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Dehydration of a Ca- and a Mg-exchanged montmorillonite (SWy-1) at elevated pressures

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ABSTRACT

The dehydration of a Ca- and a Mg-exchanged montmorillonite obtained by ion exchange of a Na-montmorillonite was determined at pressures to 1 kbar using high-pressure differential thermal analysis. Interlayer dehydration reactions of Ca-exchanged montmorillonite occur at about 70°C and 110°C above the liquid-vapor curve of water, whereas Mg-exchanged montmorillonite dehydrates at about 50°C and 110°C above this curve. At pressures above the critical point of water, the dehydration temperatures increase only slightly. These two reactions are interpreted to represent dehydration of two distinctly different H_2O molecule configurations around the interlayer cation. The data were used to determine the enthalpy of the dehydration ΔH_{dh} and the enthalpy of the interlayer water ΔH_{iw} at 1 atm. These are, for Ca-exchanged montmorillonite, first dehydration reaction, $\Delta H_{dh} = 49.5 \pm 0.5$ kJ/mol and $\Delta H_{iw} = 12.1 \pm 0.5$ kJ/mol and second dehydration reaction $\Delta H_{dh} = 58.2 \pm 2$ kJ/mol and $\Delta H_{iw} = 22.6 \pm 2$ kJ/mol; and, for Mg-exchanged montmorillonite, first dehydration reaction, $\Delta H_{dh} = 49.3 \pm 0.5$ kJ/mol and $\Delta H_{iw} = 11.1 \pm 0.5$ kJ/mol and second dehydration reaction, $\Delta H_{dh} = 66.2 \pm 2$ kJ/mol and $\Delta H_{iw} = 31.1 \pm 2$ kJ/mol. Comparison with Na-montmorillonite and a K-exchanged montmorillonite shows that the enthalpy of the first dehydration reaction of the alkali montmorillonites is significantly lower than for Ca- and Mg-exchanged montmorillonites. The high value of ΔH_{iw} of 31.1 kJ/mol suggests a unique environment for H_2O molecules around Mg, perhaps indicating that these molecules are located partly within the sixfold silicate ring of the 2:1 layer in this montmorillonite.

In sedimentary sequences, smectites often coexist with brines. Also, P_{H_2O} is often less than P_{load}. In these systems, the activity of H_2O is significantly reduced and may be buffered by the dehydration of montmorillonite. Substantial amounts of smectite in altered ocean floor and in ocean sediments may have important bearing on the introduction of water to the upper mantle.

INTRODUCTION

In recent experimental studies on the effect of pressure on the dehydration of a Na-montmorillonite and a K-exchanged montmorillonite (Koster van Groos and Guggenheim, 1984, 1986), it was found that a modest increase in pressure greatly extends the stability of the interlayer water and that dehydration occurs in two separate reactions at approximately 40 to 50 deg and at 100 to 110 deg above the boiling temperature of water at the same pressure. These reactions were interpreted to represent the dehydration of a voluminous but weakly bonded outer hydration shell and a more strongly bonded inner hydration shell. We define a "hydration shell" only as it corresponds to the dehydration reactions, and we do not imply any relationship to the term as is used in a purely aqueous system.

The *P-T* data on the dehydration reactions yielded enthalpies of dehydration and enthalpies of the interlayer water. These showed that the smaller interlayer cation (Na^+) bonds the inner hydration shell more strongly. No difference was found in the enthalpy of the interlayer water of the outer shell. In the current paper, we present data for the dehydration of the same montmorillonite, but with the divalent cation Ca^{2+} or Mg^{2+} at the interlayer site. The purpose of these studies is to determine the effect of the interlayer cation on the interlayer-water stability at elevated pressures.

