The effect of pressure on the dehydration reaction of interlayer water in Na-montmorillonite (SWy-1)

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Abstract

The temperature of the dehydration of interlayer water of Na-montmorillonite (SWy-1, American Clay Mineral Society Source Clay) is determined at pressures to 1 kbar, using differential thermal analysis (DTA). Two dehydration reactions occur, about 40° and 100°C above the boiling curve of water. Above the critical point of water the dehydration reactions show only a modest increase of temperature with pressure. No significant differences in temperature were found using different heating rates and different size fractions, as defined by their hydraulic diameter. The presence of two dehydration reactions suggests that not all interlayer water is bonded equally; a distinction may be made between weakly bonded and strongly bonded water. It is concluded that hydrated Na-montmorillonite is stable under normal pressure and temperature distributions in sedimentary basins; in these basins dehydration must involve more complex chemical interactions with pore fluids. The large increase in the stability of a hydrated montmorillonite with a modest increase in pressure may have important bearing in its use in nuclear waste disposal.

Introduction

Clay minerals of the smectite group are important components of many geologic systems. In addition, they have highly diverse applications in industry, ranging from pharmaceutical use to purifying agents to backfill in radioactive (and other) waste disposal sites. Furthermore, they and other diagenetic clays occur as cements and pore obstructions in sandstones and may modify the composition and quantity of pore fluids; the presence of these clays are important in both petroleum exploration and in well completion and stimulation. The varied usage of smectites is a consequence of their properties such as compaction, plasticity, catalytic activity, swelling, ion exchange, density and many others. These are determined by the nature of the interlayer material in smectites. This interlayer material (cations and water held between the relatively rigid sheets of tetrahedrally-coordinated and octahedrally-coordinated atoms comprising the 2:1 layer), readily interacts with the environment and generally determines its properties. The stability of the interlayer material with respect to temperature and pressure, therefore, is of great importance in many disciplines.

Whereas the effect of temperature on the interlayer dehydration of smectites has been studied extensively, the effect of pressure is not well established. Much of the information available is from drill cuttings and drill cores (Whittaker and Dyson, 1980) on the basis of the clay mineralogy, but it is difficult to separate the effect of pressure from that of temperature or of the fixation of potassium (which produces illite or illite/smectite mixed-layer clays) from drill core studies alone. Nevertheless, it is generally agreed that in an open system much of the interlayer water is easily removed by pressure, with the exception of either the last or last two hydration layers (Whittaker and Dyson, 1980). For example, van Olphen (1963) has calculated that in Ca-bentonites a load of 37,000 p.s.i. is required to remove the next to last water interlayer and 99,000 p.s.i. for the last interlayer. An experimental study (Khitarov and Pugin, 1966) indicates that pressure does not significantly increase the stability of the interlayer water in smectites. This is at variance with other experimental studies on smectites, which show that these clays are stable to temperatures of 400 to 500°C and pressures of 0.5 and 2 kbar (Eberl et al., 1978). Eberl et al. point out that increased water pressure should increase dioctahedral smectite stability in hydrothermal systems with a 1:1 ratio of smectite to pure water. These results suggest that the more modest pressures from overburden are generally insufficient to cause loss of water from the last hydration shells.

This paper reports the effect of pressure on the interlayer dehydration of a Na-montmorillonite from Wyoming (American Clay Society Standard, SWy-1). Because in conventional equilibrium studies dehydration of smectite

is reversible and non-quenchable, a dynamic method, high pressure differential thermal analysis (HP-DTA), was used.

