INTERACTION OF KAOLINITE WITH CALCITE ON HEATING. IV. REHYDRATED AND RECARBONATED SAMPLES

L. HELLER-KALLAI[1] and R.C. MACKENZIE[2]

1 Department of Geology, Institute of Earth Sciences, The Hebrew University, Jerusalem 91904 (Israel)
2 Departments of Chemistry and Soil Science, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland

ABSTRACT

Calcite thermally dissociated in the presence of various kaolinites was partially preserved as a discrete phase. Proximity of the clay caused corrosion of the calcite rhombs, even before decarbonation occurred and CaO formed. The kaolinite sample used determined the $CaCO_3$ polymorph formed on recarbonation and polymorphs with very different morphologies were obtained. Volatiles evolved on heating kaolinite also affected the recarbonation reaction, but to a lesser extent than contact with the clay.

INTRODUCTION

In the earlier papers of this series (1-4), it was shown that the configuration of the calcite endotherm on DTA curves for kaolinite-calcite mixtures depended on both experimental and instrumental parameters, as well as on the kaolinite sample used. Samples heated to above the calcite endotherm but below the kaolinite exotherm in static air, or with dry or wet $N_2$ flowing through the sample, reacted in part to give non-crystalline products. However, some of the dissociated calcium carbonate persisted as a separate phase and, after storage in polythene envelopes for some months, rehydrated and recarbonated to give portlandite and one or more of the three carbonate phases, calcite, aragonite and vaterite (4). Aragonite and vaterite were mutually exclusive but either could occur along with calcite. The calcite phases formed depended on the kaolinite sample used (4).

Distortion of the carbonate peak was due to variation in the rate of evolution of $CO_2$ and has tentatively been associated in some way with the effect of volatiles evolved along with water on the dehydroxylation of kaolinite (4). This, however, is not a simple relationship, as separation of the kaolinite and calcite by an inert layer greatly reduced the degree of distortion of the DTA curve (1, 3). Particle surfaces are therefore likely to be involved (4).

Because of this, it was considered that a further study involving scanning electron microscopy of rehydrated and recarbonated samples might throw some light on the mechanism: the results are given below.


EXPERIMENTAL


The samples examined were mainly those for which product identification has already been given (Table 2, ref. 4), but some additional samples were heated to the requisite temperatures in a Stanton Redcroft Model 673 apparatus with $N_2$ flowing over the specimens. The kaolinites used are identified as previously (4),

C-1       Well-ordered 'Al BP' kaolinite from Cornwall, England (1) - as
          received, and the <4 μm fraction.
Ga-1      well-ordered kaolinite (K Ga-1) from Georgia, USA, used in the Clay
          Minerals Society inter-laboratory study (5) ; <2 μm fraction, Na-
          saturated.
Ga-2      Poorly-ordered kaolinite (K Ga-2) from Georgia, used in the same
          study, as received.
P-K       Well-ordered kaolinite from Pugu, Tanzania, described by Robertson et
          al. (6), <5 μm fraction.
P-D       Poorly-ordered kaolinite from the same locality, rock sample,
          unseparated.
Ione      Well-ordered kaolinite from Ione, California, USA, Na-saturated.
WaG       Well-ordered kaolinite from "Warsaw geodes", Keokuk, Iowa, USA (7)
          (10-20 μm fraction).

The calcite was AnalaR calcium carbonate consisting of rhombs with edge lengths of 3-12 μm.

Electron microprobe analyses were carried out on a Jeol JXA-8600 microprobe and scanning electron micrographs were obtained with the same instrument and with a Jeol JSM-840 scanning electron microscope. Chemical analyses were per-formed in the energy dispersive mode.

RESULTS AND DISCUSSION


Electron microprobe analysis of samples heated to between the calcite endo-therm and the kaolinite exotherm revealed that at least part of the Ca was in a separate phase with no detectable amounts of Al or Si. Scanning electron microscopy showed that the particles retained the calcite outline, although their surface morphology was markedly different (see Fig. 12, ref. 1).

