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THE STRUCTURE OF THE INTERLAYER WATER IN MONTMORILLONITE

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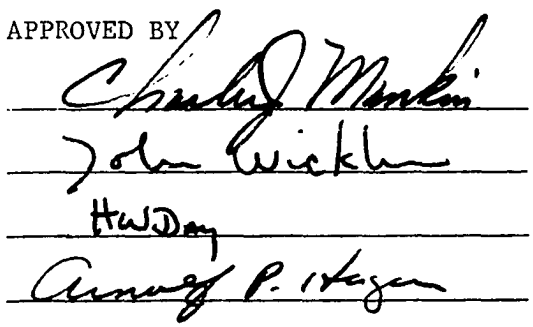
THE STRUCTURE OF THE INTERLAYER WATER

IN MONTMORILLONITE

APPROVED BY



DISSERTATION COMMITTEE

THE STRUCTURE OF THE INTERLAYER WATER

IN MONTMORILLONITE

ABSTRACT

A purified sample of essentially monomineralic montmorillonite (A.P.I. #23) was size fractioned to obtain the 1/8 - 1/16 micron size. This was split into six portions each of which was exchanged for one of the six cations, Li, Na, K, Mg, Ca, and Ba.

The six samples were chemically analyzed and investigated by x-ray diffraction and gravimetric methods at controlled temperature and partial pressure of water.

A change in the b-axis dimension is found and correlated with c-axis dimension and with water content.

A structure of initially adsorbed water is suggested in which the oxygen of the adsorbed water is bonded to both the interlayer cation and the silicon of the clay structure. It is suggested that this structure explains the high hydrogen ion activity in the interlayer space and the hydrogenation of some materials adsorbed by the clay. The decrease in entropy of adsorbed water is explained by strong bonds between the interlayer water and both the interlayer cation and the silicon cation of the tetrahedral layer.

The relative maximum expandability of montmorillonite as a function of the type of interlayer cation is explained by differences in electrostatic bond strengths as a function of the number of coordinated water oxygens around the interlayer cation.

ACKNOWLEDGMENTS

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I also wish to thank David M. Patrick and Richard P. Lockwood for the many helpful discussions that we have had.

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INTRODUCTION

Purpose of Investigation

The crystal structure and chemical composition of montmorillonite have been investigated by many workers in many fields including clay mineralogy, chemistry, soils engineering, and soil chemistry. The exchangable interlayer cations and the adsorbed interlayer water which results in expansion of the clay platelets in the c-axis direction during uptake of water are among the topics that have been most extensively studied.

The interlayer water appears to be structured, that is, less randomly oriented than liquid water (Woessner and Snowden, 1969; Grim, 1953). The structure also appears to be affected by the interlayer cation present (Grim, 1953; Kittrick, 1969 a; Kijne, 1969).

This study was undertaken to determine the structure of the interlayer water in hydrated montmorillonite and to determine the factors that affect that structure. There are several properties observed in hydrated montmorillonite that should be explained by the structure of the adsorbed interlayer water. These include step-wise hydration, variability in hydration characteristics as a function of interlayer cation

type, high hydrogen ion activity in the interlayer space and hydrogenation of some adsorbed interlayer materials, and the entropy decrease of the adsorbed water. As is discussed in a later section the previously suggested structures for the interlayer water explain one or more but not a satisfactory number of these observations. The present study has attempted, by determination of some properties and by incorporation of the observations of other workers, to derive a structure which is consistent with most, if not all, of these observations.

Scope of Investigation

In the present study a sample of a relatively pure montmorillonite (A.P.I. # 23) was used as a starting material. This was divided into six aliquots, each of which was exchanged for one of six different cations. These six samples were then investigated by chemical analysis, x-ray diffraction, and gravimetric methods under controlled conditions of temperature and partial pressure of water.

The clays were examined to see what changes were brought about by a change in water content. Water content was changed by varying the partial pressure of water. Change in d(001) as a function of pH_2O was measured. This serves to define the reaction of the c-axis dimension to change in pH_2O and to provide a reference for measurement of other parameters as a function of pH_2O. The b-axis change as represented by change in d(060) was determined as a function of d(001). The reason for determination of d(060) vs. d(001) rather than as a function of pH_2O will be discussed in a later section. The b-axis change is related to pH_2O through change in d(001). The third parameter measured was change in

weight as a function of pH_2O. From this the number of water molecules per unit cell involved in change in either the b- or a-axis can be determined.

PREVIOUS WORK

Varieties and Composition

There are several minerals in the montmorillonite or smectite group which differ by more than type of cation in the interlayer space. The dioctahedral members include montmorillonite, beidellite, and nontronite. The trioctahedral members are saponite, and hectorite. The formulas for these as taken from Grim (1953) are given in Table 1.

TABLE 1

COMPOSITIONS OF MONTMORILLONITE VARIETIES

	Dioctahedral Types
Montmorillonite	$Si_8(Al_{3.34}Mg_{.66})O_{20}(OH)_4$ with $Na_{.66}$
Beidellite	$(Si_{6.34}Al_{1.66})Al_{4.34}O_{20}(OH)_4$ with $Na_{.66}$
Nontronite	$(Si_{7.34}Al_{.66})Fe_4^{3+}O_{20}(OH)_4$ with $Na_{.66}$
	Trioctahedral Types
Hectorite	$Si_8(Mg_{5.34}Li_{.66})O_{20}(OH)_4$ with $Na_{.66}$
Saponite	$(Si_{6.66}Al_{1.34})(Mg_{5.34}Al_{.66})O_{20}(OH)_4$ with $Na_{.66}$

The difference between the types is in the location and type of element substitution in the structure. There may be Al for Si substitution in

the tetrahedral layer or Mg for Al or Fe for Al substitution in the octahedral layer in the dioctahedral varieties. In the trioctahedral types there may be Al for Si substitution in the tetrahedral layer and Al or Li for Mg substitution in the octahedral layer. The resulting charge deficiencies from these substitutions are balanced by the cations present in the interlayer positions. The cations are held more or less strongly depending on the amount and proximity of the charge deficiencies. The proximity of the charge deficiency not only affects the interlayer cation but has also been shown to affect the expandability of clays on hydration (Kerns and Mankin, 1968). The charge deficiency in expandable layer silicates is less than in non-expandable layer silicates. Muscovite for instance has one-fourth of the tetrahedral silicons replaced by aluminum so that there is a large charge deficiency which is close to the interlayer space. In montmorillonite, as opposed to muscovite, the charge deficiency is essentially all present in the octahedral layer where it is removed from the immediate vicinity of the interlayer cation. The bond between the silicate layer and the interlayer cation, therefore, is weaker than in muscovite. Expansion of montmorillonite is due to water or other polar molecules entering into the interlayer space. When this occurs the clay platelets are separated with a resultant increase in the c-axis dimension.

Differential Thermal Analysis

There is extensive information on the differential thermal analysis of montmorillonite including both low and high temperature reactions. Information with regard to the interlayer water is obtained

mainly from the low temperature (0-300°C) reactions. The strongest reaction which is related to the interlayer water is a broad endotherm occurring at about 100°C. The loss of interlayer water continues above 100°C and the endotherm merges with the beginning of the loss of OH from the octahedral layer at around 300°C (Grim, 1953). The 100°C endotherm exhibits a hump on the high temperature side for some samples. This may be indicative of divalent vs. monovalent interlayer cations. It is at least indicative of water which is bonded in such a way as to produce two distinct temperatures of dehydration. This indicates that not all the water in the interlayer space is bound in the same way but rather that there is more than one type of clay-to-water linkage.

X-ray Data

The d(001) spacing is used for identification of montmorillonite because its variability is a function of the kind and amount of adsorbed interlayer material. The minimum spacing of hydrated montmorillonite is dependent on the degree of hydration or dehydration and the type of interlayer cation present. The minimum dry d(001) spacing is about 9.6 Å but is affected by the size of the interlayer cation. The c-axis dimension of sodium montmorillonite in equilibrium with atmospheric moisture varies from 10 Å to 21 Å. It can, however, take water into the interlayer space causing expansion to relatively great distances, on the order of 300-400 Å (Low, Ravina, and White, 1970). If calcium is the interlayer cation the expansion is limited to about 15.5 Å. A wide variety of organic compounds can be adsorbed and will result in varying degrees of expansion depending on molecular size and orientation.

The b-axis (060) dimension has also been observed to change as a function of the amount of interlayer water (Low, Ravina, and White, 1970; Ravina and Low, 1972). It has been shown to be affected by composition and resulting fit between the octahedral and tetrahedral layer (McEwan, 1951). The recent work by Ravina, however, indicates that d(060) decreases with decreasing water content (Ravina and Low, 1972).

Observations on the Montmorillonite-Water System

There are many observations reported in the literature that are pertinent to this study. One of the most important is the non-liquid nature of adsorbed water. Grim (1953) discusses several points including the strength and plastic properties of clay which require a change in state, from liquid to non-liquid, of the adsorbed water. Montmorillonite exhibits a high heat of wetting (Grim, 1953) which also suggests a change in the initially adsorbed water. The freezing point of the adsorbed water is depressed indicating that the interlayer water is in some way different from ordinary water. These observations apply primarily to the initially adsorbed water. The water adsorbed at higher states of hydration acts more like liquid water. This, like the differential thermal analysis indicates that there is not one type of bonding configuration for interlayer water but rather two or more. Nuclear magnetic resonance studies (Woessner and Snowden, 1969) indicate that, unlike liquid water, the adsorbed water has a preferred orientation with respect to the clay layer.

It has also been observed that the interlayer cation affects the adsorbed water. There is an effect on the maximum expandability that is

determined by the cation. As was mentioned previously, Na-montmorillonite will expand to c-axis spacings of 300-400 Å whereas Ca-montmorillonite is limited to about 15.5 Å. Large cations like K tend to inhibit expansion (Grim, 1953).

Stepwise hydration, where the c-axis dimension increases in increments on hydration has been observed (Grim, 1953) and interpreted as successive additions of monomolecular layers of water.

The adsorbed water has been investigated by infrared absorption methods by numerous workers. Serratosa (1968) indicates, from consideration of the dissymmetry about the maximum of the 1637 cm^{-1} water peak, the possibility that the water is bound to the silicate layers in more than one way. It is also shown that on evacuation and loss of water the amount of hydrogen bonding decreases and that the water is coordinated to the interlayer cations. Farmer (1968) has also indicated that the interlayer water is bonded to the clay in more than one way. Bonding possibilities include water bonded to the interlayer cations, water hydrogen bonded to the silicate structure, and water hydrogen bonded to other water. Durand, et al. (1972) have shown that there are reactions between the clay and organic materials which are affected by the water content of the clay. NH_3 adsorbed on the clay is converted to NH_4 under certain conditions. When the vapor pressure of water is too high the reaction does not occur, and when water is absent it does not occur. Acid catalysis is proposed as the mechanism for this reaction.

The high hydrogen ion activity in the interlayer space has also been noted. There is evidence from both infrared absorption work and nuclear magnetic resonance investigations. The nuclear magnetic

resonance work will be discussed in a later section. Fripiat, et al. (1969) indicate that Na and Ca saturated montmorillonites show a high degree of dissociation of water molecules in the interlayer space. Durand, et al. (1972) show that a high degree of dissociation is required at low water contents for the protonation of NH_3.

The hydrogen bonds between hydrogen and oxygen in the interlayer have been noted to be weaker than in liquid water. Low and White (1972) in their review of the similarities between clay adsorbed water and "polywater," note that the hydrogen bonds in clay adsorbed water are weaker than those in liquid water. Fripiat, et al. (1969) indicate the same phenomenon in their study involving the high dissociation of water and the high hydrogen ion activity. Associated with the weak hydrogen bonding and high hydrogen ion activity is the hydrogenation of some materials that are adsorbed on the interlayer. Jang and Condrate (1972) in a study of lysine adsorbed on montmorillonite noted that the amino groups were protonated. Fripiat, et al. (1969) also noted that several amines were protonated when adsorbed on montmorillonite. Farmer (1968), in his review of infrared spectroscopy in clay mineralogy, discusses hydrogenation taking place in the interlayer space. He also notes that the interlayer water undergoes ionization to a greater extent than bulk water.

There has been extensive work done in investigation of thermal dehydration and heat of wetting of montmorillonite. Kittrick (1969b) indicates that for Na-vermiculite the entropy decrease for water going from the liquid state to adsorbed water was 13.2 k cal/mole of Na. He further notes that the entropy of hydration is 6.2 k cal/mole of Na. If 6.2 k cal/mole of Na is an entropy decrease due to hydration of the

cation then there is an additional entropy decrease of 7.0 k cal/mole of Na to be explained. Kittrick attributes this to hydration of negative charge sites. Kijne (1969) notes that several workers have shown that the entropy of water adsorbed on montmorillonite is lower than that of liquid water. He shows that below a surface coverage of 0.1 for Ca-montmorillonite and 0.25 for Na-montmorillonite the adsorbed water has zero degrees of freedom. Kijne found that the entropy of adsorbed water on Ca-, Na-, and Li-saturated montmorillonites was below that of liquid water and that Cs and Rb apparently increase the entropy. The largest entropy decrease is found at low partial pressures of water with entropy values increasing to near, but below, that of liquid water with increasing partial pressure of water. Kijne also found that heat of wetting values were high at low water contents and that they decreased with increasing water content. He also showed that there is a marked discontinuity in heat of wetting vs. partial pressure of water which occurs at low partial pressure of water.

There are indications other than the previously-mentioned entropy decrease and bonding indications from infrared work that some of the adsorbed water is strongly bonded to the interlayer region. Low and White (1970) note that adsorbed water has been observed to remain on the clay at temperatures in excess of 300°C. Serratosa (1968) notes that water has been observed to remain on the clay under vacuum at 100°C.

Information on the orientation of water molecules is important to a proposed structure of the water. Low and White (1970) note that Woessner and Snowden have shown that the water molecules are oriented parallel to the clay surface. Woessner and Snowden (1969) have also

shown, with nuclear magnetic resonance, that the proton dissociation in the interlayer space is much greater than in liquid water. They suggest that the highly-ionized interlayer water has a proton exchange rate of 10^6 times per second.

An additional topic that is related to water orientation is cation position in the interlayer space. Lailach, et al. (1968) have shown that the monovalent cations tend to be closely associated with the silicate oxygen surface on hydration and that the divalent cations occupy positions midway between the layers on hydration.

Previously-Suggested Water Structures

There have been several structures suggested by previous workers for the interlayer water in montmorillonite. Hendricks and Jefferson (1938) suggest a hexagonal network of water molecules which are held together in the plane of the hexagonal ring by hydrogen bonding and which are bonded to the silicate oxygens by hydrogen bonding of one-half of the molecules in the net. In this each water molecule is hydrogen bonded to another water molecule in the plane parallel to the clay sheet. In one-half of the water molecules one of the hydrogens is pointing downward toward the clay surface oxygens. Considering the roughly-tetrahedral configuration of the charge on a water molecule this is a reasonable arrangement. However, it neglects the presence of the interlayer cation and such possible effects as cation size and hydration energy. Because cations are present in the interlayer in montmorillonite and have been shown to influence the properties of the adsorbed water, a suggested water structure must take them into account. An additional

difficulty with this structure is the bridge between the successive layers of clay. The water forms a net on the silicate surface by hydrogen bonding to the surface oxygens. This produces a new oxygen surface of water oxygens. Additional water, on further hydration, is hydrogen bonded to the other silicate surface bordering the interlayer space or it hydrogen bonds to the initially adsorbed layer. In either case there are two oxygen surfaces facing each other with no hydrogen bonds available for linkage between the two. An additional difficulty with this structure is the hydrogen bonding between water and silicate. As was mentioned previously water has been observed to be retained on the clay at high temperatures. For this to occur the bond between clay and water must be stronger than normal hydrogen bonding.

Macey (1942) has suggested that the interlayer water has the structure of ice I. This is similar in arrangement to that suggested by Hendricks and Jefferson (1938) except that the packing of water oxygens is looser. From a crystallographic standpoint the fit between ice I and the silicate oxygen surface is close. This structure has again been suggested, with modifications and extensions, by Ravina and Low (1972). The study by Ravina and Low will be discussed further in a later section. The suggested ice net of water molecules is hydrogen bonded to the silicate oxygen surface as were the water molecules in the structure proposed by Hendricks and Jefferson. The same objection with regard to the strength of the hydrogen bonding holds. Because the ice structure also propogates away from the clay surface by additional layers of water molecules hydrogen bonded to the water oxygens there is again no means of connecting successive clay sheets. Here also, as in the previously

discussed structure, the interlayer cations are not taken into account.

Barshad (1949) has proposed a structure in which the oxygens of the water form tetrahedrons with the oxygen triads of the basal planes of the silica tetrahedra. This is essentially placing water oxygens on top of the silica basal triads to produce a silicon-oxygen trigonal bipyramid. The structure suggested in this study is a modification and an extension of this structure. The objections found in the literature to this structure are few. Grim (1953) notes that Barshad's observations were dependent on the sample being pure and monomineralic. Objections from this study are that Barshad offers no reason for the configuration of water molecules from a bonding standpoint, and that the position of the interlayer cations with respect to the water net is not given. If hydrogen bonding is responsible for the bond of water to clay then the previously stated objections hold. Barshad notes that the d(001) spacing is affected by the interlayer cation but gives no suggestion as to how the cations fit into the water arrangement or interact with it.

Mering (1946) has suggested that the water is present as spheres hydrated on the interlayer cations. In this structure higher states of hydration provide successive layers of water around the cation. The water molecules are presumably hydrogen bonded to the silicate oxygens and therefore subject to the previously mentioned objections. Hydration spheres cannot be complete spheres in that each additional layer of water on the cation would increase the c-axis dimension by roughly 5.6 Å which is more than is observed. Indications from this study to

be discussed later are that the initially adsorbed water is not water of hydration.

Ravina and Low (1972) have proposed that the interlayer water has the structure of ice I. This is similar to the previously-mentioned structure suggested by Macey but is more similar to the structure suggested by Hendricks and Jefferson. In the structure suggested by Ravina and Low and in that suggested by Hendricks and Jefferson, there is epitaxy between the structured water and the silicate surface. In this structure the water is in hexagonal rings which are similar in size to the silicate rings and are hydrogen bonded to those rings. They have noted that there is a change in the b-axis dimension as a function of water content and that the b-axis dimension increases as water content increases until a maximum b-axis dimension of about 9.0 Å is reached. The interlayer cations are noted by Ravina and Low to affect the interlayer water indirectly by affecting the clay structure and thereby the epitaxial arrangement of water, and directly by producing local defects in the water. No position or structural relationship, however, is given for the interlayer cations. The water is bound to the clay surface oxygens by hydrogen bonding and is therefore subject to the previously-mentioned difficulties of water retention at high temperatures. In addition this structure requires that some of the hydrogens of the water molecules point toward the silicate layer and that some hydrogen-oxygen bonds are parallel to the layer for hydrogen bonding to additional water. It has been indicated by nuclear magnetic resonance work that the water molecules are oriented parallel to the clay platelets (Low and White, 1970; Woessner and Snowden, 1969). In the structure suggested by

Low and White, only one-half of the hydrogen-oxygen bonds are parallel to the clay layer.

Mamy (1968) suggests a structure which is similar to that of Barshad in which the oxygens of some of the interlayer water molecules are located over the hollow between the three basal oxygens of the silica tetrahedra. The water is in hexagonal rings composed of five water molecules and a fluorine ion. The fluorine is present to account for observed dielectric properties. Three (every other one) of the water molecules are above the basal oxygens of the silica tetrahedra. The other two water molecules and the fluorine ion are over the holes in the silicate rings. The hydrogen bonding in this structure ties successive clay platelets together, however, there is no position given for the interlayer cations. The cations are considered for their contribution to the dielectric properties but not for structural relationships to the ordered water.