EXPERIMENTAL METHOD

Apparatus

A detailed description of the high-pressure differential thermal analysis system (HP-DTA) has been given elsewhere (Koster van Groos, 1979). In summary, the system consists of a Cu cell, which is designed for use in an internally heated pressure vessel (IHPV) similar to the one described by Holloway (1971). It can accommodate three Au capsules, weighing about 120 mg, with a length of about 7 mm, a diameter of 3.2 mm, and a wall thickness of 0.05 mm. The capsules have a re-entry well of about 1-mm depth for a Pt-$Pt_{90}Rh_{10}$ thermocouple. In any run, two of

TABLE 1. Composition of the starting material, determined by electron-microprobe analysis

	SWy-1*	CaSWy-1†	MgSWy-1†
SiO_2	66.4	62.6	65.3
TiO_2	0.12	n.a.	n.a.
Al_2O_3	23.7	24.1	23.5
FeO	4.19	4.16	4.23
MgO	2.77	3.39	5.79
CaO	1.05	4.33	0.27
Na_2O	0.58	0.0	0.0
K_2O	0.16	0.04	0.16
Total	98.97	98.62	99.25

Note: n.a., not determined.
* Hydraulic fraction < 0.1 μm of SWy-1.
† Exchanged hydraulic fraction < 0.1 μm of SWy-1.

the capsules contained about 30-mg sample, and the third contained TiO_2 and Al_2O_3 as reference. An important feature of the HP-DTA system is that both the shape of the capsules and their position in the cell are reproducible. This facilitates comparison of the DTA signals. Furthermore, the capsules can be used either open or welded shut. The fast response time, as seen in a rapid return of the signal to the base line, allows good resolution of the signal.

The DTA signals were recorded on the 20-μV range of a Kipp recorder, and temperature deviations of 0.02 deg can be resolved. The temperature is determined from the reference temperature, after correcting it for the temperature differential. Pressures were measured using calibrated Bourdon-type Heise gauges, which are accurate to within 0.5%. The heating rate was held at 20 deg/min, using a Honeywell programmable controller. The system was regularly calibrated at different pressures against the low quartz–high quartz inversion (Koster van Groos and ter Heege, 1973), and the temperature measurements are believed accurate to within 1 deg.

Thermogravimetric analysis (TGA, DTG) and differential scanning calorimetry (DSC) were done on a Dupont 1090 analyzer at the Department of Earth Sciences of the University of Utrecht, the Netherlands. These analyses were carried out in N_2 atmosphere.

Starting material

Ca- and Mg-exchanged montmorillonite, hereafter designated CaSWy-1 and MgSWy-1, were obtained by ion exchange of Clay Mineral Society Source Clay SWy-1, a Na-montmorillonite from the Newcastle Formation, Crook County, Wyoming (van Olphen and Fripiat, 1979). Since a previous study showed that the hydraulic fraction smaller than 0.1 μm produced a DTA pattern with well-defined dehydration peaks (Koster van Groos and Guggenheim, 1984), only this fraction was used. Cation exchange was accomplished by four washings with a 1 *N* $CaCl_2$ or $MgCl_2$ solution, followed by six washings with distilled water, and drying in air. The material was stored at 55% humidity over a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$.

Table 1 shows analyses of the starting materials and of the 0.1 μm fraction of SWy-1. Each sample was fused at 1200°C for 1 min and analyzed by electron microprobe. Koster van Groos and Guggenheim (1984) found significant Na_2O loss during fusion and boil-off from the glass of SWy-1 during analysis (col. 1). The high value for SiO_2 in these analyses (Table 1) indicates the presence of colloidal SiO_2. The Ca and Mg content of the exchanged SWy-1 is reasonable for montmorillonite, and it suggests that no substantial hydrolysis occurred. The starting material was also analyzed by X-ray powder diffraction before and after glycolation. The diffraction patterns are shown in Figure 1. For comparison, the diffraction patterns of the 0.1-μm fraction of SWy-1 are shown also.

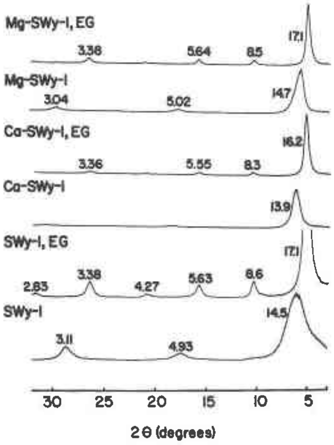

Fig. 1. X-ray powder diffractograms (Cu*K*α radiation, Ni-filtered, 1°/min) of CaSWy-1, MgSWy-1, and SWy-1 at 55% relative humidity and glycolated (EG).

