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The dehydroxylation of kaolinite

DOUGLAS YESKIS, A. F. KOSTER VAN GROOS AND STEPHEN GUGGENHEIM
Department of Geological Sciences
University of Illinois at Chicago
Chicago, Illinois 60680

Abstract

High pressure DTA experiments show that the dehydroxylation of kaolinite in dry runs with *P*(Total) = *P*(argon) proceeds at 525°C and 1 bar to 627°C at 30.5 bars. Further increase in pressure slowly increases the dehydroxylation temperature, at 5270 bars it occurs at 670°C. Under conditions of *P*(Total) = *P*(H_2O), dehydroxylation occurs at 650°C at 46.5 bars and 520°C at 1088 bars after which it increases to 571°C at 5716 bars. The results are explained by postulating the presence of a liquid-like, "meta-liquid" phase, having a pressure-dependent H_2O solubility. *P–T* relations of the kaolinite dehydroxylation reactions are best explained by assuming that they are metastable equilibrium reactions around a metastable invariant point at 625°C and 25 bars and a singular point at 640°C and 40 bars.

Introduction

It is well known (see review by Brindley, 1975) that clay minerals go through a series of transitional phases when heated to progressively higher temperatures before transforming to a stable high-temperature assemblage. In kaolinite, for example, a disordered layer structure (metakaolin) develops topotacticly during dehydroxylation. Metakaolin eventually becomes amorphous with additional heating (Brindley and Nakahira, 1959). Infrared studies (Stubican, 1959; Stubican and Roy, 1961; Pampuch, 1966) have shown that metakaolin initially retains approximately 1/8 of the hydroxyls, which are lost after prolonged heating. Furthermore, the dehydroxylation of kaolinite at one atmosphere takes place at temperatures well above the reaction kaolinite ⇆ pyrophyllite + hydralsite + montmorillonite (Roy and Osborn, 1954) which is slow, and occurs at 400°C at moderate pressures. The nature of the dehydroxylation of kaolinite is not well understood: it may represent (a) a well defined (i.e., with a sharp transition), metastable reaction or (b) a reaction from a metastable to a stable phase assemblage which, because of kinetic effects, proceeds rapidly only at the experimentally established dehydroxylation temperature. This study reports an investigation on the nature of the dehydroxylation of kaolinite by using high pressure differential thermal analysis (HP-DTA).

Previous work

Early studies on the dehydroxylation of kaolinite at elevated pressures (Stone and Rowland, 1954; Ellis and Mortland, 1962) were limited to experiments at relatively low pressures. The results of these experiments are shown in Figure 1. Stone and Rowland observed a rapid shift of the endothermic DTA peak to higher temperatures with an increase of the water pressure to 6 atm. Ellis and Mortland obtained similar results at even lower pressures, ranging from near vacuum to 3 bars. A later DTA study by Weber and Roy (1965) was carried out to pressures of 700 bars, with *P*(H_2O) = *P*(Total). They found that the dehydroxylation temperature increased with increasing pressure to approximately 40 bars, which is in good agreement with the earlier work. At higher pressures, however, dehydroxylation occurs at much lower temperatures. Their data, using the onset (characteristic) temperatures of the DTA peak, are shown also in Figure 1. This result is unusual. A dehydroxylation reaction, presumably of the type $2OH^- \rightleftarrows H_2O + O^{2-}$, is expected to occur at higher temperatures with increasing water pressure, because increasing water pressure usually inhibits dehydroxylation. Weber and Roy suggested that the reaction was metastable and that "above 400 psi, some mechanism, presumably the catalytic effect of water, facilitates structural reorganization at much lower temperatures" (p. 311). The term "metastable reaction" in context with the possible catalytic effect of water probably is used to describe a conversion of a metastable assemblage to a stable one, rather than a reaction involving two metastable assemblages.

