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High-pressure differential thermal analysis (HP-DTA) of the dehydroxylation of Na-rich montmorillonite and K-exchanged montmorillonite

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ABSTRACT

High-pressure differential thermal analysis (HP-DTA) of the dehydroxylation of a Na-rich montmorillonite (Clay Minerals Society Source Clay SWy-1) and of the same montmorillonite after being K-exchanged was carried out at pressures to 2.5 kbar. The dehydroxylation can be treated as a reaction in the binary system montmorillonite-H_2O. The dehydroxylation reaction of SWy-1, montmorillonite (M) = montmorillonite dehydroxylate (MD) + vapor (V), occurs at about 710 °C at 1–2 atm and increases to 793 °C at approximately 40 bars, where it terminates in an invariant point. At this point, three other reactions emanate. One of these, the reaction M + MD = liquid (L), also occurs at approximately 800 °C at 500 bars. At a slightly higher but unknown temperature and pressure, a second reaction (M = L + V) terminates in a singular point, from which two additional melting reactions originate: M + V = L, which decreases to 674 °C at 2460 bars, and M = L, which is assumed to lie close to the reaction M + MD = L. The fourth reaction emanating from the invariant point, MD + V = L, also occurs at approximately 920 °C at 1 atm. The reactions involving K-exchanged SWy-1 are analogous to those of SWy-1. The dehydroxylation occurs at about 705 °C at 1–2 atm, increasing to 800 °C at approximately 40 bars. The melting reaction M + V = L decreases in temperature to 728 °C at 770 bars. For both SWy-1 and K-exchanged SWy-1, the temperature range over which the reaction M + MD = L occurs becomes narrower at higher pressures. This is especially noticeable in runs with K-exchanged SWy-1. The enthalpy of dehydroxylation for SWy-1 is estimated at 300 ± 50 kJ/mol and for K-exchanged SWy-1 at 260 ± 50 kJ/mol. The above reactions represent metastable equilibria.

INTRODUCTION

The removal of hydroxyl from montmorillonite occurs as an endothermic reaction between 500 and 700 °C at 1 atm (e.g., Bradley and Grim, 1951). With a further increase in temperature, an endothermic melting reaction takes place, followed by an exothermic recrystallization reaction (e.g., Takeshi and Uno, 1971). These reactions are metastable, as is indicated by long-duration experiments (13 d), which show that Mg-Al montmorillonite is not stable above ~480 °C (Roy and Roy, 1955). The dehydroxylation reaction is readily reversible (Heller et al., 1962), and X-ray powder diffraction shows that the dehydroxylated montmorillonite is structurally very similar to the original montmorillonite (Bradley and Grim, 1951). The loss of hydroxyl groups is analogous to the dehydroxylation of other aluminous 2:1 layer silicates such as muscovite and pyrophyllite (see Brindley, 1971; Guggenheim et al., 1987).

In this paper, we present data on the effect of P_{H_2O} on the dehydroxylation of montmorillonite using Clay Minerals Society Source Clay sample SWy-1, a Na-rich montmorillonite from the Newcastle Formation in Crook County, Wyoming (van Olphen and Fripiat, 1979). A K-exchanged SWy-1 was studied also in order to establish the effect of interlayer chemistry on the dehydroxylation reaction. The same starting materials were used in our previous work on interlayer dehydration studies of montmorillonite (Koster van Groos and Guggenheim, 1984, 1986, 1987). This study is part of an investigation on the effect of the interlayer cation on the dehydroxylation of montmorillonite. The goal of this and other studies (e.g., Yeskis et al., 1985) is to understand the mechanisms of dehydroxylation in layer silicates.

