

INTERACTION OF KAOLINITE WITH CALCITE ON HEATING. II. MIXTURES WITH ONE KAOLINITE IN CARBON DIOXIDE

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ABSTRACT

The calcite endotherm on differential thermal analysis curves for kaolinite–calcite mixtures in a carbon dioxide atmosphere was affected by the ratio of kaolinite to calcite, the rate of CO₂ flow through the sample, the intimacy of particle association (sample packing) and, in some instances, heating rate. Unlike determinations in air or nitrogen, solid-state reactions affected the peak at the higher temperatures of dissociation induced by a CO₂ atmosphere. At least some of the effects observed could be due to the action of complex volatiles evolved during the dehydroxylation of kaolinite.

INTRODUCTION

The configuration of the calcite endotherm on DTA curves for mixtures of a Cornish kaolinite and calcite in a nitrogen or air atmosphere has already been shown to depend markedly on experimental conditions [1]. However, as the use of a carbon dioxide atmosphere is usually recommended for the determination of carbonates [2,3], some experiments were also carried out in this medium. The results were rather more complex than envisaged, even allowing for the possibility of solid-state reactions occurring at the higher dissociation temperatures induced by the presence of CO₂.

EXPERIMENTAL

Materials

The kaolinite and calcite used were again [1] “A1 BP Kaolin” from Cornwall, Gt. Britain, and AnalaR calcium carbonate containing rhombs with edge lengths of 3–12 μm . Mixtures with kaolinite:calcite ratios of 1.25:1 and 4:1 were prepared by dry mixing, the 1.25:1 mixture representing the optimum for gehlenite formation and the 4:1 mixture the maximum amount of calcite likely normally to occur in natural samples.

Equipment

The Stone Model DTA-200, Stanton-Redcroft Model 673 and Stanton-Redcroft STA 780 instruments [1] were again used. Infrared absorption and X-ray diffraction data were kindly supplied by Dr. J.D. Russell and Prof. L. Heller-Kallai, respectively.

RESULTS

1.25 : 1 Kaolinite / calcite mixtures

With CO₂ flowing through the sample at $\sim 15 \text{ ml min}^{-1}$ at atmospheric pressure in the Stone apparatus, the usual effects [4] were observed (curve B of Fig. 1); namely, an abrupt start to the calcite endotherm and a narrower peak at a higher temperature than is obtained with air or nitrogen. Moreover, the peak was no longer multiple (see fig. 5 of ref. 1) but was a simple peak proceeding directly into the exotherm, or possibly truncated by it. The

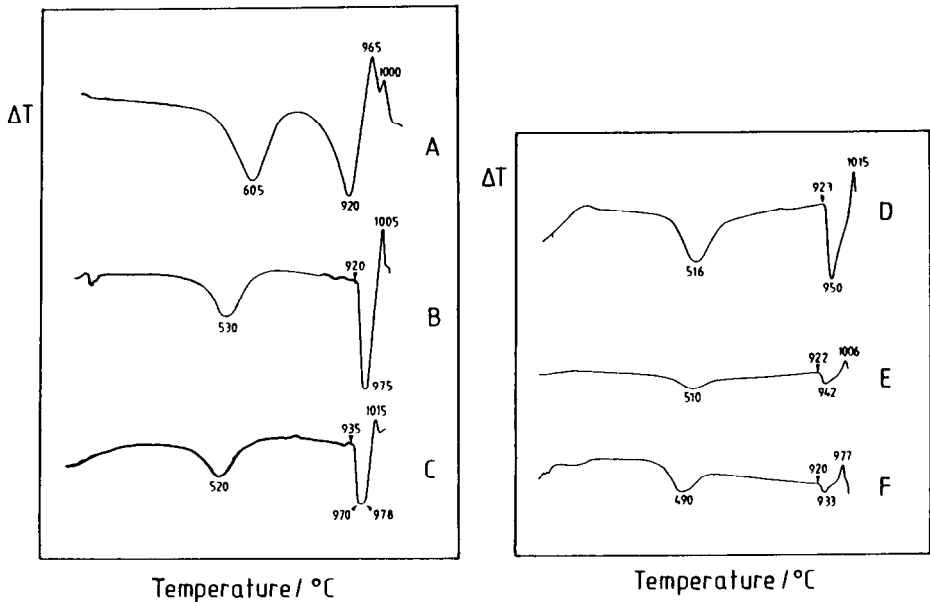


Fig. 1. DTA curves for kaolinite/calcite mixtures: A, that of Grim et al. [5] with the ordinate greatly foreshortened to facilitate comparison; B,C for a 1.25:1 mixture in the Stone instrument at $10^\circ \text{C min}^{-1}$ with CO₂ flowing through the sample at ~ 15 and $\sim 35 \text{ ml min}^{-1}$, respectively; D,E,F, for a 1.25:1 mixture sandwich-packed in the Stone instrument with CO₂ flowing through the sample at $\sim 15 \text{ ml min}^{-1}$ at 14, 10 and $5^\circ \text{C min}^{-1}$, respectively.

