REACTIONS BETWEEN CLAY VOLATILES AND CALCITE REINVESTIGATED

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Abstract—Calcite crystals exposed to clay volatiles react with some components of these volatiles, giving rise to a variety of surface morphologies. F, Cl, and S in different proportions were detected by electron microprobe analysis of the calcite surfaces. Under identical experimental conditions, volatiles from every clay mineral examined caused a specific morphology and chemical composition of the calcite surfaces, but these varied with temperature of the calcite. Changes in pH values and mass spectra of the volatiles after passage through calcite demonstrate that even on rapid heating some clay volatile-calcite reactions occur at temperatures as low as 150°C. Species other than those detectable by electron microprobe analysis also participate in the reactions in which CO_2 is liberated.

Key Words—Calcite, Clay volatiles, Mass spectra, pH measurements, Surface morphology.

INTRODUCTION

Volatiles evolved on heating clay minerals contain a variety of chemical species. Chemical analysis of the condensates and direct mass spectrometry of the gases evolved showed that they contain different anions; protons and ammonium are the dominant cations (Keller, 1986; Heller-Kallai *et al.,* 1988). Hydrogen was evolved from some samples (Heller-Kallai *et al.,* 1989a; Wicks and Ramik, 1990). The composition of the volatiles differs from one mineral to another and varies with temperature and the thermal regime. The high chemical reactivity of clay volatiles (and condensates) was manifested by their effect on the decomposition of calcite (Heller-Kallai *et al.,* 1986, 1987) and by their action as cracking catalysts for *n*-alkanes (Heller-Kallai *et al.,* 1989b; Miloslavski *et al.,* 1991).

The chemistry of the processes involved in the production of volatiles has not been entirely elucidated. Chemical analyses of the liquids obtained after condensation of the volatiles determined the nature and concentration of the cations and anions present after condensation, but some may have been lost and some may have undergone secondary reactions. On-line mass spectrometric analysis of the gases identified the entities formed in the spectrometer, which are not necessarily the same as those evolved from the clays. Thus, although the elemental composition of clay volatiles and condensates has been determined, identification of the actual moieties liberated remains uncertain. The volatile species may be incorporated in the clay mineral structures, adsorbed on the clay surfaces, trapped in micropores, or may occur as discrete impurities.

Earlier studies established that clay volatiles affect the course of the thermal decomposition of calcite (Heller-Kallai *et al.,* 1986, 1987) as well as the nature of the decomposition products. The presence of clay

volatiles caused distortions of the calcite endotherm on DTA curves (Heller-Kallai and Mackenzie, 1987; Mackenzie *et al.,* 1988). The resulting dissociation products recarbonated to different polymorphs of calcium carbonate (Heller-Kallai and Mackenzie, 1989), an effect generally associated with the presence of minor amounts of various cations, but anions may also have an effect (Tokuyama *et al.,* 1973).

In this study the reactions between clay volatiles and calcite were reinvestigated, in an attempt to locate the origin of some of the components of the volatiles and to shed some light on the chemical reactions involved. To overcome the problem of the very low concentrations of the various species present as volatiles and to facilitate electron optical analysis, single crystals of calcite and a high clay:calcite ratio were used. Since some of the reactions involved are not amenable to microprobe analysis and could not be interpreted in terms of the chemical changes observed, pH values of condensed volatiles and mass spectra of the volatiles were used as additional probes.

MATERIALS AND METHODS

Materials

The clay samples selected for study are listed in Table 1. Mass spectrometry showed that they contained no carbonates. The samples were used as supplied, except for samples K(AlBP) and M(W), which were size-separated to below 2 μm. Samples K(GW) and K(GP) were used as supplied and also after washing 10 times with distilled water.

Exposure of single crystals of calcite to clay volatiles

About 5 g of the clay samples were heated in a horizontal quartz tube under a constant stream of dry

Table 1. Samples used.

Sample	Description
K(GW)	Well-ordered kaolinite from Georgia, U.S.A. (CMS)
K(GP)	Poorly-ordered kaolinite from Georgia, U.S.A. (CMS)
K(AIBP)	Well-ordered kaolinite from Cornwall, England (designated C-1 in Mackenzie et al., 1991)
H(U)	Halloysite, Dragon Mine, Utah, U.S.A.
M(CB)	Montmorillonite, Camp Berteaux, Morocco
M(W)	Montmorillonite, Upton, Wyoming, U.S.A. (CMS)
M(SD)	Montmorillonite, South Dakota, U.S.A. (CMS)
M(T)	Ca Montmorillonite, Texas, U.S.A. (CMS)

Note: CMS—Clay minerals standard.

Table 2. Elements detected by electron microprobe analysis.