Experimental methods

Apparatus

The HP-DTA system (Koster van Groos, 1979) consists of a copper cell assembly with positions for two samples and a reference. Each position holds a uniformly machined gold capsule with a re-entry well. Pt-Pt90Rh10 thermocouples are located in and are in thermal contact with the re-entry well of the capsules. The capsule, which may be either open or sealed by welding, has a wall thickness of 0.05 mm, is approximately 7 mm long and weighs about 120 mg. The copper cell is placed in an internally heated pressure vessel (IHPV) similar to the one described by Holloway (1971). The temperature of the run is determined by using the thermocouple of the reference capsule, and adding or subtracting the temperature difference ΔT between the reference and the run. Corrected temperatures are believed to be accurate to within 1°C. The DTA signals were recorded on the 20 μV range of a Kipp recorder, enabling the detection of a temperature deviation as small as 0.02°C. Argon was used as the pressure medium and was measured using three different calibrated bourdon type heise gauges, accurate to within 0.1%. The gauges, with the ranges 0-70 bars, 0-1000 bars, and 0-7500 bars, were used to measure low, medium, and high pressures, respectively. Pressures are believed to be accurate to within 0.5%. Although the pressure medium is argon gas, it is reasonable to assume for open capsules that during the dehydration reaction the gas phase over the sample is either a mixture of H_2O and argon, $P_{total} = P_{Ar} + P_{H_2O}$, or pure H_2O gas, $P_{total} = P_{H_2O}$, which has displaced the argon. At higher pressures, where the molar volume of H_2O gas becomes small, water was added to the sample in an attempt to maintain $P_{total} = P_{H_2O}$.

The capsules were loaded with 40 mg of sample, after first pipetting the desired amount of water into the capsule. Packing of the sample was kept reasonably constant by pressing the materials in the capsule with a plunger using a constant force. Sealed capsules were checked for leaks before and for weight-loss after the experiment. Open capsules were filled up with silica wool. After inserting the capsules in the DTA cell, the sample chamber was packed with silica wool to minimize gas convection and capsule movement. In these experiments problems occurred frequently, which resulted in the loss of the data. Sealed capsules often failed at low pressures. Sometimes loss of thermal contact between thermocouple and capsule precluded registration of any peaks. Thermal drift was sometimes excessive. Electric noise occasionally "drowned" the signal. Therefore, less than half of the runs provided useful data.

Starting material

For most of the experiments American Clay Mineral Society Source Clay SWy-1, a Na-montmorillonite from the Newcastle Formation, Crook County, Wyoming (van Olphen and Fripiat, 1979), was used as received, without mechanical or chemical treatment. Twenty percent pure quartz (St. Peter Sandstone) ground to pass a 230 mesh was added as an internal standard (Koster van Groos and ter Heege, 1973; Koster van Groos, 1982). The low-high quartz inversion is a rotational transformation involving a small thermal event; it is useful to both calibrate

temperature and to determine that the thermocouples remain in thermal contact with the capsules. To ensure reproducibility in weighing and to promote sample wettability, samples were stored at 55% relative humidity, over a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$.

In order to characterize the sample, the clay was washed with distilled water and separated by centrifuging into eight size fractions (see Table 1). Some material was unavoidably lost during size separation, either through solution or by removing it with the (clear) supernatant. Each fraction was analyzed chemically, by X-ray diffraction, petrography, scanning electron microscopy, and DTA. Table 1 presents the chemical data obtained by electron microprobe analysis of fused glass beads (produced from 50 mg. clay held at 1200°C for one minute). The analysis of SWy-1 agrees well with that of van Olphen and Fripiat (1979) with the exception of Na_2O. This may be caused by Na_2O-loss during fusion and some boil off from the glass during analysis. The analyses of fractions #2, 3 and 4 are high in SiO_2 caused by the presence of quartz. The high value for CaO in #1 and 2 suggests the presence of carbonates whereas the high value of K_2O in #2 is attributed to K-feldspar. Calculation of a chemical formula from these data (Table 1) is not meaningful because of the uncertainty of the chemical composition.