Experimental method

The HP-DTA system (Koster van Groos, 1979) holds up to three uniformly machined gold sample capsules (120 mg in weight with a wall thickness of 0.05 mm and approximately 7 mm long). These capsules may be left open to an inert pressurizing medium such as argon or

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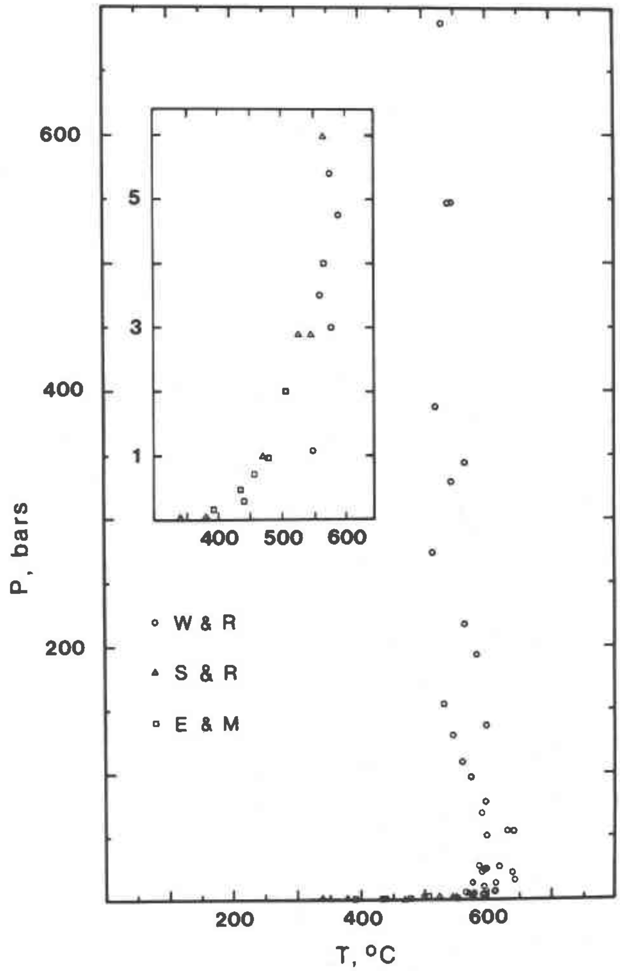

Fig. 1. A P–T diagram of previous results of the dehydroxylation of kaolinite under water pressure (W & R = Weber and Roy, 1965; S & R = Stone and Rowland, 1954; E & M = Ellis and Mortland, 1962). The inset shows an expanded pressure range from near vacuum to 6 bars.

helium, or welded shut. A Pt-$Pt_{90}Rh_{10}$ thermocouple makes thermal contact in a re-entry well at the bottom of each capsule. Two capsules containing samples and a third containing Al_2O_3 as a reference are placed in a copper cell assembly (Koster van Groos and Guggenheim, 1983) which is sealed in an internally heated pressure vessel similar to the one described by Holloway (1971).

Samples of 25 mg kaolinite with 10 wt.% pure quartz (St. Peter Sandstone), which was ground to pass a 200 mesh, were used. The quartz was added to monitor the low-high quartz inversion as a internal temperature standard (Koster van Groos, 1982) and as an indicator of thermal contact between thermocouple and capsule. Temperature, as measured by the reference capsule thermocouple, was corrected for deviations caused by the dehydroxylation reaction and by base line drift by using ΔT. The correction for the base line drift is usually less than 2°C. These temperatures are believed accurate to 1°C. For the determination of ΔT we used the 50 μv range of a Kipp recorder which can resolve temperature differences, ΔT, to 0.05°C. Calibrated high precision bourdon type gauges, accurate to within 0.1%, were used to measure the argon pressure medium. Separate gauges for low and high pressures covered ranges from 0–1000 bars and 0–7500 bars. Pressures are believed to be accurate to within 0.5%. Silica wool filler was used to prevent capsule movement and to minimize gas convection for open capsule runs. All experiments were done at a linear heating rate of 20°C/min., using a Honeywell programmable controller.