Sample	Untreated clay sample		S		Calcite after exposure to clay volatiles[1]		
	F	Cl	a	b	F	Cl	S
K(GW)	x	x	x	x	x	x	v
K(GP)	x	x	x	x	x	x	v
K(AIBP)	v[2]	x	x	x	v	v	v
H(U)	x	x	x	x	x	v	v
M(W)	x	x	v	o	x	v	v
M(SD)	x	v[3]	x	v	x	x	v
M(CB)	x	v[4]	v	x	x	v	x
M(T)	x	x	v	o	o	v	v

Symbols: a—S occurs in Ca, Sr, and/or Ba sulphates; b—S occurs in iron sulphides; x—not detected; o—minor amounts; v—present.
[1] The clay sample and calcite were heated to 500°C and maintained at that temperature for 20 min.
[2] Present in muscovite impurity.
[3] Present in biotite impurity.
[4] Present in clay and in mica and apatite impurities.

helium, at the rate of 10°C/min. Single crystals of calcite (about 50–100 mg) were inserted into the quartz tube with a cleavage face oriented towards the stream of volatiles. To avoid direct contact between clay and calcite, they were separated by a plug of quartz wool. Along the length of the quartz tube was a temperature gradient. By judicious choice of the position of the calcite crystals in the tube, their temperature could be adjusted relative to that of the clay. Thermocouples measured the temperature of the clay and calcite separately. In a standard run the clay and calcite were heated to 500°C and maintained at that temperature for 20 minutes. In some experiments the helium was wetted by bubbling through distilled water or acidified by bubbling through HCl solution before entering the reaction tube.

Microprobe analyses (EMPA)

Analyses of the original clay samples were performed with a Jeol JXA-8600 electron microprobe in both energy and wavelength dispersive modes. Preliminary experiments showed that the calcite surfaces after exposure to volatiles were very corroded and heterogeneous, rendering quantitative analyses meaningless. For qualitative analyses and studies of surface morphology, the instrument was used as a scanning electron microscope (SEM).

pH measurements

Clay (5 g) and calcite powder (500 mg), separated by quartz wool, were heated in the same reactor and under the same conditions as the samples for microprobe analysis. Part of the clay volatiles condensed at the end of the quartz tube, where they reached approximately ambient temperature. The pH of these condensates was determined at regular temperature intervals, before and after passage through calcite, using universal indicator strips: pH range 0–14 (Merck). The reproducibility of the measurements was ±0.5 units.

Mass spectra (MS)

The mass spectra of the volatiles were recorded before and after passage through calcite. Due to technical constraints the heating regime differed from that described above. The samples were heated rapidly in vacuum up to 390°C and maintained at that temperature for 20 minutes. The details were previously described (Heller-Kallai et al., 1988).

RESULTS

Microprobe analysis

The original clay samples and the surfaces of calcite crystals before and after exposure to clay volatiles were analysed. Only three additional elements were found on the calcite surfaces after exposure: F, Cl, and S. Other elements, if present, were below the detection limit or too light to be determined. The pH and MS measurements indicated that other species also participated in the reactions (see below).

In the original clay samples, F, Cl, and S were frequently below the detection limit, which is ~1500 ppm for F and ~200 ppm for Cl or S (Table 2). S, when detected, occurred in association with Ca, Sr, and/or Ba as sulphate or with Fe as a sulphide. F and Cl occurred in mica impurities, but in sample M(CB), Cl was also seen to be disseminated throughout the clay fraction. In other samples F and Cl may be part of the clay mineral structures, but in concentrations that are below the detection limit of the microprobe, e.g., kaolinite, K(AIBP) contains some structural F (Thomas et al., 1977).

The distribution of F, Cl, and S on calcite exposed to volatiles from different clay samples under a constant thermal regime is shown in Table 2. Some effects of altering the thermal regime are presented in Table 3.

Table 3. Elements detected by electron microprobe analysis.

| | Temperature °C | | | | |
Sample	Clay	Calcite	F	Cl	S
K(AlBP)	RT	—	v	x	x
K(AlBP)	500	—	v	x	x
K(AlBP)	700	—	x	x	x
K(AlBP)	500	500	v	v	v
K(AlBP)	700	200	v	o	x
M(T)	RT	—	x	x	o
M(T)	300	300	x	v	x
M(T)	400	400	x	v	x
M(T)	500	500	o	v	v
M(T)	600	600	x	v	v
M(T)	500	150	o	v	x
M(T)	700	200	v	v	x
M(T)	700[1]	200	x	x	x

[1] Previous sample reheated. Symbols as for Table 2.

Under the conditions of the experiments F, Cl, and S were concentrated on the surfaces of the calcite crystals, although they were below the detection limit in the original clay samples (Table 2). With sample M(T) Cl was detected when clay and calcite were at 300°C, whereas F was found only after the clay was heated to 500°C (Table 3). The difference may be genuine, but may also be due to the significantly higher detection limit of F. Both F and Cl, probably as HF and HCl, interact with calcite even when it is at a low temperature (150°C); in contrast, S was not found on calcite at temperatures below 500°C (Table 3).

The morphology of some of the calcite surfaces after exposure to clay volatiles is shown in Figures 1–4. Calcite heated alone maintained smooth surfaces throughout the temperature range examined. A micrograph of calcite, which was subjected to more intense heat treatment than any of the samples attacked by volatiles (heated to 600°C and maintained at that temperature for 20 minutes three times), is included for comparison (Figure 1a). Exposure to clay volatiles resulted in a variety of surface morphologies.

Kaolinites. S from K(GW) and K(GP) was fairly uniformly distributed over the calcite surfaces, without causing distinctive changes in morphology. The calcite resembled that shown in Figure 1a. In the original clay samples, S was below the detection limit of EMPA and the source of the S could therefore not be established.