EXPERIMENTAL METHOD

Apparatus

The system for high-pressure differential thermal analysis used in this study has been described by Koster van Groos (1979) and Koster van Groos and Guggenheim (1984, 1986). In summary, the system is composed of a Cu cell with positions for three capsules, two of which hold sample and the third a reference. The ability to run simultaneously two sample capsules allows the study of different starting material at the same pressure and at nearly identical temperatures, which proves very useful for the determination of small reaction-temperature differences between samples. The assembly is mounted in an internally heated pressure vessel (Holloway, 1971). Ar is the pressure me-

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dium. Temperatures were determined using Pt-$Pt_{90}Rh_{10}$ thermocouples. The temperature of the sample is obtained from the temperature of the reference after correction for the temperature differential. This differential was usually less than 3 °C, and the corrected temperature is believed accurate to within 1 °C. Pressures were determined using calibrated Bourdon-type Heise gauges that are accurate to within 0.5%. Because the method is dynamic, the gas within the vessel continuously expands. Consequently, slight overpressures may develop because the pressure release in this type of vessel is slow. In our experience, this overpressure may amount to 1–2 atm; however, the reported data are not corrected for these overpressures. Therefore, low-pressure runs are proportionally more affected than high-pressure runs. The DTA signals were recorded on the 20-μV range of a Kipp recorder, and temperature deviations of 0.02 °C can be resolved. A programmable Honeywell controller maintained a 20 °C/min heating rate, although initially a series of experiments was made using a 10 °C/min heating rate. Since no significant difference was seen between the results, the faster heating rate was used. The system was regularly calibrated against the low quartz–high quartz inversion (Koster van Groos and ter Heege, 1973) by adding 20 wt% quartz to starting material of selected runs. Sample size was approximately 30 mg.

Samples were run in Au capsules that were either open or welded shut. In runs with open capsules, the composition of the vapor phase is not known accurately because during the run the sample dehydrates (loss of interlayer water) and dehydroxylates. Furthermore, in many runs, water was added to the sample in an attempt to maintain $P_{H_2O} = P_{total}$. However, the results of these runs indicate that most H_2O is dissipated and P_{H_2O} is significantly less than P_{total}. Therefore, a series of runs using closed capsules was made with additional water to insure that $P_{total} = P_{H_2O}$. These runs were at higher pressures (above 200 bars), where the molar volume of H_2O is sufficiently small that the capsules would not burst. The sealed capsules were checked for leaks by weighing before and after the experiment. The success rate of all runs was about 30% because experiments often failed because of capsule leaks or equipment difficulties involving electric noise, excessive baseline drift, and other mishaps.

Thermal gravimetric analyses (TGA) and differential thermal gravimetry (DTG) were carried out in N_2 atmosphere, using a Dupont 1090 analyzer, by Mr. P. van der Krieken at the Instituut voor Aardwetenschappen, University of Utrecht, the Netherlands.

Starting material

The hydraulic fraction (<0.1 μm) of Clay Minerals Society Source Clay SWy-1 was used. This fraction is more pure than SWy-1 as received, but it is estimated that more than 10% of amorphous SiO_2 is still present (Koster van Groos and Guggenheim, 1984). The cation exchange was carried out by four washings with 1*N* KCl solution followed by six washings with distilled water and drying in air. Both SWy-1 and K-exchanged SWy-1 were stored at 55% humidity over a saturated solution of $Mg(NO_3)\cdot 6H_2O$. For chemical composition and X-ray diffraction information, see Koster van Groos and Guggenheim (1986).

RESULTS AND DISCUSSION

Thermal gravimetric analysis

The TGA and DTG results for SWy-1 (45-mg sample) and K-exchanged SWy-1 (35-mg sample) are shown in Figure 1. The weight loss related to dehydroxylation (note temperature range above 400 °C) is approximately 5% for both montmorillonites, which is close to the ideal value of 4.9% for sodium montmorillonite (Brindley, 1971; van Olphen and Fripiat, 1979). The DTG analysis indicates that the dehydroxylation reaction of these montmorillonites takes place in two steps. The curve for SWy-1 shows a broad asymmetric peak, which is interpreted to represent a shoulder peak at 650 °C and a main peak at 700 °C. The K-exchanged SWy-1 dehydroxylation reaction curve has two peaks also, at 650 and 670 °C. This interpretation is based, in part, on analogy to pyrophyllite and muscovite (Guggenheim et al., 1987) and is discussed further below.

