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DEHYDRATION OF K-EXCHANGED MONTMORILLONITE AT ELEVATED TEMPERATURES AND PRESSURES

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Abstract—The dehydration temperature of K-montmorillonite, obtained by ion exchange of a Na-montmorillonite, was determined at pressures to 2 kbar, using high-pressure differential thermal analysis. Dehydration reactions were found at about 50° and 100°C above the liquid-vapor curve of water. At pressures above the critical point of water the dehydration temperatures increased only slightly. The temperature of the first dehydration reaction is 10°C higher than for Na-montmorillonite, indicating a slightly greater stability of the hydration shell around the potassium interlayer cation. The second dehydration reaction occurs at a slightly lower temperature. The data were used to determine the enthalpy of the dehydration $\Delta H_{(dh)}$ and the bonding enthalpy of the interlayer water $\Delta H_{(iw)}$ at 1 atm. The first dehydration reaction of the K-exchanged montmorillonite has a $\Delta H_{(dh)} = 46.16 \pm 0.06$ kJ/mole and a $\Delta H_{(iw)} = 7.8 \pm 0.5$ kJ/mole, whereas for the second reaction, $\Delta H_{(dh)} = 56.7 \pm 2$ kJ/mole and $\Delta H_{(iw)} = 19.8 \pm 2$ kJ/mole. These values compare with a $\Delta H_{(dh)} = 46.8 \pm 0.3$ kJ/mole and a $\Delta H_{(iw)} = 7.8 \pm 0.5$ kJ/mole for the first dehydration reaction of the Na-montmorillonite and a $\Delta H_{(dh)} = 62.9 \pm 2$ kJ/mole and $\Delta H_{(iw)} = 27.1 \pm 2$ kJ/mole for the second dehydration.

Key Words—Dehydration, Differential thermal analysis, Enthalpy, Montmorillonite, Potassium, Pressure.

INTRODUCTION

Recent advances in high-pressure differential thermal analysis (Koster van Groos, 1979) allow the routine determination of dehydration reactions in clays. Koster van Groos and Guggenheim (1984) found for Na-montmorillonite that a modest increase in pressure greatly extends the stability of the interlayer water and that dehydration occurs in two stages, at about 40° and 110°C above the curve representing the boiling temperature of water (L,V(H_2O)) at different pressures (Keenan *et al.*, 1978). Although smectite stability studies are of only indirect interest in understanding interlayer dehydration reactions, the parameters affecting the breakdown of smectite may significantly influence the interlayer dehydration. Eberl (1978) showed that smectite breakdown is dependent on interlayer chemistry. In addition, Eberl and Hower (1976) suggested that small variations in the chemistry of the 2:1 layer of smectite may affect the behavior and stability of interlayer water, because of changes in the 2:1 layer charge.

In this study, we determined the effect of pressure on the dehydration of K-exchanged montmorillonite. The purpose of this work was to establish the effect of the nature of the interlayer cation on the stability of interlayer water at elevated pressures. Therefore, this study does not address the problem of the long-term stability of the clay mineralogy. To eliminate possible chemical effects that might influence interlayer dehydration, we used the same starting material as in the earlier study (Koster van Groos and Guggenheim, 1984) and kept the chemistry of the 2:1 layers constant during both the sample preparation and the experimental procedures.

These experiments were made under hydrothermal conditions, and the results should not be compared with experiments or calculations based on lithostatic (non-hydrostatic) stresses, without the appropriate corrections. Also, the results should not be directly compared to other smectites with a substantially different layer charge.

EXPERIMENTAL METHOD

Apparatus

The main features of the high-pressure differential thermal analysis system (HP-DTA) used in this study were described by Koster van Groos (1979). The apparatus consists of a copper cell with positions for three capsules, which are usually made of gold. The capsules were made uniformly, weighed ~120 mg, and have a length of ~7 mm, a diameter of 3.2 mm, and a wall thickness of 0.05 mm. They have a re-entry well of about 1 mm depth which can accommodate a Pt-$Pt_{90}Rh_{10}$ thermocouple. Two capsules contained sample and the third a reference, TiO_2 or Al_2O_3. The copper cell-thermocouple assembly was placed in an internally heated pressure vessel similar to the one described by Holloway (1971). The temperature of the sample capsules was obtained from the temperature of the reference, and corrected by using the differential temperature. This correction was as high as 3°C, but usually less. The DTA signals were recorded on the 20-μV range of a Kipp recorder, and temperature deviations of 0.02°C could be detected. Pressures were measured

