

## Chemical and mass spectrometric analysis of volatiles derived from clays

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### ABSTRACT

Chemical analyses and mass spectra of volatiles produced by pyrolysis of clays showed that these comprised a wide variety of gaseous species. The products depend on the clay but are strongly affected by the conditions of the experiments. The temperature at which gases are formed varies. Even water collected at 250 °C was acidic. Volatiles collected at 350 °C contained the same species as those collected at 700 °C but in different amounts and proportions. Mass spectra showed that the same gas may be released in early stages of heating from one clay and at higher temperatures from another. A clay-mineral mixture retained the gases to higher temperatures than the individual components.

Replicate chemical analyses of condensed volatiles from individual clays were moderately reproducible, but entirely erratic results were obtained with a clay mixture. The effect was tentatively attributed to adsorption of the gases on clay-mineral surfaces.

The chemical composition of the volatiles qualitatively accounts for their reactivity. Detailed interpretation of the information they incorporate requires much further study.

### INTRODUCTION

Volatiles derived from clay minerals have in the past been implicitly regarded as pure H<sub>2</sub>O unless the samples contained organic matter, carbonate impurities, or F<sup>-</sup>. Recently, three independent investigations showed that these volatiles are not composed of H<sub>2</sub>O only. In two, the conclusion was reached on the basis of the observed reactivity of the volatiles (Mackenzie and Rahman, 1987; Heller-Kallai and Mackenzie, 1987; Heller-Kallai et al., 1986, 1987). In the third study (Keller, 1986), chemical analyses of the condensates from 36 minerals showed that a variety of ions and compounds are driven off on heating clay minerals. Keller concluded that it was difficult to draw the line between a clay mineral and a clay rock and that the volatile fractions may serve as fingerprints to help interpret the geologic history of the samples.

Following our observations of the reactivity of clay volatiles with calcite, we analyzed condensates from various clay minerals by chemical methods similar to those used by Keller. In an attempt to correlate reactivity with chemical composition, we aimed at obtaining reproducible analyses of the volatiles derived from any particular clay and to establish the effect of changing environmental conditions on the composition of the condensates. In previous publications, we showed that the reactivity of volatiles from mixtures of clays was greater than that from the individual components. Volatiles derived from clay-mineral mixtures were therefore also analyzed (Heller-Kallai et al., 1986, 1987).

Chemical analyses were supplemented by on-line mass spectrometry of some of the samples. This served several purposes. First, some of the species evolved could be directly identified, and the change in concentration with time could be observed. Furthermore, some volatile species, which might escape in the process of collecting the condensates for chemical analysis, could be detected.

### EXPERIMENTAL DETAILS

#### Materials

The clay samples used are listed in Table 1. They were used as supplied, unless otherwise stated.

#### Collection of volatiles for chemical analysis

Five-gram samples of clay were heated to various temperatures in a quartz reactor (12.5-mm diameter) that was connected to a Pyrex trap cooled with liquid N<sub>2</sub>. The samples were held in position by quartz wool.

Two methods for deriving and collecting the volatiles, designated series I and II, were used as follows:

**Series I.** Samples were heated in vacuo at 700 °C for 30 min. Distilled water (3.5 cm<sup>3</sup>) was placed in the trap before cooling. After the temperature was raised to ambient, the liquid was transferred to a 5-cm<sup>3</sup> flask and made up to volume. This series of experiments was designed to obtain reproducible results under controlled conditions.

**Series II.** Samples were heated to various temperatures, and volatiles were collected in different temperature ranges. Some of the experiments were carried out in vacuo, as in series I; others proceeded under a stream of He that passed through the sample. The volatiles were conducted into an empty trap and either used

TABLE 1. Clay samples used in this study

Sample	Description
K(GW)	Kaolinite, Georgia, well crystallized (CMS)
K(GP)	Kaolinite, Georgia, poorly crystallized (CMS)
M(Wa)	Montmorillonite, Upton, Wyoming (CMS)
M(Wb)	Montmorillonite, Upton, Wyoming (CMS), homogenized <2- $\mu$ m fraction of M(Wa)
M(CB)	Montmorillonite, Camp Berteau, Morocco
Sep	Sepiolite, "Sepiolita," Tulsa, Spain
Hal	Halloysite no. 9, Wagon Wheel Gap, California (CMS)

Note: CMS = clay mineral standard.

as received or diluted with distilled water. This series of experiments was designed to investigate the effect of temperature and environment on the nature of the volatiles.