Two related structures, which are not, strictly speaking, interlayer water, have been suggested. Edelman and Favejee (in Grim, 1953) suggest that one-half of the silicon-oxygen tetrahedra have their apical oxygens pointing toward the interlayer space rather than toward the octahedral layer. This structure is proposed in relation to the observed cation exchange capacity. The apical oxygens pointing toward the interlayer region would have hydrogen ions attached which are available for exchange. There are several reasons why this structure is not assumed to be correct (Grim, 1953), but one point which appears to support it is the hydrogenation of some adsorbed materials which takes place in the interlayer space. A different mechanism for this will be discussed later.

McConnell (1950) suggested that some of the silicon-oxygen tetrahedra are replaced by OH_4 tetrahedrons. This structure is proposed in relation to the observed availability of OH groups in the interlayer space. A different mechanism for the availability of OH groups is included in a later discussion.

Lahav and Bresler (1973) suggest that the observed change in b-axis dimension at low water contents is due to rotation of the Si-O tetrahedra because of attractive forces between the silicate oxygens and unhydrated interlayer cations. The calculations presented assume tetrahedral rotation and show that such a rotation would result in attractive forces which would favor further rotation until repulsive forces between ions over balance the attractive forces as the cations approach the silicate oxygens. The tetrahedral rotation would result in the observed decreases in the b-axis dimension. The tetrahedral rotation which is discussed has not been observed, it is given as a possibility for explaining observed changes in the b dimension. Observations in this study, to be given in a later section, indicate that the observed decrease in b is a temporary phenomenon and that on complete dehydration the b dimension increases. This increase on complete dehydration cannot be explained by cation-silicate oxygen attractive forces and it is felt that although such attractive and repulsive forces play some role in cation-clay interactions they are not primarily responsible for the observed reaction of the b dimension to dehydration.

LABORATORY WORK

Selection and Preparation of Samples

The sample selected for this study is A.P.I. # 23 (A.P.I. Proj. 49, 1950), a relatively pure montmorillonite from Chambers, Arizona. One initial sample rather than a range of samples was chosen in order to hold the number of variables to a minimum. Because the initial sample underwent considerable refinement in preparation no data on the raw sample will be presented. Reference can be made to A.P.I. Proj. 49 (1950).

The initial sample was ground to pass an 80 mesh sieve and soaked in water to aid in dispersion. Successive size fractions were eliminated until the fraction between 1/8 and 1/16 microns was obtained. The centrifugation process used is that given by Kerns (1967).

The sample was then treated for iron removal according to the method of Mehra and Jackson (1960). Although this method probably accomplishes complete cation exchange to the sodium form (the treatment employs sodium dithionite, sodium bicarbonate, and sodium citrate), the sample was treated with excess NaCl to assure exchange to the sodium form. The sample was then washed and centrifuged repeatedly with distilled water to remove excess sodium. The removal of excess sodium is not critical because of the following treatment. The sample of clay-water suspension was then split into six aliquots. These were treated

to convert them to the Li, K, Ca, Mg, and Ba forms with one left as the Na clay. The exchange was accomplished by the method of Polyakov (1968). The samples are mixed with twenty times their weight of 1N chloride salt solution and centrifuged to remove the exchanged cations. This procedure is repeated seven times. Five washings in distilled water are followed by centrifugation to remove excess exchanged cations and chlorine.

Chemical Analysis

Samples of the six cation-exchanged forms were placed in platinum crucibles and heated to 300°C to remove the interlayer water without removing the octahedral OH. They were then weighed, heated to 1000°C for 12 hours, cooled and reweighed. The OH content of the clay was determined from this weighing and the dry clay samples were used to make brickettes for x-ray fluorescence analysis on a water free basis. The elements determined by x-ray fluorescence and the experimental error given as weight percent as determined by reproducibility are Mg, 0.15%; Ca, 0.005%; Fe, 0.06%; Si, 0.24%; Al, 0.08%; Mn, 0.0001%; Ti, 0.001%; Cl, 0.0003%; Ba, 0.001%; and K, 0.06%. Na, 0.01% and Li, 0.002% were determined by flame emission spectroscopy. The analyses are given in Table II. The analyses corrected to total 100 percent for calculation of atom content per unit cell are presented in Table III. Table IV gives the atom contents per unit cell as determined by the method of Marshall (1949). Tables II, III and IV are given in the section on Results and Analysis of Data.

Laboratory Apparatus

An x-ray diffraction sample chamber which would allow diffractograms to be obtained at controlled pH_2O and temperature was constructed. The sample holder block of a Siemens x-ray diffraction unit was modified by milling off the two back corners in order to allow an aluminum cylinder to be lowered around the sample support. Four holes were drilled through the base of the sample holder for electrical connections. The aluminum cylinder contained a large "O" ring in its base to seat against the sample holder base, and an "O" ring at the top to seat against a cover plate. Two windows were cut in the side of the cylinder for x-ray entrance and exit ports. Nylon filament across the ports was used to support mylar window material. The mylar was held against "O" rings around the windows by aluminum cover plates. The top was fitted with a pipe for connection to the pumping system. The internal surface was equipped with a heating coil for control of the cell temperature. Holes were drilled through the sides of the cylinder for these electrical connections. The Siemens sample holder block was further modified by drilling an access hole through the back to allow a thermocouple to be placed in contact with the sample slide. Two spring contacts were mounted on one side of the sample holder block where they would complete the electrical connections with the inserted sample slide. The sample slide was the same size as the glass slide which is normally employed. The slide was composed of ceramic material and contained a nichrome heating filament. The completed sample chamber allowed control of the pH_2O, the sample plate or slide temperature, and the temperature

of the chamber environment. The chamber was connected to a vacuum line by polyethylene tubing. Diagrams of the sample chamber are given in Figs. 1-5.

The vacuum line contained a source of H_2O vapor, an outlet to the atmosphere, connections to a mercury and an oil manometer, and to a weighing cell. The weighing cell was a glass tube with a quartz spring and weighing pan suspended from the center. The cell was equipped with heating coils and a thermocouple for control and monitoring of the temperature. The pumping system consisted of an oil diffusion pump and a mechanical pump on one side of the oil manometer and a mechanical pump on the other side of the oil manometer.

d(001) vs. pH_2O

Each of the six cation forms of the sample were examined to determine the change in the d(001) as a function of pH_2O. The samples were sedimented onto the ceramic heater slide. The chamber and sample were evacuated to remove the air and H_2O vapor was then admitted, reaching pressures up to saturated conditions for room temperature. The chamber and sample were flushed with H_2O vapor in this way three times so that the pH_2O was the pressure of the system. The chamber was then slowly evacuated while the sample was scanned repeatedly to determine change in the d(001) peak position as a function of pH_2O.

The dehydration by vacuum was carried out over a period of eight to ten hours, generally until no further change in d(001) was observed during sixty minutes of pumping. The procedure for measuring change in d(001) and pH_2O was to scan d(001) at the initial hydrated

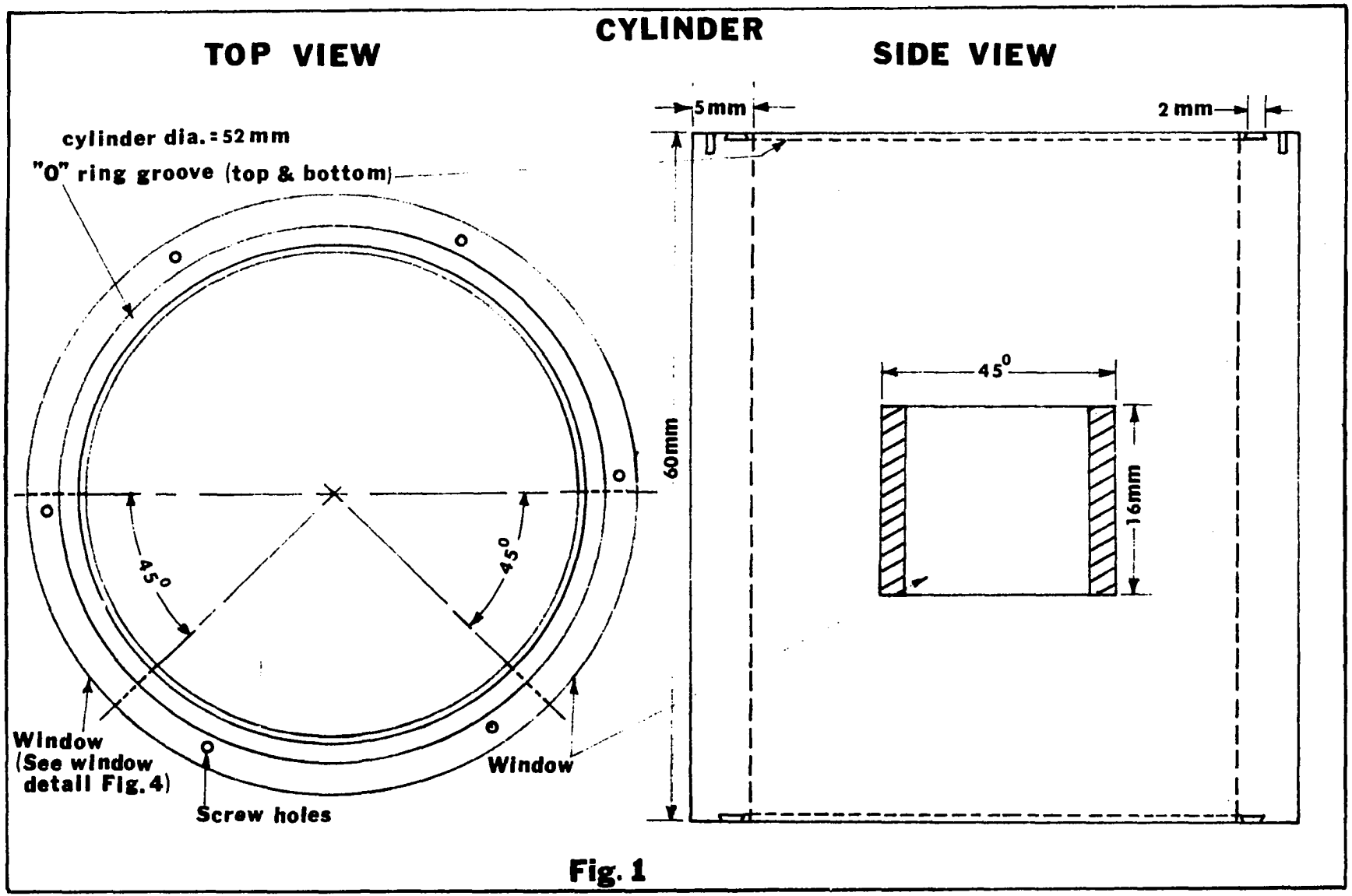

CYLINDER
TOP VIEW
SIDE VIEW
cylinder dia. = 52 mm
"O" ring groove (top & bottom)
45°
45°
Window
(See window
detail Fig. 4)
Screw holes
Window
5mm
2 mm
60mm
45°
16mm

Fig. 1

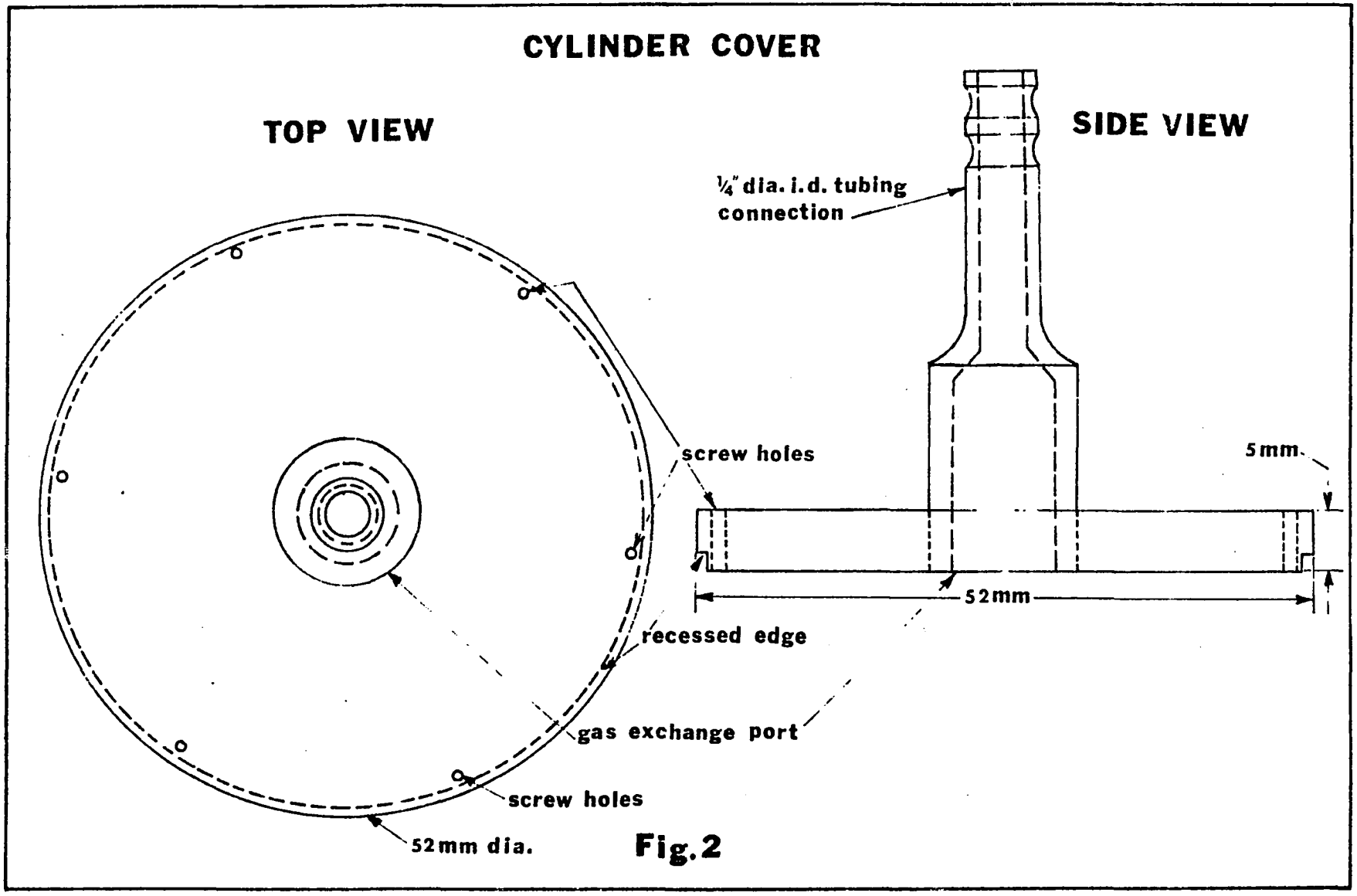

CYLINDER COVER
TOP VIEW
SIDE VIEW
¼" dia. i.d. tubing connection
screw holes
5mm
52mm
recessed edge
gas exchange port
screw holes
52mm dia.

Fig. 2

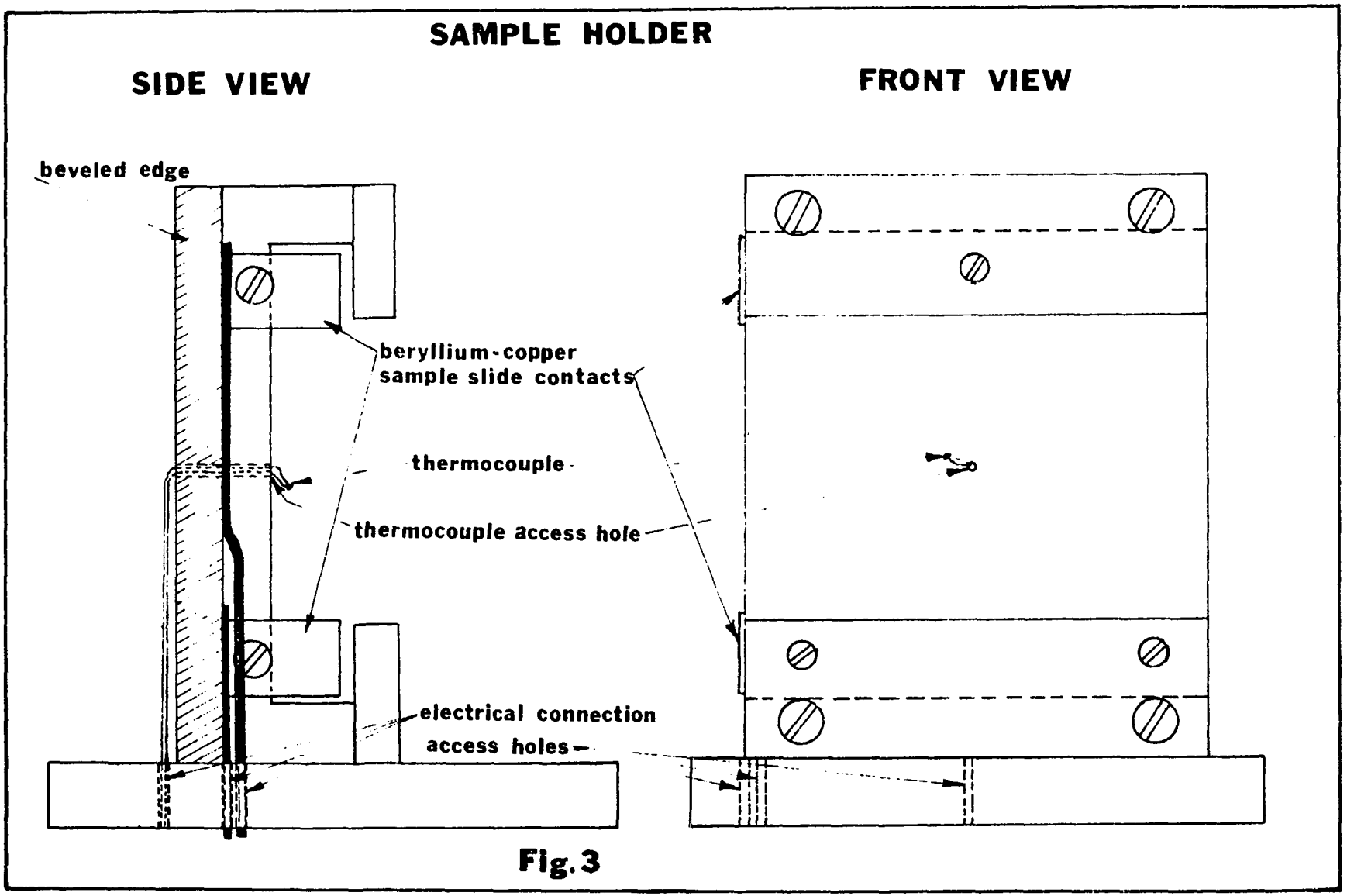

SAMPLE HOLDER
SIDE VIEW
FRONT VIEW
beveled edge
beryllium-copper
sample slide contacts
thermocouple
thermocouple access hole
electrical connection
access holes