Examination of mixtures with different kaolinites recarbonated after heating to between the calcite endotherm and the kaolinite exotherm also showed different morphologies, which are compared with that of the original calcite (Fig. 1a) in Fig. 1. Thus, the samples yielding, according to X-ray diffraction,
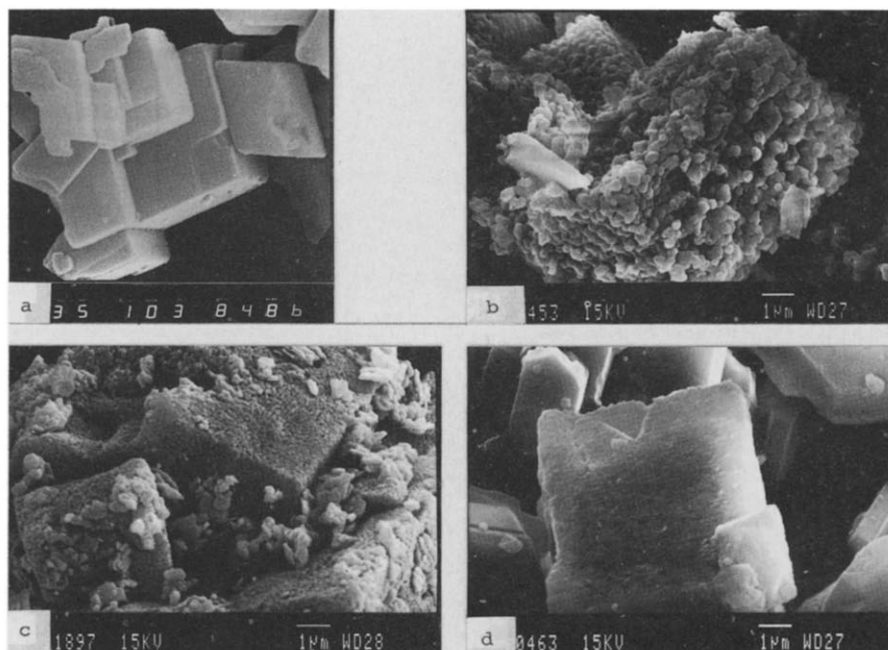
Fig. 1. Scanning electron micrographs of: (a) original calcite; (b), (c), (d) hydrated and recarbonated samples from heated 1.25:1 kaolinite-calcite mixtures for P-D (vaterite), Ga-2 (calcite+aragonite) and WaG (little effect).

vaterite (Fig. 1b) had much coarser crystals than those yielding aragonite and calcite (Fig. 1c), irrespective of the kaolinite sample used. In mixtures with WaG, the morphology of the rhombs was very well preserved (Fig. 1d). X-ray diffraction of the last showed that little recarbonation had occurred and that the dominant Ca-containing phase was portlandite. It is noteworthy that WaG is a well-ordered coarsely crystalline kaolinite with small surface area (7), which, in contrast to the other kaolinites, caused little modification of the shape of

the calcite endotherm (4).

The proximity of kaolinite not only affected the course of the recarbonation of portlandite but also the rate of hydration of the CaO initially formed. Thus, calcite alone and calcite exposed to clay volatiles from C-1 during heating to above the calcite endotherm, after storage under identical conditions in polythene envelopes for 8 days, gave only portlandite, whereas 1.25:1 and 4:1 mixtures of C-1 treated identically yielded both portlandite and CaO. For the last two samples, the intensity ratios of the two strongest peaks were 6.6 and 0.3, respectively. Consequently, contact with kaolinite seems to reduce the rate at which CaO hydrates.

The recarbonation reaction is affected by both contact with kaolinite and exposure to clay volatiles. Thus, calcite heated on its own recarbonated to calcite alone and mixtures with C-1 produced vaterite as the only carbonate phase, whereas calcite exposed to volatiles from C-1 during heating recarbonated to a mixture of calcite and vaterite. These two polymorphs were also obtained from mixtures with C-1 preheated to 1000°C, provided the mixture was tightly packed in the sample holder. A loosely packed sample recarbonated to calcite only. These observations indicate that heating under volatiles from C-1 or in intimate contact with preheated C-1 caused some vaterite to form, but neither was as conducive to vaterite formation as propinquity of the untreated kaolinite.