Figure 1b shows a curious feature observed when calcite crystals were exposed to volatiles from the K(AlBP) kaolinite. At 500°C rhombs of about 10 μm diameter, which are rich in F and Cl, appeared. In regions near the acute angles of the rhomb in Figure 1b the counting rates for F were about five times those for Cl, whereas they were similar near the obtuse an-
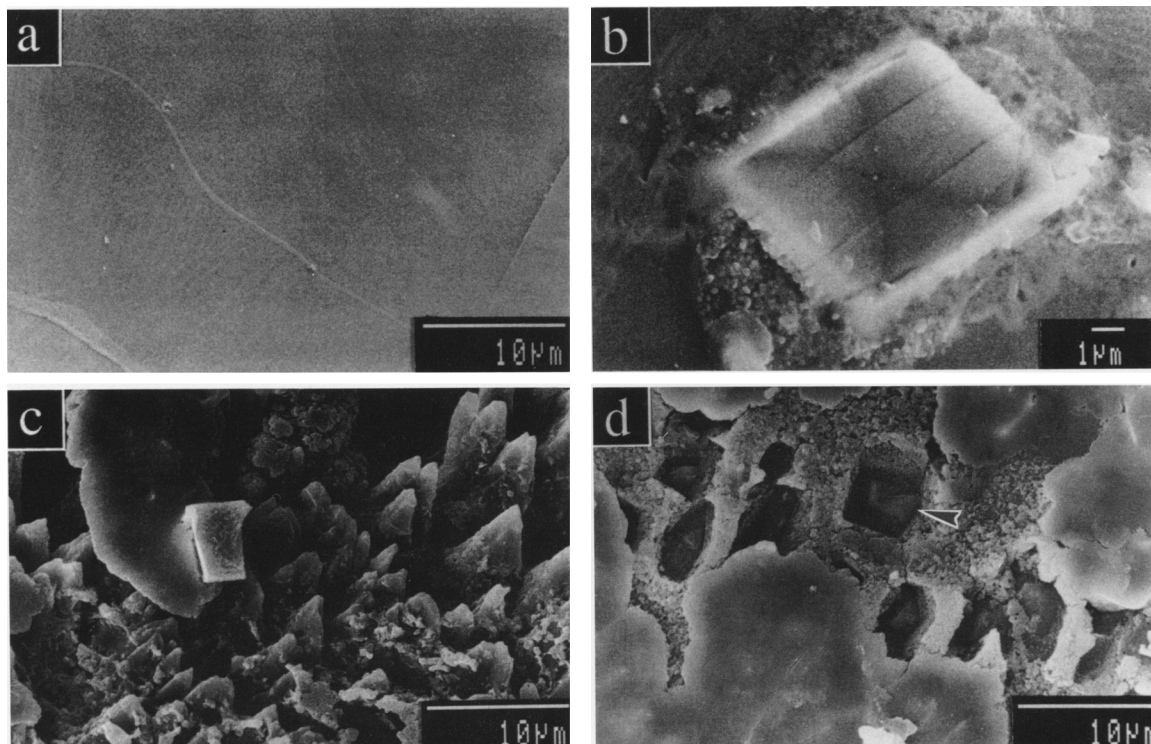

Figure 1. Electron micrographs of (a) calcite heated at 600°C; calcite exposed to volatiles from clay, both at 500°C, (b) K(AlBP); (c) and (d) H(U). The arrow in Figure 1d points to a region rich in Cl and S.
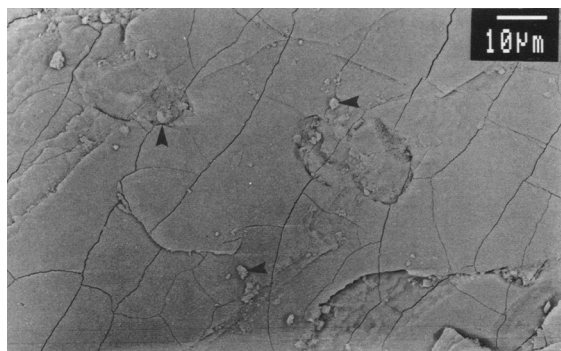
Figure 2. Electron micrograph of calcite (at 200°C) exposed to volatiles from K(AlBP) (heated to 700°C). The arrows point to some patches containing F and Cl.

gles. The centre of the rhomb is recessed. Many rhombs were present, in addition to some rectangular crystals. The small particles of irregular shape in the vicinity of the rhomb (Figure 1b) contain Cl and S. The distribution of F and Cl in the rhombs suggests that there may be some site preference for attack or that the order in which the ions reach the surfaces are of importance.

With the clay at 700°C and calcite at 200°C the entire calcite surface was covered by a thin coating, apparently of CaF_2. Some brighter F-containing patches with

small amounts of Cl and very minor amounts of S were also observed (Figure 2 and Table 3). F was present in the original kaolinite and in a mica impurity. The origin of the Cl is uncertain. EMPA showed that some F remained in the clay after heating to 500°C, but none persisted at 700°C (Table 3). It appears that between 500°–700°C, i.e., in the temperature range of the dehydroxylation of the clay, F became abundant in the volatiles and CaF_2 covered the calcite surface.