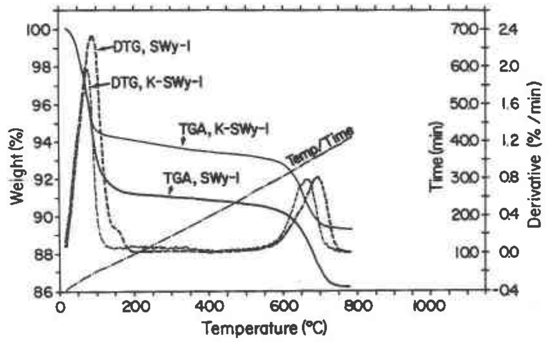

Fig. 1. DTG and TGA patterns of SWy-1 and K-exchanged SWy-1 at 1-atm pressure. Note that the interlayer water content of K-exchanged SWy-1 is significantly less than of SWy-1 (Koster van Groos and Guggenheim, 1986).

High-pressure differential thermal analysis

Approximately 45 successful runs were made in the HP-DTA study. In Tables 1 and 2 are listed (a) the onset of the dehydroxylation signal, (b) the peak temperature, (c) the temperature at which the signal sharply returns toward the baseline (we interpret this temperature, which is reproducible, as the termination of the reaction; see Koster van Groos and Guggenheim, 1984), and (d) the temperature at which the signal has returned to the baseline. The HP-DTA signals of selected runs, using open capsules, are shown in Figures 2 and 3. In these runs, the width of the peak decreases with increasing pressure, especially in runs with K-exchanged SWy-1. A similar effect was observed in a study of kaolinite (Yeskis et al., 1985). Figure 4 shows HP-DTA signals of runs of both compositions using closed capsules. No significant change in the peak width was observed in these runs. In many of these runs, the dehydroxylation peak is asymmetric (Figs. 2, 3, and 4), suggesting that perhaps the dehydroxylation occurs in more than one step.

All runs were terminated between 800 and 850 °C. The run products from open capsules of low-pressure experiments consist of a soft, fine gray-white powder, compared to the initial light-yellow color. Microscopic examination, however, showed no apparent change. The change in color is probably related to a change in the oxidation state of contaminant iron oxide. At higher pres-

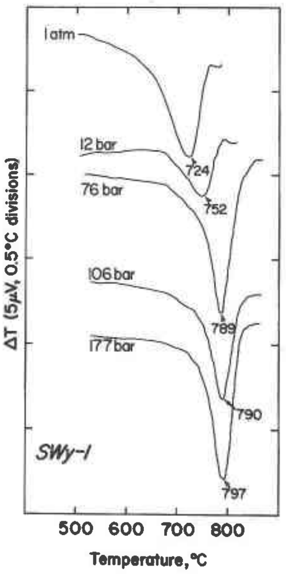

Fig. 2. Differential thermal analysis patterns of SWy-1 at different pressures, using open capsules. The peak width of the dehydroxylation reactions decreases slightly with pressure.

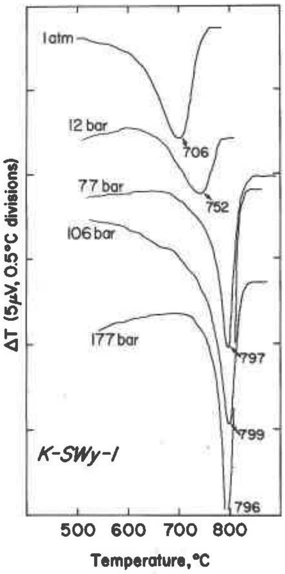

Fig. 3. Differential thermal analysis patterns of K-exchanged SWy-1 at different pressures using open capsules. The peak width of the dehydroxylation reaction decreases substantially with pressure.

sures, the appearance of the run products was very similar to that of the low-pressure runs, except that the product became more compact. The products of the closed-capsule runs were compact and glassy and dark yellow-orange to dark gray in color. Microscopically, the latter runs were glassy, but contained a substantial amount of a submicroscopic crystalline phase(s). X-ray diffraction of run products indicated that a montmorillonite-type phase was present, together with a small (<10%) amount of quartz. Microprobe analysis of these phases was not possible owing to their very fine grained nature. No evidence was found to suggest that under the experimental conditions of this study, montmorillonite melts incongruently to a liquid and other crystalline phases.

