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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

THE NATURE OF CLAY VOLATILES AND CONDENSATES AND THE EFFECT ON THEIR ENVIRONMENT

A review

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Abstract

When clays are heated, a mass loss occurs due to the evolution of volatiles. Most of these are water vapour, but in addition minor amounts of a complex assemblage of other species are liberated. The corresponding condensates are colloidal suspensions. The composition of the volatiles and condensates and the release patterns of the gases are reviewed. The nature of the assemblages varies from one clay to another and depends on the thermal regime.

Both volatiles and condensates are very reactive. Their reactivity persists even after prolonged storage. They act as acid catalysts in reactions with organic matter and decompose calcite and other carbonates. Condensates were found to etch the surfaces of quartz crystals and to dealuminate and partly destroy an Al-rich faujasite (zeolite).

Possible implications of reactions of clay volatiles and condensates for natural processes are discussed.

Keywords: acid catalysis, calcite, clay condensates, clay volatiles, quartz, zeolite

Introduction

When clay minerals, or phyllosilicates in general, are heated, a mass loss occurs, due to the evolution of volatiles. Most of these are water vapour, but in addition, minor amounts of other species are liberated. These may have been trapped in micropores or in clay interlayers, adsorbed on external or internal surfaces of the minerals, or they may derive from structural elements, e.g. F^- or Cl^- substituting for OH^-. They may also originate in associated impurities that were not eliminated by pretreatment of the clay. Like other minerals phyllosilicates trap radiogenic gases, which can be used for geological dating. The nonradiogenic volatiles evolved from phyllosilicates have been studied with different objectives:

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a) To correlate evolution of gases such as H_2, HF or HCl with structural changes of the minerals and to establish the mechanism and kinetics of these changes [1–7];

b) To use the gases or their condensates to reconstruct the geochemical history of the samples [8, 9];

c) To assist in the determination of the mineralogical composition of argillaceous rocks [10–12];

d) To monitor reactions that occur on clay surfaces [13–16];

e) To assess the impact that clay volatiles and the corresponding condensates may have on their organic [17–19] and inorganic [20–23] environments.

The present review will concentrate on the nature of the volatiles and condensates and on their potential effect on the environment.

The composition of clay volatiles and condensates

Mass spectroscopy of volatiles evolved from various clays revealed that, in addition to water vapour, they contain a variety of chemical species [24]. HF, HCl, HBr, H_2S, S, NH_3, NO, NO_2, PH_3 and HCN were identified. The composition of the assemblage depends on the thermal regime and is sample specific. An example of the changes in the release pattern of volatiles from a sample of montmorillonite with time of heating at 390°C is presented in Fig. 1. It is evident that the assemblage varied from one moment of the heating process to the next. For example, as shown by the dashed lines in Fig. 1, after 3 min the mixture was rich in HCl, NO and PH_3, whereas after 10 min NH_3 and HF were relatively more abundant. The composition of assemblages from a mixture of clays differed from the sum of the components, either due to selective adsorption or to interaction of the gases.

Some clays release hydrogen on heating in vacuo. Freund and Gentsch [1] contended that with kaolinite, as with $Mg(OH)_2$ and $Al(OH)_3$, this occurs only in the course of, or subsequent to, dehydroxylation and involves lattice vacancies. Following Freund and Gentsch, MacKenzie [2] preheated samples of kaolinite and halloysite to their dehydroxylation temperature. He attributed subsequent evolution of H_2 to in vacuo auto-oxidation reactions of transition metal cations or carbon. Similarly Wicks and Ramik [7] observed loss of H_2 from a ferroan talc and a biotite at 500°C and above. They attributed the former to auto-oxidation of Fe^{2+} and the latter, which was well correlated with evolution of F_2, to reactions with structural F^-. Heller *et al.* [26] confirmed that evolution of H_2 from two samples of kaolinite did, indeed, commence only after most of the clay was dehydroxylated (Fig. 2a). Samples of halloysite and sepiolite, however, began to liberate H_2 at much lower temperatures, though the maximum was attained above the dehydroxylation temperature (Fig. 2b). No H_2 was evolved from either of two samples of montmorillonite. Auto-oxidation of Fe^{2+} did not seem