#### Methods of chemical analysis

Anions were determined with a Dionex 2010i ion chromatograph (IC) (column HPIC-AS4A with anion microsuppressor, eluant 0.75M NaHCO<sub>3</sub>, 2.2M Na<sub>2</sub>CO<sub>3</sub>).

Na, Mg, Ca, Sr, Ba, B, Si, Al, Ti, Fe, Mn, Cd, Cu, Cr, Zn, Ni, Co, Mo, V, Be, Pb, Ag, Pb, Se, P, and S were determined with an inductively coupled-plasma atomic spectrometer (ICP-AES) (JY 48 1-m vacuum multichannel spectrometer; spectral range, 170–450 nm; resolution, 0.012 nm) fitted with a program for background correction. The accuracy and precision of the ICP determination was tested by repeat analysis of standard reference material (water NBS-1643b).

With the eluant used for IC, SO<sub>3</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> have identical retention times. Total P was therefore determined by ICP, calculated as PO<sub>4</sub><sup>3-</sup>, and SO<sub>3</sub><sup>2-</sup> was obtained by difference from the IC data. Total S was measured by ICP and expressed as SO<sub>4</sub><sup>2-</sup>. The pH was measured with a minielectrode.

#### Mass spectra

Mass spectra were recorded with a double-focusing high-resolution instrument (VG ZAB II F/25-11). Spectra collection and manipulation were executed by the data system of the instrument. Each 10-mg sample, contained in a small Pyrex tube, was introduced into the probe, which was maintained at 200 °C. The sample was heated rapidly to and held at 390 °C for each run. The instrument was operated in the electron-ionization mode under the following conditions: ionization voltage, 70 eV; reso-

lution, 3000; time per scan, 6 s; *m/z* values monitored from 10 to 250.

## RESULTS AND INTERPRETATION

### Chemical analysis of volatiles

**Series I.** The reaction temperature of 700 °C for this series was chosen to exceed the dehydroxylation temperature of the clays, in the hope that any effects due to inevitable minor changes in experimental conditions would be negligible. Three samples were chosen for analysis: M(Wb), K(GW), and a 2:1 mixture of the two, which was previously found to be very reactive toward calcite (Heller-Kallai et al., 1987). In view of problems of reproducibility encountered in a preliminary investigation, in particular with clay mixtures, experiments were repeated six times with each of the two clay samples and ten times with the mixture. The results are summarized in Table 2. Cations other than those listed were below the detection limit of ICP analysis.

It is evident that, even with individual clay minerals, reproducibility is poor. The order of magnitude of replicate experiments is, however, moderately consistent, and the average concentrations given in the table are significant. This is equally true for K(GW), which was used as supplied, and for M(Wb), which is the homogenized <2- $\mu$ m fraction of sample M(Wa).

In contrast, no two experiments with clay mixtures gave even approximately similar results. The mixtures used in the first four runs were prepared manually, the other six were aliquots of samples mixed for 40 min in a Spex mix. The suspicion that irreproducibility was caused by inadequate mixing was not borne out by these experiments. The results were completely erratic. It should be stressed that the irreproducibility was in the derivation of the condensates. Repeat analyses of any particular solution gave completely reproducible results.