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using low-, medium-, and high-pressure Bourdon-type calibrated Heise gauges, which are accurate to within 0.5%. The heating rate was held at 20°C/min by means of a Honeywell programmable controller. This rate is believed to be too rapid for partial montmorillonite dissolution, ion migration, and subsequent recrystallization, making it unlikely that the 2:1 layer chemistry changed during the run. The system was regularly calibrated at different pressures using the low quartz-high quartz inversion (Koster van Groos and ter Heege, 1973). The corrected temperature, therefore, is believed accurate to within 1°C. An important feature of this method is that the geometry of the capsules and their position in the cell are highly reproducible, allowing comparison of the DTA signals. Furthermore, the capsules may be open or welded shut.

The molar volume of water at low pressures and elevated temperatures is high. Thus, it was not possible to use sealed capsules at low pressures. At low pressures and using open capsules, the dehydration of the sample presumably resulted in the generation of sufficient H_2O vapor such that the gas phase close to the sample was pure H_2O. To maintain conditions with P(total) = P(H_2O) in runs made at intermediate pressures, it was necessary to add water because the molar volume of H_2O gas is smaller under these conditions than at low pressures. At higher pressures, where the molar volume of H_2O gas is even smaller, sealed capsules were used. In these runs, 5–10% water was added so that P(total) = P(H_2O) even during the initial stages of the run. For additional information, see Koster van Groos and Guggenheim (1984).

In the dry runs the sample material was compressed with a constant force. In the runs wherein water was added, the water was pipetted into the capsule before sample was introduced. In all runs ~30 mg of sample was used. The amounts of both water and sample were determined by weighing. The size of the samples was small, and there was little chance for overpressures to develop. Sealed capsules were checked for leaks before each experiment. If the capsule had lost weight during the run, the results were not used. Because the equipment was still under development, experiments often failed due to electrical noise, baseline drift, loss of thermal contact between capsule and thermocouple, leaking capsules, or other mishaps. The success rate was about 30%.

Starting material

Potassium-exchanged montmorillonite (designated as K-SWy-1) was obtained by ion exchanging The Clay Minerals Society's Source Clay SWy-1, a Na-montmorillonite from the Newcastle Formation, Crook County, Wyoming (van Olphen and Fripiat, 1979). The hydraulic fraction (<0.1 μm) of this clay was used. This size fraction produced a DTA pattern with well-defined dehydration peaks (Koster van Groos and Guggenheim, 1984). Cation exchange was carried out at ambient conditions to insure that the 2:1 layer was not altered. Exchange was accomplished by repeated washings with a 1 N KCl solution, followed by six washings with distilled water, and drying in air. The material was stored at 55% relative humidity over a saturated solution of $Mg(NO_3)_2 \cdot 6\,H_2O$. Table 1 shows analyses of sample SWy-1 (van Olphen and Fripiat, 1979) and the <0.1-μm fractions of samples SWy-1 and K-SWy-1. The latter two analyses were obtained from electron microprobe analysis of samples fused at 1200°C for 1 min. The data show a significant loss of Na_2O during fusion and/or boil-off from the glass during the analysis. The high value for SiO_2 in these analyses, combined with the absence of X-ray powder diffraction (XRD) reflections of quartz, suggests the presence of noncrystalline (colloidal?) SiO_2. The high values for CaO and K_2O in the analysis reported by van Olphen and Fripiat (1979) were due to the presence of calcite and K-feldspar (Koster van Groos and Guggenheim, 1984). Possibly a small amount of Ca- and K-montmorillonite was present also. The potassium content in sample K-SWy-1 is reasonable for a K-montmorillonite and suggests no substantial hydrolysis. The lack of Na indicates that the K exchange was nearly complete. The starting material was also analyzed by XRD before and after glycolation. These XRD patterns are shown in Figure 1, as are XRD patterns of the <0.1-μm fraction of sample SWy-1.