Halloysite H(U). Microprobe analysis of the original sample did not show any F, Cl, or S. Calcite surfaces exposed to volatiles from this clay were very corroded (Figure 1c). The pyramidal protrusions contained no detectable F, Cl, or S, but rectangular crystals that formed in other, strongly attacked, regions of the calcite (Figure 1d) were rich in Cl and S. The dissolution patterns, which differed from those observed with volatiles from the other samples studied, may be due to the larger amounts of water evolved. Under the prevalent thermal regime both interlayer and structural water was released from the halloysite, whereas montmorillonites lost interlayer water, but were only partly dehydroxylated.

Montmorillonites. Under the same thermal regime, volatiles from the four montmorillonites examined
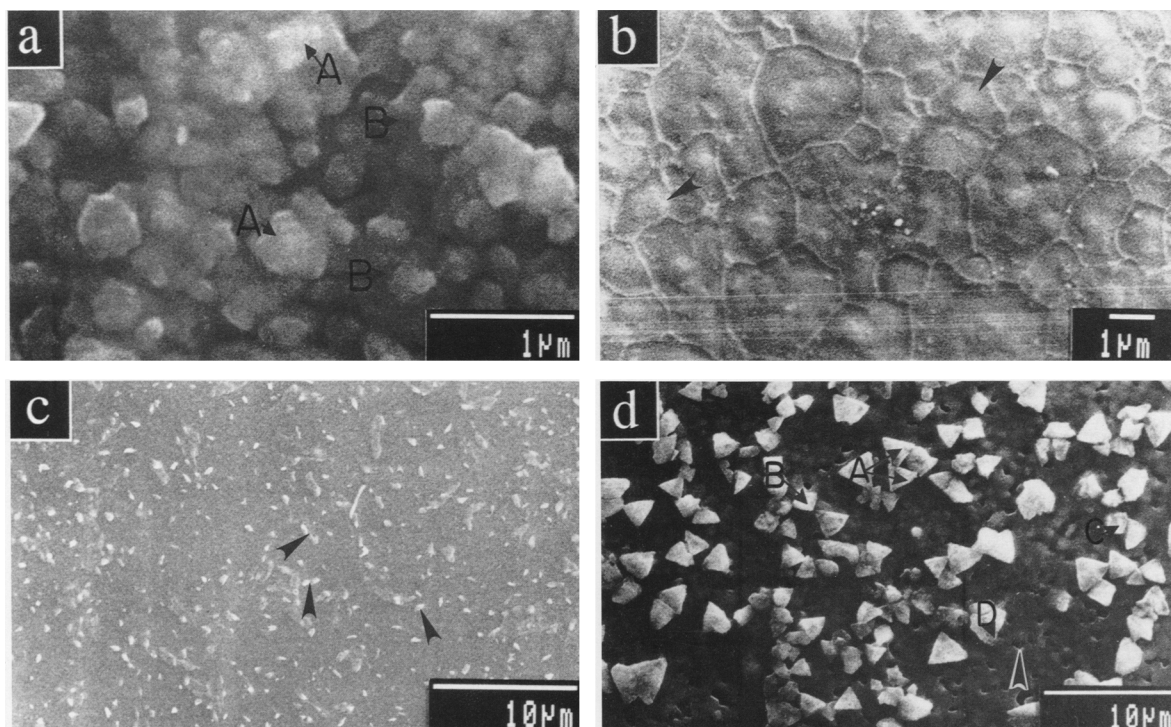

Figure 3. Electron micrographs of calcite exposed to volatiles from montmorillonites, both calcite and clay at 500°C, (a) (W), A marks region richer in Cl than S, B marks region with more S; (b) M(CB), arrows mark some regions rich in Cl; (c) M(SD), arrows mark some regions rich in S; (d) M(T), arrows point to perforations of the surface, letters A, B, C, and D mark crystals of various shapes.
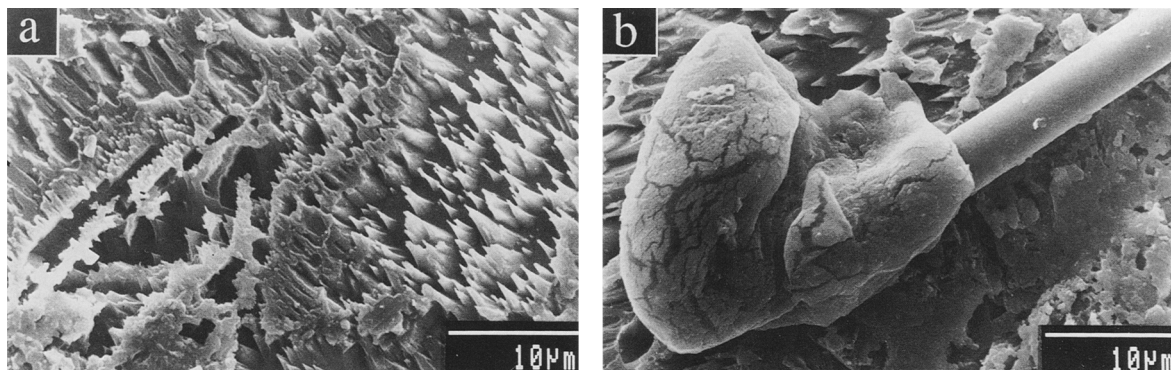
Figure 4. Electron micrographs of calcite (at 150°C) exposed to volatiles from M(T) (heated to 500°C), (a) calcite surface; (b) $CaCl_2$ crystallizing on quartz fibre.

produced very different calcite surface morphologies (Figure 3). Calcite attacked by volatiles from M(W) was covered with very fine particles, with some brighter, containing more Cl than S, and others darker, richer in S (Figure 3a).