peak obtained by Grim et al. [5] for a somewhat similar mixture in a static air atmosphere (curve A of Fig. 1) shows the same continuation from endotherm tip to exotherm and a fairly high peak temperature but also reveals the long lead-in typical of curves obtained in air. It would appear therefore, that with the large samples then in use, the dissociation of calcite proceeded as if in a CO_2 atmosphere [6] once the sample pores were filled with CO_2 . Increase of the CO_2 flow rate through the sample in the Stone instrument to $\sim 35 \text{ ml min}^{-1}$ (curve C of Fig. 1) caused the calcite endotherm not only to start at a slightly higher temperature, as would be expected, but also to appear as a doublet and to become somewhat smaller with respect to the kaolinite endotherm (characteristics suggestive of superposition of an exotherm). X-ray diffraction examination of the samples giving curves B and C after the determination showed the presence of CaO, calcite, gehlenite and larnite in both, the calcite having formed between removal from the DTA apparatus and X-ray diffraction examination [1].

Small samples of this mixture, "sandwich-packed" around the thermocouple junction in the Stone instrument between two layers of the alumina used as reference material, yielded curves showing a marked dependence of calcite peak area on heating rate (curves D–F of Fig. 1). Because of variations caused by differences in sample size and by collating the temperature scales, comparisons are only possible by assessing the relative sizes of the calcite and kaolinite endotherms on each curve. On this basis, the decrease in peak area with decrease in heating rate in curves D–F is clearly visible, as is the great reduction in size of the calcite peak for a small sample (curve E) compared with that for a large sample (curve B) at the same gas-flow and heating rates. Even at $14^\circ \text{C min}^{-1}$, where the calcite peak is largest for the small samples (curve D), its size is much smaller than would have been expected from curve B and its shape suggests the superposition of an exotherm. At $5^\circ \text{C min}^{-1}$ where the calcite peak has almost disappeared (curve F), the latter part of the curve is reminiscent of that obtained by French and Warne [7] for an oil shale containing appreciable calcite in a CO_2 atmosphere, but here the effect cannot be due to calcite–organic matter interaction. Irrespective of size, the calcite peaks on curves D–F all start sharply at about the same temperature (920°C) as that for the large sample at the same flow rate (curve B), indicating the same environment for the calcite particles in relation to CO_2 .

In the 673 instrument, with CO_2 flowing over a covered sample holder containing a loosely packed sample, the kaolinite yielded a normal curve with no peculiarities (curve A of Fig. 2). The calcite, diluted 4:1 with kaolinite precalcined at $\sim 1000^\circ \text{C}$ and examined under the same conditions, also gave the type of curve expected in CO_2 (curve E of Fig. 2) [6]. For a 1.25:1 kaolinite/calcite mixture under the same experimental conditions, however, the peak in the calcite region (curve B of Fig. 2), while still showing an abrupt start, appeared as a doublet considerably broader than would

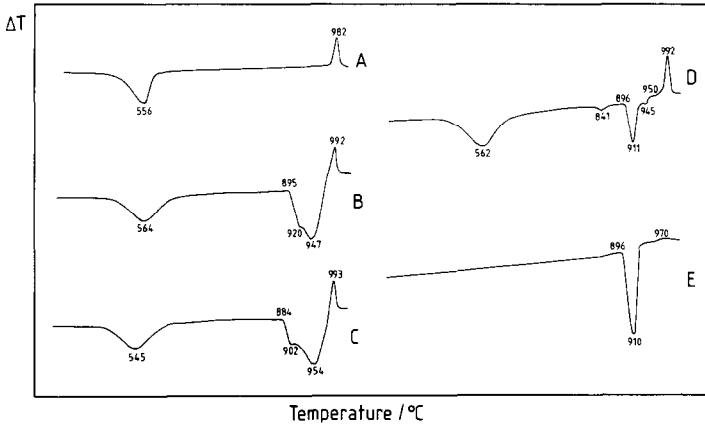


Fig. 2. DTA curves on the 673 instrument at $10^{\circ}\text{C min}^{-1}$ with CO_2 flowing over loosely packed samples: A, for kaolinite, with lid; B,C, for a 1.25:1 kaolinite/calcite mixture, with lid and without lid, respectively; D, for a 4:1 kaolinite/calcite mixture, with lid; E, for a 4:1 metakaolinite ($\sim 1000^{\circ}\text{C}$)/calcite mixture, with lid.