Table 1. Composition of Na-montmorillonite SWy-1 and K-exchanged montmorillonite K-SWy-1.

	SWy-1[1]	SWy-1[2]	K-SWy-1[2]
SiO_2	62.9	66.40	64.3
TiO_2	0.13	0.12	n.a.
Al_2O_3	19.4	23.7	23.16
FeO	3.80	4.19	4.75
MgO	2.92	2.77	3.46
CaO	1.76	1.05	0.40
Na_2O	1.53	0.58	0.00
K_2O	0.54	0.16	3.75
H_2O	5.10	n.a.	n.a.
CO_2	1.33	n.a.	n.a.

n.a., not determined.
[1] Bulk sample of SWy-1 (van Olphen and Fripiat, 1979).
[2] Electron microprobe analysis of a glass obtained from the <0.1-μm hydraulic fraction of samples SWy-1 and K-SWy-1.

Differential thermal analysis

The interpretation of a DTA pattern is still subject to discussion in the thermal analysis literature. In this study the temperatures referred to are taken from the point on a peak where the curve starts the rapid return to the base line. At this temperature the thermal event, or reaction, is complete or nearly complete. Koster van Groos and Guggenheim (1984) showed that in a Na-montmorillonite–H_2O system several reactions occur at about the same temperature, namely the boiling of

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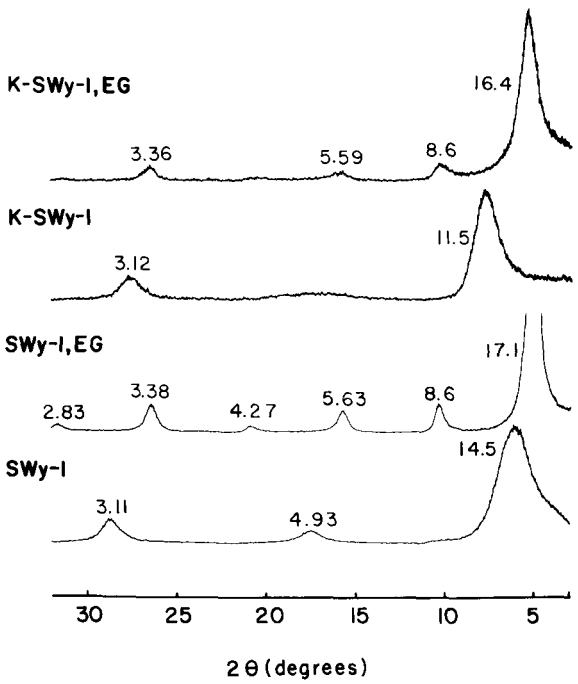


Figure 1. X-ray powder diffractograms (CuKα radiation, Ni-filtered, 1°/min) of samples K-SWy-1 and SWy-1 at 55% R.H. and glycolated (EG). Sample SWy-1 is unexchanged Na-rich montmorillonite; sample K-SWy-1 is K-exchanged. Both samples represent <0.1-μm hydraulic fraction. Numbers next to peaks are in Å units.

water and two dehydration reactions of the montmorillonite. The peaks generated by these reactions are superimposed onto each other. The boiling reaction occurs at the lowest temperature and is the strongest. As a consequence the dehydration reactions usually are indicated as a break in the slope toward the baseline; the temperature of these breaks in slope is reproducible.

RESULTS AND DISCUSSION

About 60 runs were made, of which 24 were successful (Table 2). Several runs were duplicates to verify the position of the dehydration peaks. Figure 2 illustrates the HP-DTA patterns of sample K-SWy-1 at several pressures; one pattern of sample SWy-1 at 1 atm is included for comparison. The break in slope (arrows) is usually readily identifiable and can be measured to a precision of ±1°C. In some patterns, the break in slope is not obvious (note arrow labeled 444°C at 175 bar) and, for these runs, experiments were repeated several times.