Each size fraction was analyzed by both Debye-Scherrer and powder diffractometer X-ray methods. The Debye-Scherrer method, which allows long exposure times, confirmed the presence of carbonates, K-feldspar and quartz as given in Table 1. X-ray diffractograms of three of the eight size fractions are presented in Figure 1. They illustrate the crystallinity and reaction to glycolation of the montmorillonite. (Following standard practice for reporting the d-spacing for montmorillonites (Jackson, 1979), SWy-1 was Mg-exchanged and glycolated. The 001 d-spacing of the Mg exchanged and glycolated montmorillonite is 17.09Å.) Petrographic examination showed small quantities of green biotite and tourmaline in fraction #1 and 2. Size fractions #7 and 8 are most free of impurities, although some colloidal quartz may still be present. Scanning electron microscope (SEM) photographs showed that the lateral dimensions of the individual clay particles remained fairly constant. In the coarser fractions the clay particles are clumped together forming thick aggregates. In the finer fractions these aggregates contain fewer particles. In the finest fraction (#8) the particles are present individually, they appear to be exceedingly thin, perhaps only a few layers thick.

DTA procedures

In DTA studies, a peak is defined by the temperature of the onset of the deviation, the peak temperature, and the temperature at which a deviation is no longer present. This deviation is caused by a thermal event, a reaction, in the sample. If more than one reaction occurs at approximately the same temperature, the signals of both reactions will be additive, and onset and peak temperatures of each reaction may be difficult to determine. This is illustrated in Figure 2. The curve (1) in Figure 2A shows a simplified dehydration peak of smectite. The extrapolated onset (a) and the peak (b) define the signal. At (c) most of the reaction is completed, and the curve rapidly returns to the base line. Curve (2) illustrates the effect of an additional peak, in this case an idealized peak for the boiling of water (the dashed lines indicate the separate thermal effect of the two events). The new peak temperature as illustrated by (d) has a value which is higher than the boiling temperature of water. Although the peak tem-

Table 1. Chemistry, mineralogy and preparation details of SWy-1 and size fractions

	SWy-1*	SWy-1	#1	#2	#3	#4	#5	#6	#7	#8
Centrifugal force and time used for separation:										
Force (g):			1	12	160	650	1100	1100	17300	-**
Time (minutes):			20	7	4	4	7	50	5	-
Hydraulic diameter(μ):			μ>10	10>μ>5	5>μ>2	2>μ>1	1>μ>.5	.5>μ>.2	.2>μ>.1	.1>μ
Weight fraction (%):			4.5	4.3	5.0	5.5	11.1	13.5	12.7	25.6
Chemical composition:										
SiO_2	62.9	65.75	61.44	71.83	80.69	73.19	61.43	63.56	66.49	66.40
TiO_2	0.13	0.12	0.44	0.32	0.17	0.13	0.05	0.11	0.12	0.05
Al_2O_3	19.4	20.33	11.00	12.84	12.92	16.65	28.81	23.51	22.99	23.70
FeO	3.80	3.72	1.72	2.58	2.82	3.18	2.78	4.93	4.56	4.19
MgO	2.92	2.76	1.08	1.08	1.69	2.09	1.41	3.80	2.82	2.77
CaO	1.76	1.50	15.96	3.39	0.70	0.80	0.49	1.03	1.06	1.05
Na_2O	1.53	0.82	0.77	0.72	0.24	0.28	1.16	0.43	0.88	0.58
K_2O	0.54	0.53	0.44	3.20	0.47	0.22	0.21	0.12	0.14	0.16
H_2O	5.10	na***	na	na	na	na	na	na	na	na
CO_2	1.33	na	na	na	na	na	na	na	na	na
Total	99.41	95.53	92.85	95.96	99.70	96.54	96.34	97.49	99.06	98.90
Mineralogy:										
quartz		xxx	xxx	xxx	xxx	xxx	xx	xx	x	x
carbonate		xx	xx	xx	-	-	-	-	-	-
K-feldspar		x	x	xx	-	-	-	-	-	-

* Chemical analysis from van Olphen and Fripiat (1979)
** Obtained by evaporation of the supernatant
*** Not analyzed
x Indicates the abundance: xxx, moderate; xx, present;
  x, probably present; -, not detected.

