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Dehydroxylation of Ca- and Mg-exchanged montmorillonite

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ABSTRACT

Montmorillonite is a phase in the metastable binary system (montmorillonite dehydroxylate)–H_2O. By using high-pressure differential thermal analysis (HP-DTA) of Ca- and Mg-exchanged montmorillonite (Clay Minerals Society Source Clay SWy-1) to pressures of 1.2 kbar, dehydroxylation and melting reactions were found involving montmorillonite (M), an aqueous vapor (V), and a silicate liquid (L). In addition, one dehydroxylated phase (DH) is present in the Ca-rich system, and two dehydroxylated phases (DH1, DH2) are present in the Mg-rich system. These differences are caused by the ability of Mg to move close to the residual oxygen upon partial dehydroxylation, whereas Ca is limited in its ability to migrate. The DH1 phase is an intermediate dehydrated structure with Mg paired with the residual oxygens, and DH2 is the fully dehydrated phase.

The dehydroxylation reaction of Ca-exchanged montmorillonite (M = MD + V) occurs at 715 °C and 1 bar and increases to 800 °C and 30 bars where this reaction terminates in an invariant point. Three additional reactions involving a liquid phase emanate from this point. The reaction M + DH = L is nearly temperature independent, reaction M = L + V terminates at slightly higher temperature and pressures in a singular point, and MD + V = L intersects 1 bar at about 920 °C. Two additional melting reactions emanate from the singular point. One reaction, M + V = L, decreases to 683 °C at 735 bars, and the second, M = L, is assumed to lie close to the reaction M + DH = L. In the Mg-rich system, as a result of the partly dehydrated phase (DH1), three invariant points and two singular points are present. The general topology is analogous to the Ca-rich system, although much more complex. The dehydroxylation reaction for the Mg-exchanged montmorillonite occurs at about 725 °C at 1 bar and increases to 730 °C at 1.3 bars, to terminate in an invariant point. Two dehydroxylation reactions emanate from this point, each terminating in invariant points (at 795 °C, 25 bars; 785 °C, 65 bars). At these points, a series of reactions involving silicate liquids emanates in analogy with the Ca-rich system. Below the invariant point at 1.3 bars, DH2 is more stable than DH1 because of the inability of the Mg cation to effectively interact with a newly formed residual oxygen upon dehydroxylation. An expanded interlayer region at low pressures accounts for this.

Estimates for the enthalpy of dehydroxylation range from 350 ± 50 kJ/mol for Ca-exchanged SWy-1 to 500 ± 300 kJ/mol for the complete dehydroxylation reaction at low pressures for Mg-exchanged SWy-1, 600 ± 100 kJ/mol for the partial dehydroxylation M = DH1 + V, and 400 ± 100 kJ/mol for the loss of the remaining hydroxyls in DH1 = DH2 + V.

INTRODUCTION

The dehydration and dehydroxylation of montmorillonite (ideally $(M^+_y nH_2O)(Al_{2-y}Mg_y)Si_4O_{10}(OH)_2$) has been studied previously by X-ray diffraction and infrared analysis after thermal treatment. Dehydration refers to interlayer nH_2O loss at low temperatures to about 250 °C, and dehydroxylation involves OH removal from the octahedral sheet at higher temperatures. In such studies, the montmorillonite usually is cation-exchanged to assure an end-member interlayer composition, heat-treated for several hours or days, and then examined. X-ray and infrared examination has found that for samples heated to temperatures above the reaction involving interlayer-water loss, small cations (Li, Mg, Al, etc.) can migrate into the silicate ring and sometimes into the vacant octahedral site, whereas larger cations (K, Na, Ca, etc.) are confined to the interlayer region (e.g., Hofmann and Klemen, 1950; Greene-Kelly, 1955; Tettenhorst, 1962; Glaeser and Mering, 1967; Farmer and Russell, 1967; Calvet and Prost, 1971).

Thermal analytical techniques, such as differential thermal analysis (DTA), have been used also to study water loss. Because these techniques are confined traditionally to experimental conditions at near 1 bar and because water pressures cannot be controlled easily, results have been limited. For example, DTA patterns of montmorillonites cation-exchanged with small cations cannot readily be distinguished from patterns obtained from montmorillonites cation-exchanged with large cations, although it can be expected that the process of water loss would be different for the two general types.

The use of high-pressure differential thermal analysis (HP-DTA) expands the number of dimensions of traditional studies by including the effect of pressure. Thus, the *P-T* relations of dehydration reactions can be determined and, as a consequence, thermodynamic data can be derived.

Enthalpy calculations (Koster van Groos and Guggenheim, 1986, 1987a) based on HP-DTA data for Na montmorillonite and K-, Ca-, and Mg-exchanged montmorillonite indicate that the small size and, presumably, the high field strength (a function of the ratio of cation charge to size) of Mg strongly influences interlayer dehydration. For example, the enthalpy value of interlayer water in the last stages of dehydration is considerably higher for Mg-exchanged montmorillonite than for the others. Based on these results and on the results of the earlier workers cited above, it was anticipated that Mg-exchanged montmorillonite would show a unique dehydroxylation process when compared to Na, K, or Ca analogue systems.

In this paper, we present data on divalent-cation–exchanged (Ca, Mg) montmorillonite. The starting material is identical to that used in a previous study on interlayer dehydration (Koster van Groos and Guggenheim, 1987a). The purpose of this paper is to present the effects of the interlayer cation on the kinetics of dehydroxylation and to develop a reasonable structural model to account for these data. In addition, the petrologic significance of the study is discussed.