Fig. 3

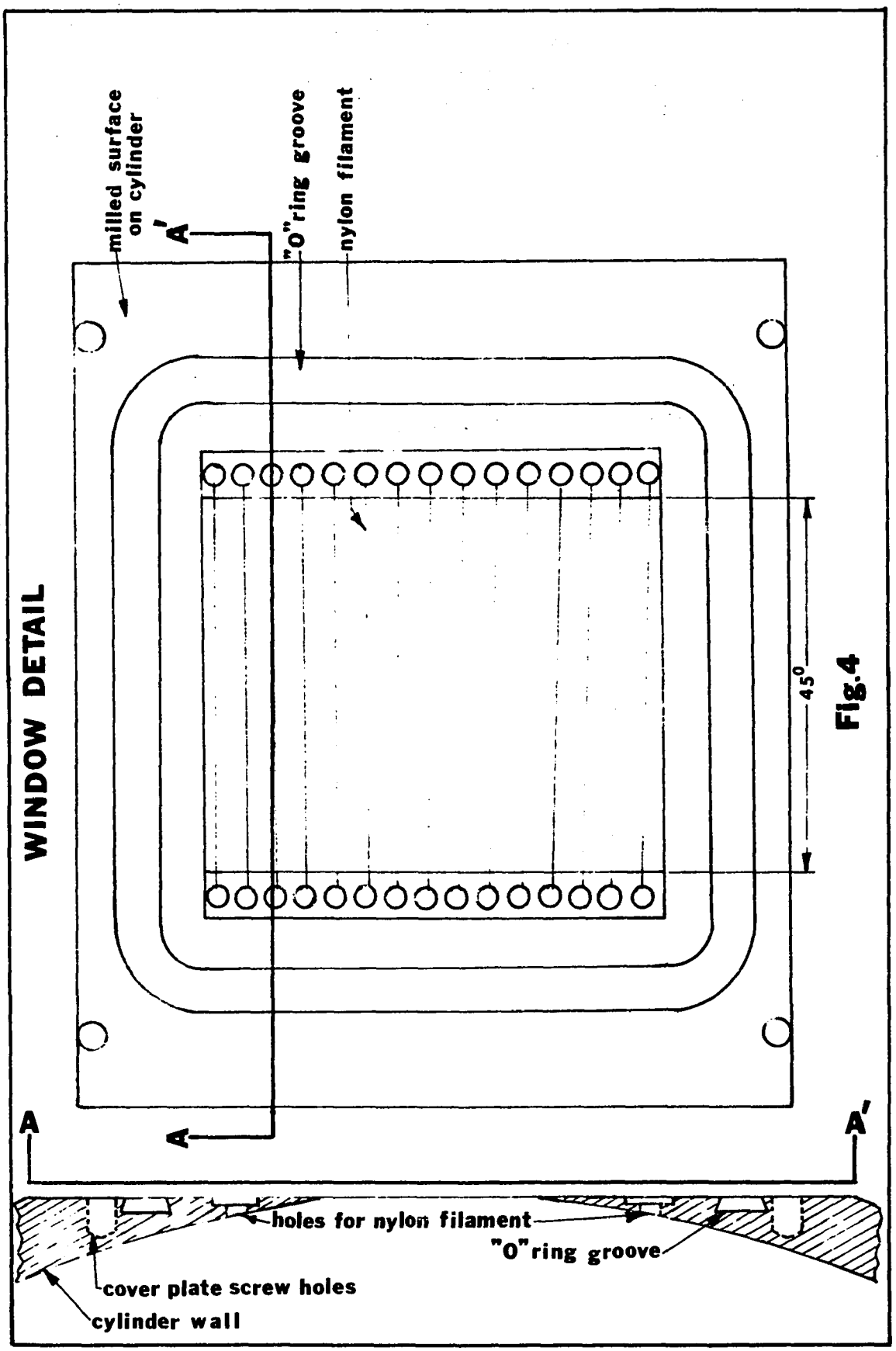

WINDOW DETAIL
milled surface on cylinder
A'
"O"ring groove
nylon filament
45°
A
A
A'
holes for nylon filament
"O"ring groove
cover plate screw holes
cylinder wall

Fig.4

PORCELAIN SAMPLE SLIDE

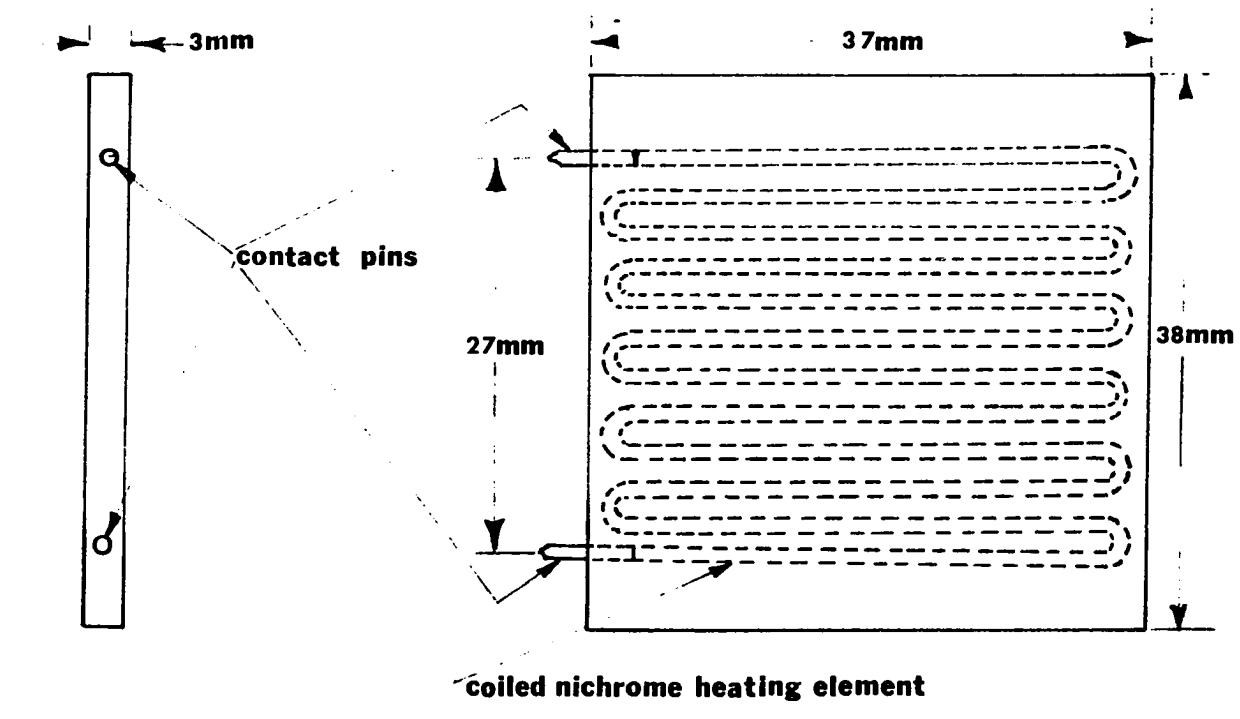


Fig.5

state and read the pressure by determining the oil level in the manometer with a cathetometer. Pumping was then begun and d(001) was repeatedly scanned with repetitions occurring as fast as scans were completed. The pressure was read as instantaneous pressure at the time the x-ray chart recorder indicated the peak of the (001) reflection. After the first one or two hours the rate of change of d(001) and pH_2O had decreased to a point that scans and pH_2O readings could be taken at successively longer intervals. Each sample was pumped continually until there was no observed change in d(001) during sixty minutes of pumping. The samples were then rehydrated by admission of H_2O vapor and the process was repeated at 35°C and 45°C. The error of determination of d(001) is relatively high at low angles on the diffractometer. The reproducibility for these determinations is 0.05 Å. The reproducibility of pressure determinations from one run to another is 0.01 torr. Within one run, however, differences of 0.005 torr are significant.

The lithium clay was dehydrated from a maximum pH_2O of 4.9 torr at 25°C (Fig. 6). In the range from 4.9 torr to full dehydration there is one major step in the curve. There are two smaller steps which occur at about 1.5 torr and 0.65 torr. These are not assumed to be significant steps with regard to water loss. The 35°C and 45°C dehydration curves are much smoother, with the major H_2O loss beginning at about 20 torr. For all of the different temperature runs the largest portion of the d(001) change takes place at pressures below 0.2 torr.

The dehydration of the sodium clay (Fig. 7) is similar to that of the lithium clay except that the initiation of the major water loss is at a higher pressure. For 25°C it begins at about 5 torr and increases

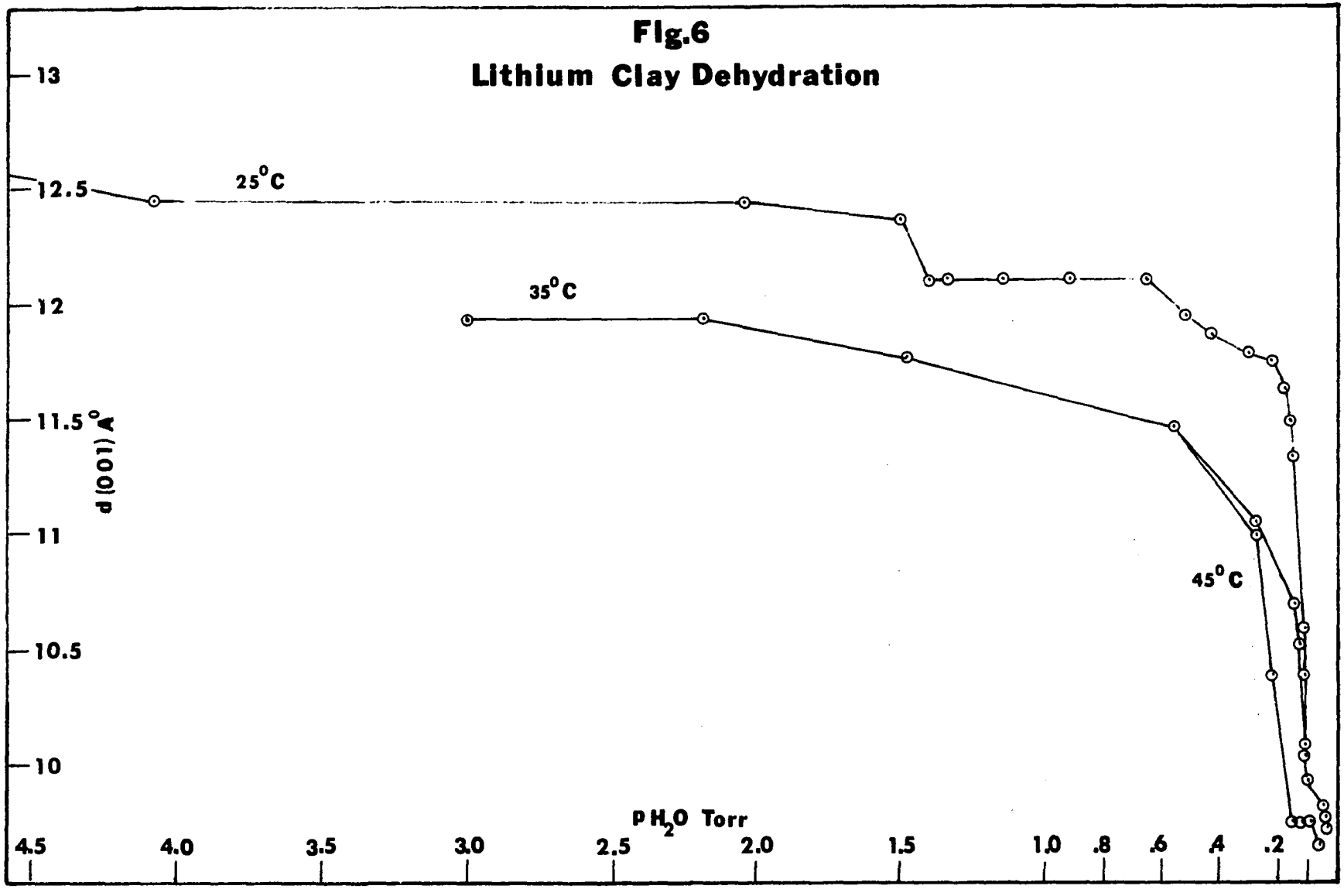


Fig.6
Lithium Clay Dehydration
13
12.5
12
11.5
11
10.5
10
d (001) Å
25°C
35°C
45°C
P H2O Torr
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.8
.6
.4
.2

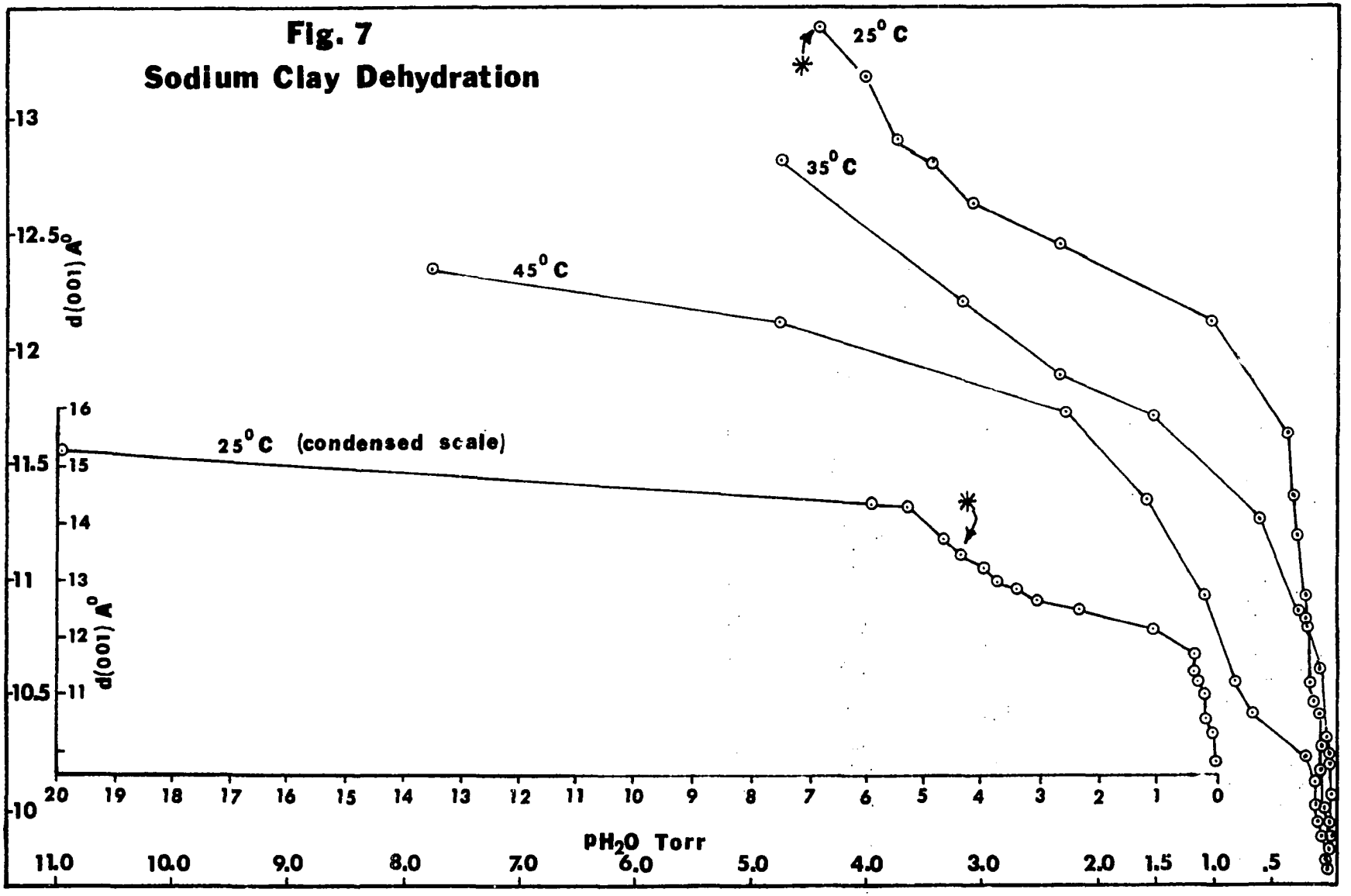


Fig. 7
Sodium Clay Dehydration
25° C
35° C
45° C
25° C (condensed scale)
d(001) Å
13
12.5
12
11.5
11
10.5
10
16
15
14
13
12
11
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
pH2O Torr
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.5 1.0 .5

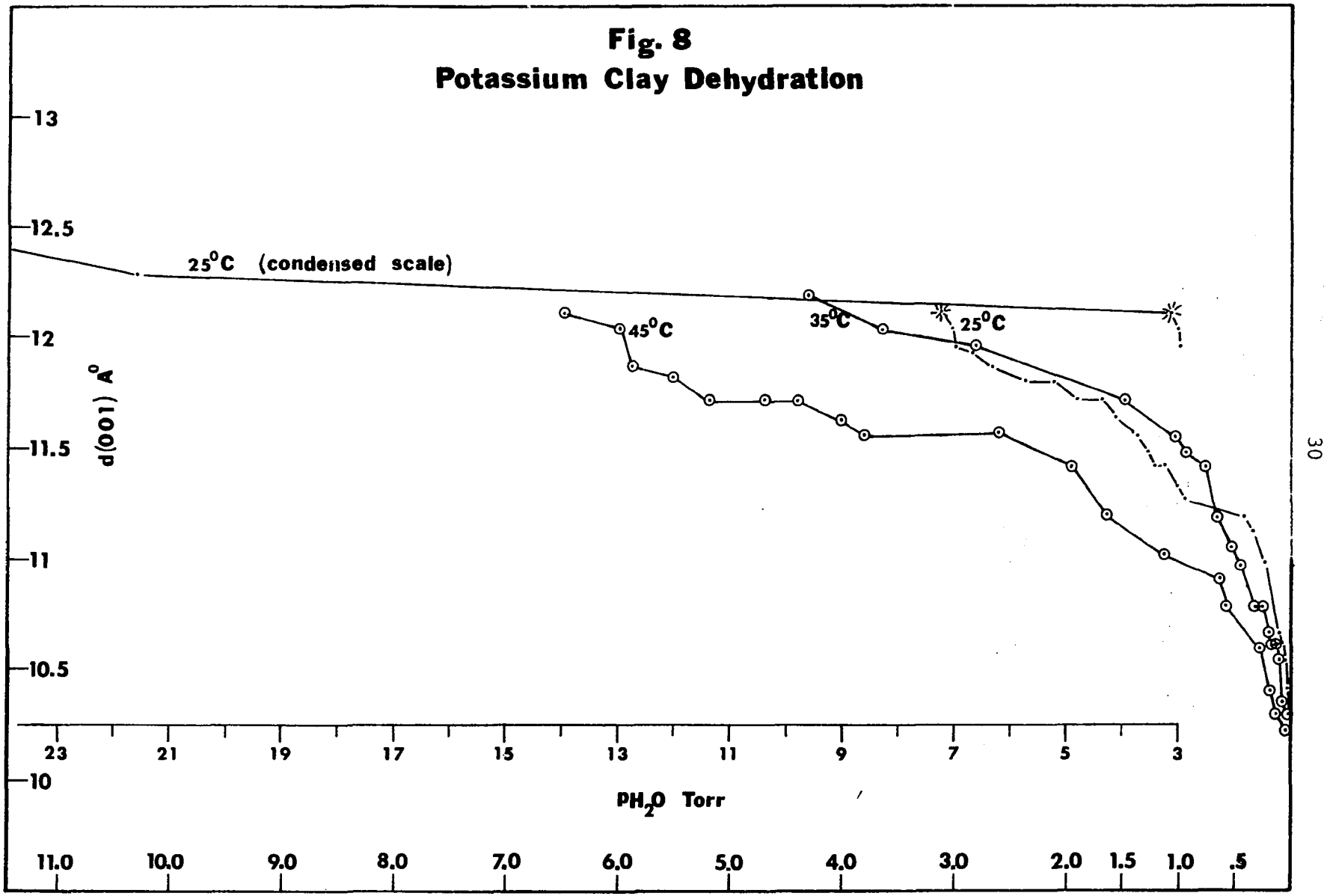
sharply at 0.5 torr. For 35°C it begins at 4.75 torr and increases at about 1.5 torr. For 45°C it begins above 12 torr and increases at about 2.3 torr.

The potassium clay shows one major loss initiated at 3.0, 4.3, and 6.0 torr for 25°C, 35°C, and 45°C respectively (Fig. 8). The curves for 25°C and 35°C cross each other. The difference is within experimental error but is due to a temporary temperature drop on evacuation during the 35°C run.