perature of the dehydration reaction is difficult to establish, the temperature at which the reaction is almost completed has not changed, and it will also occur on the combined curve as a break in the slope toward the baseline, at (c), or as a shoulder of the peak. A typical curve (Fig. 2B, curve 1) for montmorillonite is more complex due to an additional peak producing a shoulder, (e). The addition of water results in a more complex DTA signal. Also, the rate at which water evaporates at different pressures is difficult to predict. Other variables such as the degree of packing of the sample may result in small but perhaps significant over-pressures in the capsule. Although the signal was not always ideal, the DTA curve from a successful run was usually similar to the examples discussed above. However, occasionally excessive baseline drift caused by large variations in the thermal gradient in the DTA cell, loss of thermal contact between the capsule and the thermocouple, electric noise, and other experimental problems reduced the success rate to about 30 percent. To avoid incorrectly identifying an apparent peak with a reaction phenomenon, results presented here have been successfully reproduced several times.

Heating rates were initially set to 10°C/min using a Honeywell programmable controller. It was found that the results were very similar to those with a heating rate of 20°C/min. Thereafter, only a heating rate of 20°C/min was used.

Particle size effects

The DTA patterns of SWy-1 and the separated fractions, with the exception of the coarse-grained #1, were determined at 1 atmosphere and are presented in Figure 3. The arrows corre-

spond with the points (c) and (e) in Figure 2. The difference in particle size does not appear to affect the temperature of the peak or of the shoulder, as defined in Figure 2. This is supported by the fact that the SEM data did not show a significant variation in the size of the individual particles, even though they formed aggregates in the coarser fractions. Nevertheless, it is interesting to note that the finest fraction (#8) produces the sharpest peak, and the smallest secondary peak (shoulder), suggesting that the secondary dehydration peak may be related to particle thickness in Na-montmorillonite.

Because the temperatures of the primary and secondary peaks do not appear to be dependent on the size fraction, and because it is preferable to be able to compare results between laboratories, SWy-1 was used in this study as received.