In dry runs, the capsules were loaded with constant force so that they were packed equally. In runs at low pressures (Table 2), no additional water was added. At these pressures, the molar volume of water vapor is sufficiently large so vapor will continuously evolve from the sample during the dehydration reaction and expell the Ar gas pressure medium, which, presumably, acts only as a piston (see Koster van Groos and Guggenheim, 1984, for details). Thus, it is believed that sufficient water vapor remains associated with the sample so that P_{H_2O} approximates P_{total}. At moderate pressures, where the molar volume of water is much smaller, water was added to the runs to maximize P_{H_2O}. The water in these runs was pipetted into the capsule before the sample was introduced.

TABLE 2. HP-DTA peak positions for the interlayer dehydration reaction in CaSWy-1

(wt%) H_2O	First peak *P* (bar)	*T* (°C)	Second peak *P* (bar)	*T* (°C)
dry	1	177	1	219
dry	1	173	1	200
dry	1	173	1	219
10	21.8	289	22	340
10	22.3	292	22.6	323
5	81	408	81	420
5	85	400	86	420
10	122	412	—	—
10	136	440	136	460
10	170	453	—	—
10	182	458	—	—
10	190	447	—	—
10	192	457	—	—
25*	400	445	412	486
12*	478	495	477	520
10*	1075	500	—	—

* Closed capsule.

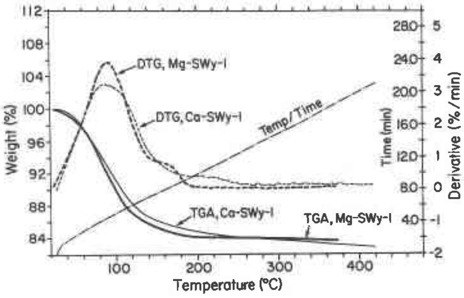

Fig. 2. TGA and DTG diagrams for CaSWy-1 and MgSWy-1. Note the weak shoulder peak in CaSWy-1 between 200 and 260°C.

Under conditions where the molar volume of water vapor is small, several sealed capsule runs were made (note runs in Table 2 between 0.5 and 1 kbar). The amount of both water and sample was carefully determined by weighing. Sealed capsules were checked for possible leaks before the experiment. If the capsule had lost weight during the run, it was assumed that it leaked during the experiment, and the results were not used.

RESULTS AND DISCUSSION

Thermogravimetric analysis

The TGA and DTG results for CaSWy-1 (25-mg sample) and MgSWy-1 (25-mg sample) are shown in Figure 2. The water loss of both smectites is about 16%, and the temperature of the main peak was approximately 90°C for each. The dehydration of MgSWy-1 takes place in two well-defined reactions about 80 deg apart, as is shown by the DTG curve. The DTG signal for CaSWy-1 indicates that the main (low-temperature) dehydration occurs over a wide temperature range. A small second dehydration reaction begins at 200–220°C and terminates at 260°C. Using the same apparatus, SWy-1 had a water loss of 9%, and a K-exchanged SWy-1, hereafter referred to as KSWy-1, had a water loss of 6% (Koster van Groos and Guggenheim, unpub.). Van Olphen and Fripiat (1979) reported an interlayer water content of SWy-1 of 4.99%, which is significantly lower than our values of 9%; we have no explanation for this discrepancy. It is concluded that the nature of the interlayer cation strongly affects the amount of interlayer water that montmorillonite can absorb at 55% humidity.

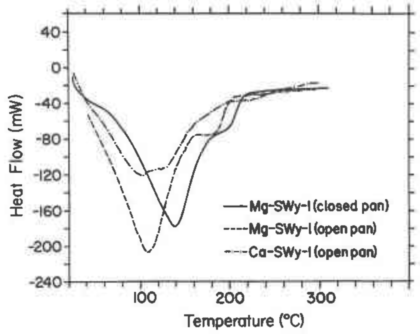

Fig. 3. DSC diagrams for CaSWy-1 and MgSWy-1. The shift of the pattern of MgSWy-1, using an open pan and a closed pan is attributed to the partial pressure of H_2O; see text. Note the two peaks for CaSWy-1 between 100 and 140°C.