Montmorillonites typically exhibit a secondary peak, which Koster van Groos and Guggenheim (1984) suggested is a result of the dewatering of more strongly bonded interlayer water. Both the primary and secondary dehydration temperatures for sample K-SWy-1 were reproducible. The primary dehydration of sample K-SWy-1 occurred at a slightly higher temperature

Table 2. High-pressure differential thermal analysis peak positions for the interlayer dehydration reaction in K-exchanged SWy-1.

	First peak		Second peak	
H_2O (wt. %)	P (bar)	T (°C)	P (bar)	T (°C)
Dry	1	155	1	205
Dry	1	155	1	190
Dry	1	142	1	200
Dry	1	148	1	195
5	1	147	—	—
5	10.2	238	—	—
Dry	20	266	—	—
10	34	300	—	—
5	67.5	330	68	376
5	84	335	—	—
10	84	358	—	—
16	106	355	107.5	395
25	165	410	—	—
10	166	426	166	438
20	174.5	416	175	444
10	195	440	196	475
5[1]	283	470	—	—
16	368	466	—	—
25	412	437	412	486
5[1]	515	480	—	—
10[1]	638	494	—	—
10[1]	1010	485	—	—
9[1]	2100	410?	—	—

[1] Closed capsule.

(150°C) than for sample SWy-1 (140°C) at 1 atm. The second dehydration peak of sample K-SWy-1 appears to be weaker than that of sample SWy-1. These results may be due to a lower enthalpy of reaction or to a smaller amount of water in the first hydration shell around the interlayer cation in sample K-SWy-1. Also, the primary dehydration peak for sample K-SWy-1 may partly mask the peak. In the DTA patterns of sample K-SWy-1 heated in the presence of water at 34 and 175 bar, the vaporization peak of water is dominant: sometimes only one dehydration peak was observed for some samples. At higher pressures the enthalpy of evaporation of water, $\Delta H_{(ev)}$ decreases sharply (e.g., Keenan *et al.*, 1978). Inasmuch as it is an important part of the total enthalpy of dehydration at higher pressures, the dehydration peak should be much smaller. At pressures above the critical point of H_2O the transition of liquid to gas occurs over a range in temperature and may overlap the dehydration of montmorillonite (see the run at 368 bar, Figure 2). In many of these patterns the dehydration peak is less well defined; e.g., in the closed capsule run at 638 bar the first peak is assumed to represent the dehydration.

The pressure-temperature relationships of the dehydration of sample K-SWy-1 are shown in Figure 3, as well as the boiling curve for water (L,V(H_2O)). As was found with the results of sample SWy-1 (Koster van Groos and Guggenheim, 1984), the dehydration reactions of sample K-SWy-1 are parallel to the boiling curve and occur about 50° and 100°C higher. These

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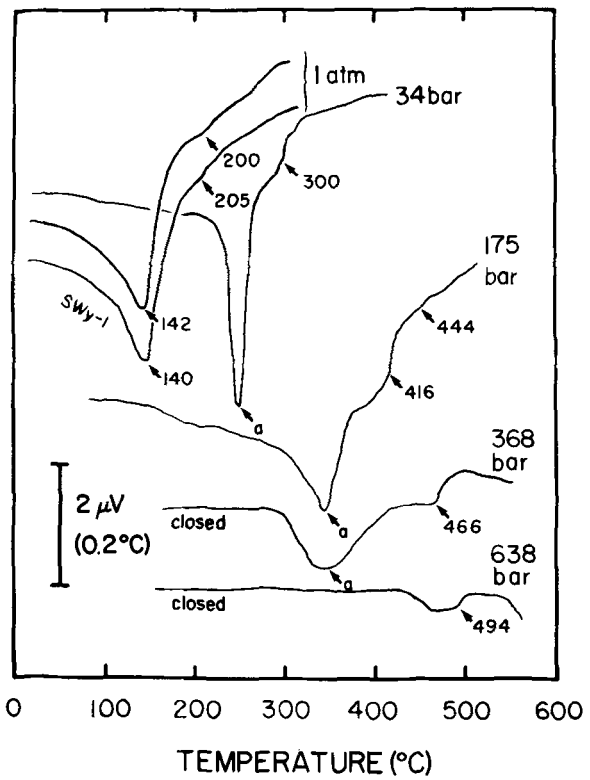


Figure 2. Differential thermal analysis patterns of samples made at different pressures. For comparison, a 1-atm pattern for sample SWy-1 is given; all other patterns are of sample K-SWy-1. Peaks labeled (a) represent liquid = vapor reaction of H_2O, which was present when water was added. Temperature scale is only approximate.