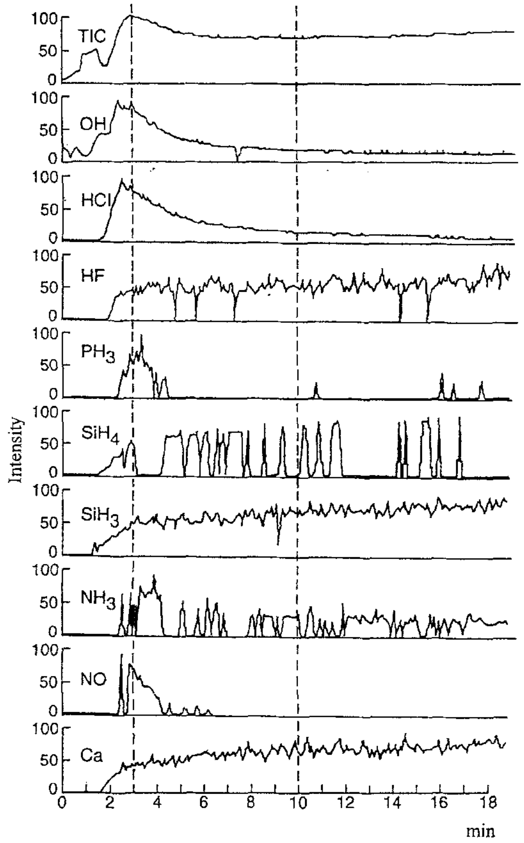

Fig. 1 Single-ion reconstruction traces of selected volatiles derived from montmorillonite (Camp Berteau, Morocco) at 390°C. TIC=total ionic counts. Adapted from [24]

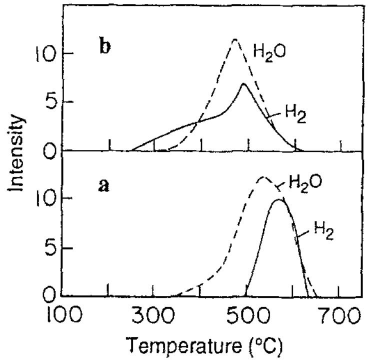

Fig. 2 Mass spectra of H_2 (solid line) and H_2O (dashed line) evolved from a) kaolinite; b) halloysite. Most of the H_2O was frozen out of the volatiles before these reached the mass spectrometer. Adapted from [26]

to have occurred, nor was evolution of H_2 correlated with the total iron content or the amount of Fe^{2+} in the clay.

Clay condensates are colloidal solutions that are formed by cooling the volatiles. They are frequently transparent initially, but become turbid on standing. The composition of these multicomponent systems varies widely with the clay and with the heating and cooling regimes [8, 24]. Separation of the colloidal particles from the liquid was achieved by distillation [19]. Microprobe analysis showed that condensate solids derived from montmorillonite, halloysite and kaolinite contained Si and Al in the approximate ratio of 4:1, as well as minor amounts of Fe and Mg. Such material was also obtained when the reactions were carried out in a stainless steel reactor. Particulate matter derived from laponite was composed mostly of Si and Mg, but no Al. These observations indicate that the solid particles were, indeed, derived from the clay [27]. The liquid fractions of the condensates contain most of the anionic species, with charge balance maintained mainly by ammonium ions and/or protons. Keller [8] and Heller-Kallai *et al.* [24] found that most of the volatiles and condensates analyzed contained HF and HCl. Similarly, Whitney and Landis [9] reported HF and HCl among the gases evolved from clays. F and Cl are also frequently evolved from