EXPERIMENTAL METHOD

Apparatus

The HP-DTA system was developed by Koster van Groos (1979). Briefly summarized, it is composed of a Cu DTA cell, holding two capsules for sample and a reference capsule, placed in an internally heated pressure vessel (Holloway, 1971). Pt-$Pt_{90}Rh_{10}$ thermocouples are placed in a small re-entry well at the bottom of the capsules, and the temperature of the samples is determined using the reference temperature with a correction for the temperature differential. They are believed accurate to within 1 °C. Pressures are determined using low-, medium-, and high-pressure–calibrated Bourdon-type Heise gauges that are accurate to within 0.5%. Ar is the pressure medium. The DTA signals are recorded on the 20-μV range of a Kipp recorder, and temperature deviations of 0.02 °C can be resolved. In this study a heating rate of 20 °C/min was selected, using a programmable Honeywell controller. The system is regularly calibrated at different pressures against the low quartz–high quartz inversion (Koster van Groos and ter Heege, 1973).

Samples of approximately 30 mg were run in Au capsules that were either open or welded shut. In runs using open capsules and at elevated pressures, 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 during the runs, and P_{H_2O} is significantly less than P_{total}. Closed-capsule runs were made at pressures above 200 bars, where the molar volume of H_2O is sufficiently small, so that the capsules would not burst. In these runs $P_{total} = P_{H_2O}$. The sealed capsules were checked for leaks by weighing before and after the experiment.

Thermal gravimetric analysis of the samples (TGA, DTG) were obtained through the courtesy of Mr. P. van der Krieken at the Instituut voor Aardwetenschappen, University of Utrecht, the Netherlands. The data were collected in a N_2 atmosphere using a Dupont 1090 analyzer.

Starting material

The starting material was obtained by cation exchanging the hydraulic fraction (<0.1 μm) of Clay Mineral Society Source Clay SWy-1 (van Olphen and Fripiat, 1979) using four washings with 1*N* solutions of either $CaCl_2$ or $MgCl_2$, followed by six washings with distilled water and drying in air. Both the Ca-exchanged and the Mg-exchanged SWy-1, hereafter referred to as CaSWy1 and MgSWy1, were stored at 55% humidity over a saturated solution of $Mg(NO_3)\cdot 6H_2O$. Chemical composition and X-ray diffraction data were given by Koster van Groos and Guggenheim (1986). It should be noted that in the starting material, more than 10% amorphous SiO_2 is present (Koster van Groos and Guggenheim, 1984).

RESULTS AND DISCUSSION

Thermal gravimetric analysis

Thermogravimetric analyses (TGA, DTG) of CaSWy1 and MgSWy1 are shown in Figure 1. The weight loss related to the dehydroxylation is approximately 5% for both montmorillonites. This is similar to the weight loss observed for SWy-1 and for the K-exchanged SWy-1 (Koster van Groos and Guggenheim, 1987b) and is close to the ideal value of 4.9% for Na montmorillonite (Brindley, 1971; van Olphen and Fripiat, 1979). The DTG analyses indicate that the dehydroxylation reaction of these montmorillonites takes place over a broad temperature range, between 600 and 750 °C, in one or possibly two steps.

High-pressure differential thermal analysis

Approximately 20 successful runs were made with each starting composition. The results for CaSWy1 are tabulated in Table 1. The temperature for the onset of the dehydroxylation signal, the peak temperature, the temperature at which the signal sharply returns toward the baseline, and the temperature at which the signal has returned to the baseline are listed. Table 2 shows the results for MgSWy1. Because open-capsule runs with MgSW1 have a double peak, the peak temperature of each peak is given.

The HP-DTA signals of the selected runs for both compositions using open capsules are shown in Figure 2. The signals are very similar in runs at 1 bar. However, the

TABLE 1. Pressure (in bars) and temperature (in °C) data for the DTA peaks of CaSWy1

H_2O (wt %)	Onset of peak		Peak		Return		End of peak	
	P	*T*	*P*	*T*	*P*	*T*	*P*	*T*
dry	1	640	1	714	1	724	1	750
dry	1	645	1	717	1	733	1	755
10	24	710	24	782	24	784	24	820
5	90	780	90	808	90	808	91	820
10	93	760	93	796	93	796	93	807
10	186	790	187	800	187	805	187	815
10	196	780	196	798	196	800	197	813
10	198	785	198	800	198	802	198	812
10	199	780	200	798	200	800	200	810
10	205	785	205	800	205	800	206	812
30	452	787	454	798	454	798	754	805
10*	216	707	218	733	218	735	219	747
7*	322	695	323	712	323	715	323	735
dry*	360	660	367	706	367	706	370	730
dry*	728	660	735	683	735	683	745	696
8*	1160	620	1180	693	1180	693	1200	710

* Closed capsule.

DTA patterns for the two compositions at elevated pressures differ significantly. CaSWy1 runs exhibit a sharp and narrow asymmetric peak with a possible shoulder peak at the low-temperature side, whereas runs with MgSWy1 have a broad double peak. The relative intensity of the peak varies and suggests that, with increasing pressure, the higher-temperature peak becomes stronger. The results of several runs using closed capsules are shown in Figure 3. The DTA patterns of both compositions are very similar although with MgSWy1, the peaks tend to be broader. All peaks are asymmetric.

Runs were terminated between 800 and 850 °C. Products from low-pressure runs consist of a soft, fine white to gray-white powder, compared to an initial white-yellow color. Microscopic examination showed no apparent change. The change in color is probably related to a change in the oxidation state of contaminant iron oxide. In the open runs at higher pressures, the product is white-gray to gray, compact, hard, and brittle. The products of the closed-capsule runs are compact and glassy and white-gray to dark yellow-orange 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 indicates the presence of a montmorillonite-like phase, together with a small amount of quartz.