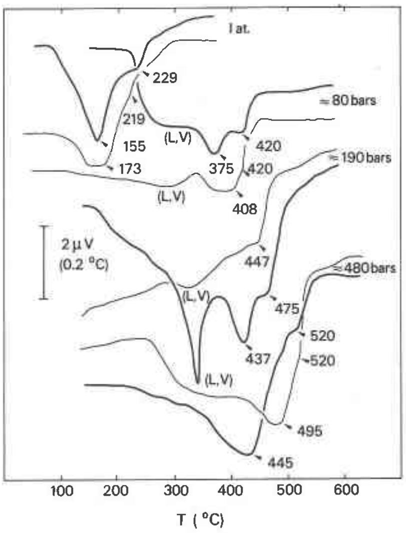

Fig. 4. DTA patterns of samples made at different pressure. The heavy lines represent MgSWy-1 and the light lines CaSWy-1. The baseline drift in these patterns is very apparent for CaSWy-1 at 190 bars and in both patterns at 480 bars. The peak labeled (L,V) represents the vaporization of water.

Differential scanning calorimetry

Figure 3 gives the results of DSC analyses. The results are very similar to the DTG curves. The most important difference is that the CaSWy-1 signal for the first dehydration reaction shows a double peak, with the apices separated by 20 deg. The second dehydration reaction for CaSWy-1 is present as a small peak between 200 and 260°C, similar to the peak present in the DTG analyses. In a series of analyses, it was found that the dehydration temperatures varied significantly more than the precision of the system. On the basis of the results of Koster van Groos and Guggenheim (1984), it is reasonable to assume that these variances are the result of different P_{H_2O}. DSC scans made using both a closed and an open pan (Fig. 3) showed that, in the anhydrous N_2 atmosphere of the apparatus, MgSWy-1 in the closed pan had a higher dehydration temperature. Since P_{H_2O} in the closed pan must have been higher, these results confirm that P_{H_2O} is a critical factor in smectite interlayer dehydration.

High-pressure differential thermal analysis

In these high-pressure experiments, analysis of the DTA patterns is complicated, especially when several reactions occur together. The most rapid change in a reaction rate often occurs when the reaction is nearly completed. In a DTA pattern, this is usually at the peak, where the curve starts the rapid return to the baseline. When several different reactions are superimposed, deconvolution of the signal may establish the approximate peak temperatures

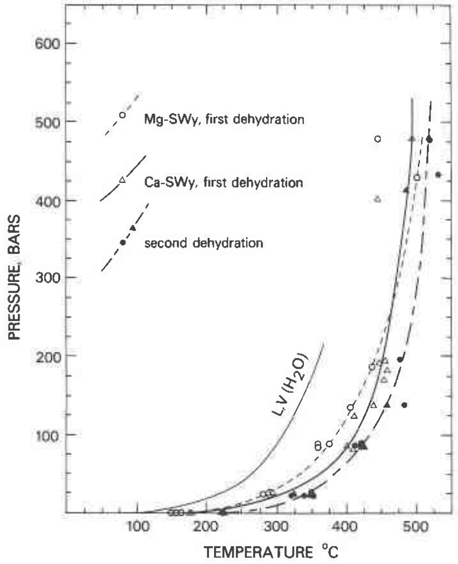

Fig. 5. A *P-T* projection of the dehydration reactions for CaSWy-1 and MgSWy-1 montmorillonite. The curve labeled L,V_{H_2O} is the boiling curve of water. The triangles represent the first and second dehydration reaction of CaSWy-1 as listed in Table 2, the circles the first and second dehydration reaction of MgSWy-1 (Table 3). The data for the second dehydration reaction are shown using closed symbols.

TABLE 3. HP-DTA peak positions for the interlayer dehydration reaction in MgSWy-1

(wt%) H_2O	First peak *P* (bar)	First peak *T* (°C)	Second peak *P* (bar)	Second peak *T* (°C)
dry	1	158	1	227
dry	1	155	1	224
dry	1	165	1	220
dry	1	155	1	227
dry	1	155	1	230
10	21	290	21	350
10	21.8	286	22	340
10	22.6	292	22.6	320
10	24	294	24	348
10	24	294	24	350
10	81	360	83	420
10	85	358	86.5	411
10	87	375	88	420
10	134	405	136	483
20	185.5	437	192	473
15*	429	500	432	526
12*	478	445	476	520

* Closed capsule.

of each reaction. This method is especially effective if the shape of the peaks is symmetrical or, at least, known. However, the shape of the dehydration curve is not known in these experiments. Therefore, we chose to interpret the DTA signal in clay-water mixtures as the superposition of the dehydration reaction of the montmorillonite on the L-V reaction of water. The peak of the dehydration reactions, which occurs at the higher temperature, is represented by a break in the slope toward the baseline (Koster van Groos and Guggenheim, 1984). These breaks in slope are referred to as shoulder peaks.

