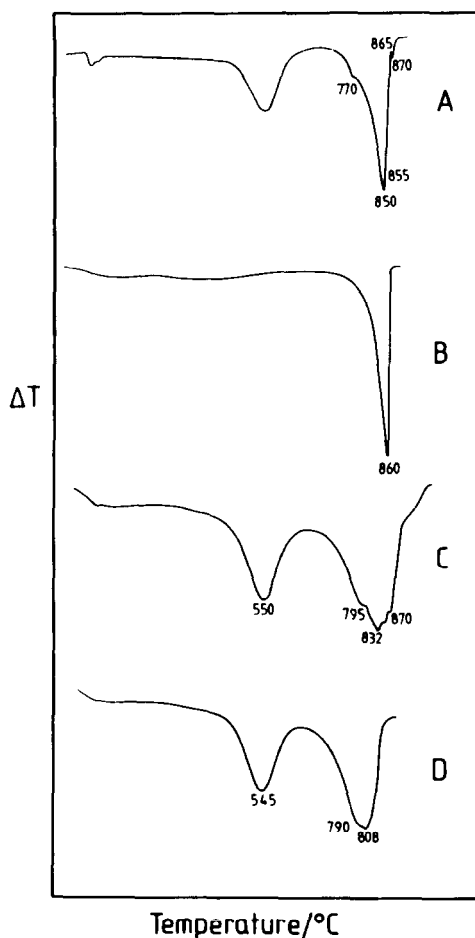


Fig. 8. DTA curves on the Stone instrument at $10^{\circ}\text{C min}^{-1}$ for: A – calcite above kaolinite without intervening alumina, in static air; B – calcite above alumina, in static air; C, D – wet-mixed 1.25:1 kaolinite/calcite mixture with dry N_2 flowing through sample at 12 ml min^{-1} and with moist N_2 flowing through sample at 12 ml min^{-1} , respectively.

Effect of particle size

The kaolinite was separated at about $4\ \mu\text{m}$ equivalent spherical diameter into two fractions and 1.25:1 mixtures were made up with each fraction. DTA curves for the coarse fraction (Fig. 9, curves A–C) were reminiscent of those for mixtures with the original kaolinite (Fig. 5) apart from a slight broadening of the peaks. The fine fraction, however, gave somewhat different results (Fig. 9, curves D–F), showing a three-peak system even in static air. As usual, peak resolution was improved with dry nitrogen flowing through the sample and the first component of the complex peak was enhanced with moist gas. Clearly, particle size exercises some effect but this

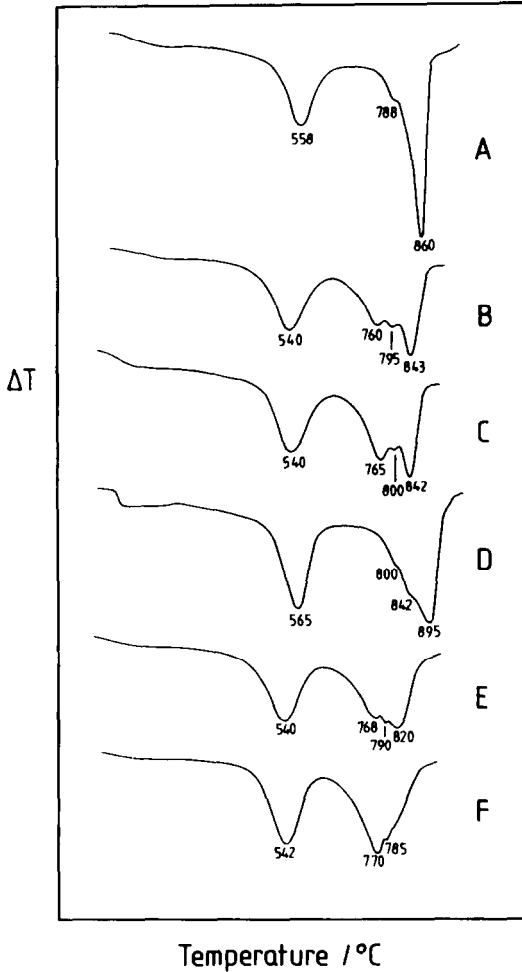


Fig. 9. DTA curves on the Stone instrument at $10^{\circ}\text{C min}^{-1}$ for: A, B, C – 1.25:1 kaolinite ($> 4 \mu\text{m}$)/calcite mixture, in static air, with dry N_2 flowing through sample at 12 ml min^{-1} , and with moist N_2 flowing through sample at 12 ml min^{-1} , respectively; D, E, F – 1.25:1 kaolinite ($< 4 \mu\text{m}$)/calcite mixture, in static air, with dry N_2 flowing through sample at 12 ml min^{-1} , and with moist N_2 flowing through sample at 12 ml min^{-1} , respectively.

could be associated with specific surface area rather than particle size, per se.