Discussion of the results

The *P*-*T* relations of the dehydroxylation reactions are shown in Figure 5. At 1 atm, dehydroxylation of the montmorillonites occurs at temperatures that are signif-

TABLE 1. Pressure (bars) and temperature (°C) data for the HP-DTA peaks of SWy-1

	Onset of peak		Peak		Return		End of peak	
H_2O (wt%)	*P*	*T*	*P*	*T*	*P*	*T*	*P*	*T*
Dry	1	620	1	710	1	715	1	745
Dry	1	643	1	717	1	720	1	770
Dry	1	635	1	717	1	724	1	755
Dry	12	690	12	742	12	752	12	780
5	39	735	39	780	39	783	40	824
10	77	743	78	785	78	789	79	830
20	106	740	106	785	106	789	106	820
Dry	110	757	112	793	112	793	113	823
Dry	122	750	122	792	122	795	123	806
20	177	745	177	793	177	797	177	830
Dry	232	766	233	787	233	790	233	820
20	359	745	358	780	358	783	357	810
10	500	767	500	810	500	810	500	827
Dry	626	766	626	790	626	795	626	815
10*	232	702	232	738	232	746	232	755
10*	232	695	232	736	232	740	232	760
10*	289	693	290	735	290	735	290	750
10*	481	620	481	710	481	712	484	740
10*	495	667	495	710	495	712	495	730
10*	566	650	568	690	568	695	570	725
10*	770	645	770	678	770	683	770	700
10*	2450	612	2460	670	2460	674	2470	696

* Closed capsules.

TABLE 2. Pressure (bars) and temperature (°C) data for the HP-DTA peaks of K-exchanged SWy-1

	Onset of peak		Peak		Return		End of peak	
H_2O (wt%)	*P*	*T*	*P*	*T*	*P*	*T*	*P*	*T*
Dry	1	623	1	700	1	708	1	760
Dry	1	620	1	700	1	706	1	745
Dry	1	627	1	710	1	715	1	765
Dry	1	683	1	710	1	716	1	765
Dry	12	697	12	745	12	752	12	780
Dry	20	730	20	780	20	780	20	834
10	39	750	39	794	40	798	40	824
10	77	780	78	793	78	797	79	820
Dry	94	775	94	798	94	800	94	810
10	96	750	96	793	96	797	97	820
10	106	745	106	799	106	799	106	820
10	177	770	177	793	177	796	177	810
10	190	750	190	780	190	782	190	795
10	198	765	199	786	199	788	200	815
10	206	780	205	785	205	787	205	803
20	359	540	358	789	358	789	357	805
10	450	710	450	800	450	801	450	810
10*	289	650	289	748	289	750	289	803
5*	514	710	514	731	514	734	514	760
10*	633	650	633	733	633	737	640	765
3*	675	710	675	728	675	730	675	740
10*	770	705	770	725	770	728	770	750

* Closed capsules.

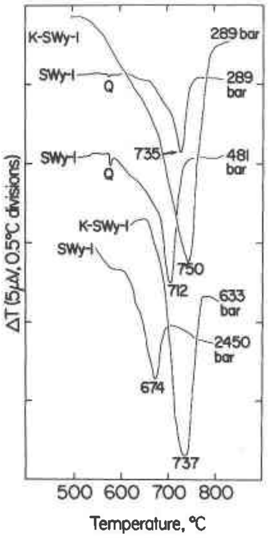

Fig. 4. Differential thermal analysis patterns of SWy-1 and K-exchanged SWy-1 at different pressures using closed capsules. Calibration peaks (labeled Q) represent the low quartz–high quartz inversion. The peak widths of the dehydroxylation reactions do not seem to be affected by pressure.