Results and discussion

Approximately 200 runs were made in this system of which about 60 were successful. Many of these were duplicate runs, made to verify the position of the dehydration peaks. Therefore, only 30 runs are considered critical and these are listed in Table 2. The effect of the presence of H_2O is illustrated in Figure 4. The runs at 5.3 bars were made simultaneously by using both sample wells of the DTA and illustrate the effect of the additional peak for the boiling of water, as was discussed above and illustrated in Figure 2. The arrows correspond with peaks (c) and (e) in Figure 2B. The DTA curves are very similar, with the exception of the additional H_2O peak. Note the
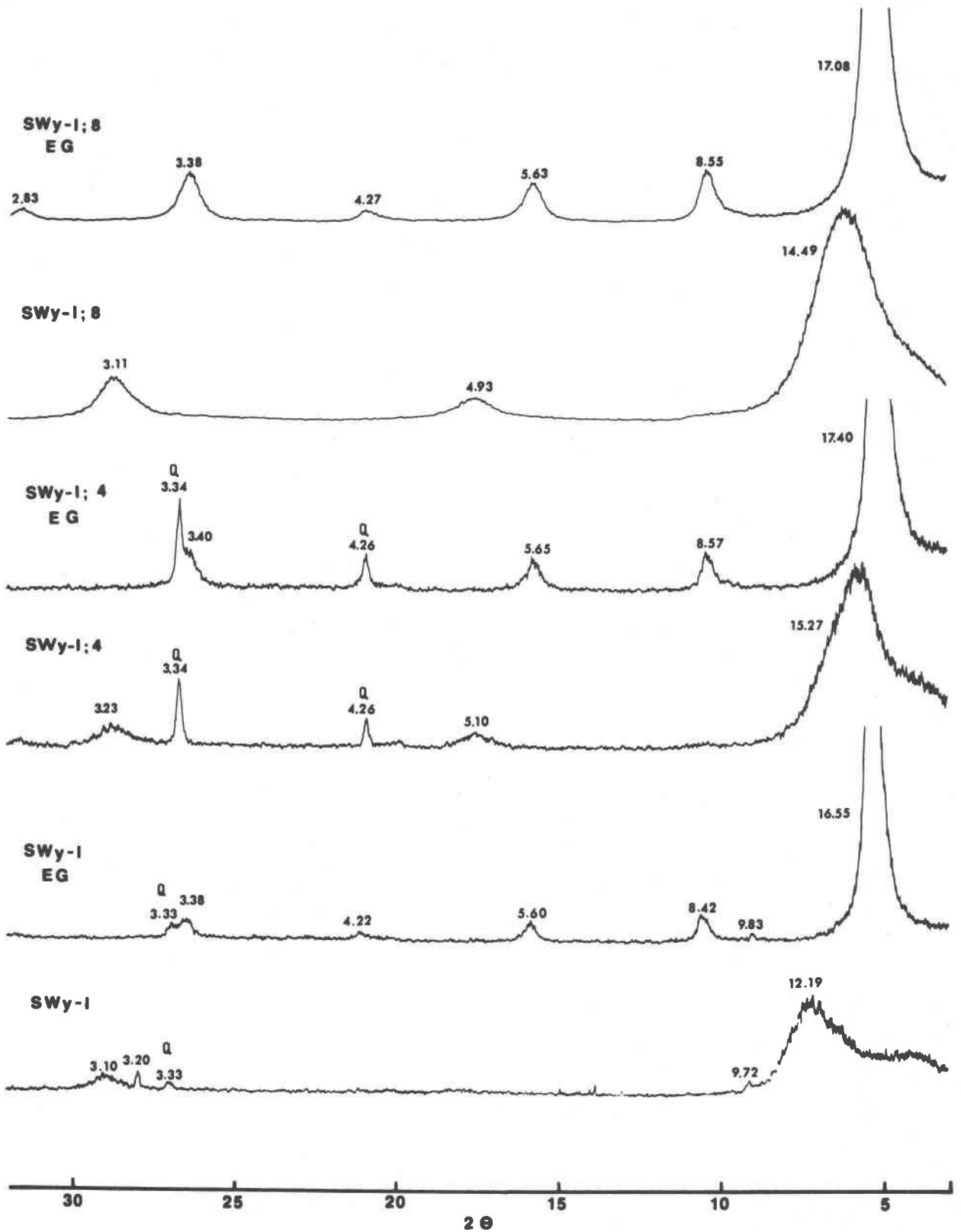
Fig. 1. X-ray diffractograms (CuKα radiation, Ni-filtered, 1°/min) of SWy-1 as received and of size fraction #4 and 8 (see Table 1) at 55% relative humidity and glycolated (EG).
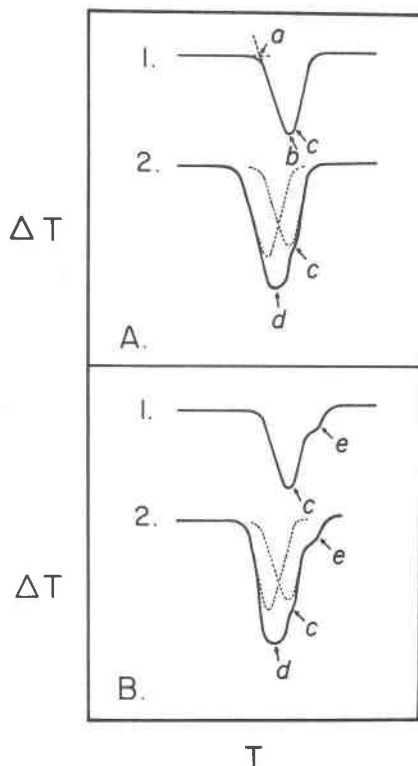
Fig. 2. (A) Curve (1) shows the extrapolated onset temperature (a) of an endothermic dehydration reaction and the peak temperature location at (b). Point (c) shows where the reaction is nearly complete. Curve (2) illustrates the effect of the presence of additional water. Shoulder (c) on curve (2) approximates the temperature of (c) on curve (1). Note that the peak temperature located at (d) is lower than (b) of curve (1), and neither represents the temperature of the boiling of water nor the dehydration temperature. Likewise, an extrapolated onset temperature of curve (2) does not provide useful information on the dehydration reaction. (B) Points (c) and (e) on curve (1) illustrate the more complex dehydration that is typical for Na-montmorillonite. As in Figure 2A, temperatures at points (c) and (e) represent temperatures where each reaction is nearly complete. Curve (2) illustrates the effect of the addition of water.
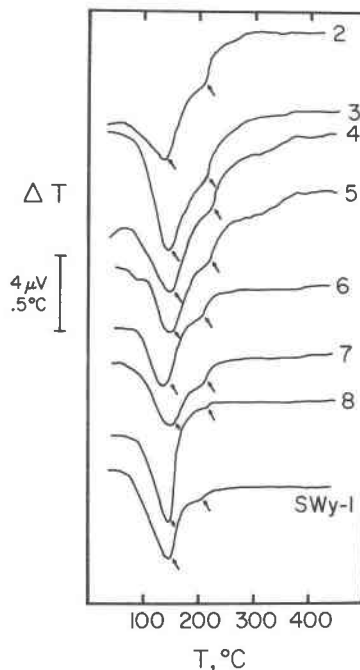