The magnesium clay remained hydrated at 25°C down to low pressures. The d(001) did not show a change until the pressure had reached 0.04 torr, the change at that point is rapid. At 25°C the complete dehydration of the magnesium clay could not be attained with the pumping system that was used. The last water to be lost comes off with great difficulty. The higher temperature runs of 35°C and 45°C, however reached final collapse of 10.048 Å and 9.717 Å respectively. There are two periods of water loss exhibited by the magnesium clay at 45°C. It is assumed that the 25°C and 35°C runs would show two periods of loss also. However, these two runs were not begun at sufficiently high pressure to observe them. The first water loss for the 45°C run is not pertinent to this study and is not shown on the scale of Fig. 9. The initial d(001) at 45°C was 14.14 Å at 15.0 torr.

Dehydration of the calcium clay is shown in Fig. 10. The curves for the 25°C, 35°C, and 45°C runs are all similar in shape. Again as with the magnesium clay there are two periods of water loss. The dehydration at 25°C was not begun at high enough pH_2O to indicate the first loss. The 35°C and 45°C runs, however, indicate the latter portion

Fig. 8
Potassium Clay Dehydration



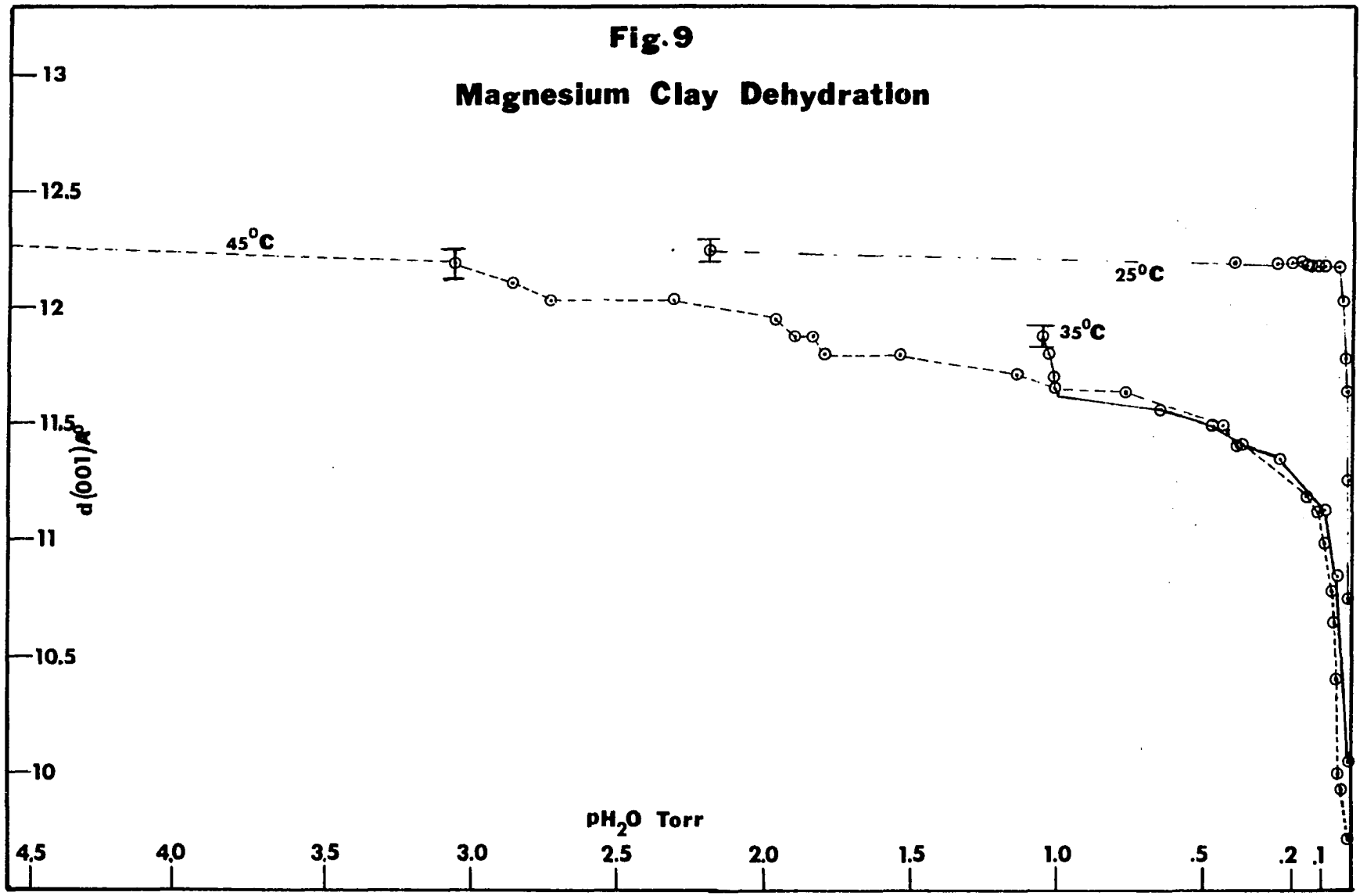


Fig. 9
Magnesium Clay Dehydration
13
12.5
12
11.5
11
10.5
10
d(100) Å
45°C
25°C
35°C
pH2O Torr
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
.2
.1

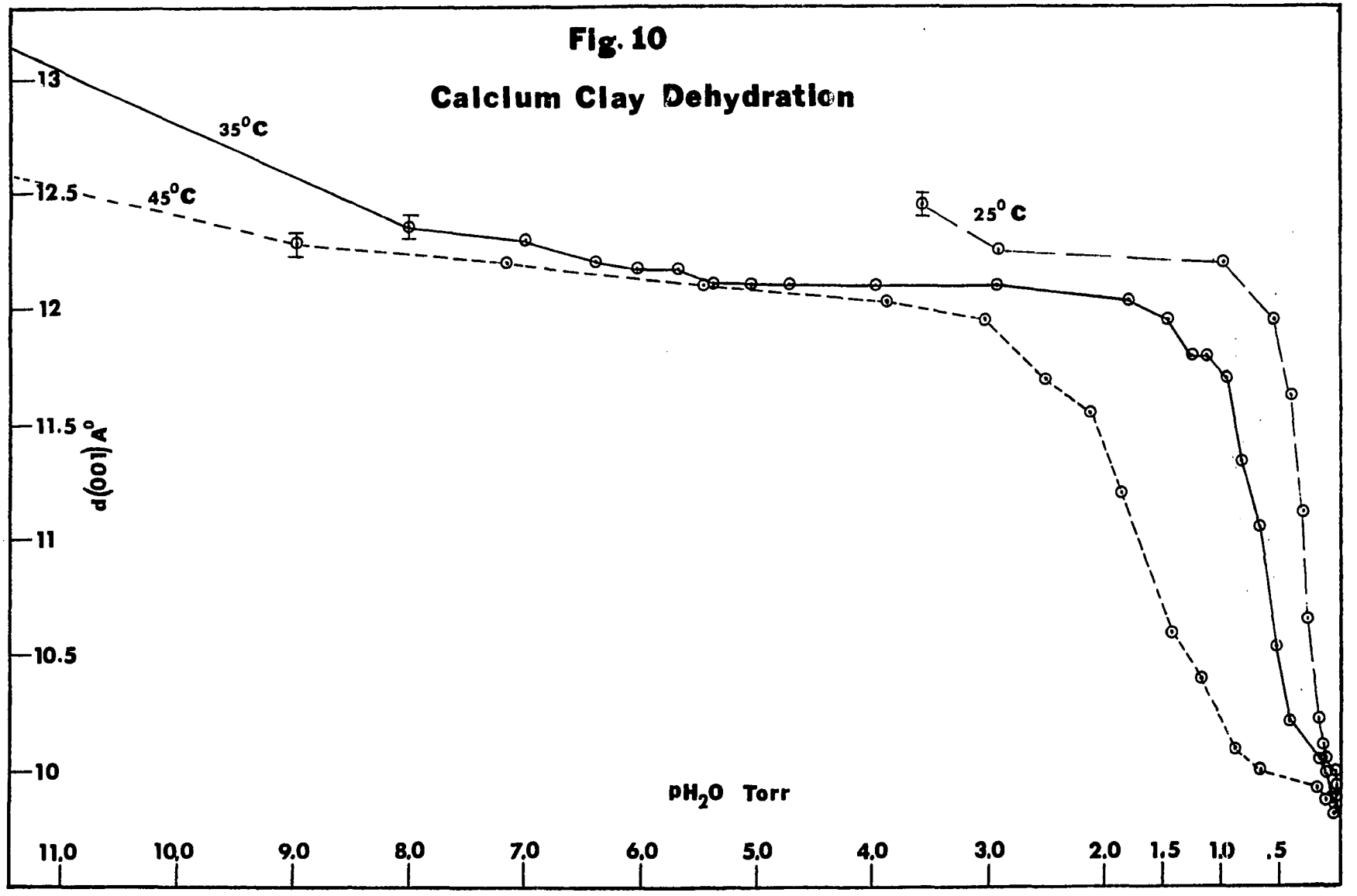


Fig. 10
Calcium Clay Dehydration
35°C
45°C
25° C
13
12.5
12
11.5
11
10.5
10
d(001) A°
pH2O Torr
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.5
1.0
.5

of that loss. The d(001) vs. pH_2O plots go off scale in Fig. 10, however the positions of the lines are correct.

Fig. 11, the dehydration curves for the barium clay, shows the latter portions of the first water loss for the 25°C and 35°C runs. The 45°C run was begun at lower pressure and shows only the last period of loss. In the divalent cation substituted clays the first water loss is not particularly significant to the present study. The fact that the divalent cation substituted montmorillonites undergo two episodes of water loss is well established in the literature.

d(060) vs. d(001)

Each of the six cation forms of the sample were run at 25°C to determine the change in d(060), or the b-axis dimension, as a function of the pH_2O. The pH_2O is indicated by the d(001) dimension as the clays are dehydrated. The d(060) measurements were made over the same time interval as the d(001) measurements, that is, eight to ten hours. d(001) was used as an indicator of pH_2O rather than measurement of pH_2O directly for facility in making the measurements. Reading both pH_2O and d(060) is difficult and time consuming and it was felt that change in d(001) was also necessary information. Rather than try to measure d(060), d(001), and pH_2O at the same time it was felt that d(001) could be used as an indicator of pH_2O.

The porcelain sample plate was used as an internal standard for accurate determination of 2θ. The peaks in the sample plate used were those closest to the montmorillonite (060) peak. It is not known what the slide material is; however, the peaks used were examined and

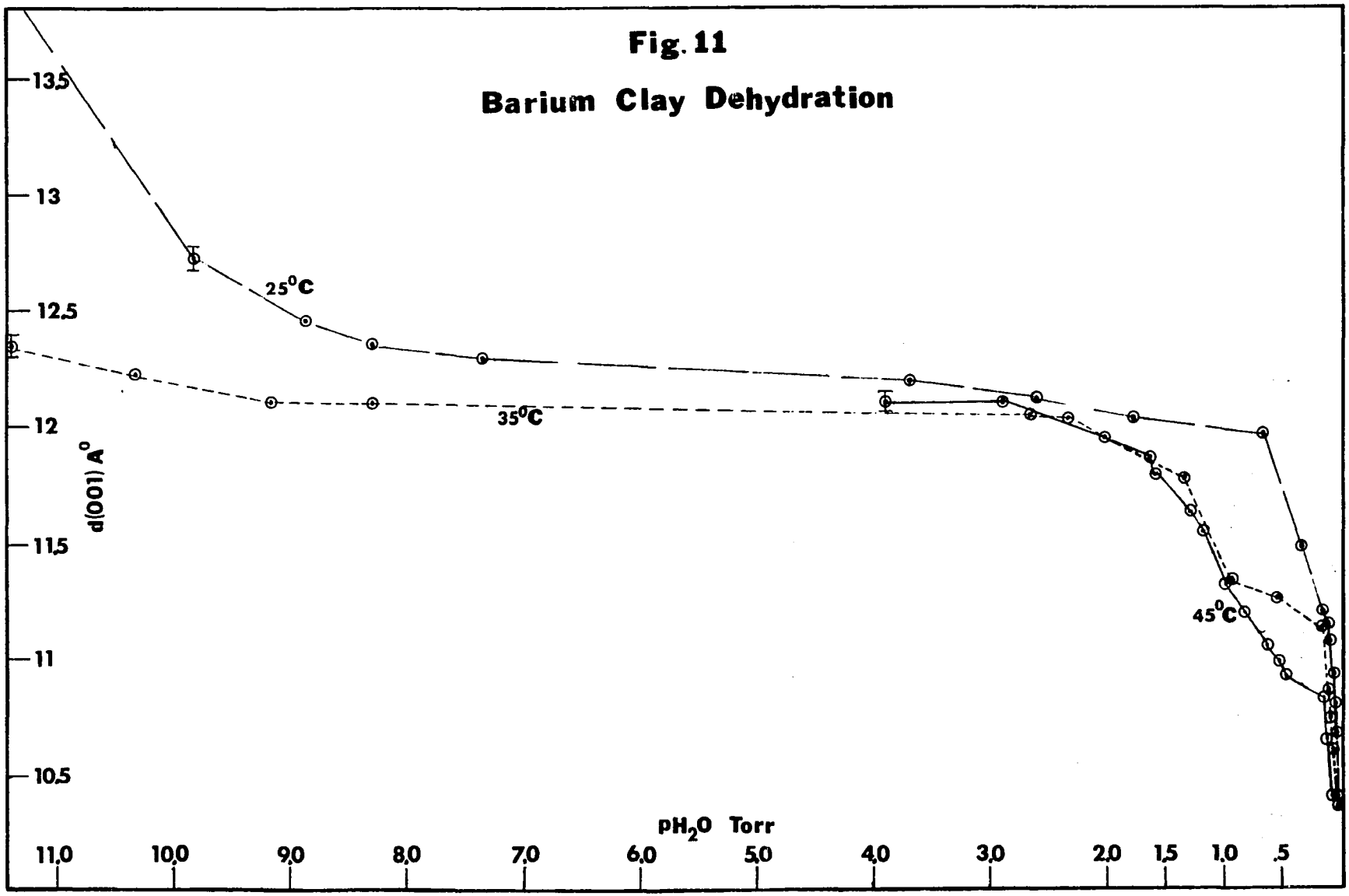


Fig. 11
Barium Clay Dehydration
13.5
13
12.5
12
11.5
11
10.5
d(001) A°
25°C
35°C
45°C
pH2O Torr
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.5
1.0
.5

determined to be stable to changes in temperature, pressure, and relative humidity. The samples were prepared by freeze-drying a clay-water suspension. The dry powders were then mounted and allowed to hydrate in H_2O vapor after flushing the chamber with H_2O vapor. The pressure was then lowered slowly while the (060) peak was scanned repeatedly with an occasional interruption for scanning of the (001) peak.

Determination of change in the (060) dimension is difficult due to the diffuse nature of the peak and the smallness of the change. In these determinations the reliability of the measurements is indicated by the standard deviation of from five to nine unidirectional scans of the (060) peak. The magnitude of the standard deviation varies from determination to determination with 1 σ being 0.0005 Å for the Mg clay, 0.0002 Å for the Na clay, the Ca clay, and the Ba clay, 0.00025 Å for the K clay, and 0.0004 Å for the Li clay. In establishing change in the b dimension no two points were considered to be significantly different unless they varied by more than four standard deviations, that is, a difference of plus or minus two standard deviations from each point. Plus or minus one standard deviation could have been used but separations of plus or minus two standard deviations indicates a higher probability that the points are in fact different. For the latter case the probability that two points are different is about 0.99.

Figures 12 through 17 show the change in d(060) as a function of d(001). In some scans there is an obvious splitting of the (060) peak into two peaks during dehydration. Fig. 18 shows the splitting observed for the Ca clay. For those samples which exhibit peak splitting the

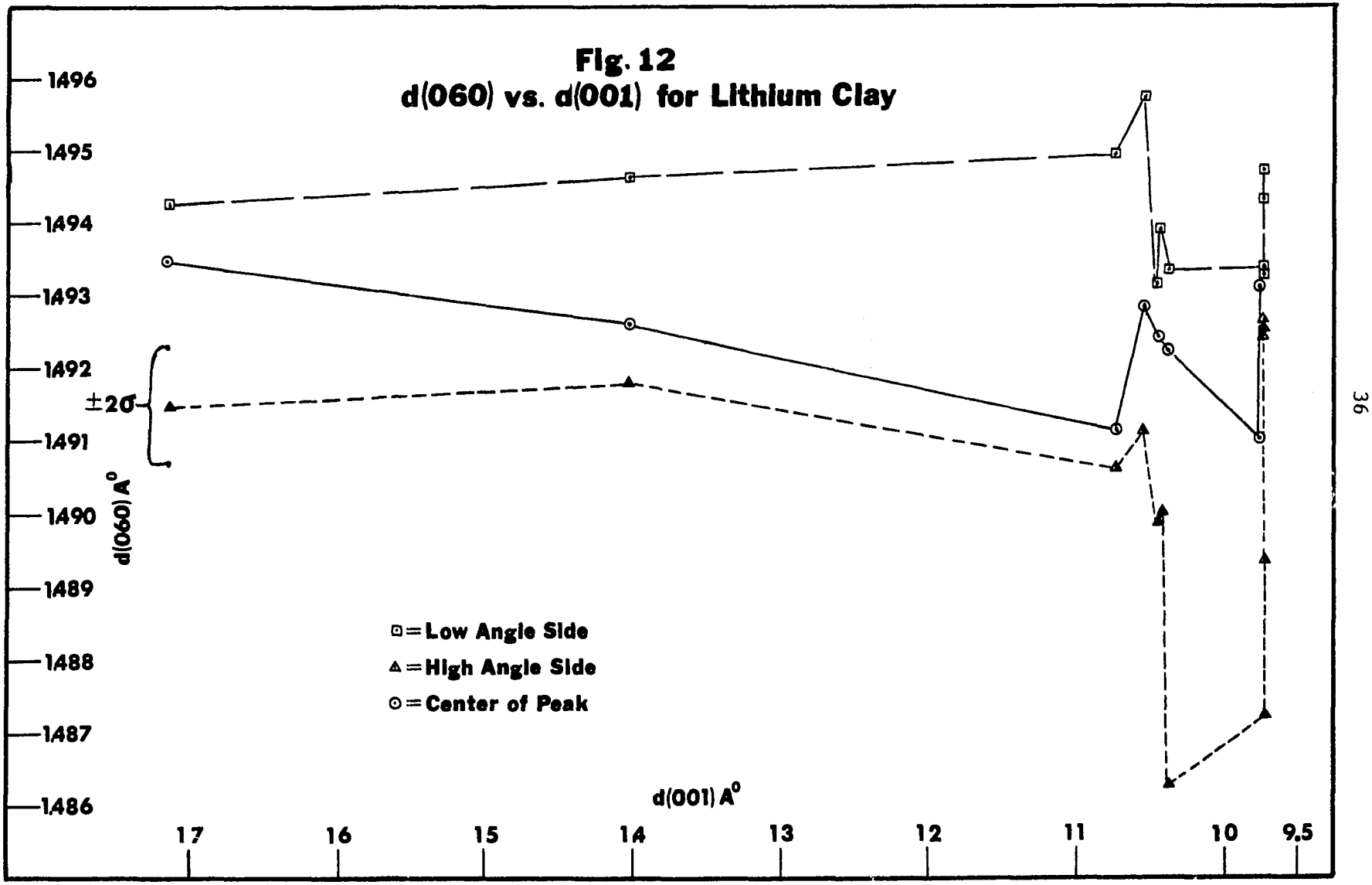


Fig. 12
d(060) vs. d(001) for Lithium Clay
1496
1495
1494
1493
1492
±2σ
1491
1490
1489
1488
1487
1486
d(060) A°
□ = Low Angle Side
△ = High Angle Side
⊙ = Center of Peak
d(001) A°
17
16
15
14
13
12
11
10
9.5

