# Effects of Heating on the Swelling of Clay Minerals

## L. A. G. AYLMORE, J. P. QUIRK, and I. D. SILLS

Department of Soil Science and Plant Nutrition, University of Western Australia

The effects of dehydration by evacuation and heating to progressively higher temperatures up to 400 C on the subsequent hydration and swelling behavior of homoionic predominately illite clay minerals has been studied. Water vapor sorption isotherms for 200-mg tablets at 25 C were determined using a volumetric doser technique, and swelling of the clays at low water suctions was measured on ceramic suction plates.

The swelling of certain illitic clays is subject to a marked reduction (e.g., from 200 percent to 35 percent water content at 10 millibars suction) after preheating, indicating the formation of very strong binding forces between individual clay particles. Although water vapor sorption at low relative vapor pressures shows that part of the water loss on heating is irreversible, it seems unlikely that any deterioration of the crystal lattice has occurred at the temperatures used. The cation exchange capacities of the clays are unaltered, and the specific surface areas are essentially the same after heating.

The nature of the bonding mechanism is not yet clear, but there is evidence that small amounts of kaolinite impurities present may be involved. It seems likely that the formation of hydrogen bonds between silicate and aluminate surfaces can occur on complete removal of the adsorbed water molecules.

•IT HAS been known for some time that heating can markedly alter the physicochemical behavior of clay mineral systems. Such techniques have been used to some extent in road research (9, 10) and also in agriculture to increase the stability of surface soils. Heating to temperatures in excess of 600 C generally results in at least some irreversible destruction of the crystal lattice with consequent deterioration in sorptive properties. However, there is a substantial amount of data to indicate that the hydrophilic properties of certain clay minerals are modified quite appreciably by desorption long before there is any significant lattice deterioration.

The data of Mooney, Keenan, and Wood (14) and others for montmorillonite show that subsequent rehydration at low relative humidities can depend markedly on the severity of the predrying technique used to obtain an "oven-dry" weight. This is largely a result of the influence of the hydration energy of the exchangeable cations on the intercalation of water. Similarly, Martin (13) and Jurinak (11) found that the sorption of water at low relative vapor pressures by kaolinite clays was influenced by preheating to temperatures up to 300 C and attributed these effects to interparticle adhesion.

During detailed studies of water sorption and swelling by clay mineral systems it was observed that the swelling of certain clays was considerably reduced by the outgassing procedure used in the determination of specific surface area and pore size distribution by low-temperature nitrogen adsorption (3). The ability of montmorillonite clays to exhibit extensive crystalline swelling [d(001) > 40 Å] at low water suctions when sodium-saturated was found to be essentially unaltered by preheating even as high as 600 C. Similarly, the relatively small swelling exhibited by kaolinite clays even when sturated with water (2) was unaffected. In contrast, several samples of clays containing predominantly illite minerals showed large reductions in swelling after desorption. This effect has been examined in some detail in the present paper.

### MATERIALS AND METHODS

The clay samples used were obtained from the following natural deposits:

•Willalooka illite-B horizon from a solonized solonetz, Hundred of Laffer, South Australia.

•Urrbrae B clay-B horizon of Urrbrae loam, a red-brown earth, Adelaide, South Australia. Clay fraction 60 percent illite and 40 percent kaolinite.

•Fithian illite-from Ward's Natural Science Establishment Inc., Illite No. 35 of the American Petroleum Institute's Research Project No. 49 (1951).

•Rocky Gully kaolinite-from pallid zone of laterite, Rocky Gully, Western Australia.

In general, samples of the clays were sodium-saturated by repeated washing with molar sodium chloride, during which the pH of the suspension was adjusted to 3.0 using hydrochloric acid. The samples were washed and finally dialyzed against distilled water using Visking cellulose casing. Initially a simple decantation process was used to remove the coarse fractions. These samples are labeled R. F. to indicate the rough fractionation used. Subsequently the  $< 2\mu$  fractions were obtained by accurate sedimentation. Samples saturated with other cations were prepared from these materials using the appropriate molar chloride solution.