Fig. 3. Representative DTA patterns at 1 atmosphere of SWy-1 and each size fraction from #2 to #8 (see Table 1). Arrows correspond to points (c) and (e) in Fig. 2 and represent two stages of dehydration. The peaks and their locations were verified by duplicate runs. Note that particle size is not a major influence in defining the dehydration temperature, but fraction #8 does show the sharpest peak and the weakest shoulder.

small signal for the second peak. No difference was observed for the dehydration temperatures between dry (no water added) and H_2O-containing runs at pressures to 30 bars. Because at these low pressures, the molar volume of H_2O is large, it appears the water vapor evolving from the interlayer region in the dry runs may flush out the argon gas from the sample volume. Probably little mixing occurs between vapor and argon. Therefore, it is assumed that the inert gas acts as a piston in these runs, so that P_{total} is equal to P_{H_2O}.

At higher pressures, to 200 bars, dehydration occurs at lower temperatures in the dry runs when compared to runs with additional water. Also the results for the dry runs were not reproducible. For these runs, it is likely that the inert gas mixes with the released H_2O so that

$P_{total} > P_{H_2O}$. In these runs the presence of additional water in the samples resulted in higher dehydration temperatures, which were reproducible. It is likely that in these runs the excess H_2O again flushed out the argon gas, so that $P_{total} = P_{H_2O}$ for the sample.

At even higher pressures the molar volume of H_2O gas is sufficiently small, that sealed capsules could be used; at lower temperatures the evolved vapor generated pressures which exceeded the strength of the capsules. In Figure 4 the effect of the use of a sealed capsule is shown. Two DTA signals, which are representative for a run using an open capsule and a sealed one, were obtained simultaneously from the same experiment at 448 bars. Both curves are very similar, except that the sealed run (C1.448) shows a dehydration peak at a temperature which is 20°C higher. It is interesting to note that, as is expected at super critical pressures, the boiling peak of water becomes much broader and poorly defined; in these runs the peaks representing dehydration, especially the shoulder, are not always clearly defined. The DTA signal at 1345 bars is very similar to the 448 bars runs, indicating that the dehydration of a montmorillonite at higher pressures is not very sensitive to variations in pressure.

The $P–T$ relations of the dehydration of SWy-1 are shown in Figure 5 along with the boiling curve of water

Table 2. HP-DTA results for the interlayer dehydration reaction in Na montmorillonite, SWy-1. For each run the pressure and temperature of points (c) and (e), see Figure 2, are given.