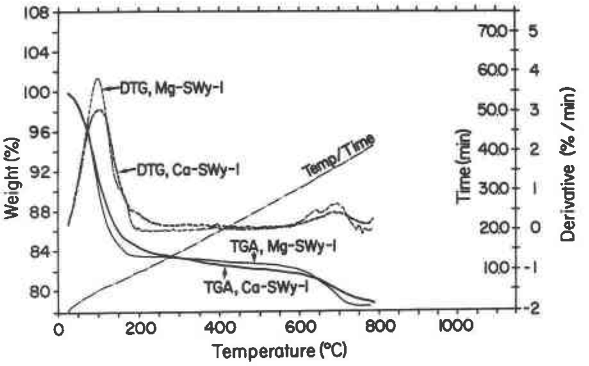

Fig. 1. DTA and DTG patterns of CaSWy1 and MgSWy1. A major H_2O-loss event occurs during the dehydration reaction between 100 and 200 °C (see Koster van Groos and Guggenheim, 1987a, for details). Dehydroxylation takes place at 600–700 °C. Note the double peak in the DTG pattern for MgSWy1.

Discussion of the HP-DTA results

The DTA patterns shown in Figures 2 and 3 suggest that three different reactions were encountered in runs using

TABLE 2. Pressure (in bars) and temperature (in °C) data for the DTA peaks of MgSWy1

H_2O (wt %)	Onset of peak		1st peak		2nd peak		Return		End of peak	
	P	*T*	*P*	*T*	*P*	*T*	*P*	*T*	*P*	*T*
dry	1	610	1	725	—	—	1	730	1	760
dry	1	650	1	732	—	—	1	733	1	750
dry	1	640	1	725	—	—	1	728	1	755
dry	1	640	1	725	—	—	1	727	1	740
dry	24	690	24	748	24	790	24	792	24	820
10	23	700	24	744	24	785	24	785	20	820
10	27	703	27	755	27	802	27	812	27	835
10	27	705	27	754	27	796	27	804	27	840
5	87	695	88	740	89	800	89	804	90	820
5	94	690	94	730	96	797	96	797	96	825
5	96	690	97	732	98	792	98	792	99	830
10	119	685	119	730	119	796	119	800	119	850
9	147	663	148	710	149	767	149	770	151	790
10	180	660	183	733	185	793	185	793	187	820
20	205	705	207	743	210	792	210	792	210	820
10	456	710	460	740	466	780	466	780	473	800
9*	216	689	218	735	—	—	218	735	219	752
7*	322	640	323	700	—	—	323	707	324	730
dry*	355	670	367	688	—	—	367	688	370	740
10*	474	620	473	675	—	—	473	685	470	702
dry*	712	630	730	663	—	—	730	668	740	685
7*	1160	618	1180	677	—	—	1180	677	1190	695

* Closed capsule.

CaSWy1 at the following conditions: open-capsule runs at 1 bar, open-capsule runs at elevated pressures, and closed-capsule runs. In experiments with MgSWy1, an additional well-defined reaction was observed in open-capsule experiment at elevated pressures. All these reactions are similar to the series of metastable dehydroxylation and melting reactions in the systems kaolinite-H_2O (Yeskis et al., 1985), SWy1-H_2O and KSWyl-H_2O (Koster van Groos and Guggenheim, 1987b), except that in these systems only one well-defined reaction was found in open-capsule runs at elevated pressures. Therefore, it is reasonable to assume that CaSWyl-H_2O behaves similarly to these systems at the conditions of this study and that four phases are present that are related in a series of metastable binary dehydroxylation and melting reactions: montmorillonite (M), a dehydroxylated montmorillonite (MD), a liquid (L), and a vapor phase (V). In the system MgSWy1-H_2O, however, the additional dehydroxylation reaction suggests the presence of a second, partially dehydyroxylated phase. The system remains binary, but the phase relations are more complex and involve the following five phases: montmorillonite (M), a partially dehydroxylated phase (DH1), a water-free dehydroxylated phase (DH2), a liquid with a variable H_2O content (L), and a vapor phase (V). The possible univariant reactions and invariant assemblages (I_1–I_3), including assemblages at singular points (S_1 and S_2), are listed below in the direction of increasing temperature:

M = DH2 + V (1)
M + DH2 = DH1 (2)
M = DH1 + V (3)
DH1 = DH2 + V (4)
M + DH1 = L (5)
M + V = L (6a)
M = L + V (6b)
M = L (6c)
DH1 + V = L (7a)
DH1 = L + V (7b)
DH1 = L (7c)
DH1 + DH2 = L (8)
DH2 + V = L (9)
DH2 = L (10)
M + L + V (S_1)
D1 + L + V (S_2)
M + DH1 + L + V (I_1)
M + DH1 + DH2 + V (I_2)
DH1 + DH2 + L + V (I_3)

The schematic P-T relations of these reactions are shown in Figure 4. The phase relations are similar to those in a system with only one dehydroxylated phase, such as the system CaO-H_2O (Wyllie and Tuttle, 1960), in which the reactions represent stable equilibria, or in a system in which the reactions are metastable, such as the system kaolinite-H_2O (Yeskis et al., 1985), except that the single invariant assemblage in these systems is split into three different invariant assemblages because of the presence of a second dehydroxylated phase. Several features of this system should be noted. Dehydroxylation of the phase M at low pressures must produce the water-free dehydroxylated DH2 directly, following Reaction 1. With increasing temperature, the phase assemblage produced in this reaction reacts to form a liquid phase following Reaction 9. With increasing pressure, liquids are produced at decreasing temperatures, along Reactions 6a and 6b, 7a and 7b, and 9, and generally require an increase in the H_2O content of the liquid phase. The smooth curve that is composed of the different melting reactions is interrupted at the invariant reactions I_1 and I_2, which represent incongruent melting of the relatively stable M and DH1. In addition, a series of vapor-absent reactions is present. The volume change in these reactions is probably small, and, therefore, they are nearly isothermal.