Figure 4 shows representative examples of HP-DTA patterns of CaSWy-1 and MgSWy-1, obtained at several pressures. The break in slope (arrows) is readily identifiable and can be measured to within 2 deg. The DTA patterns of the two montmorillonites differ substantially. In general, CaSWy-1 has a broad first (lower-temperature) peak and a very weak second (higher-temperature) peak. This is consistent with the DSC results, which showed a double peak (20 deg apart) for the first dehydration reaction. In contrast, MgSWy-1 has both a pronounced first peak and a strong second peak. This is illustrated by the DTA patterns from the 1-atm runs. The shape of the DTA curve at 1 atm is very similar to the DTG and DSC curves (Figs. 2, 3), except that the temperatures are slightly higher. Since the pressure vessel was kept at 1 atm, it is evident that P_{H_2O} was probably very close to 1 atm.

At higher pressures, water was added to the sample, and in the DTA patterns of these runs, both dehydration peaks are usually present as shoulder peaks. A large peak labeled as (L,V) represents the heat of evaporation of the added water. Sometimes only the lower-temperature dehydration peak was observed.

At pressures near the critical points, the enthalpy of evaporation of water ΔH_{ev} decreases sharply (Keenan et al., 1978). Because ΔH_{ev} is an important part of the total enthalpy of dehydration, the dehydration peak must become much smaller at these pressures. At pressures above the critical point of water, the transition of liquid to gas occurs over a range in temperature, and it may overlap the dehydration of montmorillonite. This is illustrated by the runs near 480 bars (Fig. 4). The first dehydration peak, at 495°C for CaSWy-1 and 455°C for MgSWy-1, is small but well defined. The shoulder peak of the second dehydration reaction, here at 520°C for both montmorillonites, often is difficult to identify, especially in experiments with CaSWy-1.

Approximately 75 HP-DTA runs were made, 33 of which were successful (Tables 2, 3). Several runs were duplicated in order to verify the position of the dehydration peaks. The *P-T* relationships of the dehydration reactions are shown in Figure 5. The boiling curve for water (L,V_{H_2O}), taken from Keenan et al. (1978), is shown also; it agrees well with our DTA determinations. The dehydration curves are drawn through the data points at the various pressures, but with a bias toward the higher temperatures. It is probable that the temperatures of these data points represent a minimum value, because a reduction in the water fugacity, caused by the presence of some Ar in the vapor phase near the samples, would result in a lowering of the dehydration temperature. As was found in the earlier results with SWy-1 and KSWy-1 (Koster van Groos and Guggenheim, 1984, 1986), the dehydration reaction curves have approximately the same shape as the L-V curve of H_2O, but lie at higher temperatures. The main dehydration in CaSWy-1 occurs approximately 20 deg higher than in MgSWy-1, and the second dehydration

TABLE 4. Enthalpy (kJ/mol) of dehydration of CaSWy-1 and MgSWy-1 for the first and second dehydration reactions, and the enthalpy of interlayer water, with the values for SWy-1 and KSWy-1 shown for comparison

	Dehydration	ΔH_{dh}*	ΔH_{dh}†	ΔH_{dh}‡	ΔH_{iw}
CaSWy-1	first	49.4	49.59	49.5 ± 0.5	12.1 ± 0.5
	second	57.42	59.12	58.2 ± 2	22.6 ± 2
MgSWy-1	first	49.12	49.56	49.3 ± 0.5	11.1 ± 0.5
	second	66.88	65.57	66.2 ± 2	31.1 ± 2
KSWy-1	first	46.1	46.22	46.2 ± 0.5	7.8 ± 0.5
	second	54.86	58.64	56.7 ± 2	19.8 ± 2
SWy-1	first	46.45	47.1	46.8 ± 0.5	7.8 ± 0.5
	second	61.14	64.7	62.9 ± 2	27.1 ± 2

* Taken from two data points.
† Using least-square analysis.
‡ Obtained by averaging.