Experiments using open capsules with added water showed minor differences from open capsule runs without additional water, suggesting that at the moderate temperatures for which dehydration occurs (i.e., greater than 500°C), most water vapor present in the capsule is replaced by argon through convection. For these runs, it may be assumed that P(argon) approaches P(Total). Experiments with $P(H_2O) = P(\text{Total})$ were made in closed capsules. In these runs, first a small amount of water was pipetted into the capsule after which the sample was added, and the capsule was welded shut. Capsules were checked for leaks before and after the run. Some capsules showed a weight loss after the run; because the capsules are fragile, it is likely that small leaks may have originated during pressurization.

American Clay Mineral Society Source Clay (KGa-l), a well crystallized kaolinite, from the Coss Hodges Pit, near Sandersville, Washington County, Georgia (van Olphen and Fripiat, 1979), was used as received. The sample was powdered in a mixer/miller for aproximately 25 minutes and passed through a 200 mesh screen. Scanning electron microscope (SEM) examination indicates an average grain size of about one micron. Debye–Scherrer X-ray photos indicate that the clay is relatively well-crystallized and pure. van Olpen and Fripiat (1979) report that the weight loss upon dehydroxylation (after DTA) is 13.11% (theoretical limit is 14%). These results, they suggested, indicate that the sample contains less than 7% impurities. However, it is likely that some water remains behind in metakaolin as is shown by infrared data (see Introduction) and therefore, the purity is probably considerably higher. A complete chemical analysis is given by van Olphen and Fripiat (1979).

Results and discussion

Approximately 20 successful runs were made in this study, see Table 1. Examples of representative DTA patterns for runs in open and close capsules are shown in Figures 2 and 3, respectively. Note that the dehydroxylation peak in the open capsule runs tends to be much sharper than in the closed capsule runs. This difference indicates that dehydroxylation is more rapid in the open

Table 1. DTA results for the dehydration reaction in kaolinite (KGa-l)

	Onset		Peak		Return	
wt.%H_2O	P, bar	T, °C	P, bar	T, °C	P, bar	T, °C
dry	1	525	1	595	1	647
dry	1	540	1	600	1	647
dry	30.5	627	30.5	666	30.5	685
16*	30.5	621	30.5	668	30.5	686
5*	46.5	650	46.5	670	47	684
3*	46.5	639	46.5	672	47	687
2*	69.5	627	70	667	70	685
3*	69.5	629	70	669	70	687
3*	110	621	111	657	111	677
dry	114	630	115	666	116	693
24+	188.5	617	190	665	191	686
2*	218	555	222	619	224	665
dry	250	635	251	660	252	679
33+	369	643	371	657	372	672
4*	606	538	613	570	618	597
dry	644	634	651	655	651	665
16*	1088	520	1026	564	1038	593
16*	1223	617	1232	641	1234	651
dry	1234	645	1238	654	1238	663
30*	5270	557	5270	575	5270	590
10	5270	650	5270	660	5270	670
10*	5716	560	5725	571	5750	591
20*	5716	571	5725	572	5745	585