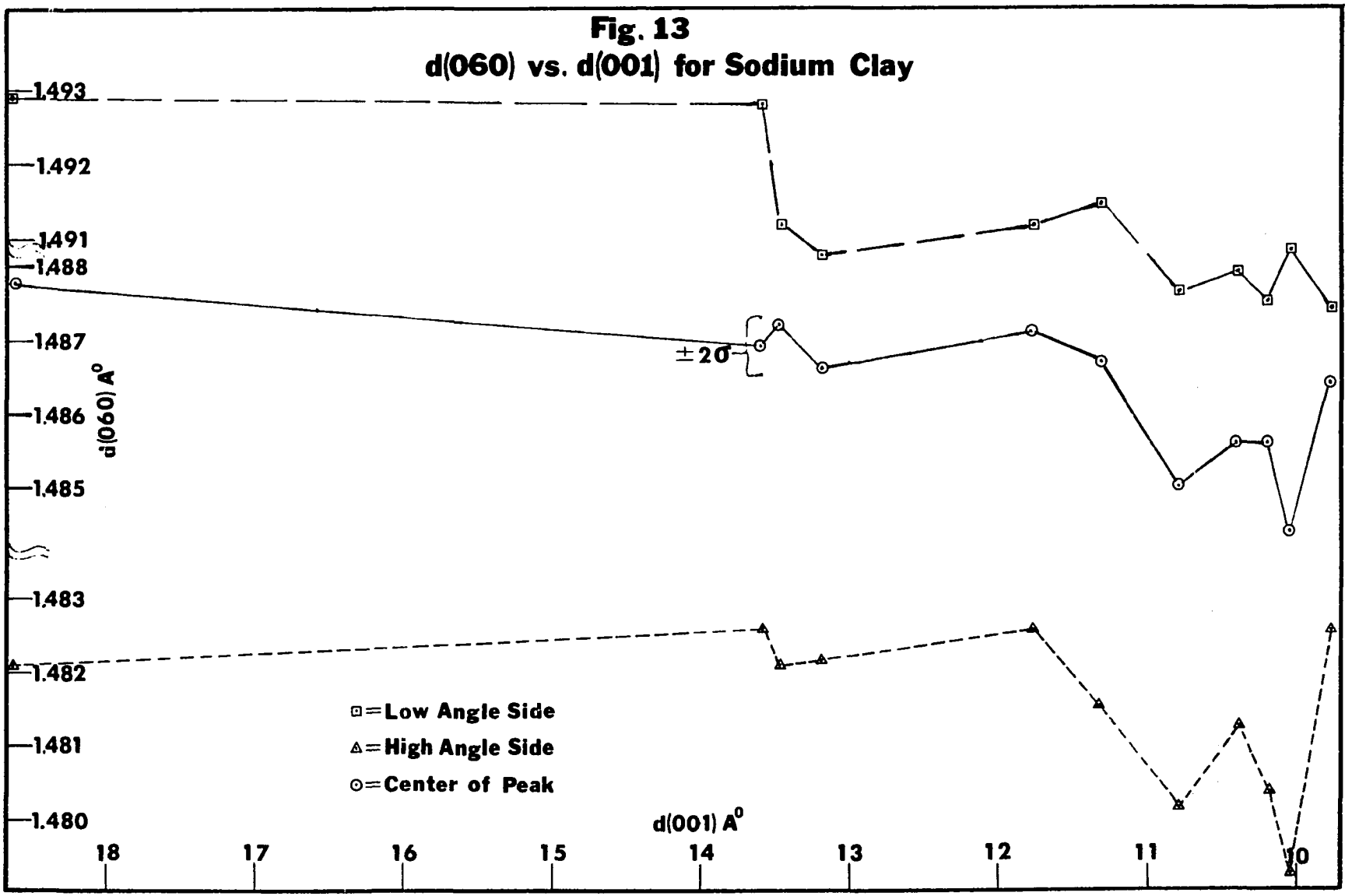
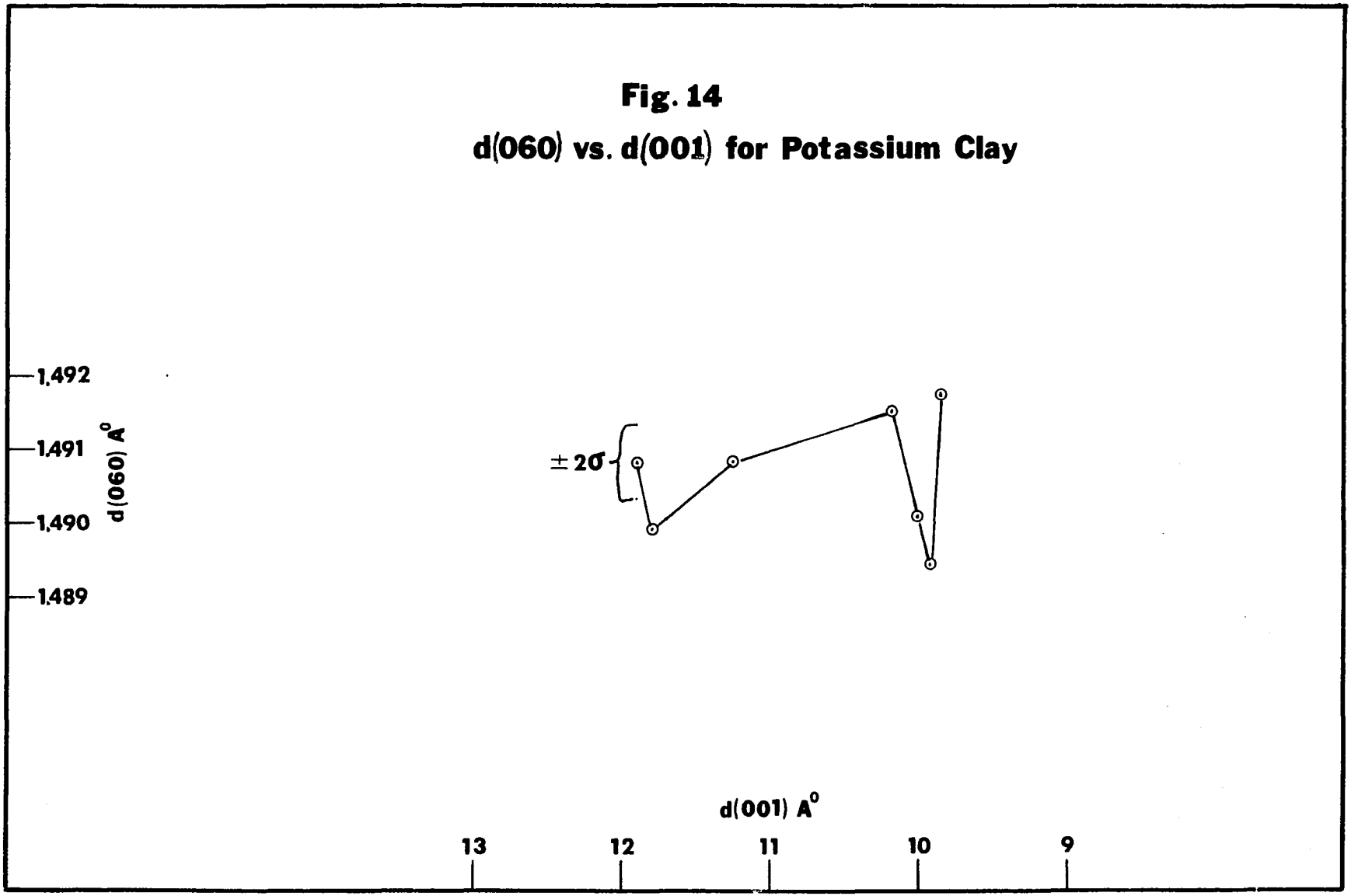


Fig. 13
d(060) vs. d(001) for Sodium Clay
1.493
1.492
1.491
1.488
1.487
1.486
1.485
1.483
1.482
1.481
1.480
d(060) A°
±2σ
□=Low Angle Side
△=High Angle Side
⊙=Center of Peak
d(001) A°
18
17
16
15
14
13
12
11
10

Fig. 14

d(060) vs. d(001) for Potassium Clay



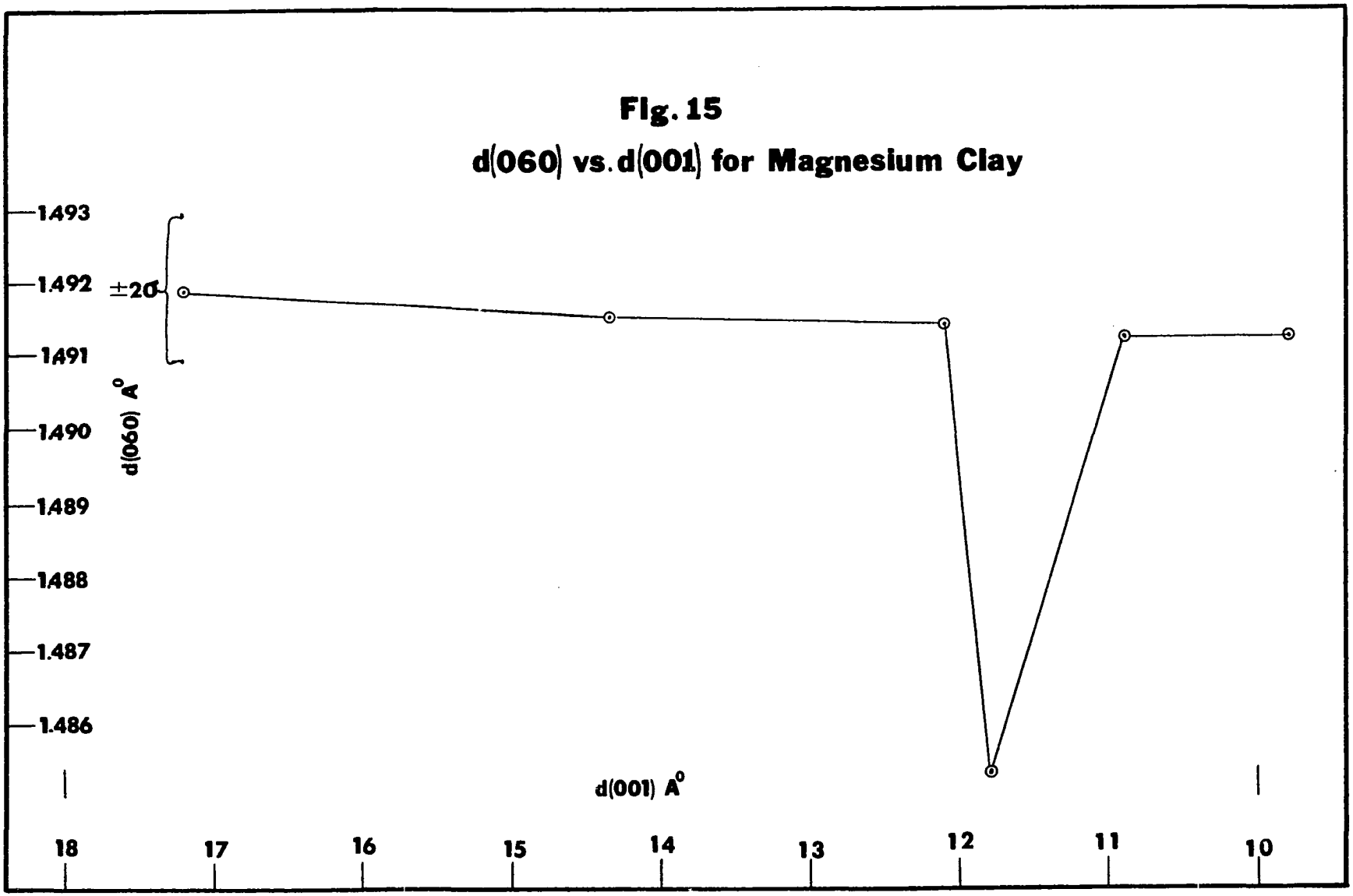


Fig. 15
d(060) vs. d(001) for Magnesium Clay
1.493
1.492
±2σ
1.491
d(060) A°
1.490
1.489
1.488
1.487
1.486
d(001) A°
18
17
16
15
14
13
12
11
10

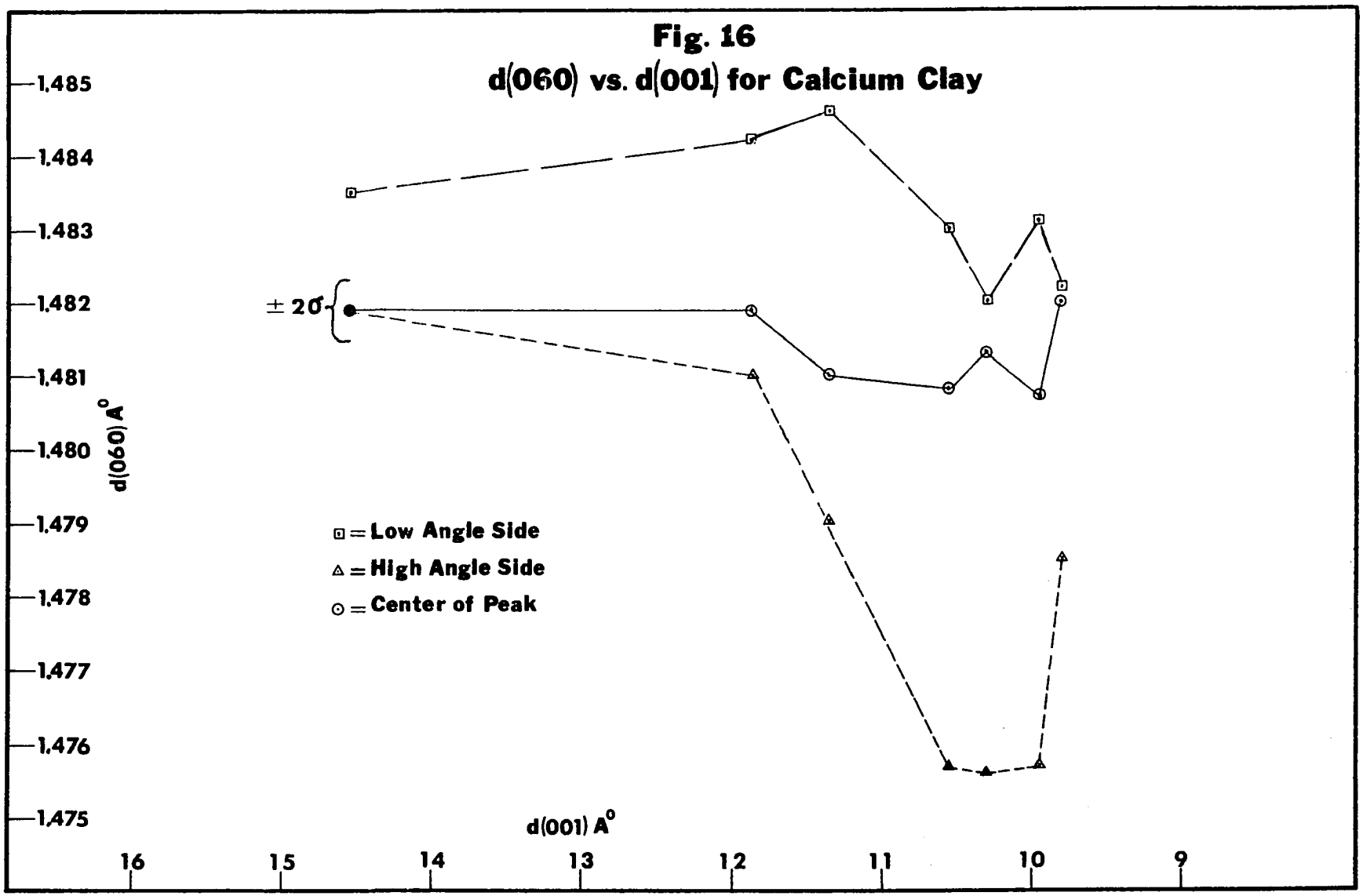


Fig. 16
d(060) vs. d(001) for Calcium Clay
1.485
1.484
1.483
1.482
1.481
1.480
1.479
1.478
1.477
1.476
1.475
d(060) A°
± 2σ
□ = Low Angle Side
△ = High Angle Side
⊙ = Center of Peak
d(001) A°
16
15
14
13
12
11
10
9