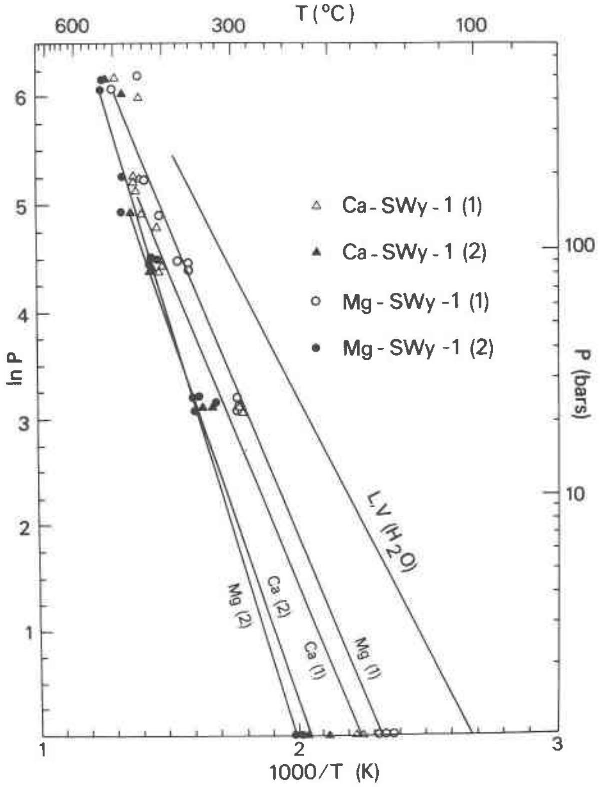

Fig. 6. A ln P vs. 1000/T projection of the dehydration reactions for CaSWy-1 and MgSWy-1 montmorillonite, and of the boiling curve of water, L,V_{H_2O}. The data points for L,V_{H_2O} were taken from Keenan et al. (1978).

occurs in CaSWy-1 approximately 10 deg lower than in MgSWy-1. Because of the similarities of the second dehydration temperatures, only one curve representing this reaction is shown in Figure 5.

THERMODYNAMIC CONSIDERATIONS

Figure 6 shows the data for CaSWy-1 and MgSWy-1 in an ln P vs. 1000/T diagram. The L-V line for H_2O is plotted for comparison. The data for the dehydration reactions of CaSWy-1 and MgSWy-1 have a linear relationship. The lines for the first dehydration reactions are not obtained by an averaging method, such as least-square analysis, but are drawn through the dehydration temperatures at 1 atm, and at 182 bars for CaSWy-1 and 429 bars for MgSWy-1. The lines representing the second dehydration were obtained using the data at 1 atm, and at 136 bar for CaSWy-1 and 432 bar for MgSWy-1. These runs were selected because they provide a maximum temperature for the dehydration reaction (see the discussion in the preceding paragraph).

The experimental data were used to obtain the enthalpy of dehydration ΔH_{dh}. The enthalpy of dehydration is a combination of the enthalpy of the interlayer water ΔH_{iw}, an expression of the bond energy, and the enthalpy of evaporation of this water ΔH_{ev} at the temperature of dehydration and 1 atm. The latter can be obtained with excellent precision using *Steam Tables* (Keenan et al., 1978) by extrapolation of the enthalpy of evaporation to higher temperatures. By subtraction, we obtained ΔH_{iw}. As was discussed previously (Koster van Groos and Guggenheim, 1986), the derivation of these enthalpies is not without problems. The effect of pressure on various thermodynamic parameters of hydrated and dehydrated clay minerals, such as activity, molar volume, enthalpy of formation, and others, is not well known. Furthermore, the fugacity coefficient of water vapor γ_{H_2O} varies considerably in this P-T range (Helgeson and Kirkham, 1974).