The objective of introducing water into the trap was to dissolve the trapped gases on raising the temperature to ambient. This objective was not completely achieved. Some acidic gases could be observed escaping both dur-

TABLE 2. Chemical analyses of volatiles for series I experiments

Clay		F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Total P*	Total S*	
M(Wb)	range	<0.1	17–27	3–6	300–850	40–80	18–54	5500–22000	
	average	<0.1	21	4	496	58	40	12057	
K(GW)	range	<0.5–0.6	1–1.7	0.3–0.6	2–11	2–10	<1–5	13–70	
	average	~0.5	1.4	0.4	5	5	3	27	
M(Wb) + K(GW)	range	<1–64	1.5–52	0.2–3	8–1650	2–96	1–45	180–20000	
Clay		Al	Si	Ca	Ag**	Ba**	Cu**	Fe**	Zn**
M(Wb)	range	<0.1–0.2	<0.1–0.7	0.6–2.2	<10	<10–20	<10–60	50–150	90–180
	average			1.1				107	135
K(GW)	range	<0.1	<0.1–0.6	<0.2–0.6	<10	<10	<10	<50†	<50
M(Wb) + K(GW)	range	<0.1–0.7	<0.1–4	<0.1–0.8	<10–650	<10	<10‡	<50–500	<50–180

\* Total P (ICP) calculated as PO<sub>4</sub>; total S (ICP) calculated as SO<sub>4</sub>.

\*\* Values in ppb of original clay; other values in ppm.

† One sample showed 150 ppb.

‡ One sample showed 25 ppb.

TABLE 3. Chemical analyses of volatiles for series II experiments

Conditions and samples	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub>	NO <sub>3</sub>	SO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>
Sample M(Wa)						
20–350 °C; vacuum						
Original clay		1		1	1	2
Clay washed and dried		1	1	1		2
350–600 °C; vacuum						
Original clay		1		1		4
Clay washed and dried		1		0	0	3
20–350 °C; in He stream						
Original clay	1	2		0	4	4
Clay dried at 110 °C	0	0		0	2	1
350–600 °C; in He stream						
Original clay	1	2		0	4	4
Clay dried at 110 °C		0		0	0	4
Sample K(GW)*						
20–350 °C; vacuum	0	1	0	0		1
350–625 °C; vacuum	0	1	0	0		1
20–350 °C; in He stream	0	2	0	0		1
350–555 °C; in He stream	1	1		0		1
Sample Sep*						
20–400 °C; vacuum		1	1	0		0
20–600 °C; in He stream	1	1		1	0†	2
Sample Hal*						
20–600 °C; in He stream	3	2			0†	0

Note: Amount of volatiles varies from only a trace (0) to abundant (4).

\* Original clay sample only.

† + PO<sub>4</sub><sup>-</sup>.

ing the experiments, despite the low temperature of the trap, and on raising the temperature of the trap.

The undiluted liquids were viscous, and occasionally large drops were observed on the walls of the trap. Mechanical disturbance caused these drops to burst and virtually disappear. Evidently, entrapped gases escaped in the process. The viscous nature of the liquids may, at least in part, be an artifact due to the low temperature of trapping but may also be a true feature of the condensates.

No convenient method for determining small amounts of NH<sub>4</sub><sup>+</sup> was available to us. A smell of NH<sub>3</sub>, together with other, sometimes pungent, odors was frequently detected. This is in agreement with the results reported by Keller (1986) and with our mass spectra, which show NH<sub>3</sub><sup>+</sup> together with other N-containing species (see below). Moreover, no other cations were detected in sufficient amounts to balance the negative charge of the anions.

**Series II.** The semiquantitative results obtained in this series of experiments are summarized in Table 3. It is evident that the experimental conditions affected the composition of the volatiles, but in view of the difficulty of obtaining reproducible results under standard conditions, the data must be interpreted with caution.