* Closed capsule runs

\+ He pressure medium

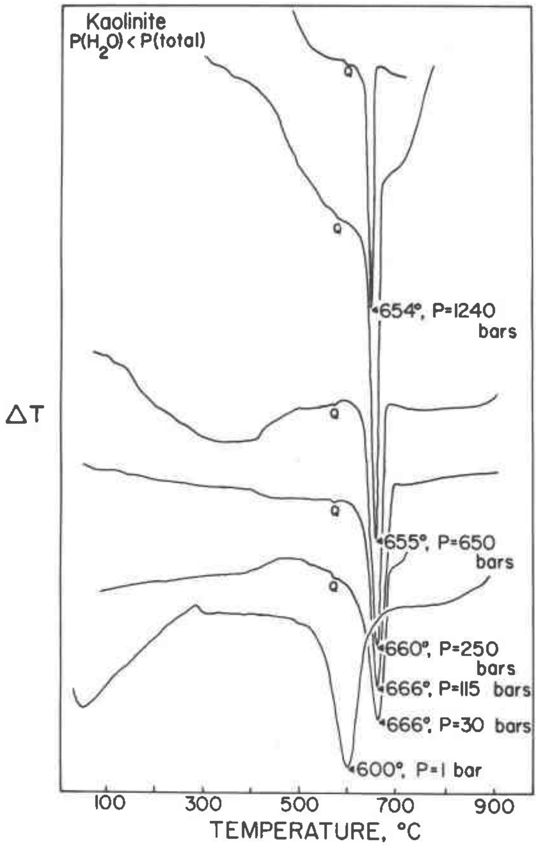

Fig. 2. Representative DTA patterns of kaolinite (KGa-l) for open capsule runs without added water. Note that the peaks become sharper with increasing pressure. (Q = Quartz).

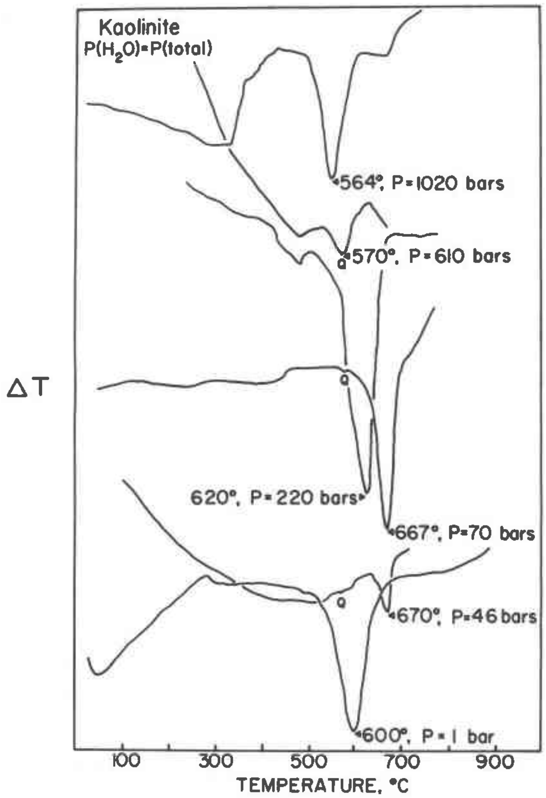

Fig. 3. Representative DTA patterns of kaolinite (KGa-l) for closed capsule runs with added water. Although the peaks become sharper with increasing pressure, peak widths are significantly different than those shown in Fig. 2. All runs made with the recorder at the 50 μv range, except the 610 bar run, which was made at the 100 μv range.

capsule runs and suggests that differences in $P(H_2O)$ may be important. For both cases, an increase in pressure reduces the peak width, which indicates that the dehydroxylation proceeds more rapidly. This reduction is especially evident in the open runs, where a peak width of more than 100°C at 1 bar becomes approximately 20°C at 1240 bars. In order to indicate the shape of the DTA peak the extrapolated onset, the peak, and the extrapolated return temperatures are listed in Table 1 and shown in Figure 4. The temperatures for each open capsule run are shown as solid lines and for closed capsule runs as dashed lines. Because the extrapolated onset temperature indicates the beginning of the reaction, the *P–T* curves of the reactions are based on these temperatures. The results for the closed capsule runs at pressures around 600 bars as shown in the inset of Figure 4 match the data of Weber and Roy (1965) very well (closed circles). The lower pressure data of Weber and Roy (1965), Stone and Rowland (1959) and Ellis and Mortland (1962) also correspond well to our data. This suggests that in the closed capsule runs $P(H_2O)$ closely approaches P(Total). The agreement between the various sets of data using well-