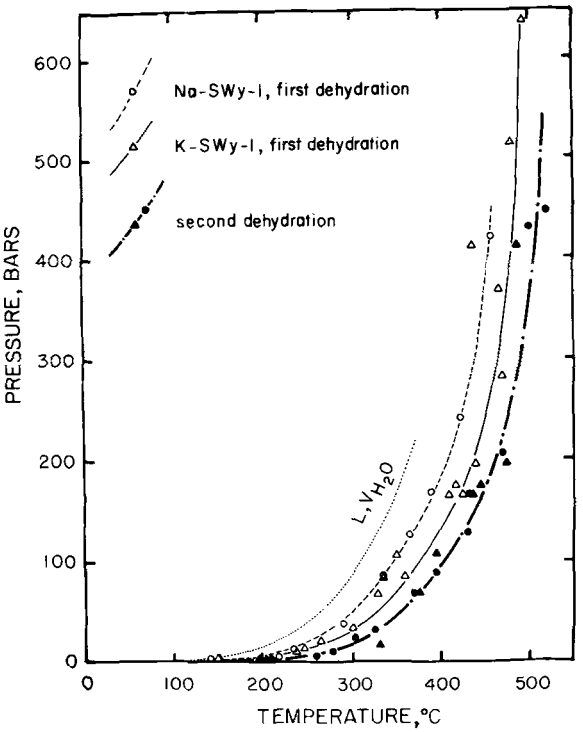


Figure 3. Presure-temperature projection of dehydration reactions of montmorillonite samples K-SWy-1 and SWy-1. Curve labeled L,V(H_2O) is boiling curve of water. Triangles represent first and second dehydration reaction of sample K-SWy-1, as listed in Table 2. Data for sample SWy-1 (circles) were taken from Koster van Groos and Guggenheim (1984).

dehydration temperatures at elevated pressures support the conclusion reached by Koster van Groos and Guggenheim (1984) that in sedimentary basins, pressure alone cannot remove the last one or two layers of water from the interlayer region of montmorillonites. It should be noted that most of the interlayer water in sample K-SWy-1 left the structure at a slightly higher temperature than that in sample SWy-1. The second dehydration occurred at about the same conditions as for sample SWy-1, except at 1 atm, where it was about 15°C lower. The higher temperature of the primary dehydration peak (Figure 3) of sample K-SWy-1 indicates that the more weakly bonded, outer hydration shell of water in sample SWy-1 was more easily lost than that in sample K-SWy-1. These results suggest that weakly bonded water was more readily expelled as the hydration shells of the interlayer cations increased in size. Thus, Na, which is more hydrated than K, tended to lose its outer hydration shells at a lower temperature than K.

The amount of heat transferred between the system and the surroundings as determined from the DTA signal is related to the quantity and change in the enthalpy of the system. Because the interlayer region is principally affected in the dehydration reaction, the bonding energy holding the water in the interlayer may be expressed by the enthalpy of dehydration. Here, bonding energy includes interactions between the interlayer cation and water, between the surface charge and water, and any other bonding effects. To determine directly the energy involved in the dehydration reactions, the system must be calibrated, which is difficult, and has not been done at this time. It is possible, however, to compare the peak area of the dehydration reactions of samples K-SWy-1 and SWy-1. After normalizing for sample weight differences, the DTA signal from sample K-SWy-1 is about 10–20% smaller than for sample SWy-1. This difference indicates that the average bonding energy of the interlayer water in sample K-SWy-1 is less than in sample SWy-1, or that sample K-SWy-1 is less hydrated, or both.