TABLE 4. pH of volatiles from sample Hal (He atmosphere)

Temperature range (°C)	pH
20–150	5.6
20–250	5.2
150–250	4
280–430	2.9
150–600	2.9

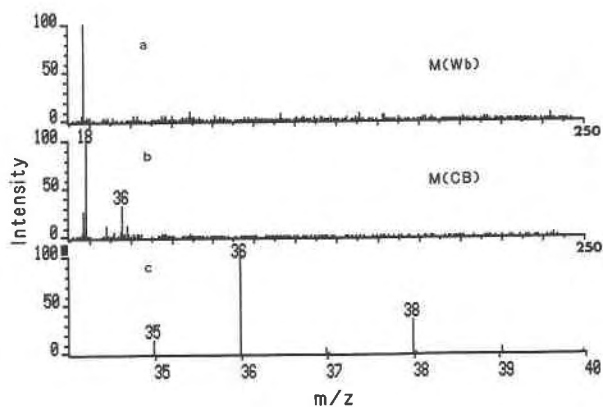


Fig. 1. Mass spectra of volatiles from (a) M(Wb),  $m/z = 10$ –250; (b) M(CB),  $m/z = 10$ –250; (c) M(CB),  $m/z = 34$ –40.

For sample M(Wa), washing before pyrolysis had little effect on the volatiles, but predrying at 110 °C reduced them considerably. S-containing species tended to be evolved in larger amounts at higher temperatures. The other species were less sensitive to changes in temperature. More volatiles were obtained in experiments carried out under a stream of He than under vacuum. The pH of all the condensates was acidic. The pH of four undiluted solutions obtained at both low and high temperatures (250 and 600 °C) ranged from 3.4 to 4.1; the values obtained for nine other samples ranged from 2.4 to 4.6 after dilution.

The concentration of volatiles obtained in all the experiments on sample K(GW) was much lower than with M(Wa). The composition did not vary greatly with experimental conditions. The pH of the solutions was acidic, ranging from 4.2 to 6.2. The higher values were observed with condensates obtained below 350 °C.

It appears that for sample Sep as with sample M(Wa), the S-containing species were evolved more efficiently under more drastic conditions of pyrolysis. The pH of the solutions ranged from 3.2 to 5.

Chemical analysis of sample Hal showed that only two anionic species occur in appreciable amounts, F<sup>-</sup> and Cl<sup>-</sup>. The changes in pH of the condensates with the temperature of pyrolysis is shown in Table 4. It appears that the amount of acidic gases increases systematically with increasing temperature.

Aliquots of the various liquids were evaporated to dryness at temperatures not exceeding 60 °C and examined by X-ray diffraction and IR spectroscopy. The patterns are very complex and have not yet been interpreted. They do, however, confirm that no colloidal particles of the original clay minerals were carried into the trap by the escaping gases.

#### Mass spectra

All the samples gave rise to mass spectra with many peaks that were only partly identified. As expected, H<sub>2</sub>O<sup>+</sup> ( $m/z = 18.0105$ ) and its fragments are the most abundant

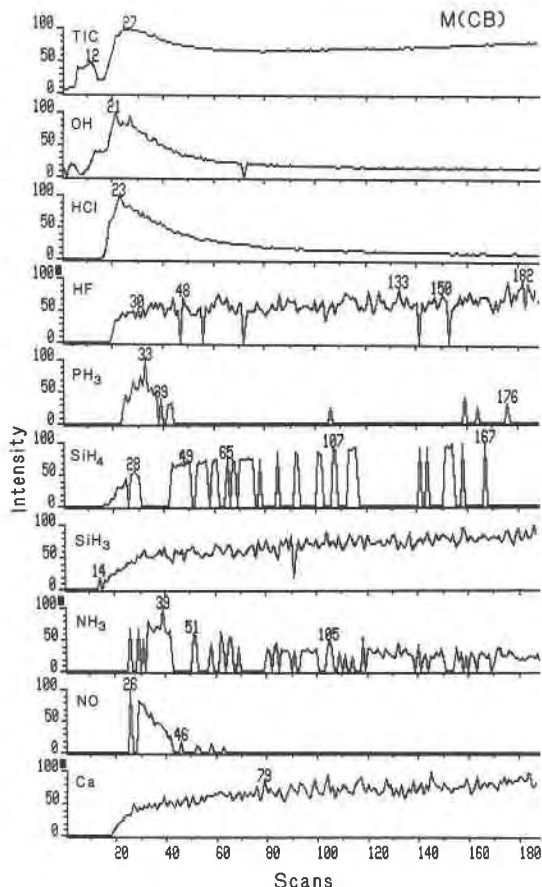


Fig. 2. SIR traces of selected volatiles derived from M(CB).