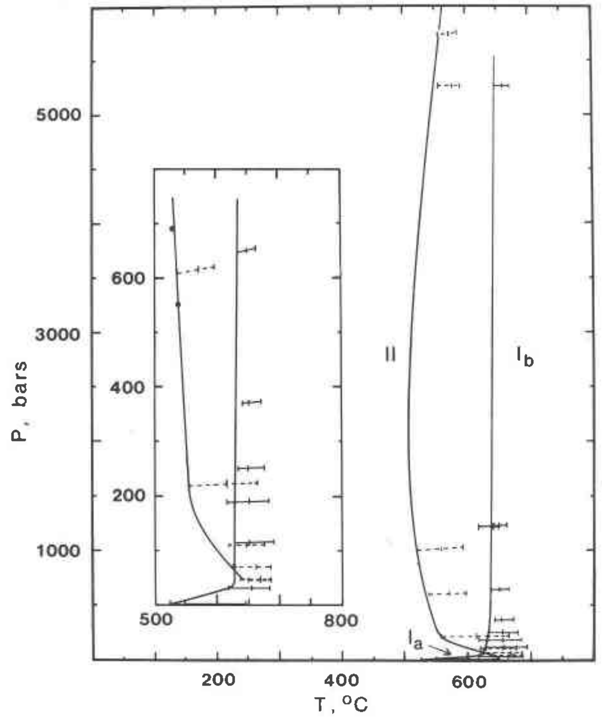

Fig. 4. The results as plotted in a *P–T* diagram. The inset shows details at low pressure. The bars designate the extrapolated onset temperature, the peak temperature, and the extrapolated return temperature. Solid bars are open capsule runs and dashed bars are for closed capsule runs. Reaction curves are drawn through the extrapolated onset temperatures for open capsule runs at low pressure (Ia), at high pressures (Ib) and for closed capsule runs (II). The two solid circles (see inset) are data from Weber and Roy (1965).

crystallized material and with $P(H_2O) = P(\text{Total})$ indicates that the dehydroxylation of kaolinite is not dependent on different experimental conditions.

In microscopic examination no difference was seen between the starting material and the run products. Also, the quartz that was present as an internal standard did not change in appearance.

X-ray powder data obtained using the Debye–Scherrer technique confirmed the breakdown of kaolinite. Run products were quartz, which was present in the starting material, and a phase with a few very weak reflections. This suggests the presence of a semi-amorphous phase, which may be metakaolin (Roy et al., 1958; Brindley and Nakahira, 1959).

The *P–T* diagram in Figure 4 shows that the data obtained from the open runs differ greatly from that of the closed runs (compare curves I and II). Furthermore, the curve obtained from the open runs is divided into two parts: a portion (Ia) from 1 to about 30 bars where the pressure affects the reaction temperature strongly, and another (Ib) at pressures above 30 bars where the effect of pressure on the reaction temperature is very small.

Because these *P–T* curves are at conditions at which kaolinite is not stable, it must be assumed that they represent metastable reactions. These reactions may be presented as:

$$\text{Kaolinite} \rightleftharpoons \text{X} \qquad \text{(Ia)}$$

$$\text{Kaolinite} \rightleftharpoons \text{Y} \qquad \text{(Ib)}$$

$$\text{Kaolinite} + \text{Vapor} \rightleftharpoons \text{Z} \qquad \text{(II)}$$

In these reactions, the following phases are assumed to participate: kaolinite, vapor, and the assemblages X, Y, and Z. The assemblage X is identified as metakaolin + vapor. Metakaolin is a disordered layer structure with some hydroxyl present (Roy et al., 1958; Brindley and Nakahira, 1959) and probably has the same Al/Si as kaolinite. The vapor phase is considered to be pure H_2O. In reaction (Ib) the volume change is probably small, which suggests that assemblage Y does not contain vapor. In reaction (II), the phase assemblage Z is stabilized with pressure; the negative slope of the reaction suggests strongly the presence of a liquid-like phase which has a varying solubility of H_2O, increasing with pressure. Above pressures of 2,000–3,000 bars, the slope of the curve becomes positive, which may indicate that this phase approaches a maximum in H_2O solubility. We will call this phase Z a meta-liquid. We do not know whether it is quenchable. It may have the same Al/Si as kaolinite or it may be enriched in SiO_2 or Al_2O_3. It has been suggested that in this system γAl_2O_3 can be present (Roy et al., 1958), although this phase may be formed at somewhat higher temperatures. If γAl_2O_3 is produced together with the meta-liquid, then the meta-liquid is enriched in SiO_2.