Evolved gas analysis

As the above results give no information on the nature of the volatiles evolved, an opportunity was taken of having some samples examined on the Stanton-Redcroft STA-MS equipment. The results, while confirming that the conformation of the peak in the calcite region depended on packing

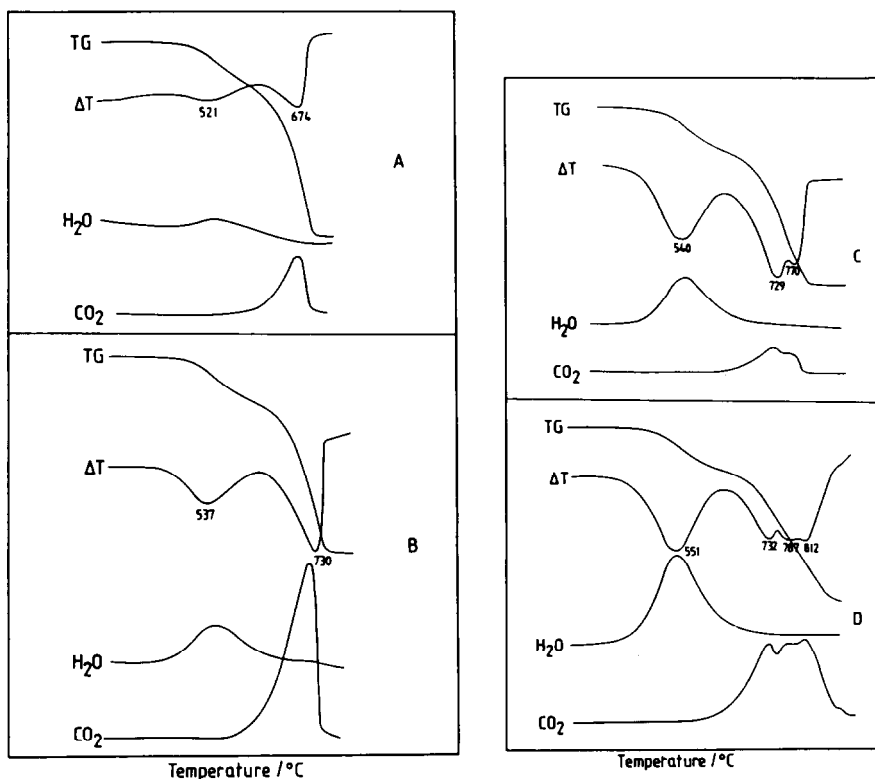


Fig. 10. Curves obtained on the STA-MS instrument at $15^{\circ}\text{C min}^{-1}$ with N_2 flowing over sample at 50 ml min^{-1} for loosely packed 1.25:1 kaolinite/calcite mixture: A – 4 mg sample; B – 9.5 mg sample; C – 19 mg sample; D – 39 mg sample.

density, revealed that only CO_2 was evolved in this region and that the pattern of evolution slavishly followed the shape of the DTA curve, thus confirming the absence of exotherms (Fig. 10D). The absence of detectable moisture in this region does not necessarily refute the involvement of water in the mechanism, as the water from the kaolinite dehydroxylation may have affected the system prior to the development of the calcite peak, chemisorbed moisture may have been retained to higher temperatures, or sorbed moisture may have been released so slowly that the amounts were below the limits of detection. The fact that CO_2 evolution commenced before dehydroxylation was complete is in accord with infrared evidence (see below).

The most striking evidence from these experiments, however, was the influence of sample size. For loosely packed (tapped) samples, no complexity developed on the calcite peak below about 9.5 mg (Fig. 10A and B); at this point a slight break in regularity is just observable and complexity increases through 19 to 39 mg samples (Fig. 10C and D). Although this could, a priori, be ascribed to decreasing ease of egress of CO_2 with larger

sample sizes, the difficulty of simplifying peak shape by flowing gas rapidly through the sample (Fig. 2) suggests it may well be a separate effect.

X-ray diffraction

The only detectable impurity in the original kaolinite was mica at about 5%. Examination of the two particle-size fractions showed mica to be present in both but to be somewhat concentrated in the coarse fraction. Amounts were difficult to assess, but if the original had 5% mica, the coarse probably contained about 7% and the fine about 3%.