When the boiling curve of water is plotted on a ln P vs. 1000/T diagram (see Fig. 6), a straight line results. From its slope, the enthalpy of evaporation may be calculated, using $\Delta H = -R(\ln P_2 - \ln P_1)/(1/T_2 - 1/T_1)$ (see, e.g., Anderson, 1977). For H_2O an enthalpy of evaporation of 39.5 kJ/mol is obtained at 1 atm and 100°C, where $\gamma_{H_2O} = 0.98$ (Helgeson and Kirkham, 1974). This compares well with the value of 40.886 kJ/mol from Robie et al. (1978), which is surprising considering the nonideal character of H_2O. Since the departure from ideality in the dehydration reaction is mainly in the behavior of the fluid phase, a similar derivation of the enthalpy of dehydration is equally valid. When this procedure was used for SWy-1 (Koster van Groos and Guggenheim, 1986), the calculated value of ΔH_{iw} was in excellent agreement with a calorimetric determination of ΔH_{iw} for a Na-montmorillonite. Thus, it appears possible to obtain reasonable values also for ΔH_{dh} for CaSWy-1 and MgSWy-1 at 1 bar.

The following procedure was used to derive the enthalpy of dehydration ΔH_{dh}. Using the maximum dehydration temperatures (Fig. 6), a dehydration enthalpy was calculated (Table 4), which produces an enthalpy value that is probably low. Next, a slope for the reactions was obtained using linear regression, and the corresponding enthalpy values were calculated (Table 4). For many data points used in the regression, the temperatures are low because P_{H_2O} may be less than P_{total}. Therefore, the value for ΔH_{dh} based on the regression is too high. The "best value" is based on the average of the two values (Table 4). It is difficult to evaluate the standard error, so we assume that our "best value" is confined by the two determinations. In the linear regression of the data of the second dehydration, the line is forced through the temperature values for 1 atm, because we consider these the most reliable. Otherwise, the same procedure was used to obtain ΔH_{dh}.

The data show only a small difference in ΔH_{iw} for the first dehydration reaction of the two montmorillonites. ΔH_{iw} of the second dehydration reaction for MgSWy-1, however, is significantly larger. The montmorillonites with a univalent interlayer cation (SWy-1 and KSWy-1) behave similarly, with little or no difference for ΔH_{iw} of the first dehydration reaction but a large difference for the second dehydration (Table 4). Clearly, the nature of the interlayer cation affects the enthalpy of the interlayer water, with the smaller, higher-charged cation having a significantly higher ΔH_{iw} for the more tightly bonded interlayer water.

A PHYSICAL MODEL

Additional comments on the data

The total interlayer water loss at approximately 55% relative humidity as determined from the thermal gravimetric data is about 16% for CaSWy-1 and MgSWy-1, 9% for SWy-1, and 6% for KSWy-1. The average number of H_2O molecules per exchangeable cation for each dehydration reaction may be estimated from the gravimetric data and the chemical analyses: Mg has a total of 14 H_2O molecules in its hydration shell, the last 2 of these are lost during the second dehydration reaction. The hydration shell of Ca contains approximately 13 H_2O molecules; 12 of these are expelled by the first dehydration reaction and the last H_2O molecule is removed during the second dehydration. The DSC results suggest that the first dehydration reaction for CaSWy-1 may be a combination of two closely spaced (20 deg) events. SWy-1 and KSWy-1 contain twice as many cations in the interlayer site as compared to CaSWy-1 and MgSWy-1. Therefore, the total number of H_2O molecules per cation is approximately half. This is consistent with the thermogravimetric analyses that show that the hydration shell of Na and K contains 4–5 and 3–4 H_2O molecules, respectively.

The SWy-1 data indicate that for each two cations, approximately one H_2O molecule remains after the first dehydration. It is expelled during the second dehydration. KSWy-1 has only a slight peak for the second dehydration reaction; therefore, the number of H_2O molecules that remained after the first dehydration reaction must be very small.

The enthalpy of the second dehydration for Mg-exchanged montmorillonite is much higher than for the other exchanged montmorillonites. Furthermore, the number of H_2O molecules involved in the second dehydration reaction is also much higher.