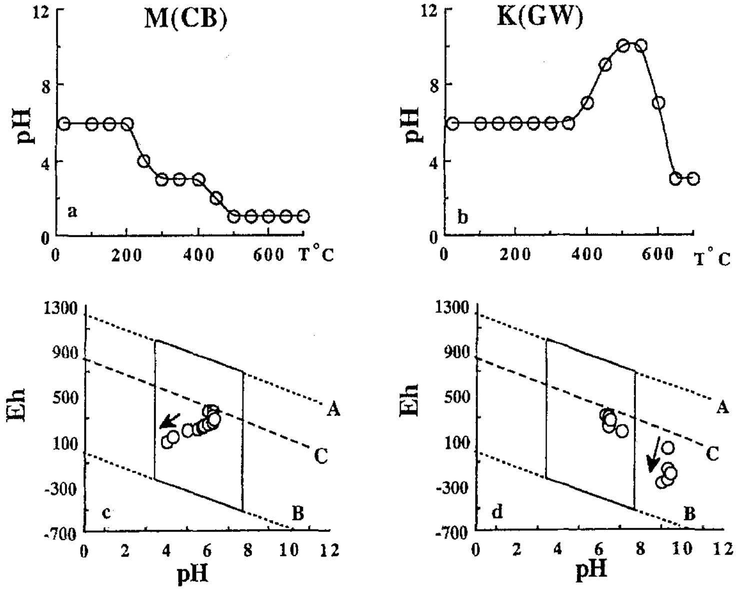

Fig. 3 a) and b) Changes in *pH* of condensates with temperature; c) and d) changes in *pH/Eh* of condensates with temperature. a) and c) montmorillonite (Camp Berteau, Morocco); b) and d) kaolinite (Georgia, USA, well-ordered). Lines A, B and C correspond to upper and lower limits of water stability and to complete oxidation/reduction neutrality respectively. The arrows indicate the direction of increasing temperature. Adapted from [22, 27]

micas [25]. In contrast, Wicks and Ramik [7] claimed that, while HF was common, HCl was only rarely released from hydrous minerals and Paulik *et al.* [10] contended that, on heating clays, only three gaseous decomposition products are formed: H_2O, SO_3 (SO_2) and CO_2. The reason for these disagreements is unclear. They may be due to different sensitivities of the apparatus or to a fortuitous choice of the minerals studied.

pH/*Eh* values of the condensates differ from one clay mineral to another and, like the composition of the volatiles and condensates, they change with the heating regime. On raising the temperature the *pH* of a condensate may increase, decrease or remain unchanged. *pH* values ranging from 1.6 to 11 have been observed (Figs 3a and b). All the condensates examined had two features in common: during dehydroxylation of the clay they were acidic and the *Eh* values tended towards the reducing field (Figs 3c and d) [22]. A low *pH* of dehydroxylation water may be caused by concomitant release of anions. For example, 0.02% of structural Cl^-, which would escape detection in most routine analyses of the parent clay, if released as HCl together with 5% hydroxyl water, would lower the *pH* of this water to 1. Evolution of H_2 may account for the reduction in *Eh* of some of the condensates, but neither of these explanations is generally applicable to all hydrous phyllosilicates.

The composition of clay volatiles and condensates is sample specific. Clays of the same mineral group give rise to very different assemblages. On the basis of the limited number of experiments published it seems that evolution of H_2 may be a group characteristic related to the structure of the minerals.

Catalytic effects of clay volatiles and condensates in organic reactions

The catalytic effect of clay minerals on a wide range of organic reactions has been extensively studied and utilized. Their reactivity is generally attributed to intrinsic properties of the clay, such as large surface area, surface acidity or the ability to participate in redox reactions. The question arises whether this reactivity is, indeed, entirely due to the clay itself or whether volatiles or condensates may contribute to the catalysis.

Figures 4b and f show the effect of volatiles and condensates from montmorillonite on cracking of tetracosane ($C_{24}H_{50}$). Similar experiments were performed with nonadecane ($C_{19}H_{40}$). The reactions with volatiles were carried out in an open system, those with condensates were batch reactions in sealed ampoules. The effects of direct contact of the hydrocarbon with the parent clay under similar experimental conditions are shown for comparison (Figs 4a, c and e). Both volatiles and condensates catalyzed cracking of the long-chain hydrocarbon to give a product assemblage, denoted *A*, in the entire temperature range in-