Volatiles derived from M(CB) caused a more roughly corroded calcite surface with bright patches rich in Cl (Figure 3b—note the lower magnification).

With volatiles from M(SD) small S-containing particles were scattered over the calcite surface (Figure 3c). No Cl was discerned, although some was found in a biotite impurity in the original clay sample. Probably, the biotite was stable in the temperature range studied.

The morphology presented by calcite exposed to volatiles from M(T) differs profoundly from the others (Figure 3d). The calcite surface is perforated and partly covered by triangular, rectangular, rhombohedral, and irregularly shaped crystals. The larger, darker crystals are rich in Cl; the brighter, shapeless ones contain more S. Some F was also detected. With the clay at 500°C and the calcite crystals at 150°C the calcite surfaces are very corroded (Figure 4). The protrusions shown in Figure 4a contain some Cl. On some of the quartz fibres, which separated the clay from the calcite in the reactor, particles approaching the composition of $CaCl_2$ were formed (Figure 4b). It appears from Figure 3d that at higher temperatures the calcite surfaces were partly healed and calcium chloride recrystallised, incorporating S in some form.

Sulphur in clay samples. Sulphate impurities were not decomposed by heating to 500°C; but whenever sulphides were detected in the original samples, S occurred on the calcite surfaces, provided that the calcite was at a temperature of at least 500° (Tables 2 and 3). To elucidate the reactions between volatiles derived from sulphide impurities present in the clay samples and calcite, pyrite was used as the source of volatiles in a series of experiments similar to those carried out with clay volatiles. When pyrite was heated to 600°C

under dry He, only sporadic S-containing patches were formed on the calcite. In contrast, when the stream of He was wet, significant amounts of S were released at 550°–600°C. The species formed on the calcite surfaces depended on the temperature of the calcite. At 200°C globules of elemental S were formed, whereas CaS was obtained when the calcite crystals were at 600°C. When the wet He was acidified, very little S was detected on the calcite crystals at 200°C, and the small amounts present were not in the globular, elemental form. When the temperature of the calcite was raised, more CaS was observed. Evidently with pure water, elemental S is the dominant species, whereas H_2S is formed with acidified water. However, the equilibrium constant for the reaction

$$CaCO_3 + H_2S \leftrightharpoons CaS + H_2O + CO_2 \qquad (1)$$
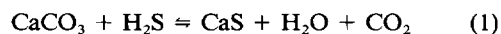
is small at temperatures below 500°C (Gmelin, 1961).

In experiments with clay volatiles, no globules of elemental sulphur were detected on any of the calcite surfaces. Since all these experiments were carried out under a stream of dry He, any water present was entirely supplied by the clay samples. It appears that the clay volatiles contain sufficient amounts of acidic water to cause evolution of H_2S from sulphides. The pH measurements confirmed that above 500°C the volatiles were, indeed, acidic (see below).

pH of clay condensates

Figures 5 and 6 show the changes in pH values of the condensates with increasing temperature, before and after passage through calcite.