Fig. 17

d(060) vs. d(001) for Barium Clay

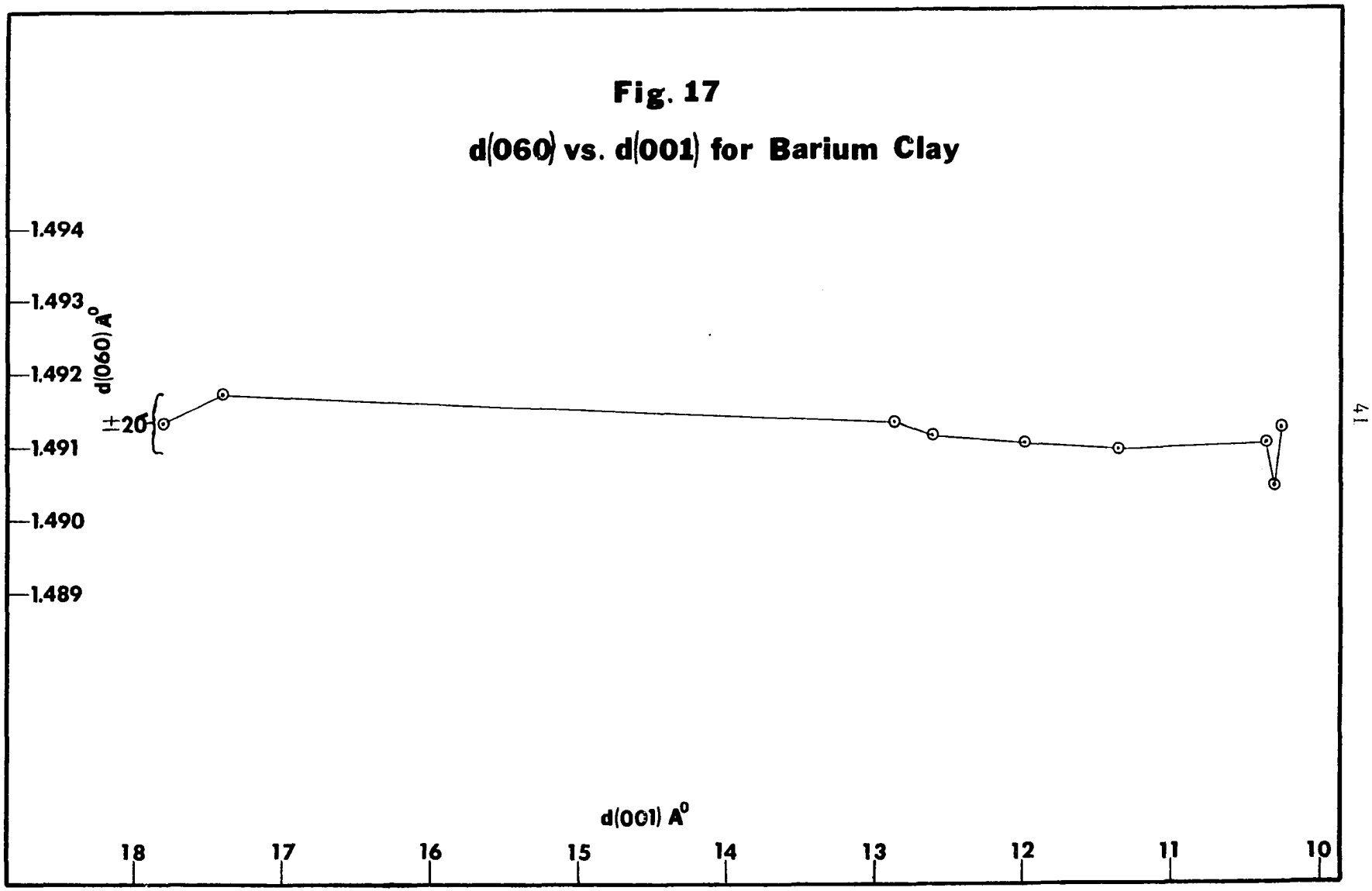
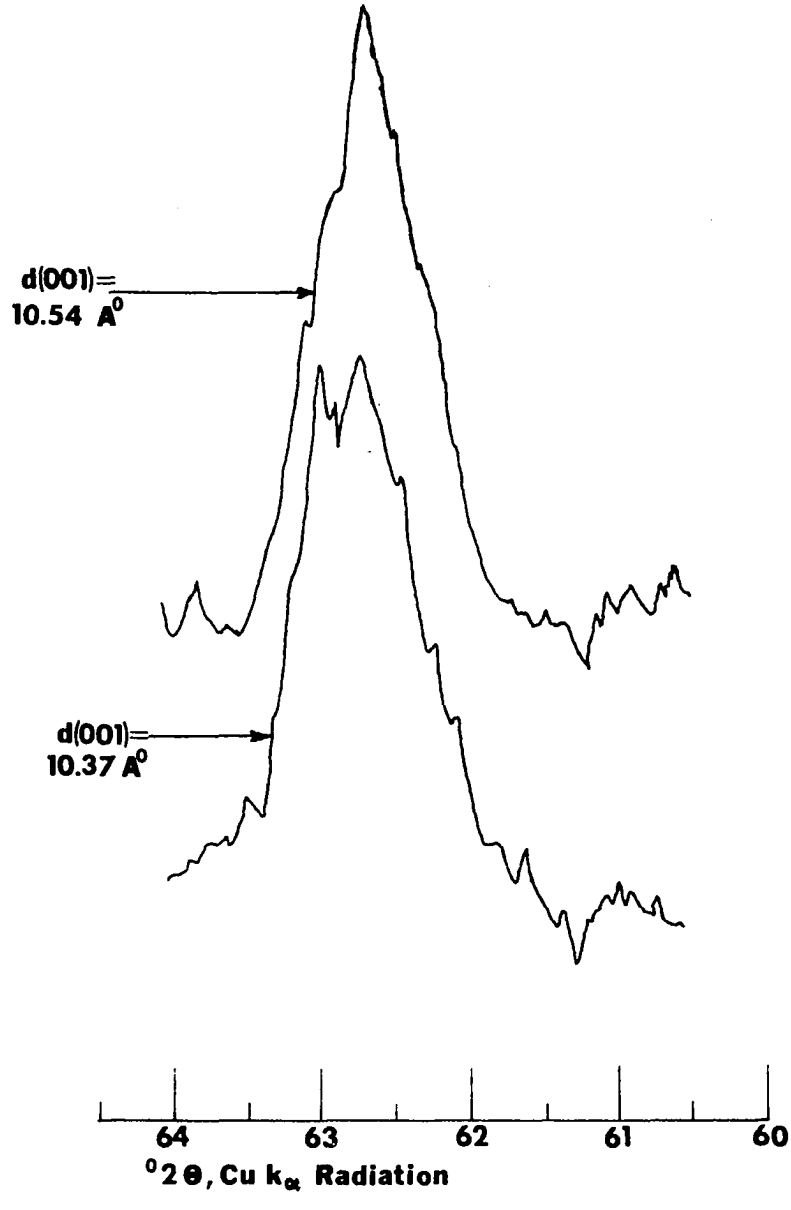


Fig. 18



(060) Peak Splitting on Dehydration for Calcium Clay

graphs show change with dehydration for the peak center, the high angle side, and the low angle side of the peak.

Fig. 12 shows the b-axis change for the Li clay. The line for the center of the peak shows a decrease in the b-axis dimension beginning at 10.55 Å. The change is greater than four σ and is considered significant. The line for the high angle side shows a larger change and the decrease is considered indicative of b-axis change. It should be noted that there is a return to near the initial b-axis dimension upon maximum water loss.

The sodium clay (Fig. 13) also shows a decrease in the b-axis dimension on dehydration followed by return to near the initial b-axis dimension with loss of the last water. The amount of decrease for both the peak center and the high angle side is greater than four σ.

The potassium clay (Fig. 14) shows a varied response to decreasing pH_2O. The decrease in b at low water content is present as is the notable increase at dehydration to the dry state. The b-axis dimension starts at an intermediate value, decreases slightly, then increases to above the initial spacing before undergoing the large decrease at the last water loss. Whatever the cause of the initial drop in d(060), the change at low water content is greater than four σ and is considered to be a significant change.

The magnesium clay (Fig. 15) shows little variation throughout most of the dehydration until d(001) equals 12.1 Å. At that point there is a sharp decrease followed by a sharp increase to near the initial value. There was no observable peak splitting and traces for the high and low angle sides are not plotted.

The calcium clay (Fig. 16) reacts as the other samples do with lowered water content. The decrease begins at 11.87 Å and is interrupted by a slight increase at 10.3 Å. It then continues down again to a minimum at d(001) = 9.95 Å and then increases to a point above the original value on complete dehydration. The line for the high angle side shows a much more marked decrease in the b-dimension followed by an increase to a point below the initial value.

Dehydration of the barium clay (Fig. 17) shows a decrease in the b-axis dimension at 10.35 Å which is different from the initial d(060) by more than four σ, but barely so. The peak splitting of the type shown in figure 18 may occur for the barium clay but the background on the diffractometer trace is high and identification of the peak motion is not possible.

The change in b-dimension, as mentioned before, has been indicated by other workers. For all six of the cation forms under investigation there is a significant decrease in the b-dimension with decrease in water content. The point that has not been indicated previously is that there is an increase in the b-cell dimension which occurs at very low water contents. This increase is also exhibited in all six of the cation forms used in this study.

There is great difficulty in obtaining reliable data on change in the b-cell dimension. Although the b-axis change was found in all of the samples and is statistically significant in each, corroboration of the findings was sought by a different approach. Each of the samples was examined by a step scan procedure. The step scan interval was 0.02° 2θ and a mechanical printer was used to record the diffracted

x-ray intensity during the one minute count at each angle. With this procedure, and using the porcelain sample holder as an internal standard, the b-dimension can be determined with a reproducibility of 0.00025 Å. There is an important difference between this procedure and that of scanning with a diffractometer trace. The b-axis change is a transient phenomenon. It occurs over a very short period of time with respect to the total time of pumping during dehydration. Figures 12 through 17 demonstrate this quite well. In additional x-ray work on observing the b-dimension change it was found that if pumping were terminated after initiation of the b-axis decrease that it would increase again on sitting at constant pressure. This is interpreted as a non-equilibrium situation created by continual decrease in the number of water molecules per unit cell. As loss of water is interrupted or terminated the b-dimension returns to an equilibrium condition, presumably by reorientation of the water which remains. The time required for the step scan to encompass the internal standard and (060) peaks is in excess of two hours. During one step scan, then, the decrease to minimum b-dimension and increase to maximum or initial value could occur and not be noticed. Since the decrease in b is established and not in question the principle value of the step scan data is to show that the b-dimension increases to near its initial value at complete dehydration. In figure 19 the points plotted are the determined b-dimension at peak center vs. the d(001) dimension observed at initiation of the step scan. It should be noted that the line for a given cation saturated clay in figure 19 does not represent the mode of

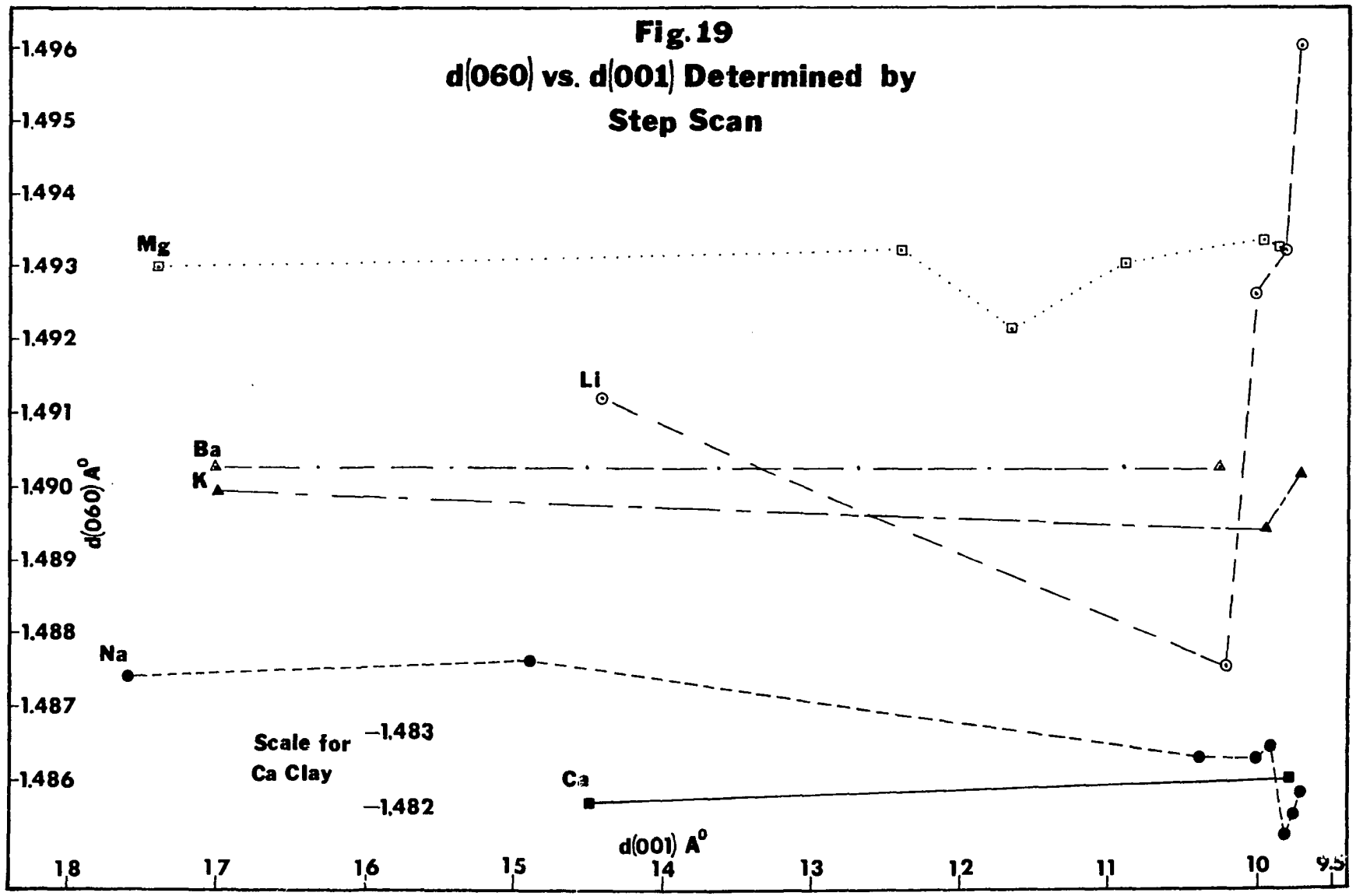


Fig. 19
d(060) vs. d(001) Determined by
Step Scan
1.496
1.495
1.494
1.493
1.492
1.491
1.490
1.489
1.488
1.487
1.486
d(060) A°
Mg
Li
Ba
K
Na
Ca
Scale for
Ca Clay
1.483
1.482
18
17
16
15
14
13
12
11
10
9.5
d(001) A°

b-axis change on dehydration but are only to connect points which refer to the same cation saturated clay.

The lithium clay shows the largest decrease in b and also the largest increase on complete dehydration. The sodium clay shows decrease and increase but not as great an increase as indicated by the diffractometer trace. For the potassium clay there is a slight decrease followed by an increase to a point above the starting b-dimension.

The magnesium, calcium, and barium clays all show increase in b at final dehydration to a point above the starting point.

Weight Loss vs. pH_2O

A glass cell for measurement of weight loss of the clay during dehydration was constructed. The cell contained a heating coil and thermocouple for control. A quartz spring and weighing pan were suspended from the inside center of the cell. The motion of the weighing pan during dehydration was observed with a cathetometer. The weight loss data were accurate to within 0.5 mg. The reproducibility of a complete curve, with the same sample, was $\pm$ 10 mg. For determination of the weight loss a portion of sample was placed in the weighing pan and suspended from the quartz spring. The cell was evacuated and flushed with H_2O vapor and then left to equilibrate for 24 hours. The dehydration was accomplished in the same manner as the previous determinations of pH_2O vs. d(001) and d(060). The times of dehydration were again eight to ten hours. The temperature inside the cell was maintained at 25°C.

Figures 20-25 give the weight loss data for the six samples as number of milligrams lost and as percent lost. There is a relatively

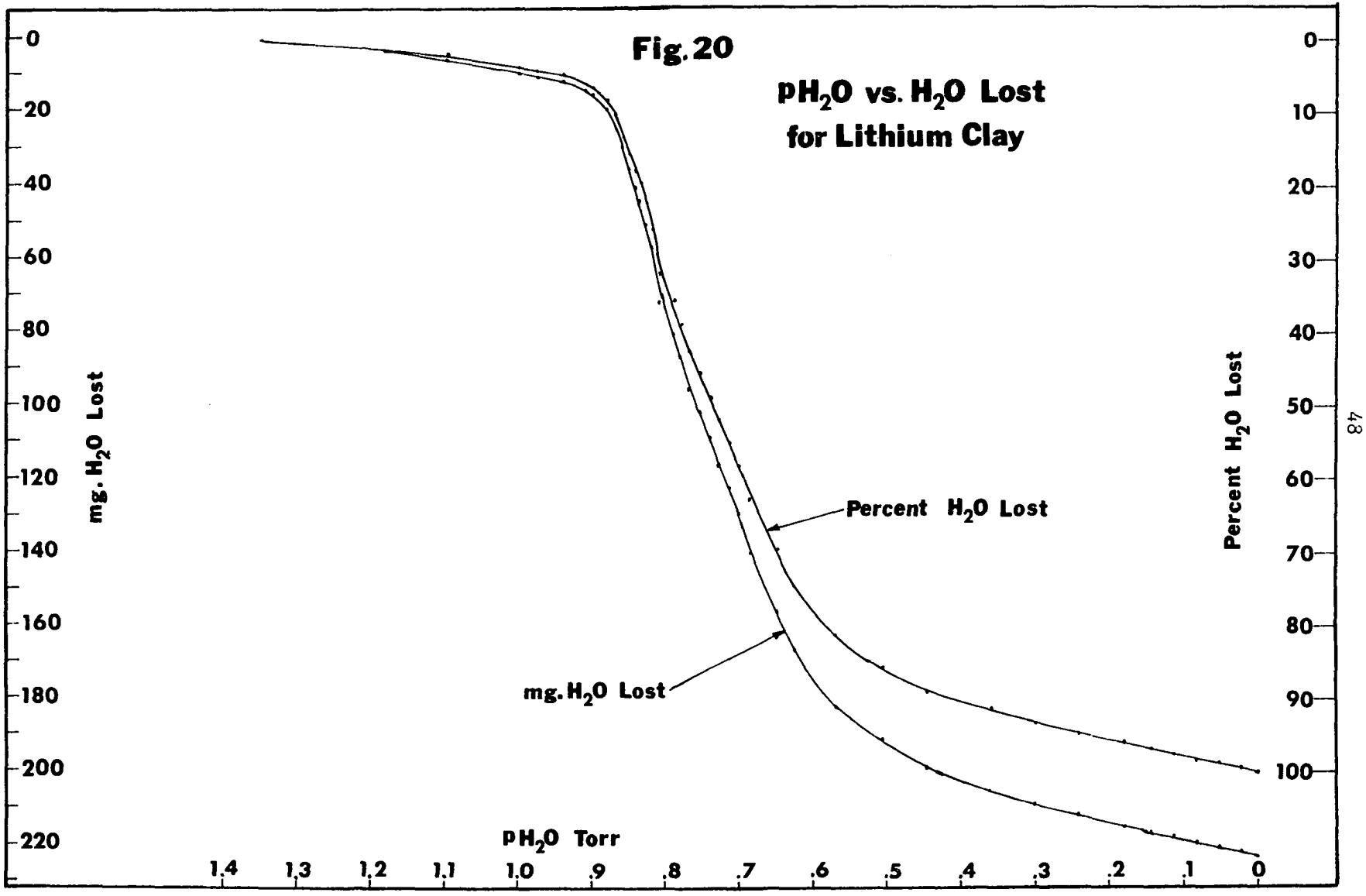


Fig. 20
pH2O vs. H2O Lost
for Lithium Clay
mg. H2O Lost
Percent H2O Lost
pH2O Torr
0
20
40
60
80
100
120
140
160
180
200
220
0
10
20
30
40
50
60
70
80
90
100
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

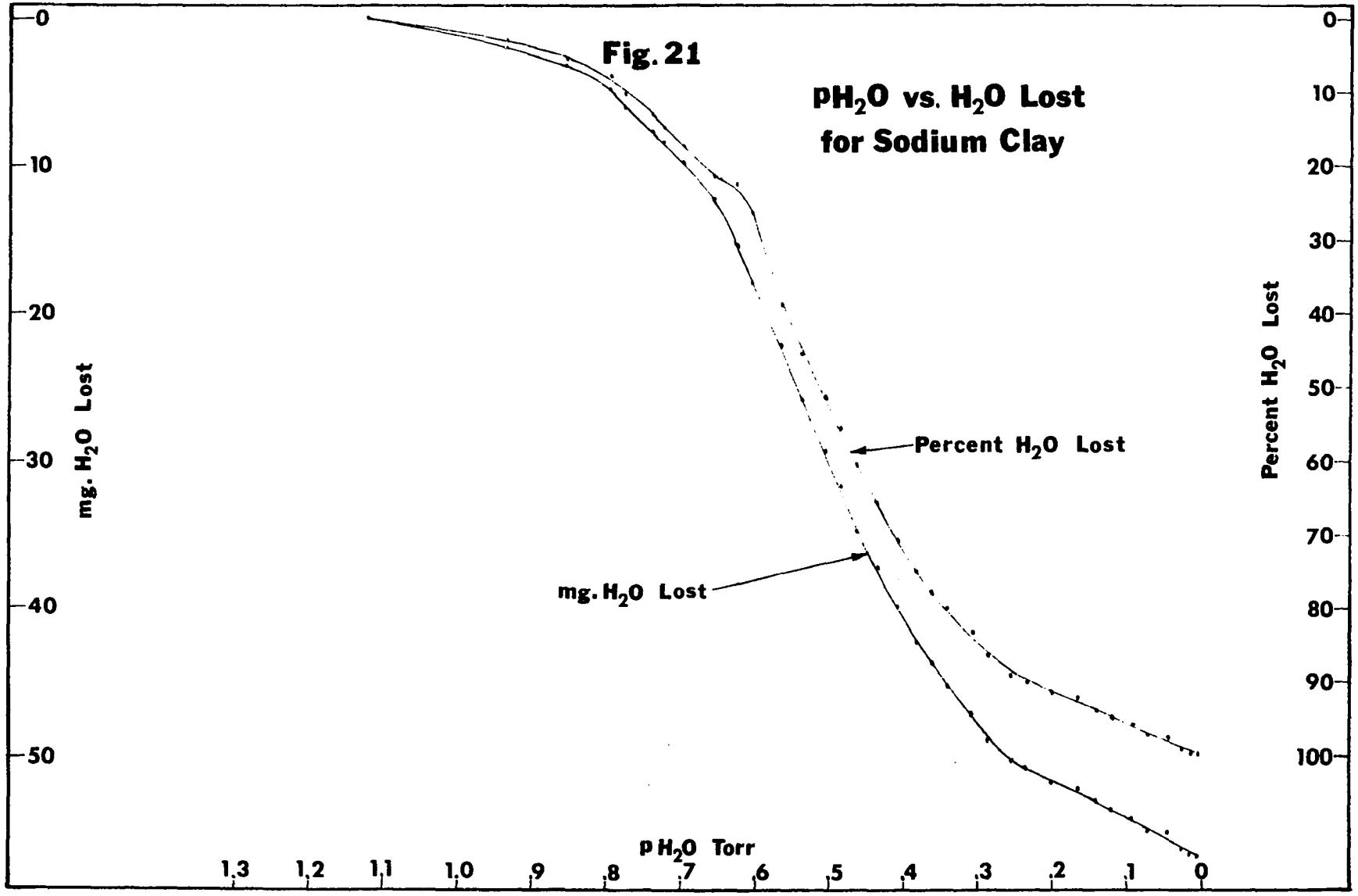


Fig. 21
pH2O vs. H2O Lost
for Sodium Clay
mg. H2O Lost
Percent H2O Lost
mg. H2O Lost
Percent H2O Lost
p H2O Torr
0
10
20
30
40
50
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