The phases in this system are: kaolinite (K), metakaolin (MK), meta-liquid (ML), vapor (V), and possibly γAl_2O_3 (C). Thus, there are four, or possibly five phases present in these reactions. The phase rule is applicable to a system when conditions of constant pressure, temperature, and chemical potential are met, even in a metastable equilibrium. If the chemical potential of the components participating in the above reactions is constant, then the phase rule applies. Assuming this, the system must behave as a binary join if Al/Si of the condensed phases is constant, or as a ternary system if not. The four (binary) or five (ternary) phases present in the reaction is the maximum possible. We now can list the possible reactions in this system, assuming it is binary:

$$\text{K} \rightleftharpoons \text{MK} + \text{V} \qquad (1)$$

$$\text{K} \rightleftharpoons \text{ML} + \text{V} \qquad \text{(2a)}$$

$$\text{K} + \text{V} \rightleftharpoons \text{ML} \qquad \text{(2b)}$$

$$\text{K} \rightleftharpoons \text{ML} \qquad (3)$$

$$\text{K} + \text{MK} \rightleftharpoons \text{ML} \qquad \text{(4a)}$$

$$\text{K} \rightleftharpoons \text{MK} + \text{ML} \qquad \text{(4b)}$$

$$\text{MK} + \text{V} \rightleftharpoons \text{ML} \qquad (5)$$

$$K + MK \rightleftharpoons ML + V \quad (6a)$$

$$K + V \rightleftharpoons MK + ML \quad (6b)$$

The reactions (2a), (4a), and (6a) assume that ML contains less H_2O than kaolinite, in reaction (3) ML contains the same amount of H_2O as kaolinite, and in reactions (2b), (4b), and (6b) ML contains more water than kaolinite. Assuming that at low pressures ML will contain less H_2O than kaolinite, then the reactions (2a), (4a), and (6a) are possible. If metakaolin and H_2O are end members and the join is binary, then reaction (6a) is invariant, from which four reactions emanate, forming a Schreinemaker's bundle around the invariant reaction, see point I in Figure 5. The relevant reactions are 1, 2a, 4a, and 5, which are also shown. An increase in pressure will increase the solubility of H_2O in ML so that in reaction (2a), at some elevated pressure, meta-liquid will contain the same amount of H_2O as kaolinite, and reaction (3) becomes possible; a further increase of pressure also stabilizes reaction (2b). Clearly then, reactions (2a), (3), (2b) terminate in a singular point S. The arrangement for all reactions is shown in Figure 5.