The pH of condensates from the three kaolinites and the halloysite decreased sharply above 500°C, in the temperature range of dehydroxylation of the clays. With condensates from K(GW) this decrease is preceded by a drastic increase in pH at about 400°C. With both K(GW) and K(GP) the pH values of condensates from the original clays and from these samples after washing
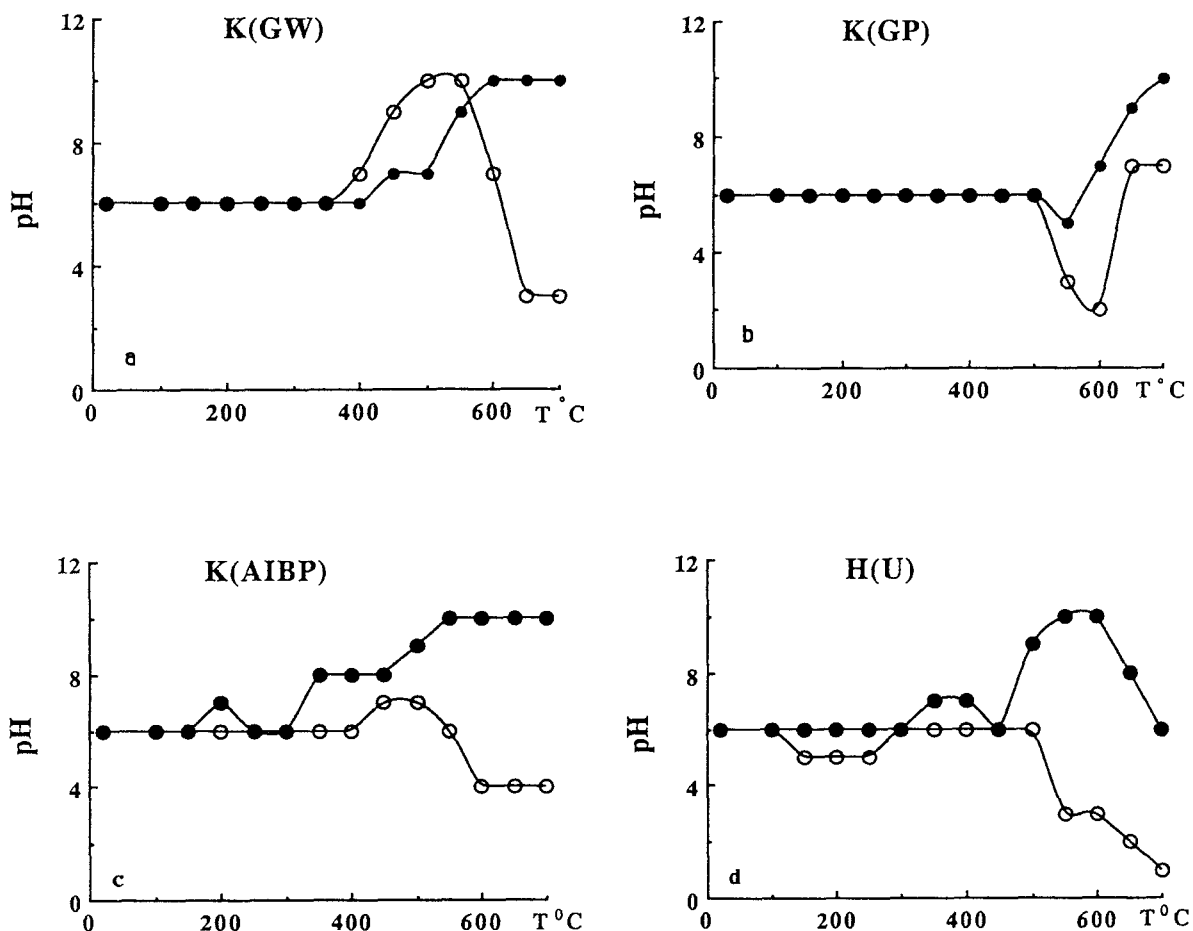
Figure 5. Changes in pH with temperature of volatiles from kaolinites and halloysite. O original clay; ● volatiles after passage through calcite.

10 times are very similar, which proves that the changes observed are not due to soluble impurities. Condensates from the halloysite sample show a small decrease in pH at about 150°C, associated with loss of interlayer water.

The changes in pH of condensates with temperature from the four montmorillonites differ greatly from one sample to another. Condensates derived from M(T) and M(CB) were very acidic above 150°–200°C, whereas those from M(W) and M(SD) fluctuated in the heating range studied, reaching minimum values of 3 at 550°C and 5 at 200°C, and again at 400°C, respectively.

As expected, passage through calcite increased the pH of acidic condensates. However, when the initial pH of the condensates was high, passage through calcite caused a decrease, as in samples K(GW) and M(SD).

The pH curves show that condensates from each of the clays examined were acidic in the temperature range of 500°–550°C, some much more than others. Some reactions with calcite commenced at quite low tem-

peratures, e.g., at 150°C with M(T) (Figure 6a). Microprobe analyses showed that Cl was present on the surface of calcite crystals exposed to volatiles from this clay at various temperatures (Table 3). A simple reaction between HCl in the volatiles and calcite would explain these observations, but other reactions may occur simultaneously. Changes in pH values of condensates from other clays cannot always be directly correlated with the results of the corresponding microprobe analyses, e.g., the high pH observed with volatiles from K(GW), which was reduced by passage through calcite (Figure 5a).