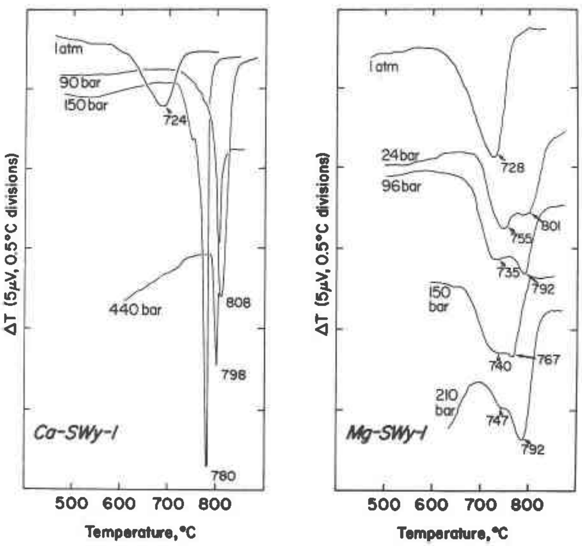

Fig. 2. HP-DTA patterns of CaSWy1 and MgSWy1 at different pressures using open capsules. Note the similarity in the 1-atm patterns. The patterns of CaSWy1 at elevated pressures show a reaction occurring over a small temperature range whereas the two peaks in the patterns of MgSWy1 indicate the presence of two distinct reactions.

Figure 5 shows the phase relations in the system CaSWy1-H_2O, based on the peak temperatures of the runs listed in Table 1. The dehydroxylation temperature of CaSWy1 increases rapidly from 715 °C at 1 bar to approximately 800 °C at about 30 bars, where it terminates in an invariant reaction. At higher pressures, the presence of two closely related vapor-absent melting reactions is inferred. However, it is not possible to differentiate be-

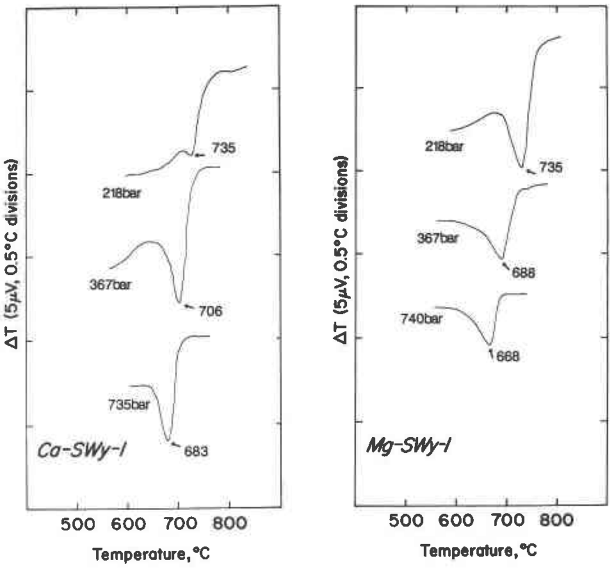

Fig. 3. HP-DTA patterns of CaSWy1 and MgSWy1 at different pressures using closed capsules. Note the similarity in the patterns with respect to pressure and composition.

tween these reactions on the basis of HP-DTA data. Increasing pressure does not change the reaction temperature appreciably. Runs in closed capsules show a sharp decrease in the reaction temperature with pressure. This reaction is interpreted as a metastable melting reaction of CaSWy1 in the presence of excess H_2O.

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, 1987b). Assuming an uncertainty in the invariant point of 2 °C and 10 bar, the dehydroxylation enthalpy for CaSWy1 is 350 ± 50 kJ/mol. The dehydroxylation of CaSWy1, therefore, requires more energy than that of SWy1 (300 ± 50 kJ/mol) and KSWy1 (260 ± 50 kJ/mol), indicating a slightly higher bond strength of the hydroxyl groups.

The phase relations in the system MgSWy1-H_2O are shown in Figure 6. They are based on the peak temperatures listed in Table 2 and on the geometry of the phase relations as presented in Figure 4. The run at approximately 148 bars yielded temperatures that are approximately 20 °C too low to be consistent with the other data; the difference is not understood. The dehydroxylation temperature of MgSWy1 at 1 bar occurs at approximately 726 °C, which is 11 °C higher than in runs with CaSWy1. At higher pressures, two peaks are found that represent Reactions 3 and 4 as well as Reactions 2, 5, 6c, 7c, and 8 that are vapor-absent. Runs in closed capsules show a sharp decrease in the reaction temperature with pressure similar to that in the system CaSWy1-H_2O, although the temperature of the metastable melting reaction at higher pressures is approximately 15 °C lower than that in the Ca-bearing system.