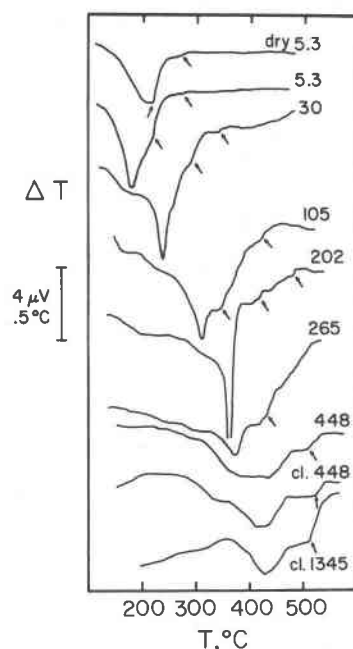| wt.%H₂O	P, bar	T, °C	P, bar	T, °C
dry	1	140	1	222
dry	1	142	1	214
dry	1	140	1	210
dry	1	140	1	214
5	1	148	1	214
dry	5.3	218	5.5	260
5	5.3	218	5.5	263
15	10	238	10.2	278
dry	12.5	236	-	-
5	22.5	273	23	305
dry	22.5	270	-	-
5	30.5	260	31.5	326
10	33.5	269	35	342
dry	38	290	-	-
dry	48	292	-	-
10	48	290	-	-
5	67	330	68	370
5	76	324	80	390
15	85	335	88	395
20	103	340	104	400
10	105	353	109	420
10	126	352	128	430
30	165	374	-	-
10	167.5	390	166.5	430
20	175	391	-	-
20	206	415	206	470
15	242	422	245	500
20	276	417	282	485
18	368	466	-	-
20*	422	460	430	500
30	448	430	447	510
20*	448	447	447	520
15*	1352	450	1385	530

* Sealed capsule runs

Fig. 4. DTA patterns in runs made at different pressures. The pressure, in bars, is indicated by the numerical value. The effect of excess water (water added) on the DTA pattern is shown for runs made at 5.3 bars and the effect of open and closed (cl.) capsules for pressures at 448. All runs, unless otherwise labelled, contain additional water (see Table 2). Arrows point to (c) or (c) and (e) as shown in Fig. 2. Peaks not indicated with arrows were not reproducible and do not represent reactions.

(L,V) for comparison. The open circles represent the first dehydration peak, the closed ones the second. The DTA results are remarkably consistent; the first dehydration curve (A) lies approximately 40°C above the boiling curve of water and the secondary dehydration curve (B) about 60 to 70°C higher. The dashed part of the curves (A) and (B) are less well defined. The data at higher pressures, however, suggest that dehydration becomes much less dependent on pressure.

The results, using dry runs at low pressures, wet runs at intermediate pressures, and wet runs in sealed capsules at high pressures, are remarkably consistent. While the individual data are somewhat limited in value as a consequence of the lack of precise knowledge of the water fugacity in these runs, the consistency and reproducibility of the data does suggest that the $P–T$ curves for the dehydration of SWy-1 as shown here probably represent closely pressure conditions of $P_{total} = P_{H_2O}$.

The presence of the two dehydration peaks is common in DTA signals of Na-montmorillonite (e.g., Grim, 1968, p. 288). The higher temperature peak is usually significantly smaller than the lower temperature one. The significance of the two DTA peaks may be that not all interlayer water is bonded equally. This is supported by the suggestion of Farmer (1971), Farmer and Russell (1971), Low (1979), and Carieti et al. (1981, 1983) that a

distinction may be made between those interlayer water/OH groups that are bonded by strong hydrogen interactions and those with weak interactions with the surface of the 2:1 layer of smectites with high water content. Thus, the primary dehydration peak may be the result of the expulsion of the weakly bonded water and, after the hydration shells of the ions have been reduced, a secondary dehydration peak results from the removal of the remaining and more strongly bonded water. It is evident that pressure does not appreciably alter the relationship of dehydration between the weakly bonded and strongly bonded interlayer water in Na-montmorillonite.