icantly higher than those determined by TGA because of the lower water fugacity in the latter. The low f_{H_2O} in the TGA is a consequence of the experimental method, which requires the almost instantaneous escape of the evolving H_2O vapor into the N_2 atmosphere. The dehydroxylation temperature of SWy-1 increases rapidly from 710 °C at 1 atm to approximately 790 °C at 40 bars. In open-capsule runs, a further increase in pressure does not change the reaction temperature appreciably. Runs in closed capsules show a decrease in the reaction temperature with pressure greater than 40 bars. K-exchanged SWy-1 behaves very similarly, except that at 1 atm, dehydroxylation occurs at 700 °C. The lower dehydroxylation temperature is consistent with DTA experiments at near-atmosphere pressures on a similar Wyoming bentonite (Heller et al., 1962). At higher pressures, the dehydroxylation of K-exchanged SWy-1 occurs at a slightly higher temperature. The main difference between the results for the two montmorillonites is the higher reaction temperature in the closed-capsule runs of K-exchanged SWy-1. As the two montmorillonites differ only in the interlayer cation, the variation in the reaction temperature in the closed-capsule runs relates to the interaction of this interlayer cation with the melt structure produced in this reaction. Thus, K-exchanged SWy-1 is significantly more stable than SWy-1 with respect to silicate liquid at elevated pressures in the presence of an aqueous vapor.

In order to model the phase relations, it is important to determine which phases participate in these reactions. Clearly present are (a) montmorillonite, (b) a silicate-rich liquid, as is indicated by the presence of a glass in the run products of the closed-capsule experiments, and (c) an aqueous vapor. In addition, as shown by X-ray diffraction patterns of run products, a montmorillonite-type phase is present. This suggests that a montmorillonite dehydroxylate phase exists much like the high-temperature metastable forms of pyrophyllite, muscovite, and kaolinite. Previous direct evidence for the montmorillonite dehydroxylate phase is limited and comes from the work of Bradley and Grim (1951). They noted the close similarities of the powder-diffraction patterns of montmorillonite before and after heating. By analogy to pyrophyllite and muscovite, however, the evidence for a montmorillonite dehydroxylate phase becomes compelling: (1) Structural determinations of muscovite dehydroxylate (Udagawa et al., 1974) and pyrophyllite dehydroxylate (Wardle and Brindley, 1972) established that the low-temperature and high-temperature phases are similar but that the coordination of Al becomes fivefold at high temperatures. Because all other aspects of the structure remain the same, the powder-diffraction pattern of the low-temperature and high-temperature forms are very similar, as is observed for montmorillonite in this study. (2) Montmorillonite chemistry is analogous to that of pyrophyllite and muscovite. It has an Al octahedral sheet identical to pyrophyllite and muscovite. Furthermore, the tetrahedral