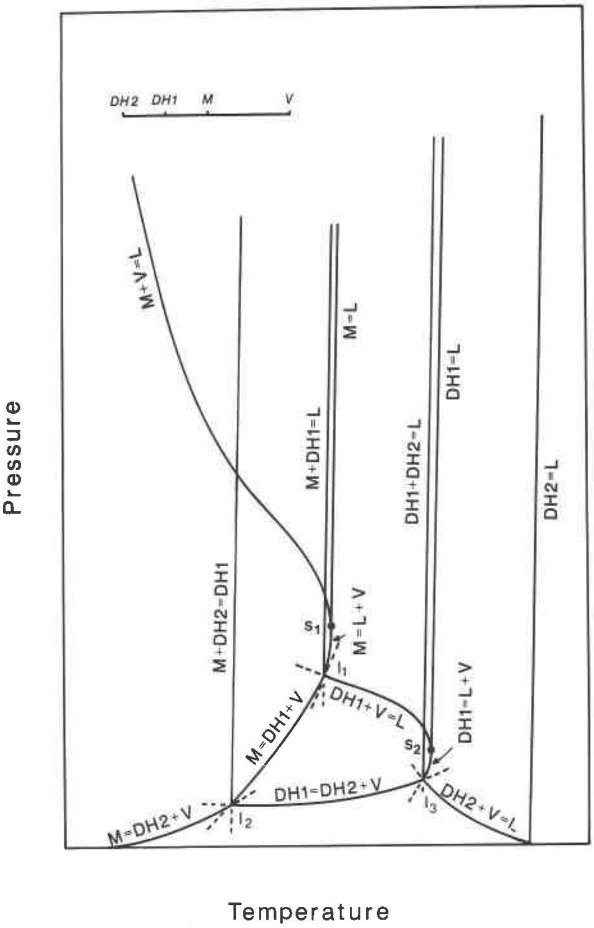

Fig. 4. Schematic pressure-temperature diagram for a system with two dehydroxylated phases, such as the system (MgSWy1 dehydroxylate)-H_2O. The relative compositions are shown in the upper left corner. See text for discussion. Abbreviations: M = montmorillonite; DH1 = partially dehydroxylated phase; DH2 = fully dehydroxylated phase; L = silicate liquid; V = aqueous vapor.

The pressure at the three invariant points in the system MgSWy1-H_2O is determined in part on estimates for the enthalpy of the dehydroxylation reactions in this system. If it is assumed that the dehydroxylation enthalpy of Reaction 1 is slightly higher than in CaSWy1, then I_2 lies at 730 ± 2 °C and 1.3 ± 0.2 bar, and the enthalpy of Reaction 1 is 500 ± 300 kJ/mol. The substantial error is a result of the relatively large uncertainty in the slope of Reaction 1. There is little doubt, however, that this invariant point is very close to 1 bar. Thus, it is likely that the two peaks in the DTG curve for MgSWy1 (Fig. 1) are the result of a slight overpressure of H_2O. The *P-T* conditions of the two other invariant points can be derived using the experimentally determined temperatures and assuming that (a) the partial dehydroxylation reaction (3) has a higher enthalpy than Reaction 1, (b) that the dehydroxylation energy for Reaction 4 is similar to that in

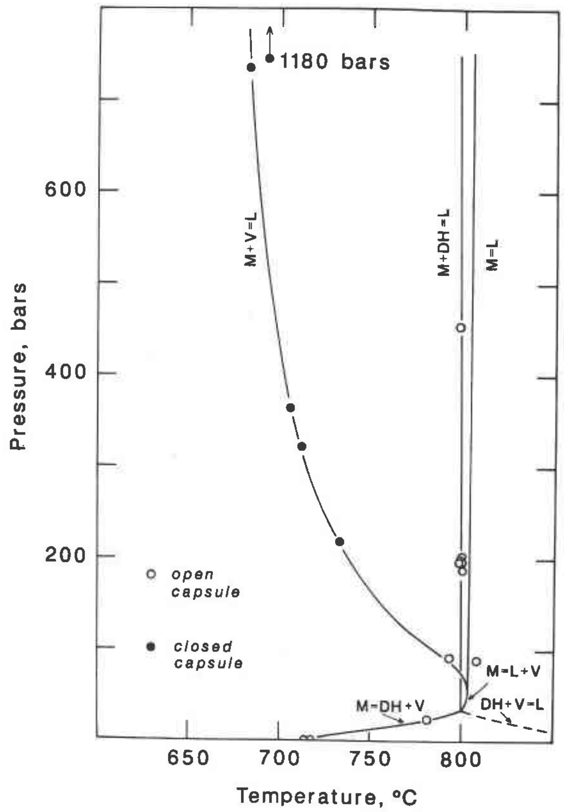

Fig. 5. Pressure-temperature diagram for the system (CaSWy1 dehydroxylate)-H_2O. The dashed line represents the melting reaction that intersects the 1-bar isobar at approximately 920 °C (van Olphen and Fripiat, 1979). Abbreviations: DH = dehydroxylate; see Fig. 4 for other abbreviations.

the system CaSWy1-H_2O, and (c) that the combined enthalpy of the latter two reactions is similar to that of Reaction 1. Thus, I_1 lies at 785 ± 2 °C and 65 ± 10 bar, and I_3 at 795 ± 2 °C and 25 ± 10 bar. The corresponding enthalpies for Reactions 3 and 4 are 600 ± 100 kJ/mol and 400 ± 100 kJ/mol, respectively.