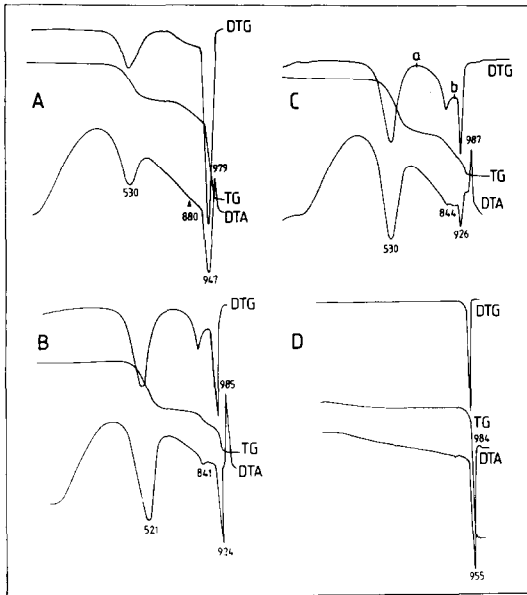


Fig. 3. TG—DTG—DTA curves at $10^{\circ}\text{C min}^{-1}$ with CO_2 flowing over the sample at $\sim 40\text{ ml min}^{-1}$ for: A, 1.25:1 kaolinite/calcite mixture, loosely packed; B,C, 4:1 kaolinite/calcite mixture, loosely packed and hard packed, respectively; D, 4:1 metakaolinite ($\sim 1000^{\circ}\text{C}$)/calcite mixture, loosely packed. Curves A—C determined on the STA 780 instrument, curve D on the STA 781 instrument with computerized output.

have been expected from curve E. Clearly, therefore, even in a CO₂ atmosphere, the dissociation of calcite is affected by the dehydroxylation of kaolinite. With an uncovered specimen holder under the same conditions, dissociation, as might have been expected, started at a slightly lower temperature (curve C of Fig. 2), but the doubling was even more pronounced and the peak was somewhat wider. Despite the difference in shape, however, the calcite : kaolinite endotherm area ratios were sensibly the same on curves B and C (1.90 and 1.85, respectively).

In the STA 780 instrument, the DTA curve for the mixture, when loosely packed with CO₂ flowing over the sample, showed a shoulder on the low-temperature limb of the calcite peak, this shoulder being rather better expressed on the DTG curve (Fig. 3A). With a hard packed sample, the shoulder, although still present, was rather less well expressed on both the DTA and DTG curves and the main calcite endotherm, at 942°C, was very sharp, apparently being truncated by an exotherm peaking at 980°C, just before the main exotherm at 994°C. Because of the shoulder, neither curve showed an abrupt start to the calcite peak.

4:1 Kaolinite / calcite mixture

In the Stone instrument, samples “sandwich-packed” around the thermocouple junction between two layers of alumina, and examined at 10 and 14°C min⁻¹ and at similar CO₂-flow rates, yielded very similar curves (Fig. 4). Both showed a sharp calcite endotherm with an abrupt start, the start and peak temperatures being slightly higher, as would be expected, at the higher heating rate: the calcite : kaolinite endotherm area ratios were essentially the same at 0.27 and 0.28, respectively, in contrast to the results for the 1.25:1 mixture (curves D–F of Fig. 1). In addition to the kaolinite and

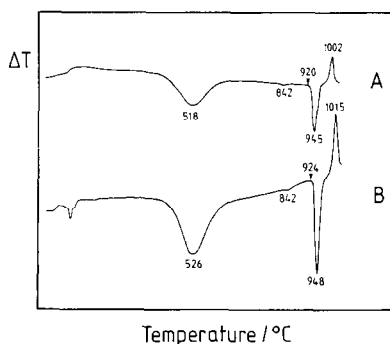


Fig. 4. DTA curves for a 4:1 kaolinite/calcite mixture sandwich-packed in the Stone instrument with CO₂ flowing through the sample at ~15 ml min⁻¹: A, B, at 10 and 14°C min⁻¹, respectively.