X-ray diffraction examination of a sample heated to almost the end of the complex calcite peak in the STA 780 instrument and then quenched showed the presence of CaO, Ca(OH)₂, vaterite and a trace of calcite, the Ca(OH)₂ and CaCO₃ phases having formed between the time of sampling and examination (about 2 weeks). No calcium silicates were detected. Several other samples from the 673 and STA 780 instruments, taken after commencement of the kaolinite exotherm, showed the presence of gehlenite and possibly anorthite, although no exotherms associated with such neoformations were observed. Presumably, either these phases formed so slowly that no exotherms developed or the heat involved in their formation was occluded in the kaolinite exotherm. The silicate phases formed under various conditions and the recarbonation of some samples to vaterite rather than to calcite are matters of considerable interest but are outside the scope of the present study. Their immediate relevance is their confirmation of the fact that the complexity of the calcite peak is not due to the superposition of exotherms and that such calcium silicates as are formed appear at higher temperatures.

Infrared absorption spectrometry

Examination of the metakaolinite samples prepared at 600 and 750°C showed that both contained OH groups, most likely associated with the mica component, and that the amounts differed little, if at all: differences in behaviour are therefore unlikely to be due to the mica impurity. A sample of the 1.25:1 mixture heated in the Stone instrument until the end of the kaolinite endotherm (point a, Fig. 11) with dry nitrogen passing through and then quenched showed the presence of CaO, as Ca(OH)₂, in agreement with the EGA results. The possibility of CO₂ adsorption by metakaolinite as an explanation for the complex peak was tested by heating a sample to well before the largest component of the calcite peak in the Stone instrument, quenching and examining within an hour by infrared spectrometry. The result was inconclusive: although no adsorbed CO₂ could be detected, any that might have been present could have been lost during quenching, sample transference and sample preparation.

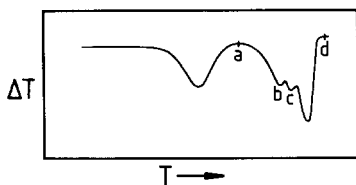


Fig. 11. Formalized DTA curve showing sampling points.

Scanning electron microscopy

In addition to the original mixture, samples heated in the Stone instrument, with dry nitrogen flowing through the sample, to the points a, b, c and d, Fig. 11, and then quenched were examined. Samples were dusted on to an adhesive surface on a sample stub, loose material gently blown off and a 20 nm gold coating applied before examination. Interest was concentrated on the behaviour of the calcite particles, which generally appeared somewhat larger than the kaolinite particles. The original mixture showed calcite particles with characteristic shapes (Fig. 12A) and sharp edges with a certain amount of adhering material that is presumably kaolinite. On heating to point a, Fig. 11, the sharpness of the edges, and particularly of the corners, of the calcite crystals had decreased (Fig. 12B), indicating that some dissociation had occurred—an observation in agreement with infrared and EGA evidence. By point b, Fig. 11, the calcite crystals had developed very rounded edges (Fig. 12C) and by point c they showed the wavy surface (Fig. 12D) characteristic of particles partially decomposed by heating in a furnace in air [5]. At point d, Fig. 11, extremely fragmented pseudomorphs of lime after calcite can be recognized. A sample heated to point b, Fig. 11, with moist nitrogen flowing through seemed to show rather less “blunting” of the edges and corners (Fig. 12F) than the corresponding sample with dry nitrogen through (Fig. 12C) and a sample of the 1.07 : 1 750 °C metakaolinite/calcite mixture (that giving curve E, Fig. 6) heated to the temperature of point b, Fig. 11, with dry nitrogen through, showed even less blunting of the corners and edges. Sintering, as observed in CO₂ [7], and the characteristic appearance of samples from the pyroprobe [5] were nowhere apparent. One interesting observation was that the amount of kaolinite, or metakaolinite, adhering to the calcite crystals appeared to increase as dissociation proceeded: whether this is so or reflects field selection cannot at present be decided. Examination of the samples giving Fig. 12C–E by infrared absorption spectrometry showed the usual mixture of Ca(OH)₂, CaCO₃ and metakaolinite but no new phases.