In conclusion, a series of metastable binary reactions occurs in the systems CaSWy1-H_2O and MgSWy1-H_2O at elevated pressures and modest pressures. HP-DTA indicates that the dehydroxylation of CaSWy1 proceeds as a single event. Dehydroxylation of MgSWy1, on the other hand, occurs in two distinct events, suggesting the presence of an intermediate dehydroxylate phase. This intermediate phase is not stable at 1 bar, but forms at a slightly higher pressure, estimated at 1.3 bar. The significance of the difference in the dehydroxylation between CaSWy1 and MgSWy1 is discussed in the following section. Similar to the binary systems with kaolinite (Yeskis et al., 1985), SWy-1, or K-SWy-1 (Koster van Groos and Guggenheim, 1987b), a metastable liquid phase containing 10–15% H_2O is formed at remarkably low pressures.

STRUCTURAL MODELS FOR THE DEHYDROXYLATION OF Na, K, Ca AND Mg-EXCHANGED MONTMORILLONITE

Because the starting materials used in these experiments and in a parallel study (Koster van Groos and Guggenheim, 1987b) were K, Ca, and Mg cation-exchanged at ambient conditions from the Na form (SWy-1), the 2:1 layer chemistry is constant in these samples. A reasonable preliminary assumption, therefore, is that observed DTA differences between these materials are related to the interlayer chemistry. Variables include the number of interlayer sites occupied, cation size, and cation charge. K-exchanged montmorillonite is intermediate in chemistry between pyrophyllite and muscovite, which are known to have similar dehydroxylation mechanisms (Guggenheim et al., 1987). It is assumed, therefore, that K-exchanged montmorillonite follows a similar dehydroxylation process. In addition, at least for the K-rich series, it is clear that the number of interlayer sites occupied does not have a major effect on the nature of the process or the resulting dehydroxylated structure.

Guggenheim et al. (1987) used Pauling bond-strength (PBS) summation calculations to propose a physical model for the dehydroxylation of dioctahedral 2:1 layers, with emphasis on pyrophyllite and muscovite. The general aspects of this model are adopted here, although modifications can now be made to include the effects of interlayer chemistry. The major effect of dehydroxylation relates to the octahedral sheet where a "residual" oxygen remains behind in the dehydroxylated structure (the high-temperature phase that develops topotactically from the low-temperature form). Octahedrally coordinated cations in the low-temperature form become five-coordinated in the dehydroxylated structure, but other topologic features remain very similar between the two forms. Upon dehydroxylation, the two associated OH groups in the low-temperature form react to form an H_2O molecule, which leaves the structure, and one residual oxygen, which moves to the position midway between what was formerly the OH···OH shared edge of the octahedra in the low-temperature form (see Fig. 6 in Guggenheim et al., 1987). PBS summation calculations showed that the residual oxygen is very undersaturated with respect to positive charge and requires a readjustment of first, second, and third nearest neighbors to help compensate for the disruption of local charge neutrality. If the PBS calculations are made for a structure in transition, the resulting atomic adjustments can be shown to have a major effect on further dehydroxylation. For details of the procedure and the results, see Guggenheim et al. (1987).

Although most previous investigations on the effect of temperature and interlayer chemistry in montmorillonites have not been made on dynamically derived (quenched after rapid heating to temperature) samples, studies on annealed samples indicate that small cations such as Li and Mg can enter well into the silicate ring (Tettenhorst, 1962) and into the vacant octahedral site