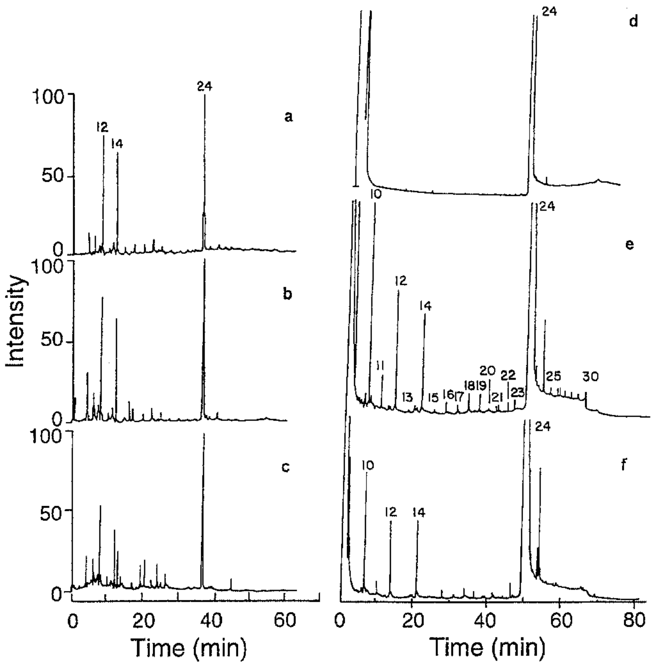

Fig. 4 Gas chromatograms of liquid products from tetracosane with a) clay, 250°C; b) volatiles, 500°C; c) clay, 500°C; d) acidified water; e) clay; f) condensate. Experiments a–c) were carried out in an open system, d–f) in closed ampoules at 160°C. Montmorillonite (Upton, Wyoming) was used throughout [17, 18]

vestigated (Figs 4b and f). It was also the only product assemblage obtained from mixtures of the alkane with clay minerals up to about 250°C in an open system (Fig. 4a) and at 160°C in a closed system (Fig. 4e). At temperatures above 250°C in an open system an additional assemblage, *B*, was obtained from mixtures of tetracosane with montmorillonite (Fig. 4c) or halloysite, but not with kaolinite or sepiolite. The components of assemblage *A* have been identified by gas chromatography-mass spectrometry. They conform to the criteria for acid catalysis. Products *B* are the result of direct contact with the surfaces of some reactive clays at elevated temperatures [17, 18]. The results are summarized in Table 1.

Experiments in a dynamic system confirmed that the reactions with condensates are genuinely catalytic. The conversion of tertiary butyl acetate to isobutylene and acetic acid and the decomposition of *n*-octane were used as model reactions. In these on-stream experiments the reactivity was confined to the particulate matter derived from the colloidal suspensions. Per unit mass this material was a more efficient catalyst than the parent clay. The distillates were unreactive [19]. In batch reactions in sealed ampoules, however, in which the distillates were heated with *n*-octane for 3 days at 150°C, they did catalyze cracking of

Table 1 Experiments performed with *n*-alkane

System	Reagents	Temperature	Product
Open	volatiles	<500°C	*A*
"	clay	<250°C	*A*
"	clay: kaolinite	250–500°C	*A*
"	sepiolite	"	"
"	montmorillonite	"	(*A*+*B*)
"	halloysite	"	"
Closed	condensate	160°C	*A*
"	clay+H_2O	160°C	*A*

n-octane [27]. Initially these distillates were clear liquids, but they became turbid on standing. It is therefore uncertain which components of the system are capable of exerting catalytic effects, but there is no doubt that the particulate matter is more effective than the distillate. The aqueous medium may reduce reactivity, but it does not destroy it. The reactivity of the condensates persists even after several years' storage [18].

Decarbonation and recarbonation of calcite

Clay volatiles react with carbonates, liberating CO_2. This was first detected by monitoring the CO_2 evolved on pyrolysis of calcite powder in an apparatus of the Rock Eval type [20, 21] used for typing kerogen. The amount of CO_2 evolved was proportional to the clay:calcite ratio, provided that only one clay mineral was used. Clay mixtures did not react like the sum of their components, as was also noted for the composition of their volatiles [24]. The temperature at which decomposition of calcite occurred was appreciably reduced by the presence of clay volatiles, causing evolution of inorganically derived CO_2 at temperatures less than 400°C, which is usually regarded as the limit between organic and inorganic CO_2 in Rock Eval analysis. The residue after calcite decomposition appears to have been carried off as an aerosol in the stream of He which was passed through the pyroprobe during the experiments. Passage of volatiles through calcite frequently increased their *pH*, but in at least one instance an unexplained decrease was observed [22].

In a different set of experiments cleavage surfaces of large crystals of calcite were exposed to clay volatiles [23]. Electron microscopy revealed that various components of the volatiles, such as F, Cl or S attacked calcite, giving rise to a variety of surface morphologies (Fig. 5). The reactions commenced at temperatures of about 150°C or less. Reactions of this type may account for the distortion of the calcite endotherm observed in DTA curves of calcite exposed to vola-