The DTA technique is a dynamic method which does not necessarily yield data representative of an equilibrium reaction. Kinetic problems may prevent the establishment of equilibrium at lower temperatures. However, in this study, the dehydration reaction probably does represent a close approach to equilibrium. This conclusion is based on the following: (1) the variation of the heating rate did not show a discernable effect on the hydration temperature—runs made at heating rates of 10°/min give results similar to runs at 20°/min, (2) no grain size effect was encountered, as is shown in Figure 3, (3) if a kinetic problem delays dehydration, it can be expected to be less pronounced at higher temperatures and pressures. How-
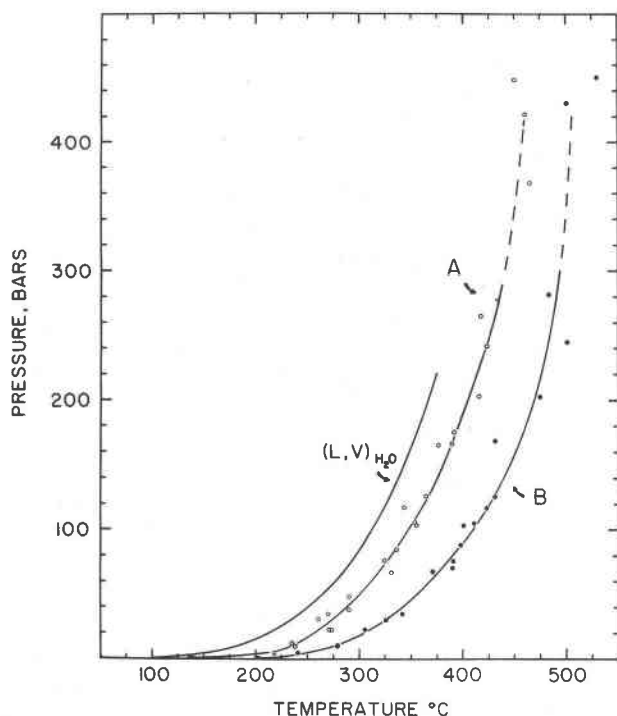
Fig. 5. The results as plotted in a *P–T* diagram. The curve labelled (L,V)$_{H_2O}$ is the boiling curve of water as determined by Keenan et al. (1978). Curve A represents the first dehydration peak (open circles) and curve B the shoulder (closed circles). Runs in excess of 500 bars are not shown (see Table 2).

ever, the results of all runs are remarkably consistent in that dehydration appears to be related to the (L,V) curve of H$_2$O. DTA data do not establish the nature of the reaction; it may represent a stable or a metastable equilibrium. Long term synthesis experiments in similar systems in which hydrated montmorillonite was formed (Eberl et al., 1978), do suggest that this reaction represents a stable equilibrium at *P–T* conditions of our study.

The dehydration of SWy-1 was found to take place at a considerably lower temperature at 1 atmosphere (primary peak: 140°C, shoulder 210°C) than the reported (van Olphen and Fripiat, 1979) value of 185°C, with a shoulder at 235°C. Large samples, such as those used by van Olphen and Fripiat (1979) may produce a slight internal overpressure during DTA and cause the dehydration peaks to occur at higher temperatures. As is shown in this study, an increase in pressure of 1 bar increases the dehydration temperature by 40 to 180°C for the primary peak. It is also possible that in the larger samples thermal gradients occur which would result in a broadening of the peak. This also causes a displacement of the peak to higher temperatures.

It is shown also that Na-montmorillonite is remarkably stable in the absence of other components at moderate pressures. For example, at 200 bars, it is stable to temperatures well over 400°C. This indicates that in

sedimentary basins under normal ambient pressure and temperature conditions a hydrated Na-montmorillonite may be stable. Of course, in the presence of additional components such as potassium, mixed-layer clay minerals or illite may be formed, which would result in the expulsion of the interlayer water.

The large increase in stability of the hydrated Na-montmorillonite with only a small increase in pressure suggests that this type of clay mineral may be highly useful in backfill of nuclear depositories. However, this study does not provide data on the effect of other chemical components, which may have an important influence on dehydration.

Acknowledgments

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