Mass spectra

Mass spectra of the volatiles from all the clay samples confirmed that they were complex mixtures of many chemical species and that their composition changed with temperature, as previously shown (Heller-Kallai *et al.,* 1988). The release patterns of the individual components were altered by passage through
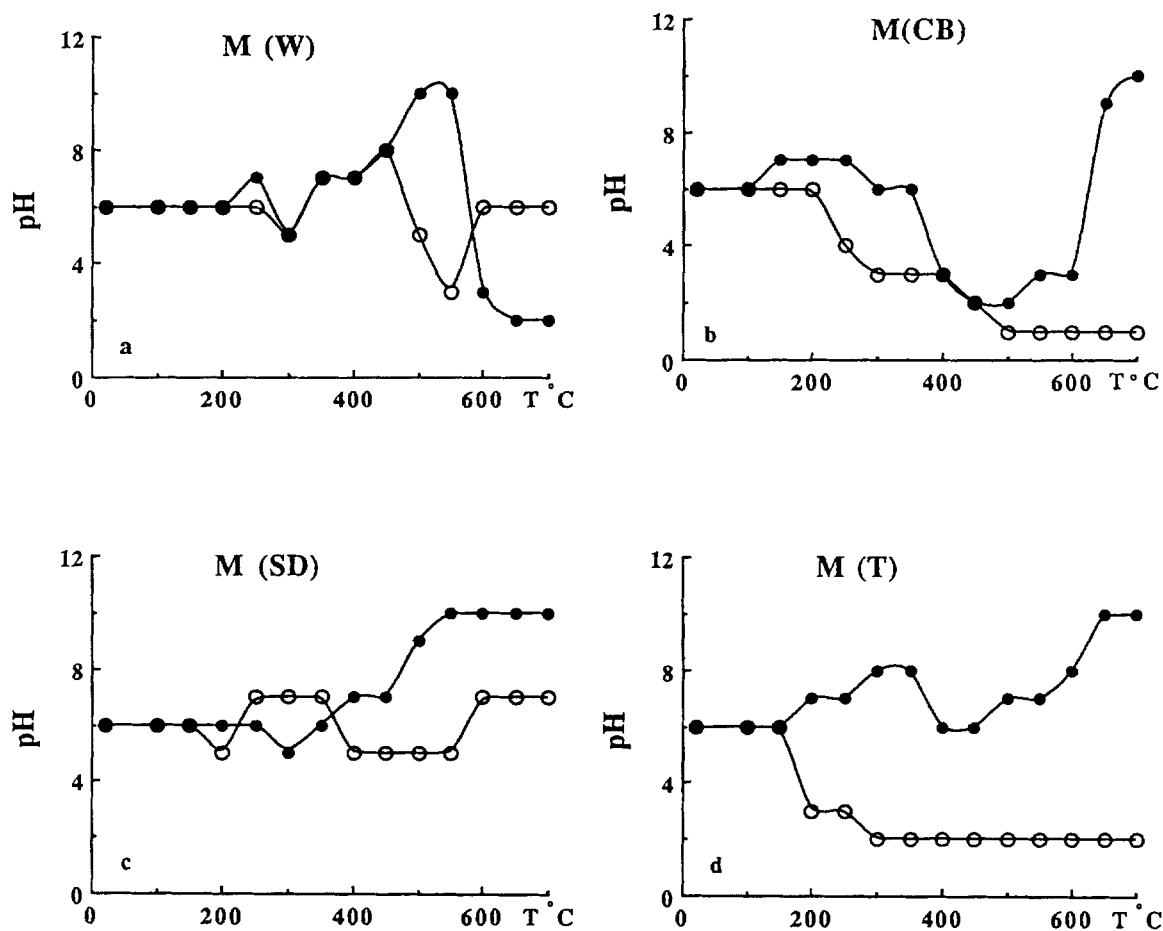
Figure 6. Changes in pH with temperature of volatiles from montmorillonites. ○ original clay; ● volatiles after passage through calcite.

calcite. Single-ion reconstruction (SIR) traces of selected species evolved from K(AIBP) before and after passage through calcite are presented to illustrate this point (Figure 7).

As before (Heller-Kallai *et al.*, 1988), HF^+ and HCl^+ were obtained from each of the clay samples. H_2S^+ was present in all the volatiles except those from M(CB). This is in agreement with the microprobe analyses, which showed no S on calcite exposed to volatiles from M(CB), in contrast to all the other volatiles examined. NH_4^+ and NH_3^+ were observed with each of the samples, again with the exception of M(CB). None of the volatiles except from Ca(M) contained any detectable amounts of organic matter. No CO_2^+ was detected in any of the original volatiles, but was always present after passage through calcite. Evolution of CO_2^+ started early in the course of heating (Figure 7d), in agreement with the changes observed in the pH values, indicating that reactions with calcite and some of the volatiles began at low temperatures. Due to the much lower sensitivity of the microprobe analyses, the small con-

centrations of reaction products formed at low temperatures frequently could not be detected.

DISCUSSION AND CONCLUSIONS

Although the three methods of analysis furnished results that are partly complementary, some important distinctions must be noted. The mass spectra record *dynamic* changes in the volatiles before and after passage through calcite. The method is the most sensitive of the three. The species identified are not necessarily those that were evolved from the samples, but the differences that were observed when the volatiles passed through calcite are genuine indicators of changes taking place. The pH measurements reveal changes in the composition of the condensates, which are affected by the solubility of the gaseous components in water and perhaps also by secondary reactions. As with mass spectra, changes observed on passage of the volatiles through calcite are reliable evidence that reactions occurred. SEM and EPMA reveal the morphology of the calcite crystals and the distribution of F, Cl, and S on