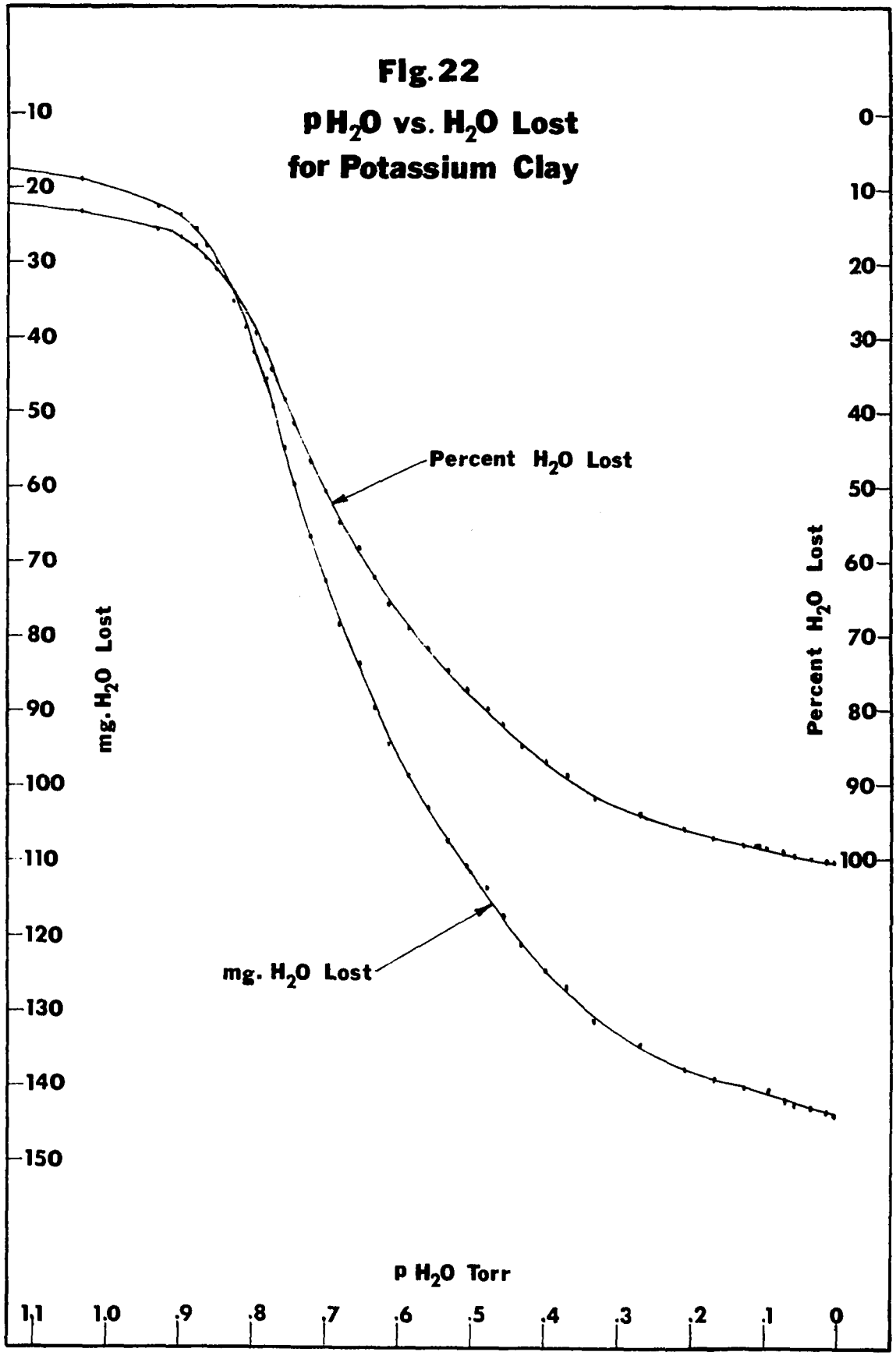


Fig. 22
p H2O vs. H2O Lost
for Potassium Clay
mg. H2O Lost
Percent H2O Lost
Percent H2O Lost
mg. H2O Lost
p H2O Torr
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
0
10
20
30
40
50
60
70
80
90
100
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

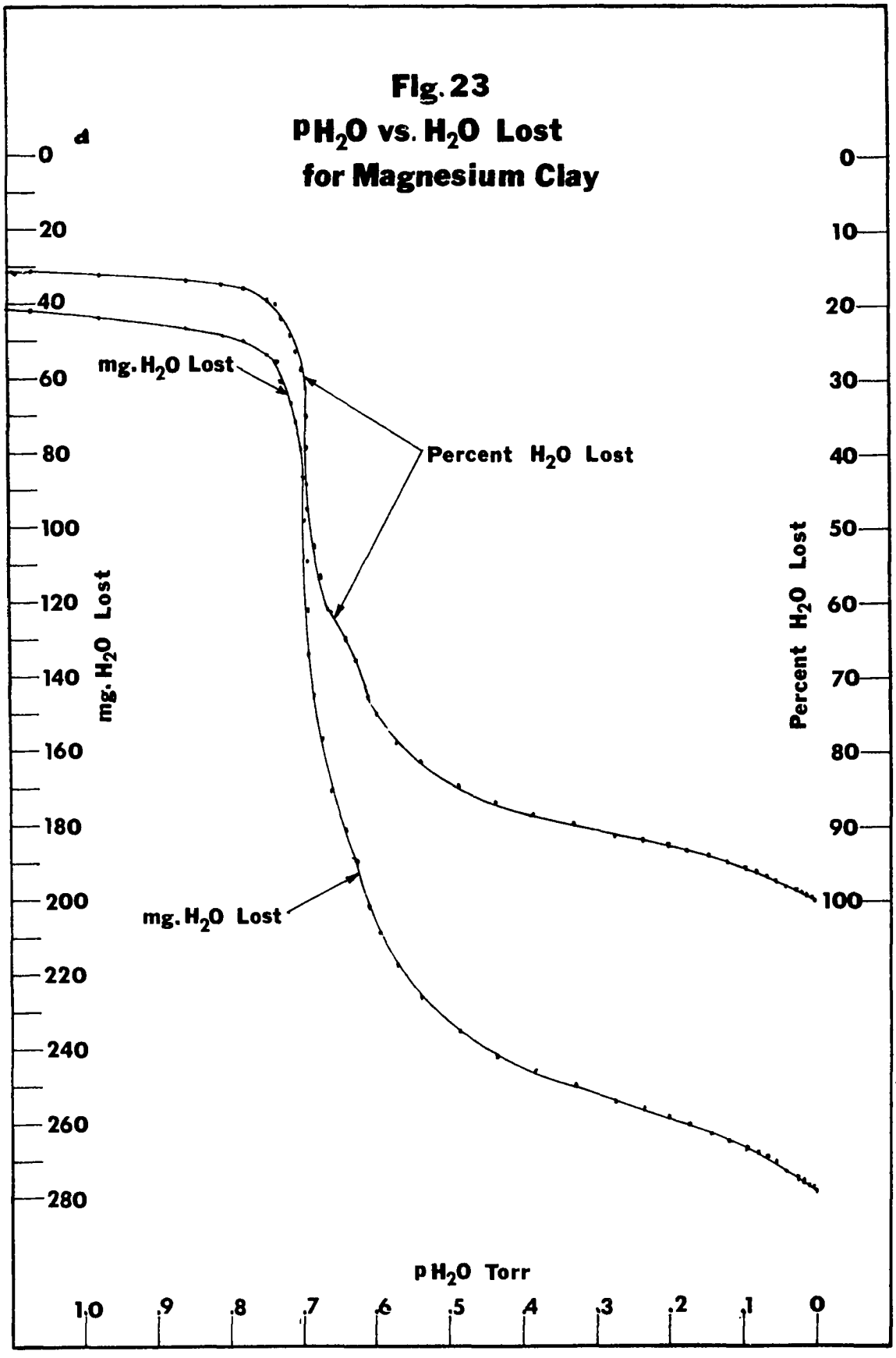


Fig. 23
pH_2O vs. H_2O Lost
for Magnesium Clay
mg. H_2O Lost
Percent H_2O Lost
mg. H_2O Lost
mg. H_2O Lost
Percent H_2O Lost
pH_2O Torr
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
0
10
20
30
40
50
60
70
80
90
100
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

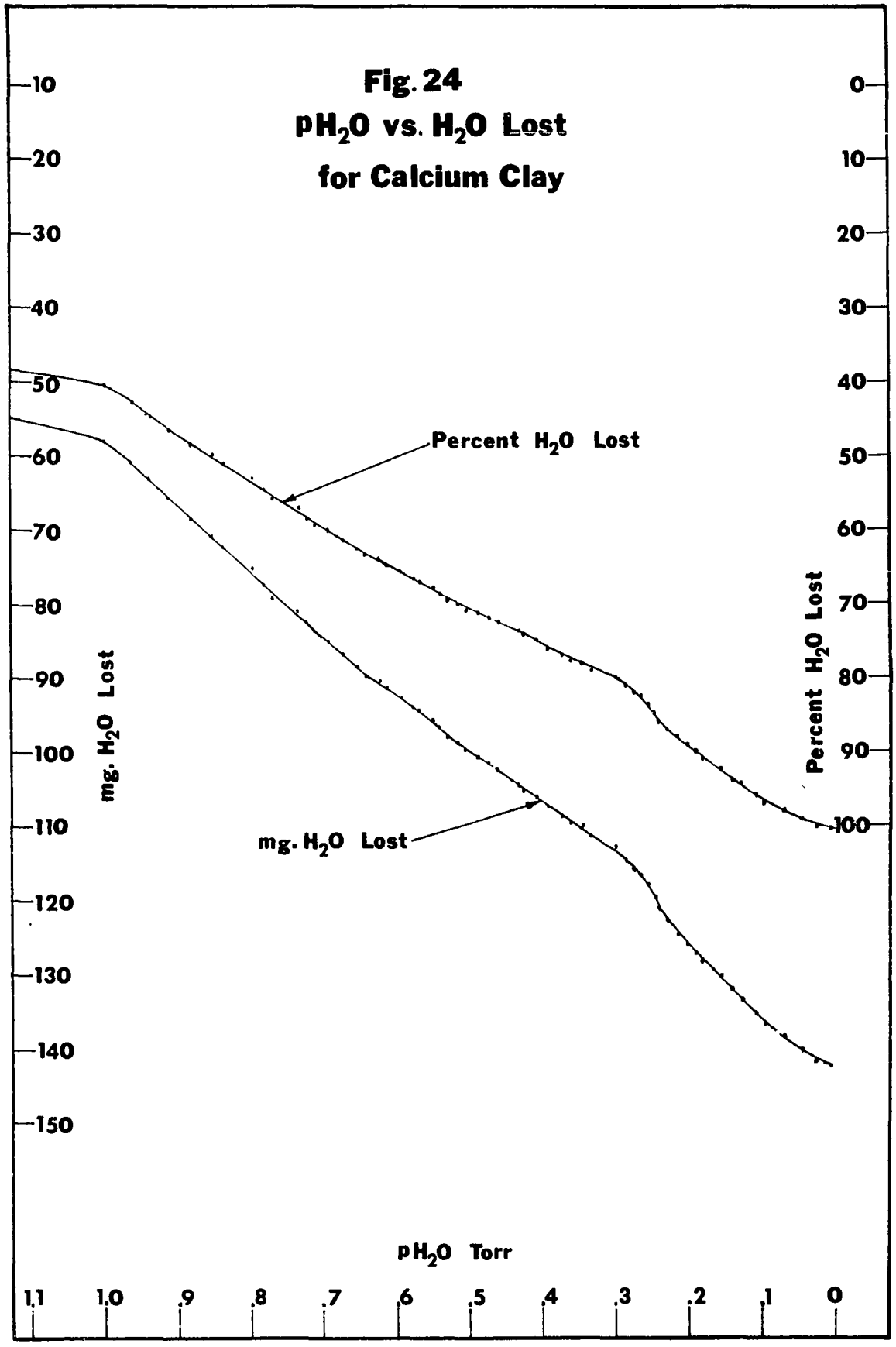


Fig. 24
pH2O vs. H2O Lost
for Calcium Clay
Percent H2O Lost
mg. H2O Lost
mg. H2O Lost
Percent H2O Lost
pH2O Torr
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
0
10
20
30
40
50
60
70
80
90
100
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

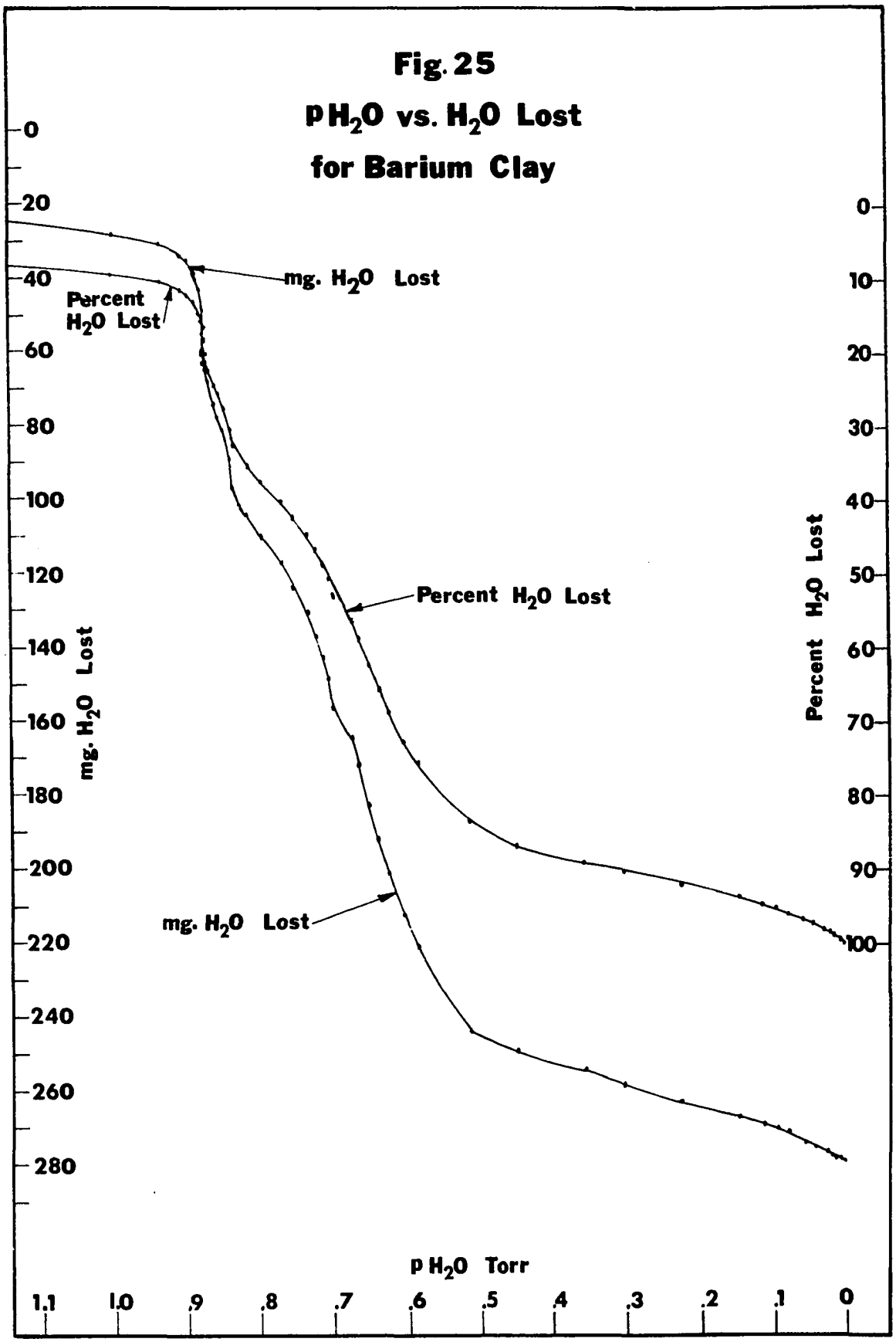


Fig. 25
p H2O vs. H2O Lost
for Barium Clay
mg. H2O Lost
Percent H2O Lost
Percent H2O Lost
mg. H2O Lost
mg. H2O Lost
Percent H2O Lost
p H2O Torr
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
0
10
20
30
40
50
60
70
80
90
100
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0

rapid water loss in all of the samples down to a pressure of 0.3 or 0.4 torr. This coincides with the plateau formed in the graphs of d(001) vs. pH_2O. The small percentage of water lost from 0.3 or 0.4 torr down to complete water loss results in all of the last period of c-axis decrease.

RESULTS AND ANALYSIS OF DATA

Table II gives the chemical analysis of the six samples used. Table III gives the analyses corrected to 100 percent. Table IV gives the calculated atom contents per unit cell.

The data in figures 6-11 indicate that the type of interlayer cation affects the way that water is lost from the interlayer space. This has also been demonstrated with regard to increasing temperatures (Kittrick, 1969a). These effects may be due to factors such as ion charge, size, hydrated radius, or number of waters of hydration.