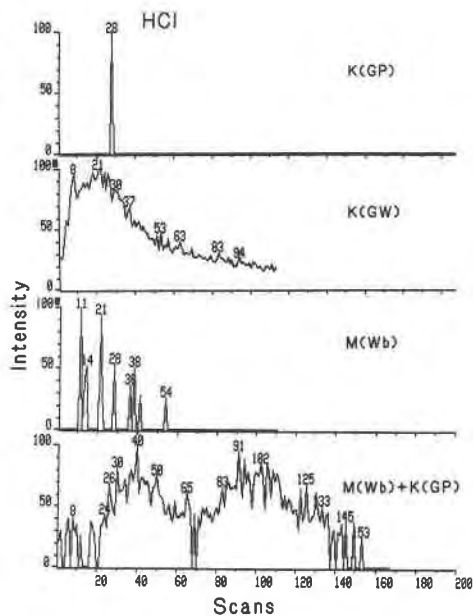


Fig. 3. SIR traces of HCl<sup>+</sup>.

species. Figure 1 shows part of the spectra obtained from two samples of montmorillonite. With M(CB) the four characteristic peaks of HCl ( $^1\text{H}^{35}\text{Cl}$ ,  $^1\text{H}^{37}\text{Cl}$ ,  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$ ) dominate the spectrum in the natural abundance ratio, with a host of much smaller peaks appearing in the background. The pattern obtained from M(Wb) also has many peaks, but no single species other than  $\text{H}_2\text{O}$  and its fragments predominates (Fig. 1a).

Figure 2 shows single-ion reconstruction (SIR) traces, i.e., the change in concentration with time, of several of the species released from M(CB) during 18 min (180 scans) at 390 °C. It is evident that the profiles of the traces of the various species are very different. For example, the profile of HCl<sup>+</sup> is almost parallel to that of OH<sup>+</sup>, whereas HF<sup>+</sup> was liberated at a fairly constant rate throughout the period of heating.  $\text{H}_2\text{S}^+$  was produced just after most of the  $\text{H}_2\text{O}$  was volatilized.

Both the species formed and the SIR profiles are properties of individual clays and are not group characteristics; e.g., Figure 3 shows the traces of HCl<sup>+</sup> from two samples of kaolinite from the same locality. The difference is striking: HCl<sup>+</sup> is evolved in the early stages of heating from the poorly crystalline sample, but much more gradually from the well-crystallized one. The profiles of

HF<sup>+</sup> are more similar (Fig. 4). With the two montmorillonites, however, the profiles of HF<sup>+</sup> differ more than those of HCl<sup>+</sup>. HF<sup>+</sup> was predominantly produced in the early stages of heating M(Wb) (Fig. 4), but it was formed throughout the entire run with M(CB) (Fig. 2).

Figure 5 shows SIR traces of water obtained from the various minerals studied. OH<sup>+</sup> was monitored to avoid distortion of the pattern due to oversaturation of the  $\text{H}_2\text{O}^+$  response. The profiles of OH<sup>+</sup> are approximately parallel to those of total ionic counts (TIC) (e.g., Fig. 2). Table 5 presents a very simplified account of the release patterns of selected species. It also shows the relative amounts of these species, as given by the computer. The experiments do not purport to be quantitative. The figures give some indication of the relative integrated intensities, but calibration would be required to establish proportionality factors.