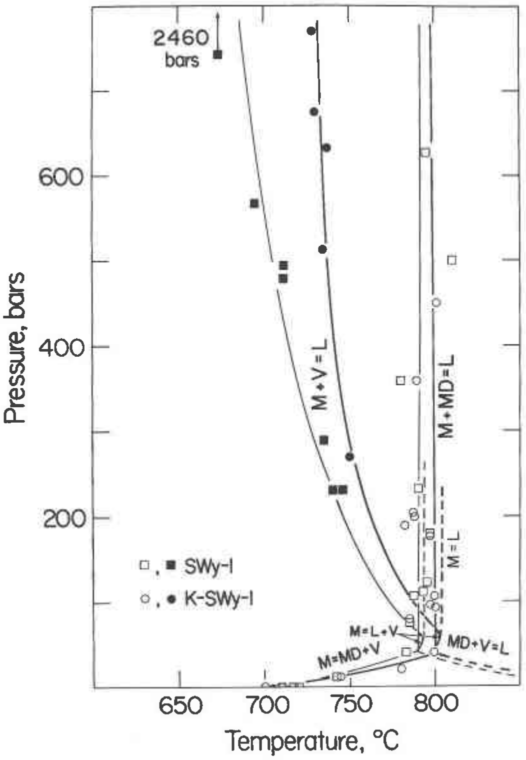

Fig. 5. Pressure-temperature relations of the system montmorillonite-H_2O. The solid lines represent reactions determined in this study, whereas the dashed lines represent reactions inferred from the phase relations. The thin lines represent dehydroxylation and melting reactions of SWy-1, whereas the thick lines indicate the same reactions for K-exchanged SWy-1. Abbreviations: M = montmorillonite, MD = montmorillonite dehydroxylate, L = liquid, V = vapor.

site chemistry is between that of pyrophyllite and muscovite. Likewise, the occupancy of the interlayer cation sites is midway between pyrophyllite and muscovite for the K-exchanged montmorillonite after interlayer water is removed. Guggenheim et al. (1987) discussed the crystal-chemical aspects of dehydroxylation and suggested that the process should be similar to other aluminous 2:1 layer silicates with univalent interlayer cations, although they noted also that small variations in thermal stability would be dependent in part on the number of interlayer sites occupied and the type of the interlayer cation.

It should be noted that dehydroxylation in Na-rich montmorillonite and K-exchanged montmorillonite is analogous to the dehydroxylation reaction of pyrophyllite and muscovite. Heller et al. (1962) found it relatively easy to rehydroxylate a partially dehydroxylated montmorillonite, similar to pyrophyllite and muscovite (e.g., Gaines and Vedder, 1964; Vedder and Wilkins, 1969; Aines and Rossman, 1985). In addition, the two-step mechanism for dehydroxylation of muscovite and pyrophyllite suggested by Guggenheim et al. (1987) appears valid also for montmorillonite, as is indicated by the broadness and asymmetry of the thermal analysis peaks above 600 °C (this study). This mechanism is based on variations of bond strength of the Al–OH bond, which in turn depends on the coordination of neighboring polyhedra as dehydroxylation progresses. Initially, polyhedra are in sixfold coordination but, as dehydroxylation proceeds, more and more polyhedra become fivefold in coordination, with the remaining OH groups being affected by their neighboring polyhedra. The Al–OH bonds are stronger when neighboring polyhedra are all of the fivefold type after partial dehydroxylation, as can be derived from Pauling's rules, and further dehydroxylation is delayed until the thermal energy increases sufficiently.

The process of dehydroxylation, as proposed by Guggenheim et al. (1987), explains both the asymmetry and broadness of the dehydroxylation reaction (Fig. 1) as two overlapping and poorly resolved dehydroxylation peaks. The two sets of peaks are broad and poorly resolved because there are many intermediate structures with different amounts of both sixfold- and fivefold-coordinated polyhedra. The decrease in width of the peak with increasing pressure, most prominently displayed in the patterns of K-exchanged SWy-1 (Fig. 3), indicated that the 2:1 layer is significantly affected by both pressure and the nature of the interlayer cation (cf. Figs. 2 and 3). Further study is necessary to clarify these effects.

It is possible to model the results using a phase-equilibria framework in the system montmorillonite-H_2O, with the understanding that at the pressure and temperature conditions of this study, the phase assemblages represent metastable equilibria. Summarizing the results, at 1 atm, SWy-1 dehydroxylates at approximately 710 °C. An increase of pressure to about 40 bars increases the dehydroxylation temperature to 790 °C. This reaction is strongly pressure dependent, and the participating phases are montmorillonite, montmorillonite dehydroxylate, and vapor. Above approximately 40 bars, two reactions are observed. One of these is almost pressure independent, which indicates that vapor is probably absent. The other reaction has a negative slope, and the run products are glassy. The phases participating in the latter reaction are montmorillonite, liquid, and vapor. A fourth reaction is inferred from the melting of montmorillonite dehydroxylate at 1 atm, which occurs at approximately 920 °C (van Olphen and Fripiat, 1979). In this reaction montmorillonite is absent. In all, four phases can be assumed to participate in these reactions: montmorillonite (M), montmorillonite dehydroxylate (MD), a liquid phase (L), and H_2O-rich vapor (V). Quartz is found in the run products as well, but it is most probably derived from the crystallization of amorphous silica, which is abundant in the starting material.