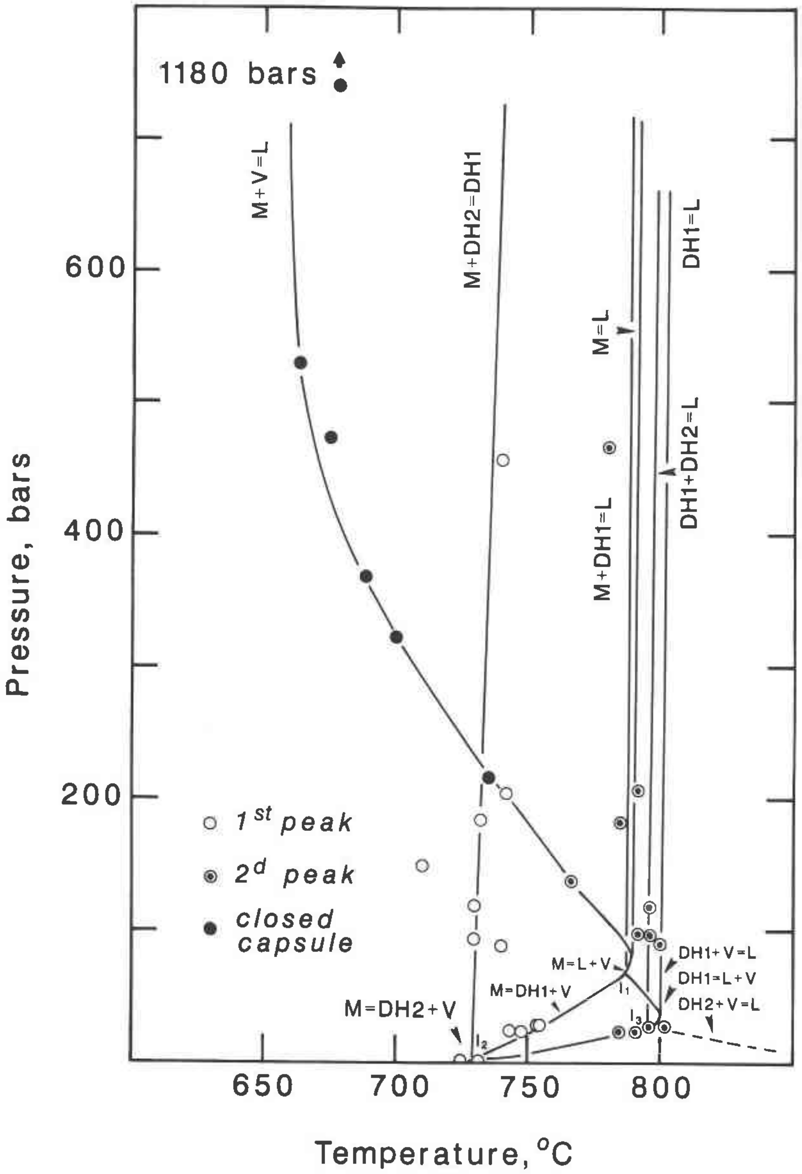

Fig. 6. Pressure-temperature diagram for the system (MgSWy1 dehydroxylate)-H_2O. The dashed line represents the melting reaction that intersects the 1-bar isobar at approximately 920 °C (van Olphen and Fripiat, 1979). See Fig. 4 for abbreviations.

(e.g., Hofmann and Klemen, 1950; Greene-Kelly, 1955; Farmer and Russell, 1967; Calvet and Prost, 1971) upon dehydration, whereas Ca, Na, and K are severely limited in the extent of their migration. Although the experiments described here are at higher temperature, the data are consistent with the Mg phase being unique in comparison to the Ca, Na, or K phases, presumably because of the small size of Mg and its ability to migrate readily into the 2:1 layer. The key in understanding the effect of interlayer chemistry on the dehydroxylation process is in recognizing how the interlayer cation can help maintain local charge balance by associating with the residual oxygen.

Applications to the HP-DTA results

Above about 1.5 bar, it is apparent that initial dehydroxylation in MgSWy1 occurs at lower temperatures than the (single) peak for the other Na-, Ca-, or K-bearing forms. This suggests that Mg initially destabilizes the fully hydroxylated 2:1 layer, presumably because of its high field strength and repulsive interactions with the H^+. Therefore, MgSWy1 has a lower thermal stability than the K, Na, or Ca forms above about 1.5 bar.

Upon initial dehydroxylation, Mg can stabilize the structure by entering the silicate ring and neutralizing the undersaturated residual oxygen. Charge balance of the residual oxygen is essentially complete, because the Mg cation can reach an equilibrium distance to the residual oxygen. It is because of this degree of freedom that the Mg cation stabilizes the structure around the residual oxygen and, in contrast to muscovite undergoing dehydroxylation (Guggenheim et al., 1987), the Al cation in fivefold coordination does not require a significant positional readjustment. Dehydroxylation can proceed in a similar manner until all the interlayer Mg cations are paired with residual oxygens (about a third of the available interlayer sites are filled by Mg in the low-temperature structure). This structure represents the DH1 phase, with part of the structure having residual oxygens associated with Mg and the other portion of the structure retaining OH. A second series of dehydroxylation events occurs with increasing temperature to produce a fully dehydroxylated phase (DH2). The formation of DH2 produces a (second) peak at a temperature similar to the single-peak dehydroxylations of the other forms. Therefore, the DH1 phase is nearly equivalent in thermal stability to NaSWy1, KSWy1, and CaSWy1. This accounts for the topology of the two phase diagrams (cf. Figs. 5 and 6) with M = DH + V (Fig. 5) having a similar slope and disposition to DH1 = DH2 + V (Fig. 6).

Two general models to explain "end-member" dehydroxylation processes now have been considered: (1) dehydroxylation of K-rich forms (pyrophyllite, K-exchanged montmorillonite, and muscovite), which involves little or no interlayer-cation migration during dehydroxylation, and (2) dehydroxylation of Mg-exchanged montmorillonite, which requires interlayer-cation migration during dehydroxylation. Although both processes produce asymmetric thermal peak shapes at low pressures (up to about 60 bar for the former, but from about 1.5 bar to 60 bar for MgSWy1), the differences in the processes become especially apparent when comparisons are made at higher pressures (20–60 bar). Because Al···O,OH bond strengths change upon initial dehydroxylation in pyrophyllite and K-rich forms (Guggenheim et al., 1987), further dehydroxylation is delayed, and, as a consequence of this delay, an asymmetric peak forms. This asymmetry is evident throughout the 1- to 60-bar range. In contrast, the asymmetry of the peak in MgSWy1 is a result of a different process, which involves Mg cation migration, with the two thermal peaks for the MgSWy1 not completely resolved until higher pressures (above about 20 bar). At higher pressures, the dehydroxylation reactions are replaced by melting reactions (e.g., M + V = L), and the DTA peaks become considerably sharper.

Considering the single DTA peak associated with dehydroxylation, it is clear that Na- and Ca-rich montmorillonites react more like the K-rich forms. However, because both processes discussed above produce peak asymmetry, HP-DTA cannot determine the extent to which interlayer-cation migration is involved in dehydroxylation in the Na and Ca forms. The process involving Mg montmorillonite is distinguished from the process involving K-rich forms by the ability of the interlayer cation to migrate into the silicate ring and, therefore, appears to relate to cation size rather than cation charge. Na and Ca are intermediate in size between K and Mg and are nearly equal in size (Shannon, 1976). On the basis of simple size considerations alone, therefore, the Na and Ca position is intermediate between the K position in K-SWy-1 (nearly centered in the interlayer) and the Mg position in MgSWy1 (closely associated with the residual oxygen), and, consequently, peak characteristics for the Na and Ca forms are intermediate between them. Although this interpretation may appear adequate to explain the DTA peak shapes, charge differences should not be ignored. Because of the higher charge on Ca relative to Na, it is likely that Ca can move closer to the residual oxygen than a simple comparison of radii from Shannon (1976) might indicate. Radii values from Shannon, although useful as a first approximation, are average values from structures with generally regular sites, but deviations from these values for individual bond lengths are common (e.g., Brown and Wu, 1976). Such deviations are caused by unsaturated anions and, in the case for the highly undersaturated residual oxygen, a large deviation from the average would be expected, with a greater deviation for the divalent Ca than for the Na. A closer approach of Ca to the residual oxygen may be envisioned as an asymmetric positioning in the interlayer cavity. This may suggest that the process of dehydroxylation in CaSWy1 is slightly different than in (Na-rich) SWy-1, although the DTA data are not sufficient to determine this. We emphasize, however, that the peak shapes indicate that the Na and Ca forms react more like the K-rich forms than the Mg form.