The air-dried clays were gently ground to a powder, equilibrated with 0.75 relative water vapor pressure, and compressed into 200-mg cores at 1200 atmospheres pressure by means of a hydraulic jack (1). This was done to facilitate subsequent experimental handling and to ensure that the clays were in an overconsolidated condition.

Heating of the clays was carried out by allowing a number of cores in weighing bottles to equilibrate for 3 days at a given temperature in a muffle furnace and cooling the ground glass stoppered bottles over phosphorus pentoxide powder before weighing.

Water content-energy data at low suctions were obtained using ceramic-perspex pressure plate systems. The cores were wet up in small stages using vacuum desiccators containing saturated salt solutions to prevent disruption of the cores by rapid differential swelling.

Surface areas were determined by application of the B. E. T. theory (7) to lowtemperature nitrogen adsorption isotherms determined volumetrically in the usual way. Water vapor sorption isotherms were determined volumetrically in equipment similar to that used by Jurinak (11) incorporating a modified Pearson gage (<u>16</u>).

Cation exchange capacities were obtained by first saturating the clays using an utral solution of molar strontium bromide and removing excess salt by washing with distilled water. The exchange capacities were then determined as the difference between the strontium and bromide contents of the dried clays determined using an X-ray fluores-cence spectrographic method.

## RESULTS AND DISCUSSION

The specific surface areas and cation-exchange capacities of the clay cores are given in Table 1. In Table 2 the decrease in weight of the Willalooka illite and Urrbrae

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SPECIFIC SURFACE AREAS AND CATION EXCHANGE CAPACITIES OF CLAY MATERIALS				
Clay	Specific Surface Area (m²/g)	Cation Exchange Capacity (me/100 g)		
Willalooka illite (R. F.)	150	39.1		
Willalooka illite (< $2\mu$ )	188	-		
Urrbrae B clay (R. F.)	91	27.6		
Fithian illite (< 2µ)	99	-		
Rocky Gully kaolinite (< 2µ)	39.3	4.0		

TABLE 2 WEIGHT LOSS BETWEEN SUCCESSIVE TEMPERATURES AND 400 C FOR ILLITIC CLAYS

Clay	Weight Loss (g/100 g clay at 400 C)				
	20 C	110 C	200 C	300 C	
Ca <sup>++</sup> Willalooka illite	16.39	4.92	2.47	1.22	
Mg <sup>++</sup> Willalooka illite	21.07	4.82	2.36	1.20	
Na <sup>+</sup> Willalooka illite	18.47	4.58	2.28	1.21	
K <sup>+</sup> Willalooka illite	17.36	3.89	1.87	1.10	
Ca <sup>++</sup> Urrbrae B clay	12.83	3.71	1.67	0.75	
Mg <sup>++</sup> Urrbrae B clay	13.07	3.92	1.80	0.85	
Na <sup>+</sup> Urrbrae B clay	13.47	3.27	1.58	0.80	
K <sup>+</sup> Urrbrae B clay	11.27	3.24	1.53	0.73	

B clay cores between successive temperatures and 400 C has been expressed as a percentage on the basis of the weight of clay after drying to 400 C. The possible sources of weight loss on heating are surface-adsorbed water, water of hydration of the exchangeable cations, hydroxonium ions in interlayer positions normally occupied by potassium ions in unweathered micas (6), and hydroxyl groups from the clay lattice. Some weight loss may also occur from the charring of any organic matter present but this is relatively small in these materials. In general, the water contents from 110 C to higher tem-

peratures show some relationship to the hydration energies of the exchangeable cations and the specific surface areas of the clays but the variation between different ions is not as large as might be expected if the weight losses were entirely associated with dehydration of the exchangeable cation [see Table 1 in Keenan, Mooney, and Wood (12)].



Figure 1. Water contents (cc/100 g at 110 C) for Willalooka illite cores saturated with sodium (△), potassium (□), calcium (X), and magnesium (O) cations on rewetting at 100 mB suction vs initial water content (cc/100 g at 400 C) after preheating to various temperatures.