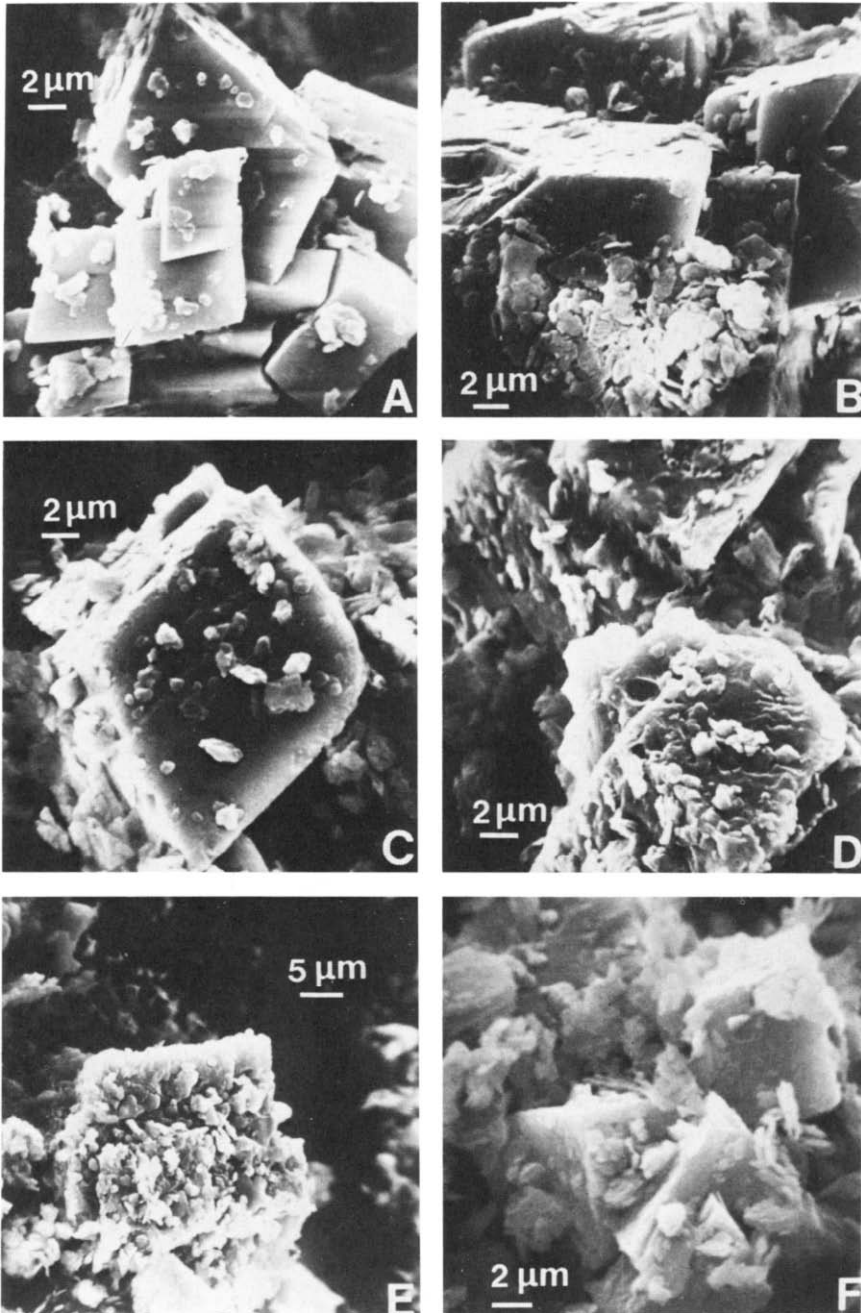


Fig. 12. Scanning electron micrographs of 1.25:1 kaolinite/calcite mixture: A–E – before heating and after heating to points a, b, c, d, Fig. 11, respectively, in the Stone instrument with dry N_2 flowing through sample; F – after heating to point b with moist N_2 flowing through sample.

DISCUSSION

The above results clearly indicate that the complex calcite endotherm is not due to the occurrence of solid-state reactions and that the manner in which calcite apparently decomposes in kaolinite/calcite mixtures in air or nitrogen depends on (a) ease of egress of CO_2 , (b) the presence or absence of water vapour, (c) intimacy of mixing, (d) particle size and (e) sample size, at least for the particular kaolinite used in this study. The effects of instrumentation (Figs. 3 and 4) can probably be explained by combination of these factors. Examination at appropriate points by non-thermoanalytical techniques threw little light on the mechanism.

As the typical curve in Fig. 11 was obtained with gas flowing through the sample, the multi-peak calcite endotherm cannot be explained on the basis of occasional slight suppression of CO_2 evolution by high CO_2 partial pressure in the sample pores. An explanation on the basis of the effect of moisture on the calcite itself [6] is also untenable, being inconsistent with many of the above results, especially the absence of complexity for mixtures with metakaolinite prepared at 750°C and above, even with moist gas through the sample. Some other explanation must therefore be sought.