Contact with kaolinite and exposure to clay volatiles affected calcite surfaces even below the temperature of the calcite endotherm. A scanning electron micrograph of rhombs of calcite heated to 710°C in contact with kaolinite (Fig. 2a) reveals strongly corroded crystals - an effect that increased with the kaolinite:calcite ratio. Exposure of calcite to volatiles from C-1 during heating to the same temperature caused only rounding of crystal edges but no apparent corrosion (Fig. 2b).
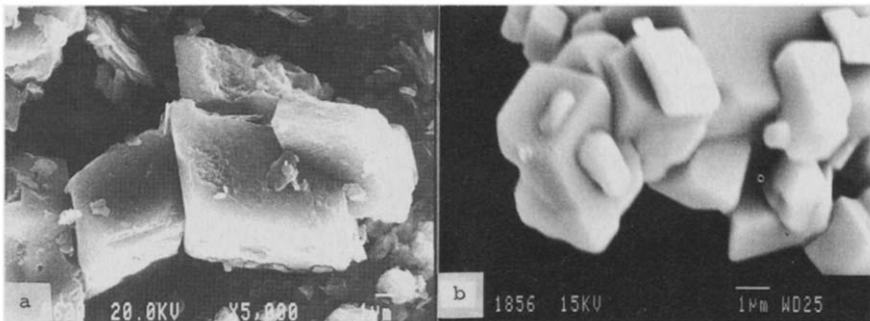


Fig. 2    Scanning electron micrographs of calcite heated to 710°C: (a) in mixture with C-1; (b) exposed to volatiles from C-1.

The effect of clay volatiles on rhomb surfaces is well exemplified by the micrographs in Fig. 3, where a shows a rhomb surface of calcite heated to just above the endotherm and rehydrated to portlandite, and b the surface of a corresponding rhomb that was exposed to clay volatiles. Neither sample had recarbonated. The surface of the rhomb exposed to clay volatiles is etched and shows channels that are absent from that of the calcite heated alone.
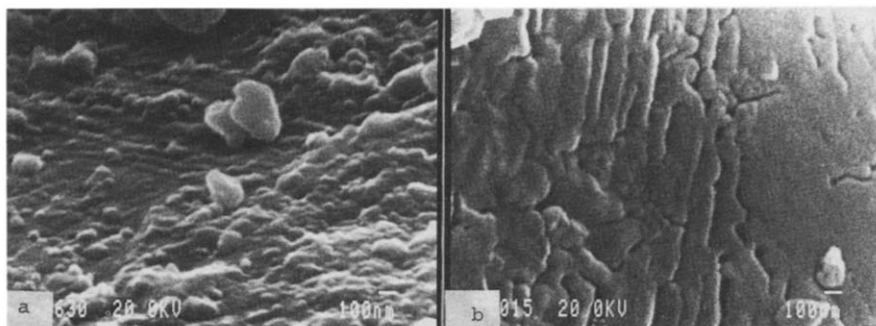


Fig. 3    Scanning electron micrographs of hydrated samples of thermally dissociated calcite: (a) heated alone; (b) exposed to volatiles from C-1.

CONCLUSIONS

Proximity of kaolinite affects the course of rehydration and recarbonation of thermally dissociated calcite, even when this is preserved as a discrete phase. The calcite is strongly corroded before dissociation occurs, but rehydration of CaO after dissociation is retarded. Thermally dissociated calcite recarbonated  to calcite alone, but in the presence of various kaolinites vaterite or aragonite (with very different morphologies) were also obtained.

Clay volatiles also affect the course of rehydration and recarbonation of thermally dissociated calcite, but to a smaller extent. Mixtures with C-1 yielded vaterite as the only recarbonated phase, whereas with volatiles from C-1 and with mixtures with calcined C-1 both vaterite and calcite were obtained. A common denominator seems to direct crystallization towards the same $CaCO_3$ polymorph. The involvement of volatiles suggests that this must be sought in the chemical composition. But whether the effective elements are concentrated at the clay surface and are partially lost on calcining the clay or whether, when kaolinite and calcite are in close contact, other factors are involved requires further investigation.

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