Figure 3. Water vapor adsorption isotherms at 25 C for sodium Willalooka illite degassed at various temperatures.



Figure 4. Water vapor desorption isotherms at 25 C for sodium Willalooka illite degassed at various temperatures.

The water contents on wetting the cores against 100 millibars (mB) suction after heating to successively higher temperatures up to 400 C, calculated on the subsequent oven-dry (110 C) basis, are shown in Figures 1 and 2 for Willalooka illite and Urrbrae B clay cores respectively when saturated with sodium, potassium, calcium, and magnesium cations. At this low suction the differences in swelling due to the exchangeable cation and increasing heat treatments become most apparent. For both clays the cores saturated with divalent magnesium and calcium cations, although unaffected by preheating to 200 C, show appreciable reductions in swelling after preheating to higher temperatures. The cores saturated with monovalent cations, and in particular those sodium-saturated, show a marked continuous reduction in swelling with increasing temperature. The large swelling of the unheated sodium clays can be attributed to the unrestrictricted development of diffuse ionic double layers. However, previous work (1) has indicated that there is an electrostatic potential barrier restricting the swelling of these clays when saturated with polyvalent ions. It is apparent that the restrictions due to the heating process either enhance or exceed these restrictions.

The cause of these restrictions is not immediately apparent. Grim  $(\underline{8})$ , in reviewing the dehydration properties of illites used by numerous workers, indicates that there is no loss of structure even with the loss of hydroxyl groups until temperatures exceed 850 C. In addition, Brooks (5) found that the surface area of an illite clay was essentially constant after the loss of surface-adsorbed water and cation hydration water, until temperatures in excess of 600 C were reached. In Figures 3 and 4 are shown water sorption and desorption isotherms obtained on sodium-saturated Willalooka illite cores outgassed at various temperatures until the pressure in the volumetric system remained below  $10^{-3}$  mm mercury after 30 minutes isolation from the pumps. Since

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these isotherms were obtained on the  $< 2\mu$  fraction of the clay and the clays were heated under vacuum there is of course no direct correspondence in weight loss at a particular temperature between these and the previous samples. Evacuation should result in greater dehydration at any given temperature.

The adsorption isotherms (Fig. 3) are of similar shape with the main vertical displacement occurring between outgassing at room temperature (20 C) and at 100 C. The additional water uptake obtained on the 100 C sample above the uptake after outgassing at 20 C is essentially equivalent to the additional loss of 2. 7 cc at STP that occurs on heating from 20 C to 100 C. The weight loss to this stage is thus probably due largely to a reversible dehydration of the surface and cations. On further outgassing at 200 C the subsequent water uptake is slightly less and this may be attributed to a small drop in specific surface area resulting from a more intimate contact of the clay crystals on removal of the last water molecules most strongly held between regions of closest approach. Both Martin (13) and Jurinak (11) have reported such a loss of surface area. Also a decrease in B. E. T. nitrogen area of some 5 to 10 percent on desorption between 100 C and 200 C for Willalooka illite has been repeatedly observed by the authors in studies on the surface area of clays with presorbed water (4).

The weight losses on outgassing at temperatures above  $\overline{100}$  C are far greater than those regained on subsequent water sorption. These values are given in the following table for convenience in comparing with Figures 3 and 4:

Temperature	100 C	200 C	300 C	400 C
Water loss (equivalent cc at STP/g)	2.7	16.3	25.1	47.3

The increases in subsequent water uptake observed after outgassing at 300 C and 400 C required considerably longer times for equilibration; this and the increased hysteresis effect on desorption (Fig. 4) suggest that these weight losses could be due to the loss of hydroxonium or hydroxyl ions from within the clay lattice. However, it is apparent that at least part of this loss is regained under these conditions.

Thus it seems unlikely that the reduction in swelling on heating can be attributed to deterioration of crystal structure or marked changes in the sorptive properties of the clay surfaces.