calcite endotherms, however, there was observed on both curves in Fig. 4 a tiny endotherm at 842°C that also appeared on curves obtained on both the 673 and STA 780 instruments (curve D of Fig. 2; Fig. 3B,C). The surprising consistency of peak temperature (841–844°C) for three instruments of such widely different characteristics suggests association with a phase transition or something similar. On the other hand, its clear connection with a sharp mass loss at the same temperature on the DTG curve (Fig. 3B,C) would indicate that it represents a stage of dissociation. Samples heated to points a and b on the curve in Fig. 3C and cooled in CO₂ yielded typical infrared bands for calcite at point a but a different set of bands that might be interpreted as a bicarbonate or a basic carbonate artifact at point b, whereas X-ray diffraction revealed calcite as the only crystalline species in both, although a minor component might have been missed because of the small amount of sample available. As heating and cooling experiments in the 673 instrument tend to confirm that the 842°C endotherm is not directly associated with calcite dissociation, the coincidence of the DTA and DTG peaks on the curves in Fig. 3B,C may be fortuitous. The exact nature of this peak is under further investigation.

In the 673 instrument, the main calcite region (curve D of Fig. 2) shows a simple peak starting abruptly at 896°C and followed by an endothermic–exothermic “step” at 945–950°C before the main exotherm at 992°C. Comparison with the sharp simple calcite peak on the curve for a 4:1 mixture of kaolinite precalcined at ~1000°C with calcite (curve E of Fig. 2), determined with a similar sample size at the same sensitivity, suggests that the peak system on curve D must represent an endotherm starting at 896°C and finishing at 950°C with a broad exotherm, caused by a relatively slow solid-state reaction peaking at ~935°C, superposed.

In the STA 780 instrument, the 4:1 mixture, whether loosely or tightly packed (Fig. 3B,C), yielded distinct double DTG and DTA peaks in the calcite region, but the size of the main DTA calcite peak decreased the harder the packing. This is consistent with the occurrence of a more pronounced solid-state reaction the more intimate the mixture. If, as suggested above, the small 842°C endotherm is not directly related to the DTG peak at about the same temperature, the first stage of mass loss must be represented by the broad shoulder on the low-temperature side of the main calcite endotherm. However this may be, the start of calcite dissociation never seems so abrupt on the STA 780 instrument as on the other two instruments, suggesting incomplete removal of air from the sample by CO₂. The curves for the 4:1 metakaolinite (~1000°C)/calcite mixture obtained on a STA 781 instrument with computerized output (Fig. 3D), like that on the 673 (curve E of Fig. 2), shows a single sharp peak but, again, the start is not so abrupt. The small exotherm on both curve E of Fig. 2 and Fig. 3D after the calcite peak indicates incomplete destruction of the kaolinite exotherm during the precalcination [1].

DISCUSSION

It was originally envisaged that the complexities observed on the DTA curves for kaolinite–calcite mixtures in nitrogen or air [1] would be greatly reduced, or even eliminated, in a CO_2 atmosphere because (a) the higher temperature of calcite dissociation would ensure that decarbonation would not overlap with kaolinite dehydroxylation and the complex volatiles then evolved [8,9] (referred to below, for consistency, as ‘kaolinite volatiles’) would be less likely to interfere [10]; (b) at the higher temperature, the metakaolinite surface would be likely to be less reactive; (c) the curve obtained by Grim et al. [5] (curve A of Fig. 1) was relatively simple and, during the latter part at least, the atmosphere inside the sample was likely to be CO_2 . It was also appreciated that the higher dissociation temperature induced by CO_2 might lead to more ready solid-state reaction between freshly-formed CaO and metakaolinite.

For the Stone instrument, at least, these anticipations appeared justified, as all peaks in the calcite region (Figs. 1 and 4), apart from the small 842°C endotherm which is under further investigation, could be explained in terms of endotherm–exotherm superposition. Thus, the calcite endotherm on curve B of Fig. 1 may well be slightly truncated by the commencement of a solid-state reaction exotherm and, as noted above, the peak on curve C appears to be doubled at the tip by superposition of an exotherm. The change in peak conformation with faster gas flow was unexpected but could possibly be due to earlier complete removal of traces of kaolinite volatiles sorbed on the metakaolinite surface, thus permitting earlier reaction. Alternatively, as some particles of sample were often found on top of the specimen holder below the lid after determinations at fast flow rates, it is possible that particles moved around within the sample and that collisions caused earlier reaction. The marked decrease in the calcite : kaolinite endotherm area ratios with decrease in heating rate for thin “sandwich-packed” samples (curves D–F of Fig. 1) could also be explained by the occurrence of a slow solid-state reaction between the CaO being formed and the metakaolinite, provided the rate of this reaction was independent of heating rate. This would lead to virtual cancellation of the endotherm at slow heating rates but to an increase in its size (as well as in that of the final exotherm) as the heating rate increased: precisely the pattern observed. The fact that the “sandwich-packed” 4 : 1 mixture yielded calcite endotherms of a size apparently independent of heating rate (Fig. 4) may, in some way, be connected with the 1.25 : 1 mixture possessing the exact proportions for gehlenite formation; it is, for example, noteworthy that the two mixtures generally behaved differently. The small size of the “sandwich-packed” samples and the inevitable mixture with alumina precluded X-ray diffraction examination after heating. There is also, however, a marked discrepancy between the curves for the 1.25 : 1 mixture determined on the Stone instru-