Thermodynamic considerations

The data presented in this paper were used to obtain the enthalpy of dehydration $\Delta H_{(dh)}$ at 1 atm for the dehydration reactions of sample K-SWy-1. In addition, the corresponding information from Koster van Groos and Guggenheim (1984) was used to obtain the enthalpy of dehydration for sample SWy-1. The derivation of these enthalpies on the basis of these exper-

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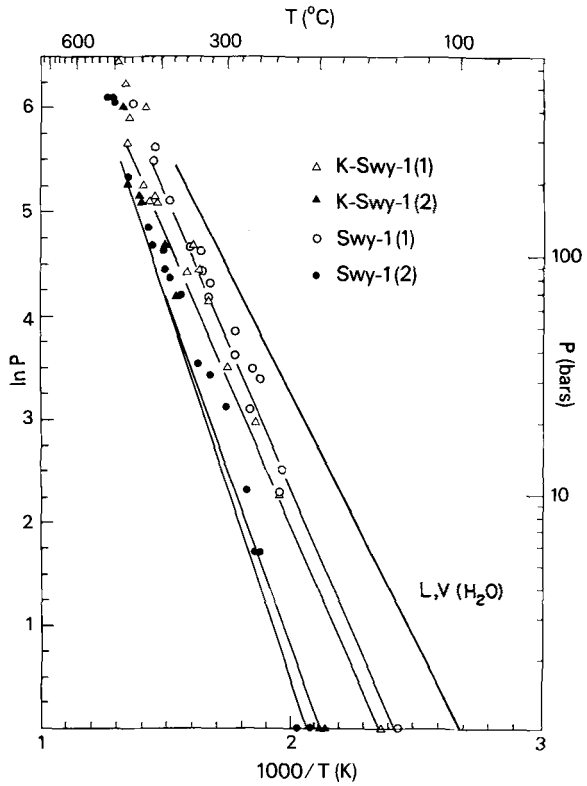


Figure 4. ln P vs. 1000/T projection of the dehydration reactions for montmorillonite samples K-SWy-1 and SWy-1 and of the boiling curve of water, L,V(H_2O). Data for sample SWy-1 are taken from Koster van Groos and Guggenheim (1984), for L,V(H_2O) from Keenan *et al.* (1978). Straight lines do not represent an average of the data, but rather the lower slope limit of the data set (see text). These lines, from left to right, are for sample SWy-1 (second dehydration), sample K-SWy-1 (second dehydration), sample K-SWy-1 (first dehydration), sample SWy-1 (first dehydration), and boiling curve of water (L, V(H_2O)).

imental data is, however, not without problems. The effect of pressure on various thermodynamic parameters of hydrated and dehydrated clay minerals, such as activity, molar volume, and enthalpy of formation, is not well known. Furthermore, the fugacity coefficient of water vapor $\gamma(H_2O)$ varies considerably in this P-T range. Figure 4 shows the data from Table 2 on an ln P vs. 1000/T plot, along with the boiling curve of H_2O. It is well known that the fugacity of water vapor in equilibrium with water varies considerably (see e.g., Helgeson and Kirkham, 1974). If the fugacity coefficient $\gamma(H_2O) = 1$ and $\Delta C_P \sim 0$, the data should lie on a straight line. The slope of this line represents the enthalpy of reaction, following the relation $\ln P_2 - \ln P_1 = -\Delta H/R(1/T_2 - 1/T_1)$ (see e.g., Anderson, 1977). This slope is only valid where $\gamma(H_2O) \sim 1$ and, therefore, to pressures as high as about 1 bar, where $\gamma(H_2O) = 0.98$ (Helgeson and Kirkham, 1974). This slope yields a value for the enthalpy of evaporation for H_2O of 39.5 kJ/mole at 1 bar and 100°C, close to the generally accepted value of 40.886 kJ/mole (Robie *et al.*, 1978). Therefore, reasonable values were expected from our experiments for $\Delta H_{(dh)}$ for sample K-SWy-1 and SWy-1 at 1 bar, although the simplifications are significant.

Koster van Groos and Guggenheim (1984) showed that the dehydration temperature is reduced when $P(H_2O) < P(total)$. Consequently, we believe that in the runs which gave higher water dehydration temperatures, $P(H_2O)$ approached P(total). Therefore, the data indicating the highest dehydration temperatures were considered to represent runs in which the $P(H_2O) = P(total)$. A straight line drawn through these data represents the upper temperature limit for each reaction. In Figure 4 the straight lines representing the first dehydration were obtained using the dehydration temperatures at 1 atm for sample K-SWy-1 and SWy-1, at 283 bar for sample K-SWy-1, and at 242 bar for sample SWy-1. For the second dehydration the data at 1 atm and at 196 bar for sample K-SWy-1 and 206 bar for sample SWy-1 were used.