Since there is a decrease in surface area evident on vigorous outgassing it is reasonable to assume that the subsequent restrictions to swelling arise from the formation of bonds at the regions of contact of the individual clay crystals. A conceivable origin for strong electrostatic attractive forces at these points would be through the dehydrated cations sandwiched between the negatively charged clay crystals. However, this would require that the cation exchange capacity of the heated material be significantly reduced, and accurate measurements indicate that there is no such loss of exchangeable cations.

Martin (13) observed a decrease in the specific surface area and water uptake of kaolinite clays stored under a vacuum of  $10^{-5}$  mm pressure for long periods and attributed this effect to twinning of the crystals in close juxtaposition. The mechanism of twin formation was considered to be hydrogen bonding between the oxygen surface of one crystal and the hydroxyl surface of its neighbor. Similarly, Jurinak (11) observed a degree of "coalescence" of kaolinite crystals after desorption that was related to the size of the exchangeable cation on the clay surface. The Urrbrae B clay used in the present work contains some 40 percent and the Willalooka illite about 2 percent kaolinite. Hence, it seems quite possible that the formation of interparticle hydrogen bonds on the removal of adsorbed water molecules may prevent the re-expansion of the domains of oriented clay particles despite the formation of diffuse ionic distributions on the surfaces. Such forces have been suggested by Aylmore and Quirk (2) as being responsible for the small swelling exhibited by kaolin clays.

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WATER	CONTENTS	ON V	WETTING	TO 10	mB SUCTION H	OR
	SODIUM FI	ТНІА	AN ILLITE	΄ (< 2μ)	SAMPLES	

Treatment	Water Content (g/100 g)	
Unheated	92.5	
Preheated 300 C	133.9	
Unheated plus 1 percent Rocky Gully kaolinite	92.8	
1 percent Rocky Gully kaolinite added and heated to 300 C	90.8	

This suggestion is strongly supported by the data in Table 3 for sodium-saturated Fithian illite that X-ray examination shows to be free of kaolinite impurity. Far from restricting the swelling of this clay, heating to 400 C results in an appreciable increase in water uptake at 10 mB suction, probably through the removal of organic binding materials. The addition of 1 percent Rocky Gully kaolinite as an impurity before heating seems to cancel this increase due to the removal of organic matter. However, it is difficult to control the intimacy of mixing of the two constituents and this would obviously influence the extent of bonding that occurs.

Dimethyl sulfoxide (DMSO) has been shown to be an effective hydrogen bond breaker (15) and hence it should be possible to at least partially restore the swelling of these clays by treatment with DMSO if hydrogen bonding is in fact responsible. This possibility was investigated by shaking samples of preheated sodium Willalooka illite with a 90 percent solution of DMSO in water for periods of two weeks and two months at 60 C. The samples were washed with distilled water, air-dried and compressed into cores as before. The water contents of these DMSO-treated cores at 10 mB suction are compared in Table 4 with control cores of the unheated clay and heated samples shaken for two weeks with distilled water.

It is apparent that the DMSO treatment is not only capable of restoring the swelling capacity of the Willalooka clay but actually increases the water uptake of the heated material beyond that of the unheated clay if carred out long enough. This may indicate the presence of some restrictions in the original clay but obviously a more detailed investigation of the DMSO treatment is warranted to establish the nature of this interaction.

From the previous results it is reasonable to conclude that the presence of the kaolinite clay is responsible for the restriction to swelling observed on heating the Willalooka and Urrbrae B clay samples. It seems very likely that the formation of hydrogen bonds between oxygen and hydroxyl surfaces on the complete removal of adsorbed water is in fact the mechanism of crosslinking that occurs. Further work is at present being undertaken in an attempt to confirm these conclusions and to determine the extent of hydrogen bonding that occurs in the different systems.

10 mB SUCTION				
Treatment	Water Content (g/100 g)			
Untreated	246			
Heated 300 C, shaken with water for 2 weeks	80			
Heated 300 C, shaken with 90 percent DMSO for 2 weeks	154			
Heated 300 C, shaken with 90 percent DMSO for 2 months	355			

TABLE	4
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EFFECT OF DMSO TREATMENT ON WATER CONTENT OF SODIUM WILLALOOKA ILLITE (< $2\mu$ ) ON WETTING TO

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