The model

The high enthalpy of the second dehydration reaction of Mg-exchanged montmorillonite, combined with the two H_2O molecules associated with the Mg cation, requires that these molecules are more tightly bonded to the structure. Therefore, it is likely that these two H_2O molecules are at least partially located within sixfold silicate rings. Such an arrangement is appealing since the charge on the dipole of a water molecule can be satisfied by the cation at one end and the charge-undersaturated basal oxygens associated with Al-substituted tetrahedra at the other. The small size of Mg allows the H_2O molecules to partially enter the silicate ring, whereas large cations may inhibit the process. This interpretation is consistent with the large enthalpy (31.1 kJ/mol) and the high temperature of the second dehydration reaction (225°C) for MgSWy-1. We do not know whether these H_2O molecules are nearest neighbors to the Mg cation when it is fully hydrated. The 12 additional H_2O molecules in the complete hydration shell possibly form two layers of six molecules each; however, we have no experimental data to suggest such a configuration. This model should be considered tentative until independent data, for example from infrared analysis (IR), become available.

In contrast to MgSWy-1, KSWy-1 has a low value of ΔH_{iw} for the second dehydration reaction. Also, only a small number of H_2O molecules are involved in this dehydration. Presumably, the large size of the K cation prevents H_2O molecules from being directly associated with the silicate rings. The smaller Na and Ca cations would be less effective at preventing H_2O molecules from entering this site. Therefore, a small number of these molecules would be expected to become directly associated with the silicate rings.

This model provides a simple explanation for the persistence of a part of the interlayer in Mg-exchanged montmorillonites. Furthermore, the association of the Mg cation with the two H_2O molecules may provide a basis for the development of a brucite-like layer, which can be a precursory stage for the formation of chlorites. For example, Curtis et al. (1985) suggested a possible evolutionary pathway between swelling chlorites, developed from smectite, to chlorite with increasing depth of burial. However, the stability of these phases and the mechanism of transformation is a function of the chemistry of the smectite-chlorite system, and much work is needed to evaluate the effect of temperature, pressure, and composition on the stability of smectite with respect to chlorite.

GEOLOGIC APPLICATIONS

In this study, the stability of interlayer water in montmorillonite was determined as a function of the interlayer cation species. The effect of the chemical environment, which may result in illitization was not considered. The reaction resulting in illite formation is dependent on the activity of K^+ (Garrels, 1984; Rosenberg et al., 1985), and consequently, montmorillonite may be stable over long periods of time in K-poor systems.

The aqueous-fluid pressure in sedimentary strata usually varies from the hydrostatic pressure in open systems to the lithostatic pressure if the strata are sealed. Because of the small but finite permeability of the seal, a lithostatic fluid pressure cannot be sustained over the long term, and the fluid pressure will decline to the hydrostatic values. The water pressure in these strata, therefore, may be 45 to 50% of the lithostatic pressure. Furthermore, these fluids usually are brines, so that the activity of H_2O in the fluid is lowered. Under these conditions, dehydration of montmorillonite will occur at substantially lower temperatures than obtained in this study, where P_{H_2O} was equal to P_{total}.

Because the enthalpy of the interlayer water for a particular montmorillonite is constant, it is possible to evaluate the effect of lower activity of H_2O in sediments. For example, if the fugacity of H_2O in the aqueous fluid is approximately 40% of the lithostatic pressure, the dehydration temperature may be reduced by 30°C at 1 atm or reduced by more than 100°C at 600 bars. This indicates that in sedimentary strata, montmorillonite can dehydrate at temperatures below the boiling of water. Consequently, water pressure in these strata may be buffered by the presence of montmorillonites. A sudden reduction of the fluid pressure, which may occur, for example, during drilling operations, would result in a rapid dehydration of montmorillonite.

Montmorillonite represents a very important mineralogical component in ocean sediments and altered ocean crust. For example, smectite and mixed-layer smectite-chlorite are present over the total 1000-m penetration of Deep Sea Drilling Project Hole 504B (leg 69 and leg 83) in altered oceanic crust of 5.9 Ma (Honorez et al., 1983; Alt et al., 1985). These smectites tend to be FeO-MgO rich. When the ocean crust is subducted, considerable amounts of H_2O are transported with the descending crust. Extensive early dehydration may not take place if the descending crust is sealed dynamically, i.e., isolated in the down-thrusted slab. If the temperature remains relatively low for several million years, smectites may be transported to significant distance and depth, while retaining their interlayer water. At some stage, smectites will recrystallize at low to moderate temperatures to chlorite- and stilpnomelane-rich assemblages, which also contain a large amount of structural H_2O. It is concluded that the stability of interlayer water in smectites may have important bearing on the introduction of H_2O to the upper mantle.

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