The data sets include points with a dehydration temperature that is probably too low, as was seen above. Consequently, the result of a linear regression of each data set establishes a lower temperature limit for the dehydration reaction. This procedure effectively placed more weight on the higher dehydration temperatures. The higher pressure data for sample K-SWy-1 and the value at 5.3 bar for sample SWy-1 were not used in the regression analyses, because these were apparently of lower quality. The linear regression for the data of the second dehydration was forced through the temperature values at 1 atm, because we consider these data superior. The P-T relations of the dehydration reactions were, thus, confined. The corresponding val-

Table 3. Enthalpy of dehydration $\Delta H_{(dh)}$ for samples K-SWy-1 and SWy-1 for the first and second dehydration, and the enthalpy of interlayer water $\Delta H_{(iw)}$.[1]

Sample	Dehydration reaction	1 $\Delta H_{(dh)}$	2 $\Delta H_{(dh)}$	3 $\Delta H_{(dh)}$	4 $\Delta H_{(iw)}$
K-SWy-1	First	46.1	46.22	46.16 ± 0.06	7.76 ± 0.5
	Second	54.86	58.64	56.7 ± 2	19.8 ± 2
SWy-1	First	46.45	47.1	46.8 ± 0.3	7.8 ± 0.5
	Second	61.14	64.7	62.9 ± 2	27.1 ± 2

[1] Energies are expressed in kJ/mole. Values in column 1 are based on highest temperature values, in column 2 by using linear regression analysis, and in column 3 by averaging columns 1 and 2.

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ues for the dehydration enthalpy are listed in Table 3, columns 1 and 2. In column 3, the average of the two values is given also, together with an estimated error.

The enthalpy of dehydration is a combination of the enthalpy of the interlayer water $\Delta H_{(iw)}$ and the enthalpy of evaporation $\Delta H_{(ev)}$ of this water at the temperature of dehydration and 1 bar. The latter value can be evaluated accurately by extrapolation, using steam tables (Heil, 1965; Keenan *et al.,* 1978). Following $\Delta H_{(iw)} + \Delta H_{(ev)} = \Delta H_{(dh)}$, we obtained the enthalpy of the interlayer water (see Table 3, column 4). Our estimated error for this value is larger, because of the error this method has in the determination of $\Delta H_{(ev)}$ of water, as discussed above. The uncertainty introduced, however, is partly compensated by the fact that water vapor behaves more ideally at the dehydration temperatures than at 100°C.

The data show no significant difference in $\Delta H_{(iw)}$ of the outer hydration shells (i.e., the first dehydration reaction). The difference in the size of the DTA peak, as was observed, must therefore have been due to a smaller amount of water in the outer hydration shell of sample K-SWy-1. This conclusion is supported by the observation that in a hectorite the presence of K^+ as compared to Na^+ reduced the amount of interlayer water significantly (Tardy et al., 1980); however, although the layer charges are similar, hectorite may not be directly comparable to montmorillonite. The enthalpy defined here as $\Delta H_{(iw)}$ is directly comparable with the integral heat of adsorption of the second layer, as derived by van Olphen (1965). Using calorimetric methods, he obtained a value of 7.776 kJ/mole for a Na-vermiculite, which compares remarkably well with the present results. For the second dehydration reaction (i.e., the loss of the inner hydration shells) the difference in $\Delta H_{(iw)}$ is significant. The nature of the interlayer cation affects the bonding of H_2O, with the smaller cation Na^+ having a more energetic bond. The integral heat of adsorption (van Olphen, 1965) for the complete monolayer (15.62 kJ/mole) does not compare as well with the present data. This poorer agreement is not surprising, because in Na-vermiculite the layer charge is substantially different from that of sample SWy-1, which will affect the first hydration shell more greatly than the second hydration shell.

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