It is unlikely that the presence of quartz affects the dehydroxylation reactions, as excess SiO_2 can neither be accommodated in the dehydroxylate nor would it be expected to be a breakdown product of the montmorillonite phase. Although quartz may dissolve in the liquid phase, we assume that only a small amount enters the liquid at the temperature of the observed reaction. This does not preclude that more quartz may dissolve at higher temperatures, but even this amount is probably small because both quartz and montmorillonite dehydroxylate are found in the run products. We conclude that the melting reactions are not significantly affected by the presence of quartz.

The system, therefore, may be treated as the binary system montmorillonite-H_2O. The composition of the phases is constant, with the exception of the liquid, which has an H_2O content that is very low at 1 atm but that increases with pressure. The phase relations in this system are very similar to the systems kaolinite-H_2O (Yeskis et al., 1985) and CaO-H_2O (Wyllie and Tuttle, 1960). The varying amount of H_2O in the liquid phase requires the presence of six reactions:

$$\mathrm{M} = \mathrm{MD} + \mathrm{V} \tag{1}$$

$$\mathrm{M} + \mathrm{MD} = \mathrm{L} \tag{2}$$

$$\mathrm{MD} + \mathrm{V} = \mathrm{L} \tag{3}$$

$$\mathrm{M} = \mathrm{L} + \mathrm{V} \tag{4}$$

$$\mathrm{M} + \mathrm{V} = \mathrm{L} \tag{5}$$

$$\mathrm{M} = \mathrm{L}. \tag{6}$$

Reactions 1 through 4 emanate from an invariant point, forming a Schreinemakers bundle. The invariant point lies at approximately 40 bars and 793 ± 5 °C for SWy-1 and at the same pressure but at a slightly higher temperature, 800 ± 5 °C, for K-exchanged SWy-1. The solid lines in Figure 5 represent the reactions determined in this study, the dashed lines represent reactions inferred from the phase relations. Although the temperature differences between the corresponding reactions for SWy-1 and K-exchanged SWy-1 are small, nonetheless they are real, as both samples were routinely run simultaneously under nearly identical conditions. Reaction 4 terminates in a singular point, where the H_2O content of the liquid becomes the same as in montmorillonite. With a further increase of pressure, Reactions 5 and 6 occur. Reaction 5 was observed in the closed-capsule experiments and, although no experimental evidence for Reaction 6 was observed, it is probably very close in temperature to Reaction 2. In this study, no direct evidence was found for Reactions 4 and 6, but, as stated above, they are required by phase-relations considerations.

On the basis of *P-T* relations of the dehydroxylation reactions, the enthalpy of dehydroxylation was calculated (e.g., Anderson, 1977; Koster van Groos and Guggenheim, 1986). For SWy-1, the enthalpy of dehydroxylation for Reaction 1 is approximately 300 ± 50 kJ/mol and, for K-exchanged SWy-1, approximately 260 ± 50 kJ/mol. As these values are based on the HP-DTA data at pressures less than 40 bars, a considerable uncertainty has to be assumed for the H_2O fugacity in the low-pressure experiments. The enthalpy of dehydroxylation is reasonable for dehydroxylation reactions (Arens, 1951). It represents in large part the difference of the energy necessary to break O–H bonds and the energy released by the formation of H_2O molecules.

In summary, the results show that the dehydroxylation of montmorillonite is strongly dependent on pressure. Furthermore, at relatively low temperatures and pressures, montmorillonite melts to produce a metastable silicate liquid. Both the dehydroxylation and the melting reaction are affected by the type of the interlayer cation, with K resulting in significantly higher melting temperatures of montmorillonite at elevated H_2O pressures. The dehydroxylation and melting reactions represent metastable reactions in the system montmorillonite-H_2O.

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