The phase relations in the MgSWy1 system clearly indicate that low pressure (below about 1.5 bar) destabilizes the DH1 structure relative to DH2, the fully dehydroxylated phase. High-pressure single-crystal X-ray studies of layer silicates (Hazen and Finger, 1978) showed that bond distances in the 2:1 layer are relatively insensitive to pressure changes, even to pressures of 35 kbar, whereas the interlayer region is highly compressible. Therefore, it is likely that the instability of the DH1 structure at low pressures, where the interlayer is relatively expanded, is not related to the OH-loss portion of the process that occurs within the 2:1 layer but, rather, to the inability of the Mg interlayer cation to interact effectively with the residual oxygen. Because electrostatic attractive forces are a function of the inverse square of the interatomic distance, an expanded interlayer would limit such interactions. Furthermore, in an expanded interlayer at low pressures, if Mg resides between 2:1 layers near tetrahedral basal edges (where they can best satisfy undersaturated basal oxygens associated with any Al-containing tetrahedra) and not within silicate rings, then they are shielded partially from a newly created residual oxygen upon partial dehydroxylation. Without an immediate stabilizing effect of the Mg cation to satisfy the undersaturated charge on the residual oxygen, the dehydroxylation process would proceed much as in the K-rich forms. The location of larger interlayer cations (Ca, Na, K) in an expanded interlayer region is not directly relevant to this discussion, as larger cations are limited in their interaction with the residual oxygen because of size. Obviously, more data are needed regarding the location of the Mg cation at high temperatures immediately prior to dehydroxylation.

Because the initial loss of hydrogen is a random process, the DH1 phase represents an immediate solution to satisfy the undersaturated charge on the residual oxygen, wherever a residual oxygen may occur within the octahedral sheet. With continued dehydroxylation and as more of the vacant octahedral sites become associated with two residual oxygens in a *trans* configuration to form the DH2 phase, it would be expected that Mg could enter the vacant site, perhaps simultaneously with the formation of residual oxygen pairs. This would allow the charge saturation of two residual oxygens and a maximum degree of symmetry around the Mg cation. Although an argument can be made for Mg to enter the vacant site, this is not a necessary aspect of the model. For example, a second dehydroxylation event (to form DH2) would occur regardless of Mg remaining in the silicate ring or entering the vacant site.

The model presented above considers neither octahedral Mg as an important variable nor the possibility that interlayer Mg enters the vacant octahedral site upon interlayer dehydration at much lower temperatures. In montmorillonites, Mg^{2+} substitutes for octahedral Al^{3+}, which creates a small charge imbalance on the coordinating oxygens, including the oxygen of the hydroxyl group. Although the Mg interlayer cation is accessible to the hydroxyl group, it seems unlikely that the interlayer cation interacts strongly with that oxygen because of the very dynamic heating rate (20 °C/min), the relatively small charge imbalance on the oxygen and the relative ease of the proton to readjust its position to the oxygen to compensate, the relatively long distance between OH and the interlayer cation, and the shielding effect of the positively charged H^+. Therefore, for these DTA experiments, the lack of a significant driving force argues against Mg interlayer migration until a residual oxygen forms upon dehydroxylation Furthermore, the strong similarities between the DTA results of the Na, K, and Ca montmorillonites and muscovite and pyrophyllite suggest that the Mg substitution for Al is not, by itself, an important part of the process. For these reasons, models incorporating octahedral Mg migration or Mg interlayer-cation migration at low temperatures as important variables are not proposed, although future workers should consider if this represents an oversimplification.

PETROLOGIC APPLICATIONS

The dehydroxylation of clay minerals is capable of releasing vast quantities of fluids in the deeper continental crust and in the subducted altered ocean floor. The stability of these minerals is limited in such environments, and recrystallization will produce other layer silicates, such as chlorite. The work presented here and in an earlier study (Koster van Groos and Guggenheim, 1987b) indicates, however, that at pressures upward from 40 to 100 bars (depending on the H_2O fugacity) and at temperatures significantly below the dehydroxylation temperature, montmorillonite melts to produce a hydrous metastable liquid phase. Therefore, an upper limit of approximately 600 to 650 °C exists for montmorillonite in a hydrous environment.

The liquids produced are highly reactive and can be expected to crystallize rapidly, forming a series of hydrous and anhydrous aluminosilicate minerals. Because the temperature at which montmorillonite melts is relatively high, it seems likely that in the continental crust, montmorillonite will be consumed in metamorphic reactions before a liquid phase can form. However, during subduction of altered oceanic crust and associated sediments, the rate of temperature increase may be sufficient for metastable melting of montmorillonite to occur. Hence, subsequent crystallization would release copious amounts of aqueous fluids that would be introduced into the hot, overlying mantle wedge. The flux of these fluids to the peridotitic mantle would significantly increase production of hydrous (andesitic) magmas in this environment.

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