One mechanism that appears to explain most, if not all, of the results involves adsorption and desorption of CO_2 by metakaolinite. Thus, for the curve in Fig. 11, some CO_2 could be adsorbed during the period from start of evolution to somewhere between points a and b (a period of at least 10 min) so slowly that no exotherm develops. Some of this CO_2 , possibly, in view of the effect of moist gas, that associated in some way with water chemisorbed on the metakaolinite [4], is then desorbed endothermally to give peak b. A subsequent portion, perhaps associated with other active sites on the metakaolinite (as the presence of moisture has little effect) or as a different species of CO_2 , is evolved to give peak c. The calcite itself is also dissociating over this range and yields the final large peak.

At first sight, this explanation suffers from the obvious objection that gas flow through the sample should remove the CO_2 immediately it is formed. However, the scanning electron micrographs showed that the calcite particles had kaolinite, or, at this temperature, metakaolinite, particles so closely associated that CO_2 from the surface could well be adsorbed before it is removed by the flowing gas. Moreover, the CO_2 generated at the base of the sample has to traverse some 6 mm of sample before escaping to the atmosphere and some could, even if diluted by carrier gas, be adsorbed during transfer. There is some evidence that both mechanisms may be operative. Thus, the absence of complexity when the kaolinite and calcite were separated by alumina and gas flowed through the sample (Fig. 7), as well as the results for the wet-mixed sample (Fig. 8), lend support to the first, whereas dependence of peak complexity on sample size (Fig. 10), i.e. thickness, tends to give credence to the second. Differences in the relative

sizes of the various peaks could then be associated with variations in the amounts or species of CO₂ adsorbed on possible sites with retention time and/or partial pressure of CO₂ in the sample. Indications are that with high partial pressures and thick samples desorption from one site, or of one species, is delayed until after the dissociation of the bulk material (Fig. 3). The effects of particle size are fully consistent with differences in specific surface areas. This suggested mechanism raises the question as to whether the CO₂ and CO obtained by Garn and Anthony [8] during early stages of dehydroxylation of kaolinite arose from the presence of strongly sorbed species. Moreover, evidence for the adsorption of CO₂ by metakaolinite treated with NaCl has recently been published [9].

The absence of any complexity for mixtures containing metakaolinite prepared at 750 °C and above would indicate the absence on this material of active sites for adsorption, whereas the presence of only one additional peak on the curves for mixtures with the metakaolinite prepared at 600 °C (Fig. 6) suggests that one active site is absent. One would expect this to be the site giving rise to peak b in Fig. 11, although the temperature of the additional peak and its susceptibility to moisture would indicate that it is in fact that giving rise to peak c. In any event, it must be remembered that metakaolinite prepared by heating for 30 min at 600 and 750 °C could have a vastly different type of surface from that of samples brought to and through these temperatures at 10 °C min⁻¹ in a DTA instrument.

Although it therefore appears that the present results can be explained on the basis of a CO₂ adsorption-desorption phenomenon, it must be stressed that this is only a hypothesis that must await confirmation or otherwise. The probable reason for the results obtained by Grim et al. [1] will be considered in a later paper of this series.

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Prof. L. Heller-Kallai, The Hebrew University, Jerusalem, for X-ray diffraction studies, information and comment, to Drs. J.D. Russell, W.J. McHardy and M.J. Wilson and Mr. E. Paterson, The Macaulay Institute for Soil Research, for infrared, electron-optical, X-ray and Du Pont DTA data, to Mr. S.B. Warrington, Stanton Redcroft Consultancy Service, London, for the STA-MS determinations, and to Miss H.M. Moir, Department of Soil Science, University of Aberdeen, for technical assistance.

REFERENCES

- 1 R.E. Grim, J.S. Machin and W.F. Bradley, Illinois State Geol. Surv. Bull. No. 69 (1945) 77 pp.

- 2 D.H. French and S.St.J. Warne, *Thermochim. Acta*, 84 (1985) 197.
- 3 W.H. MacIntire and T.B. Stansel, *Ind. Eng. Chem.*, 45 (1953) 1548.
- 4 G.W. Brindley, J.H. Sharp, J.H. Patterson and B.N. Nakahari, *Am. Mineral.*, 52 (1967) 201.
- 5 L. Heller-Kallai, I. Miloslavski and Z. Aizenshtat, *Naturwissenschaften*, 73 (1986) 615.
- 6 D. Price, V. Fatami, D. Dollimore and R. Whitehead, *Thermochim. Acta*, 94 (1985) 313.
- 7 M. Maciejewski and H.R. Oswald, *Thermochim. Acta*, 85 (1985) 39.
- 8 P.D. Garn and G.D. Anthony, *J. Therm. Anal.*, 1 (1969) 29.
- 9 M. Gabor, L. Pöpl and E. Körös, *Clays Clay Miner.*, 34 (1986) 529.