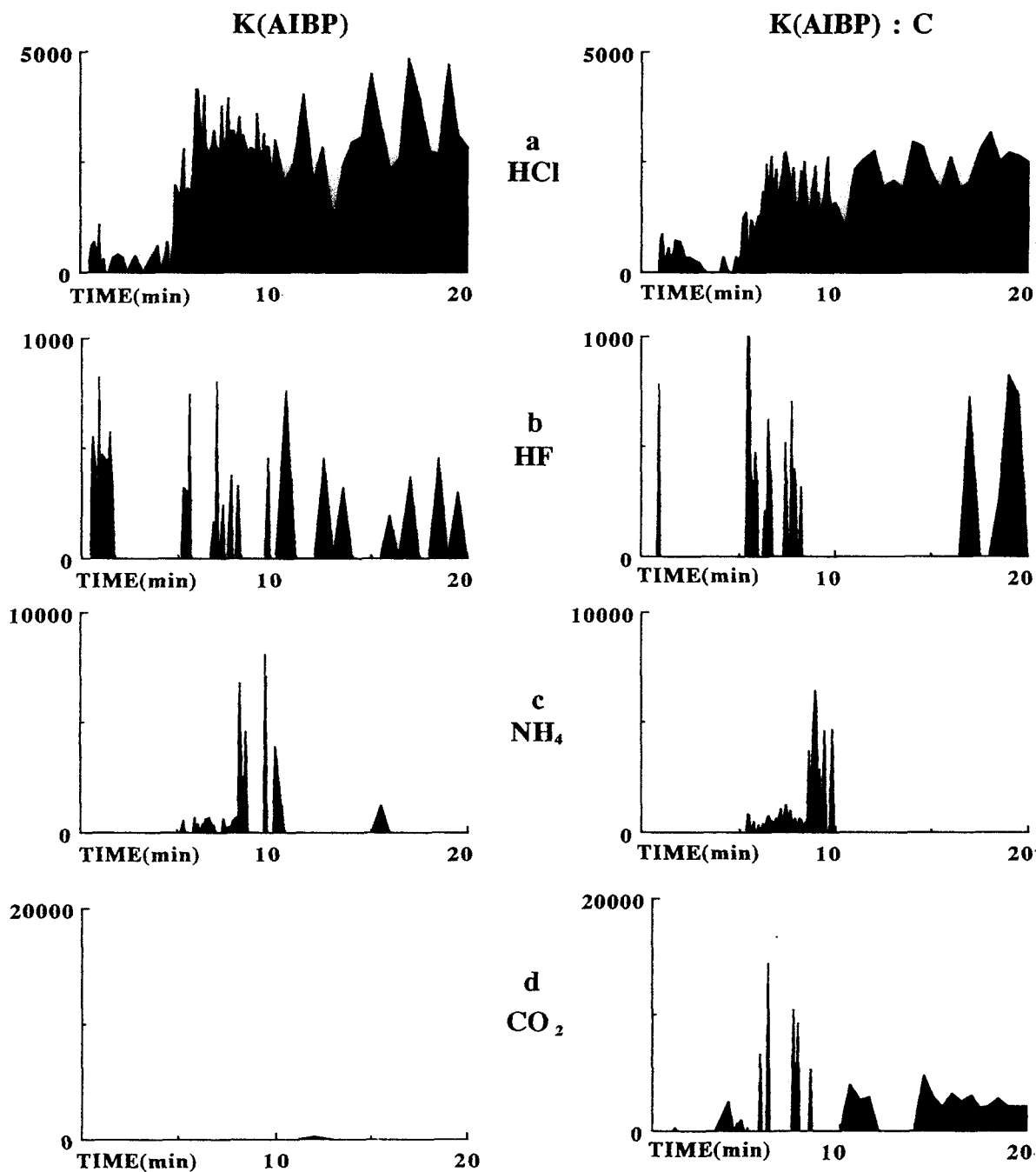## K(AIBP)   K(AIBP) : C

Figure 7. SIR traces of ion molecules obtained by electron impact from sample before, K(AIBP), and after, K(AIBP):C, passage through calcite.

them. (Other chemical species which participate in the reactions could not be detected by EPMA). The effects are cumulative throughout the heating process, although replacement of one species by another may occur. The present study, therefore, does not supply a complete interpretation of all the processes involved in the reactions between clay volatiles and calcite in an inert atmosphere, but several conclusions are warranted.

At temperatures up to 600°C F^-, Cl^-, and/or S^- present in clay volatiles react with calcite, liberating CO_2. F^- and Cl^- were derived from the clay minerals and/or from impurities present in the samples and S^- probably derived from sulphide impurities. Sulphates were

not decomposed. The clay minerals supplied water for the reactions. Frequently this water was acidic and reactions of the type

$$CaCO_3 + 2HX \rightarrow CaX_2 + CO_2 + H_2O \qquad (2)$$
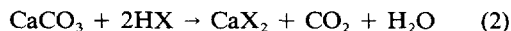
where $X = F$ or Cl, or reaction (1) with H_2S may be postulated. Possible sources of protons are interlayer H_3O^+ ions, hydrolysis of interlayer or adsorbed water, structural OH groups, or decomposition of NH_4^+ ions. However, reactions also occurred with volatiles that condensed to liquids with high pH values.

Many chemical species other than F, Cl, and S have been identified in clay volatiles and condensates (Keller, 1986; Heller-Kallai et al., 1988). Some of these may participate in the reactions with calcite, but their location in the original clay samples and the chemistry of their reactions with calcite remain unclear.

The surface morphology of calcite exposed to clay volatiles and the distribution of F, Cl, and S differed profoundly from one sample to another and changed with the thermal regime. The temperature of the clay sample affects the composition of the volatiles evolved; the temperature of the calcite affects the type of reaction it can undergo. From the point of view of natural processes, it is particularly significant that some of the reactions commenced at low temperatures (150°C or less), even on rapid heating. The variety of products obtained indicates that diagenesis of calcite (and other carbonates) may be influenced in many different ways by the presence of clay minerals. Impurities, even in concentrations too small to be detected in routine analyses, may affect the course of the reactions. The different processes of calcite attack and the various chemical species accumulating in the decomposing calcite may account for some of the effects of clay volatiles on the course of calcite de- and recarbonation previously observed (Heller-Kallai and Mackenzie, 1989).

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