It is evident from Table 5 that Cl<sup>+</sup> is correlated with HCl<sup>+</sup> and F<sup>+</sup> with HF<sup>+</sup> in all the samples. The patterns are compatible with those expected for fragmentation of HCl and HF. S<sup>+</sup> may have derived from  $\text{H}_2\text{S}$  with most of the samples, but with M(Wb) an additional source must be invoked.

All the samples examined gave rise to HF<sup>+</sup>, NH<sub>3</sub><sup>+</sup>, and NH<sub>4</sub><sup>+</sup>, and most of them also yielded SiH<sub>3</sub><sup>+</sup>, HCl<sup>+</sup>, NO<sup>+</sup>, and Ca<sup>+</sup>. The SIR profiles differ from sample to sample, except for SiH<sub>3</sub><sup>+</sup>, which, whenever formed, appeared throughout the entire run, sometimes in association with SiH<sub>4</sub><sup>+</sup>. The possibility that Si was derived from the walls of the Pyrex ampoule containing the sample cannot be excluded. BH<sub>3</sub><sup>+</sup>, which was also detected, may have been derived from the same source.

The presence of NH<sub>4</sub><sup>+</sup> in all the volatiles is in agreement with the chemical analyses of clay condensates given by

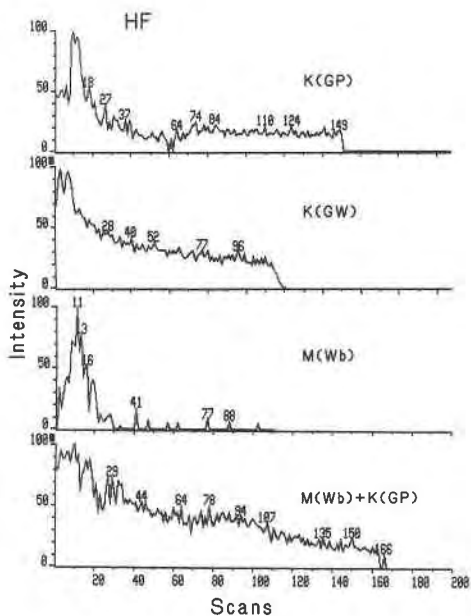


Fig. 4. SIR traces of HF<sup>+</sup>.

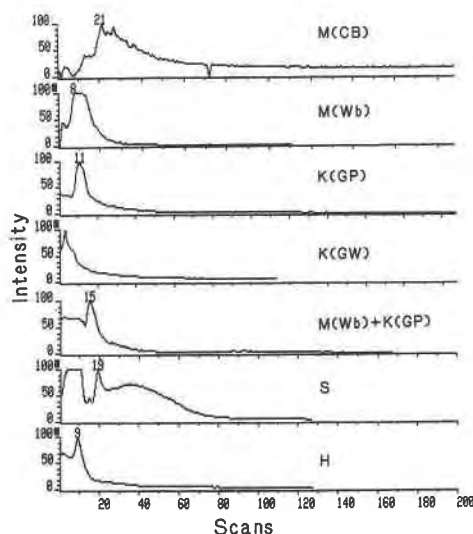


Fig. 5. SIR traces of OH<sup>+</sup> (*m/z* = 17.0027).

Keller (1986), which showed abundant NH<sub>4</sub><sup>+</sup>. A surprising feature is the appearance of a material with mass number 43.017. This corresponds exactly to *m/z* of N<sub>3</sub>H<sup>+</sup> and to no other species. It is unclear how N<sub>3</sub>H<sup>+</sup> could have formed in the course of the experiments or, indeed, whether this or any other species observed is an artifact of the mass spectrometric analysis. It is noteworthy, however, that the ratio of NH<sub>3</sub>/N<sub>3</sub>H varies from one clay to another, suggesting that N<sub>3</sub>H is not merely produced by fragmentation of NH<sub>3</sub>.

The results obtained in duplicate experiments were fairly reproducible (e.g., M(CB) in Table 5).