ment with a full sample holder and with a thin layer (curves B and E of Fig. 1) at the same heating and gas-flow rates. One possible explanation is that CO_2 flow through the sample completely removed sorbed kaolinite volatiles from the metakaolinite surface in the thin sample, thus enabling readier reaction with CaO , whereas such removal from the thick sample was incomplete. Although this postulate tends to be supported by the effects of rapid gas flow (curve C of Fig. 1), the absence of such an effect for the 4:1 mixture in thin-layer form (Fig. 4) must raise some doubt and the discrepancy may in some way be related to the temperature gradients and heat-transfer effects inevitable in a thick sample. Unfortunately, large samples of the 4:1 mixture were not examined with CO_2 flowing through the sample in the Stone instrument and this equipment is no longer available to the authors.

Despite some difficulties in correlation, all individual curves determined on the Stone instrument can thus be interpreted in terms of superposition of solid-state reaction exotherms on the calcite endotherm. Moreover, the absence of the complexities observed in a nitrogen or air atmosphere [1,10] strongly suggests that the passage of CO_2 through the sample completely removed the kaolinite volatiles before the calcite started to dissociate. Some of the volatiles might, however, remain sorbed on particle surfaces, thus affecting reactivity.

This relatively simple picture no longer holds when CO_2 merely flows over the sample. Thus, the DTG and DTA curves from the STA 780 instrument (Fig. 3A–C) indicate two distinct stages of calcite dissociation and this is confirmed by quantitative evaluation of the TG curve. Similarly, the doubling of the atypical broad calcite endotherm on curves determined on the 673 instrument (curves B and C of Fig. 2) is suggestive of a like complexity. All the complexities could, however, arise in one way or another from the presence of kaolinite volatiles. Thus, in the absence of gas flow through the sample, such materials could decompose calcite which is closely associated with the kaolinite particles undergoing dehydroxylation and the CO_2 formed could be immediately adsorbed on the fresh active surface of the metakaolinite, as suggested previously [1]. Because of the CO_2 atmosphere, this sorbed CO_2 would be desorbed at a higher temperature than in nitrogen or air but “calcite dissociation” would be revealed by TG only when the CO_2 was desorbed. This process would be expected to become more pronounced the higher the proportion of kaolinite in the mixture and the harder the packing; moreover, the DTA effect associated with desorption should be smaller than that associated with an equivalent amount of dissociation. Whether or not the 842°C endotherm is directly connected with the DTG peak at about the same temperature (see above), the first DTG peak on Fig. 3B,C is represented by a relatively small effect on the DTA curve, indicating a less energy-absorbing process than dissociation. Moreover, the shoulder on the DTG curve for the 1.25:1 mixture (Fig. 3A)

developed into a peak for the 4:1 mixture (Fig. 3B,C) and the peak increased in size with hard packing. Although experimental observations are, therefore, consistent with this explanation, it cannot be taken as proven, as the same trends would be expected if the volatiles affected the surfaces of the calcite crystals [11] in such a way that dissociation of the altered surface required less energy and occurred fairly slowly over a wide temperature range before the main dissociation. Moreover, either of these mechanisms could explain the first peak of the doublet in the calcite region on curves B and C of Fig. 2, although curve D tends to support the second.

Despite a few uncertainties, logical explanations can thus be advanced for most of the experimental observations. As most of the complexities, which seem to be associated with the complex volatiles evolved during kaolinite dehydroxylation [8,9], can be avoided or minimized by passing CO₂ through the sample during a determination, this technique is to be recommended for natural samples containing both kaolinite and calcite. However, the variability of the volatiles from one sample of kaolinite to another suggests that a much more comprehensive study of the system in CO₂ is required.

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