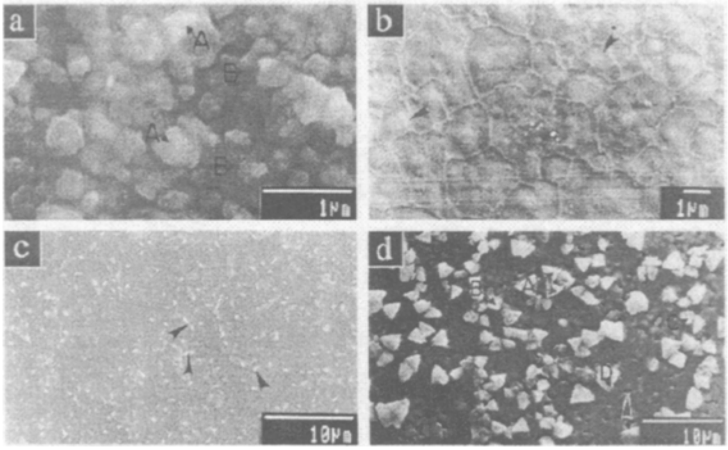

Fig. 5 Electron micrographs of calcite exposed to volatiles from different montmorillonites. The letters and arrows in a, b and c indicate regions rich in either Cl or S. Arrows in d point to crystals of different shapes [23]

tiles from kaolinite [28]. They may also explain the effect of kaolinites or their clay volatiles on the recarbonation of decarbonated calcite. Depending on the kaolinite or the volatiles to which the calcite had been exposed during decarbonation, different polymorphs of calcium carbonate with varying morphologies were formed on recarbonation [29]. It seems possible that different anions incorporated into decarbonated calcite modify the course of the recarbonation process.

The effect of clay condensates on quartz

Figure 6a shows an electron micrograph of a fragment of an *m* face of a synthetic quartz crystal after immersion in condensate derived from montmorillonite at room temperature. The spherical particles are composed of SiO_2, the dendrites consist of NH_4Cl. Such dendrites were frequently observed on quartz crystals immersed in clay condensates. This is compatible with the observation that NH_3 and NH_4^+ commonly occur in clay volatiles and condensates respectively [8, 24]. Similar dendrites were formed by immersion of quartz in NH_4Cl solution at room temperature. According to a reference dating to 1916 [30] the presence of NH_4Cl in solution enhances dissolution of quartz, but no subsequent confirmation of this observation seems to have been published. Figure 6b shows the effect of a 1/25 *M* solution of NH_4Cl on quartz at 300°C. At this temperature dendrites did not form, but the initially almost smooth quartz surface was clearly etched. Similar etch features were produced by clay condensates. It seems possible that NH_4^+, Cl^- and F^- present in many of the condensates contributed to this effect [27].

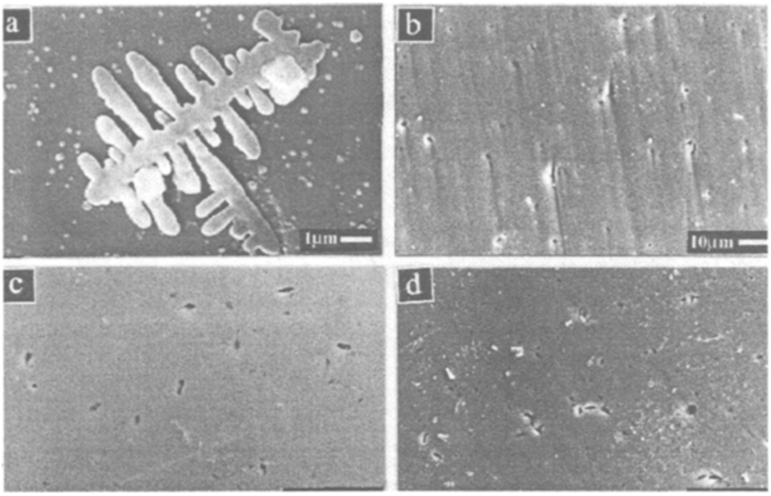

Fig. 6 Electron micrographs of quartz exposed to a) condensate from montmorillonite (Texas); b) 1/25 *M* NH_4Cl solution; c) and d) condensate from sepiolite. a) and c) room temperature; b) and d) 300°C [27]

Figures 6c and d show fragments of the same m face of the quartz crystal after exposure to a condensate derived from sepiolite at room temperature and 300°C respectively. This condensate contained only minor amounts of NH_4Cl and no dendrites appeared. The observed etching must, therefore, have been caused by other components of the suspension [27].