Table 5 and Figures 3 and 4 show the effect of mixing two clay minerals, M(Wb) and K(GP), on the release patterns of various species. It is evident that the mass chromatograms obtained from the clay mixture differed profoundly from those of the individual components, in complete agreement with the results of the chemical analyses and with the higher reactivity of clay mixtures noted in previous studies (Heller-Kallai et al., 1986, 1987). In general, the various species tend to be retained to higher temperatures by mixtures than by the individual components. This is well illustrated by the SIR traces of HCl<sup>+</sup> shown in Figure 3.

TABLE 5. Release patterns of selected volatiles from clays used in this study

Species: Mass:	OH 17.002	HCl 35.976	Cl 34.968	HF 20.006	F 18.998	H <sub>2</sub> S 33.987	S 31.972	SiH <sub>4</sub> 32.008	SiH <sub>3</sub> 31.003	NH <sub>3</sub> 17.023	NO 29.997	NO <sub>2</sub> 45.992	Ca 39.962	HN <sub>3</sub> 43.017	PH <sub>3</sub> 33.997	HBr 79.927	HCN 27.010
M(CB)-I*	14762	21114	4081	188	29			3759	413	192	607		349	405	119	37	
M(CB)-II*	14500	16180	2716	164	20			2225	329	150	484		313	400	93		
		a	a	c	c			a, b	c	c	b		c	a	a <sup>+</sup> , b	b	
M(Wb)	65500	354	123	2037	531	194	273	124	1618	1297	290	272	560	3017			491
		b	b	a, b	a, b	b	b	b	c	a, c	b	a	a, b	a			b
K(GP)	35631	28		403	83	92	39		354	845	112		108	1560			
		b		a	a	a, b	b		c	a	b		c	a			
K(GW)	43775	288	68	640	101	86	41		553	219	222		239	1085			
		a, c	a, c	a, c	a	a <sup>+</sup>	a <sup>+</sup>		c	a, c	a		c	a			
M(Wb)+ K(GP)	45964	152	44	939	172	95	57	49	1441	458	234	50	180	793			417
		c		a, c	a, c	b	b	b	c	a <sup>+</sup> , c	c	b	c	a <sup>+</sup> , c			b
Sep	65500	81	37	924	203	54		1139	393	308			129	102	103	134	
		c	c	c	c	b		b	c	a			c	a	b	b	
Hal	16231			138						71	108			159			
				a, b						c	c			c			

Note: Values are relative integrated intensities; a = species formed together with H<sub>2</sub>O; a<sup>+</sup> = species formed in late stage of H<sub>2</sub>O release; b = individual bursts; c = species formed continuously throughout period of scan.

\* I and II are duplicate experiments.

## DISCUSSION

The results obtained by the two methods of analysis, chemical analysis and mass spectra, are complementary, though both have limitations. In the course of collecting the volatiles some escaped, despite the low temperature of the trap. More were lost when the temperature of the trap was raised to ambient. This is demonstrated by HF, which was detected in all the mass spectra at 390 °C but was not found in some of the condensates collected at higher temperatures. The mass spectra suffered from two limitations: the uppermost temperature of 390 °C of the probe and the problem of distinguishing secondary from primary species.

All the experiments showed that the products differed greatly from one clay mineral to another, in agreement with Keller (1986). The SIR traces demonstrate that not only do the nature and amount of the volatiles vary, but that the release patterns may be entirely different. The same species may be evolved rapidly in the early stages of heating from one clay but only gradually from another.

Reproducibility of the chemical analyses of condensates was poor. The sample of kaolinite used for replicate analyses was used as supplied, and inhomogeneity might have been expected. Sample M(Wb), however, was a homogenized <2- $\mu\text{m}$  fraction of M(Wa). More reproducible results would therefore have been anticipated. The problem was compounded when mixtures of clays were used. Replicate analyses differed enormously, and inexplicably high concentrations of individual components were occasionally observed (Table 1). SIR traces demonstrated that gases tend to be retained to higher temperatures by clay-mineral mixtures than by the individual components. The amount of gas successfully trapped for analysis of the condensates may depend on the rate and temperature of its evolution.