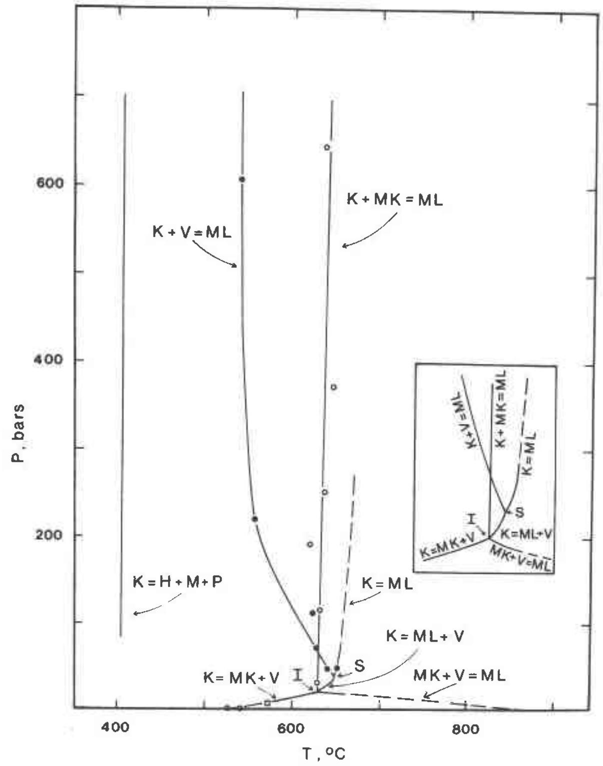

Fig. 5. The *P–T* relations of the system kaolinite–H_2O. It is assumed that metakaolin and H_2O vapor are the endmembers of a binary system, see text for discussion. The curve K = H + M + P is considered to represent the stable equilibrium reaction (after Roy and Osborn, 1954). The inset shows the low-pressure regime enlarged. (○ = open capsule runs, ● = closed capsule runs, □ = data from Stone and Rowland (1954)) Abbreviations: K = kaolinite, H = hydralsite, M = montmorillonite, P = pyrophyllite, V = vapor, ML = meta-liquid, MK = metakaolin, S = singular point, I = invariant point).

As mentioned above, it is possible that γAl_2O_3 is a participating phase in these reactions. If so, the invariant reaction is:

$$K + MK \rightleftharpoons ML + C + V, \quad (7)$$

and in the reactions, 2a, 3, 4a, 5, the phase assemblage ML is replaced by ML + C, and the other two reactions are C-absent or ML-absent:

$$K + C \rightleftharpoons MK + V \quad (8)$$

$$K + ML \rightleftharpoons MK + V \quad (8a)$$

These are identical to reaction (1) but because Al/Si of metakaolin and kaolinite is assumed to be identical, C and ML are only present in principle. We emphasize that the *P–T* relations of the ternary reactions would be the same as in the binary, except that ML would become ML + C.

The pressure and temperature of the invariant point is determined on the basis of both our data and the low pressure data of Stone and Rowland (1954), note the open square in Figure 5. The data locate the invariant point at approximately 25±5 bars and 625±5°C. The location of the singular point is 40±10 bars and 640±10°C. Of course, all these reactions are metastable with respect to the pyrophyllite + hydralsite + montmorillonite assemblage. No data are available for other reactions. The thermal effect of reaction (5) must be very small and is not detected in our experiments. We estimate it to occur at 1 atmosphere at approximately 850°C on the basis of the discussion by Roy et al. (1958, p. 204), and it may include the additional γAl_2O_3 phase (see discussion above).

The arrangement of the various reactions in the dehydroxylation of kaolinite is very similar to that of portlandite (Wyllie and Tuttle, 1960). However, while in the latter study all the phase assemblages represented stable equilibria, there cannot be any doubt that in this study we describe a series of metastable reactions.

It must be recognized that in the above discussion an additional phase, meta-liquid, is postulated. The major chemical difference between metakaolin and meta-liquid is the water content, for the meta-liquid phase must be variable in water content. It may be possible to equate metakaolinite with the meta-liquid phase. However, if this is the case, the metakaolin structure requires sites which can accommodate either OH groups or vacancies. The *P–T* relationships for this system would then degenerate to three reactions:

$$K \rightleftharpoons MK + V \quad (1)$$

$$K + V \rightleftharpoons MK \quad (2b')$$

$$K \rightleftharpoons MK \quad (3')$$

terminating in a singular point. However, the evidence does not appear to support this interpretation since the data indicate that dehydroxylation in the wet system at 46.5 bars occurs at higher temperatures than in the dry system. The temperature difference of approximately 20°C is far greater than the temperature uncertainty of our experiments.

In summary, it is concluded that the dehydroxylation of kaolinite proceeds in a series of well-defined metastable reactions around an invariant point. The development of transitional phases in other clay systems similar to metakaolin (especially in smectite), suggests the likely presence of a meta-liquid phase in those systems as well.

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