The effect of clay condensates on zeolites

Exploratory experiments were carried out with a sample of Linde X, which is a synthetic high-alumina faujasite [27]. The sample was exposed to a condensate derived from Ca montmorillonite at 105°C for one week, during which time the suspension was slowly evaporated and renewed three times. Subsequently it was Na-exchanged and dried, to render it comparable to a similarly exchanged and dried, but otherwise untreated, sample. Figure 7 shows the XRD patterns of the two samples. The differences between them are appreciable.

Faujasites are cubic crystals. Exposure to the condensate caused a contraction of 0.3% in the lattice parameter. In addition the intensity of the XRD pattern was reduced, the relative intensities of the peaks were changed and background scattering was enhanced. The decrease in pattern intensity is not apparent in the figure, due to manipulation of the intensity scale. A reduction in cell size of faujasite without other striking modifications of the XRD patterns indicates a decrease in the Al:Si ratio, leaving the (Si+Al):O ratio unchanged [31, 32]. A decrease of 0.3% in the lattice constant corresponds to a loss of about 0.04 mole

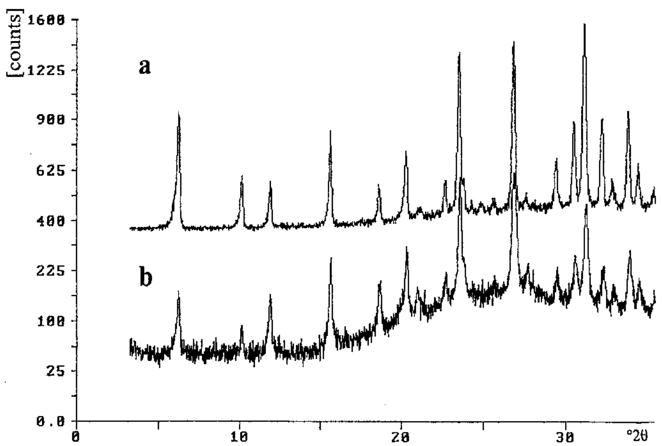

Fig. 7 XRD traces of Linde X: a) untreated; b) after exposure to condensate from montmorillonite (Texas) [27]

fraction of AlO$_2^-$ [31]. The drastic changes in relative intensity of some of the peaks, e.g. those of the 220 and 311 reflections at about 8.8 and 7.5 Å respectively, suggest that other structural changes occurred. Apparently these led to partial breakdown of the structure, which accounts for the reduced pattern intensity and the increase in background scattering. The half-width of the peaks remained unchanged, which indicates that the crystalline fraction was of uniform composition.

The changes in the XRD pattern of Linde X suggest that exposure to clay condensate caused some dealumination and partial destruction of this Al-rich zeolite. This inference received support from infra-red spectra [27]. Further investigations are required to establish the validity of the conclusions and to determine whether clay volatiles and condensates can cause dealumination and structural breakdown of other aluminosilicates.

Conclusions

Clay volatiles and condensates are reactive mixtures whose composition and release pattern from the parent clays are sample specific. Experiments to date have shown that volatiles and condensates act as genuine acid catalysts in reactions with organic material, and that, under various experimental conditions, they attack carbonates, quartz and a high-alumina zeolite. To what extent these conclusions can be extrapolated to reactions with other minerals or mineral groups remains to be established. It seems very probable that further research will reveal many more organic and inorganic substances that are attacked by these potent reagents.

Even at this stage the results may have far-reaching implications for our understanding of various aspects of rock diagenesis, and of the alteration, maturation and transport of organic matter in nature. It seems that some of the catalytic action generally attributed to clays at elevated temperatures may, in fact, be due to the fluids derived from them. These are much more easily transported than the parent clays and facilitate more intimate contact with solid organic matter, in particular with kerogen. The same fluids which transport the active catalyst can attack the surrounding rocks and dissolve cements, thereby opening up new pathways for reagents and products. Moreover, the observation that the reactivity of condensates was preserved for long periods of time suggests that the reactions are not confined to the vicinity of the parent clays. Even under laboratory conditions some of the reactions commenced at temperatures that were sufficiently low to be geologically viable.

Possible effects of volatiles and condensates should be taken into consideration in any attempt to interpret reactions involving phyllosilicates at elevated temperatures. These effects may be obscured by other processes which produce greater changes, but they are always present. Because the composition of the evolved gases differs from one sample to the next, a precise explanation may require a study of each particular assemblage. This limitation must be taken into account in designs of model experiments and in any attempt to extrapolate the results obtained with one sample to an entire mineral group.

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