The mutual effect of clays in mixtures may be tentatively attributed to adsorption-desorption effects, but chemical reaction between the gases evolved may also occur. Surface adsorption may also account for the irreproducibility of the chemical analyses. Even the <2- $\mu\text{m}$  fraction of sample M(Wb), though well mixed, comprises a wide range of particle sizes and aggregates, which may exert a chromatographic effect on the gases formed.

The concept of surface adsorption receives support from comparison of the reactions in a stream of He and in vacuo (Table 4). Higher concentrations of products were obtained under He, suggesting that the stream of gas desorbed and transported products that remained adsorbed under vacuum. Moreover, although the montmorillonite analyzed gave rise to much greater amounts of reactive gases than the kaolinite, addition of kaolinite to montmorillonite increased its reactivity, again suggesting that surface effects may be involved.

Some of the species detected in the mass spectra, such as  $\text{SiH}_3^+$ ,  $\text{SiH}_4^+$ , and  $\text{PH}_3^+$ , indicate a strongly reducing environment. Evolution of small amounts of  $\text{H}_2$  in the course of dehydroxylation of minerals in vacuo has been

reported, recently for kaolinite (Gábor et al., 1986). This requires further investigation.

Three of the clay minerals analyzed by Keller (1986) are from the same source as those we examined. The concentrations given in Keller's paper are in ppm's of liquid. Assuming that the clays gave rise to about 10% condensates by weight, the values in Table 1 of Keller's paper must be divided by 10 to render them approximately comparable with ours, which are expressed in ppm of original clay. In view of the problems encountered with replicate analyses under controlled conditions, it is hardly surprising that the agreement is poor.

The possible effect of impurities stressed by Keller (1986) is illustrated by the results obtained with CMS Wyoming bentonite M(W). The condensates examined by Keller (1986) had an alkaline pH (8–8.5), whereas 13 samples we analyzed ranged from pH 2.4 to 4.6. Anion analyses of our samples showed much higher concentrations of  $\text{SO}_3^-$  and  $\text{SO}_4^-$  than those examined by Keller. In addition, ICP analyses demonstrated that the total amount of S greatly exceeded that present in the form of  $\text{SO}_3^-$  or  $\text{SO}_4^-$ . XRF analysis of the <2- $\mu\text{m}$  fraction of the clay specimen revealed 0.7% S and scanning-electron micrographs showed that at least some of this is present as iron sulfide. This impurity may account for the striking difference between the analyses. Keller's sample was used without purification, whereas ours was the <2- $\mu\text{m}$  fraction that would be expected to be of greater purity. Inhomogeneity of the rock is one alternative, but the possibility of selective and incomplete trapping of the volatiles must also be considered.

## CONCLUDING REMARKS

Keller (1986) suggested that much of the geologic history of a clay may be inferred from a detailed analysis of the LOI (loss on ignition) fraction. Potentially this may be true, but in view of the difficulties involved in obtaining reproducible results, considerable research is required before meaningful data can be obtained. In particular, the interfering effects of coexisting clay minerals must be taken into account. Great caution must therefore be exercised in interpreting the results.

The high reactivity of the gases evolved has been demonstrated by their effect on calcite (Heller-Kallai et al., 1986, 1987). It may be speculated that these gases, some of which were released at relatively low temperatures, may play an important part in many reactions involving clays. In nature they may not only affect the course of diagenesis, but may also alter the porosity of the surrounding rocks. It seems possible that some reactions that were attributed to catalysis by clays may, at least in part, be due to the action of volatiles released in the course of the reactions. This raises the problem of using clay samples for model experiments. A particular clay mineral may not necessarily be representative of the mineral group. It may further be speculated that evolution of reactive gases may be a contributing factor that may help to account for

differences in dehydroxylation temperatures of clays with similar structure and gross chemical composition.

It is evident that much further research is required to establish the full implications of the results obtained.

#### ACKNOWLEDGMENTS

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