In this study there is water lost easily at relatively high pH_2O, then water is lost gradually as the pH_2O is decreased, and finally water is lost at very low pH_2O resulting in final collapse of the expanded c-axis. For monovalent cation clays the water loss is roughly continual and gradual up to the last major change in d(001). There is no indication of more than one major step in the curve. The large d(001) change at low (less than 4 torr) pressure is temperature dependent, that is, the higher the temperature the higher the pressure at which water is lost. This is true until the last increment of d(001) decrease. The last 0.25 to 0.50 Å decrease is also temperature dependent, but much less so than the previous change. For the divalent cation clays the dehydration data indicate that there are two periods of water loss and commensurate d(001) decrease. The first loss occurs at pressure greater than 4 torr

TABLE II

MAJOR ELEMENT ANALYSES

Oxide	Sample 1	2	3	4	5	6
SiO_2	61.49	61.30	60.52	56.76	61.97	61.72
Al_2O_3	22.27	21.74	22.05	20.73	23.10	22.04
Fe_2O_3	3.05	2.73	2.81	1.72	3.10	3.25
K_2O	1.04	3.35	.21	.28	.62	.26
MgO	6.65	6.99	6.79	5.58	6.52	9.14
CaO	.156	.086	3.88	.206	.106	.040
BaO	.040	.000	.011	11.36	.006	.015
Li_2O	.025	.021	.036	.023	.980	.029
Na_2O	2.45	.029	.400	.650	.320	.140
MnO	.009	.004	.007	.000	.022	.020
TiO_2	.478	.397	.407	.417	.447	.426
Cl	.008	.041	.005	.003	.005	.004
OH	4.737	4.506	4.805	4.307	4.616	5.221
Total	102.403	101.194	101.931	102.036	101.812	102.305

TABLE III

MAJOR ELEMENT ANALYSES
(Corrected to 100 Percent)

Oxide	Sample 1	2	3	4	5	6
SiO_2	60.01	60.39	59.35	55.63	60.87	60.33
Al_2O_3	21.73	21.42	21.63	20.32	22.68	21.54
Fe_2O_3	2.98	2.69	2.76	1.69	3.03	3.18
K_2O	1.04	3.30	0.21	0.28	0.61	0.25
MgO	6.49	6.89	6.66	5.47	6.41	8.93
CaO	0.153	0.085	3.80	0.202	0.105	0.039
BaO	0.040	0.000	0.011	11.140	0.006	0.015
Li_2O	0.025	0.021	0.035	0.023	0.964	0.028
Na_2O	2.390	0.290	0.390	0.640	0.310	0.140
MnO	0.009	0.004	0.007	0.000	0.012	0.020
TiO_2	0.467	0.392	0.400	0.409	0.440	0.416
Cl	0.008	0.040	0.005	0.003	0.005	0.004
OH	4.624	4.440	4.712	4.222	4.540	5.101
Total	99.966	99.962	99.970	100.029	99.982	99.993

TABLE IV

ATOM CONTENTS PER UNIT CELL

Element	Sample 1	2	3	4	5	6
Si	7.56	7.72	7.68	7.66	7.58	7.66
Al	0.44 } 8.00	0.28 } 8.00	0.32 } 8.00	0.34 } 8.00	0.42 } 8.00	0.34 } 8.00
Al	2.79	2.96	2.98	2.96	2.90	3.22
Ti	0.04	0.04	0.04	0.04	0.04	0.04
Fe	0.28 } 4.33	0.26 } 4.58	0.26 } 4.56	0.18 } 4.30	0.22 } 4.34	0.30 } 4.77
Mn	0.00	0.00	0.00	0.00	0.00	0.02
Mg	1.22	1.32	1.28	1.12	1.18	1.21
Ca	0.00	0.00	0.26	0.00	0.00	0.00
Na	0.58	0.08	0.10	0.18	0.08	0.03
K	0.16	0.54	0.04	0.04	0.10	0.04
Ba	0.00	0.00	0.00	0.30	0.00	0.00
Li	0.00	0.10	0.00	0.00	0.48	0.01
Mg	0.00	0.00	0.00	0.00	0.00	0.24
OH	4.00	4.00	4.00	4.00	4.00	4.00
x^a	0.74	0.72	0.40	0.52	0.66	0.32
y^b	0.74	0.72	0.66	0.82	0.66	0.56

[a]Total number of cations in interlayer.

[b]Total charges on interlayer cations.

and the second at pressures less than 3 torr. An increase in temperature results in water loss at higher pressures as it does for the monovalent cation substituted clays. This is particularly marked in the first water loss and much less so in the second. As with the monovalent cation clays the temperature has only a small effect on the pressure of the last 0.25 to 0.50 Å of d(001) decrease.

For all six of the cation substituted clays there is water which is lost easily at relatively high pH_2O and water which is lost with great difficulty at low pressure. Because of this it is concluded that the bond between the clay and the water is of more than one kind. This is also indicated by the previously mentioned thermal dehydration where stepwise change in d(001) as a function of temperature is shown (Kittrick, 1969a and b) and by infrared absorption work in which changes in the peaks representing OH bonds were observed (Serratosa, 1968; Farmer, 1968; Durand et al., 1972).

It has also been shown in figures 20-25 that the amount of water responsible for the last c-axis change is small. The water lost although small in amount is responsible for a c-dimension change of from 1.90 Å to 2.47 Å depending upon the interlayer cation present. It is apparent from the plateau formation in figures 6-11 that the last loss is water that comes off with greater difficulty than that which is lost initially. As is shown in the weight loss determinations (Figures 20-25) there is a great deal of water lost with roughly equal facility before the final loss is reached.

The determination of b-axis change as a function of water loss indicates that the last water to be lost has an influence on the silicate

sheet. The bulk of the interlayer water is lost before an effect on the b-cell dimension is observed, so that the amount of water involved in shortening the b-cell dimension is small. The change in the b-cell dimension is marked and of short duration with the b-dimension returning to near its initial value upon complete dehydration. The maximum shortening in the b-axis direction in these samples varies from 0.0054 Å in the Ba clay to 0.0396 Å in the Mg clay.

The data from the graphs of d(001) vs. pH_2O (Figures 6-11) and from weight loss vs. pH_2O (Figures 20-25) are combined to give d(001) vs. percent water lost in Figures 26 and 27. It is apparent that the major

TABLE V

WATER MOLECULES PER UNIT CELL PRESENT PRIOR TO THE LAST MAJOR d(001) DECREASE

Cation	Number of H_2O Molecules	Cation	Number of H_2O Molecules
Li	1.04	Mg	1.17
Na	1.59	Ca	2.23
K	7.89	Ba	5.86

change in d(001) is during the loss of the last 10 to 20 percent of the water. The weight of water lost between a given percentage of loss and 100 percent loss is known (see Figures 26 and 27) as is the weight of clay on which the determination was made. From these data the number of water molecules per unit cell which are present just prior to the last collapse have been calculated and are given in Table V. The estimated error in these values is $\pm$ 0.1 water molecules per unit cell. It is

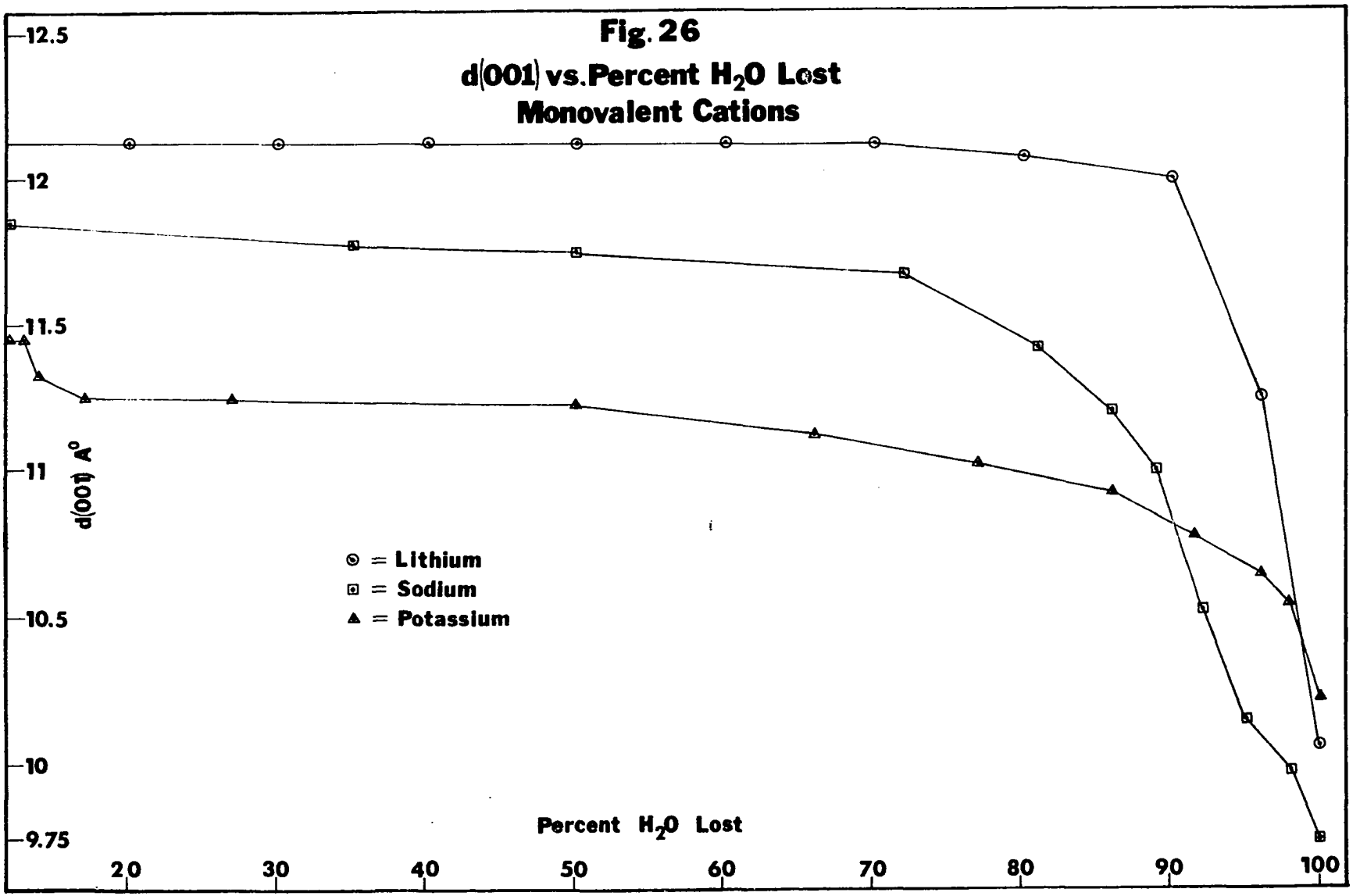


Fig. 26
d(001) vs. Percent H_2O Lost
Monovalent Cations
12.5
12
11.5
11
10.5
10
9.75
d(001) A°
⊙ = Lithium
⊡ = Sodium
▲ = Potassium
Percent H_2O Lost
20
30
40
50
60
70
80
90
100

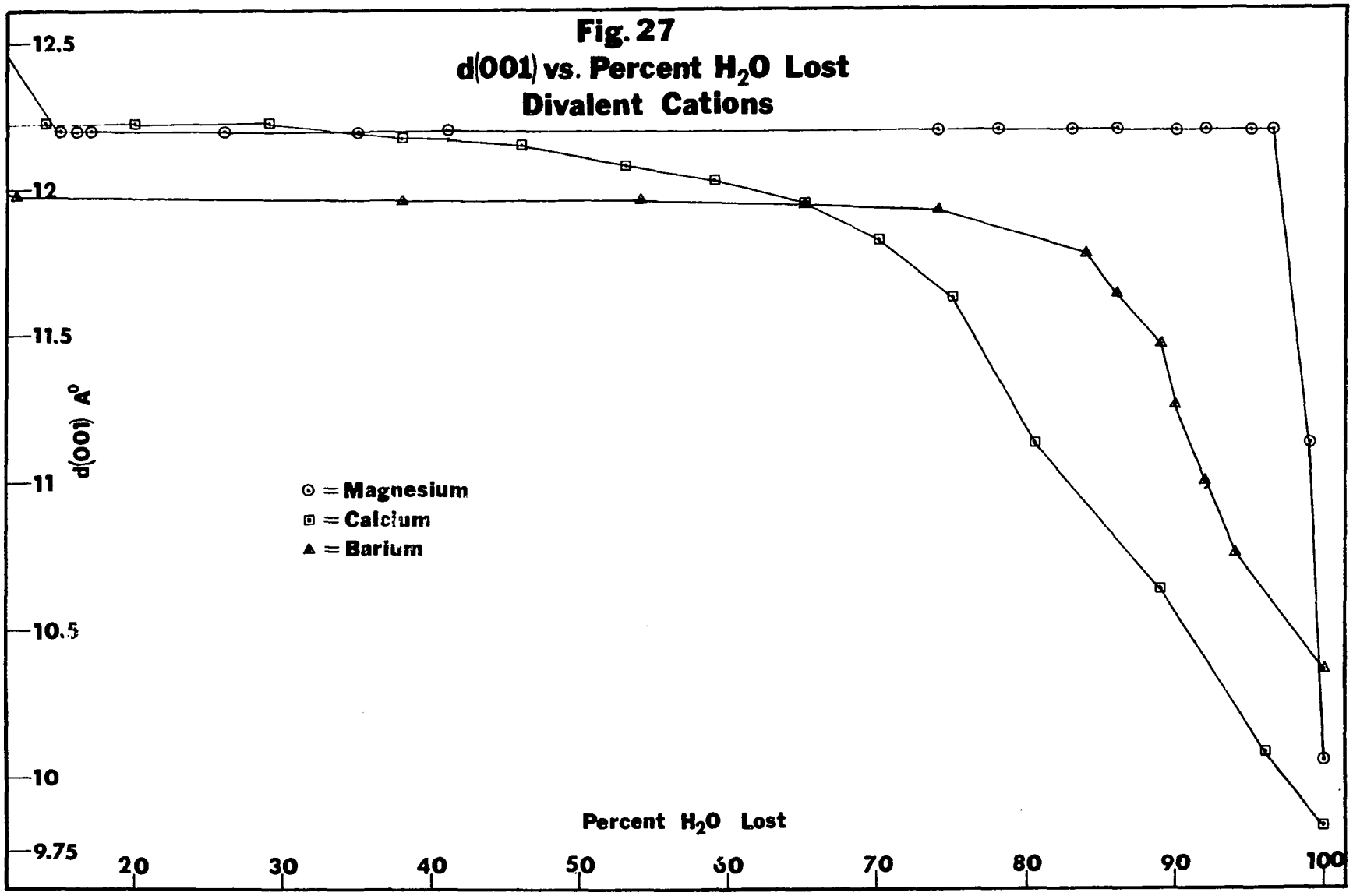


Fig. 27
d(001) vs. Percent H2O Lost
Divalent Cations
12.5
12
11.5
11
10.5
10
9.75
d(001) A°
⊙ = Magnesium
⊡ = Calcium
▲ = Barium
Percent H2O Lost
20
30
40
50
60
70
80
90
100

evident that the number of molecules of water per unit cell which are present before the last c-axis decrease is small. It should be emphasized that the data in Table V do not indicate that this is the maximum number of water molecules that may be present when the clay is expanded to "one" water layer, but only the number that are lost during final collapse, or from a different point of view, the number that are required to prop up the structure.

Figure 28 shows the number of water molecules lost during final collapse plotted against moles of H_2O hydrated on the various cations (Grim, 1953), hydration energy of the cations (Cotton and Wilkinson, 1967), and the ionic radii of the cations (Fyfe, 1964). It is seen that the number of water molecules lost during final collapse decreases as hydration energy increases. If the water were present as hydration spheres on the cations it would seem reasonable to expect the most water to be associated with the cations having the highest hydration energy. Other workers have also indicated that this is not the case (Grim, 1953). From the data in Figure 28 it appears that there is an excellent correlation between the number of molecules of water involved in the last collapse and the cation size. As the ion size increases the number of molecules increases, that is, the large cations coordinate more water than the small. On the basis of the data presented in Figure 28 it is concluded that the last water to be lost is not water of hydration and that the cation size has more influence on the water structure than has hydration energy. The break in the line for ionic radius vs. water loss is compatible with the allowable coordination numbers of the cations if a radius of 1.40 Å is assumed for the water molecule. It must again be emphasized

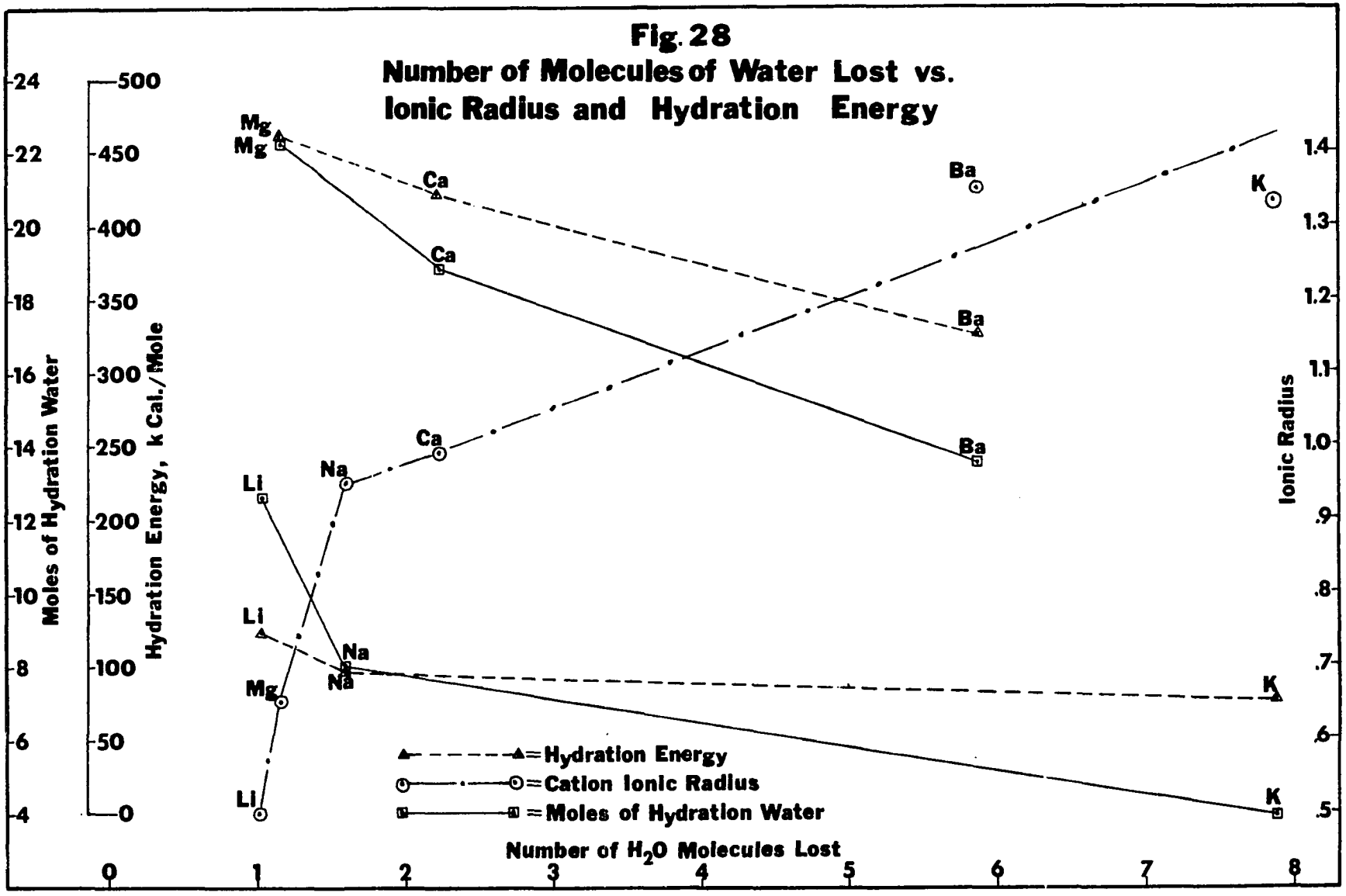


Fig. 28
Number of Molecules of Water Lost vs.
Ionic Radius and Hydration Energy
Moles of Hydration Water
Hydration Energy, k Cal./Mole
Ionic Radius
Number of H_2O Molecules Lost
Mg
Ca
Ba
K
Li
Na
=Hydration Energy
=Cation Ionic Radius
=Moles of Hydration Water

that the data in Figure 28 apply only to that water necessary to prop up the structure. This does not negate the possibility of the presence of hydration water on the cations or water hydrogen bonded to the silicate oxygen surface at slightly higher water contents. In fact this is likely in view of the large amount of water lost without appreciable c-dimension change just prior to the final collapse.

SUGGESTED STRUCTURE OF THE INTERLAYER WATER

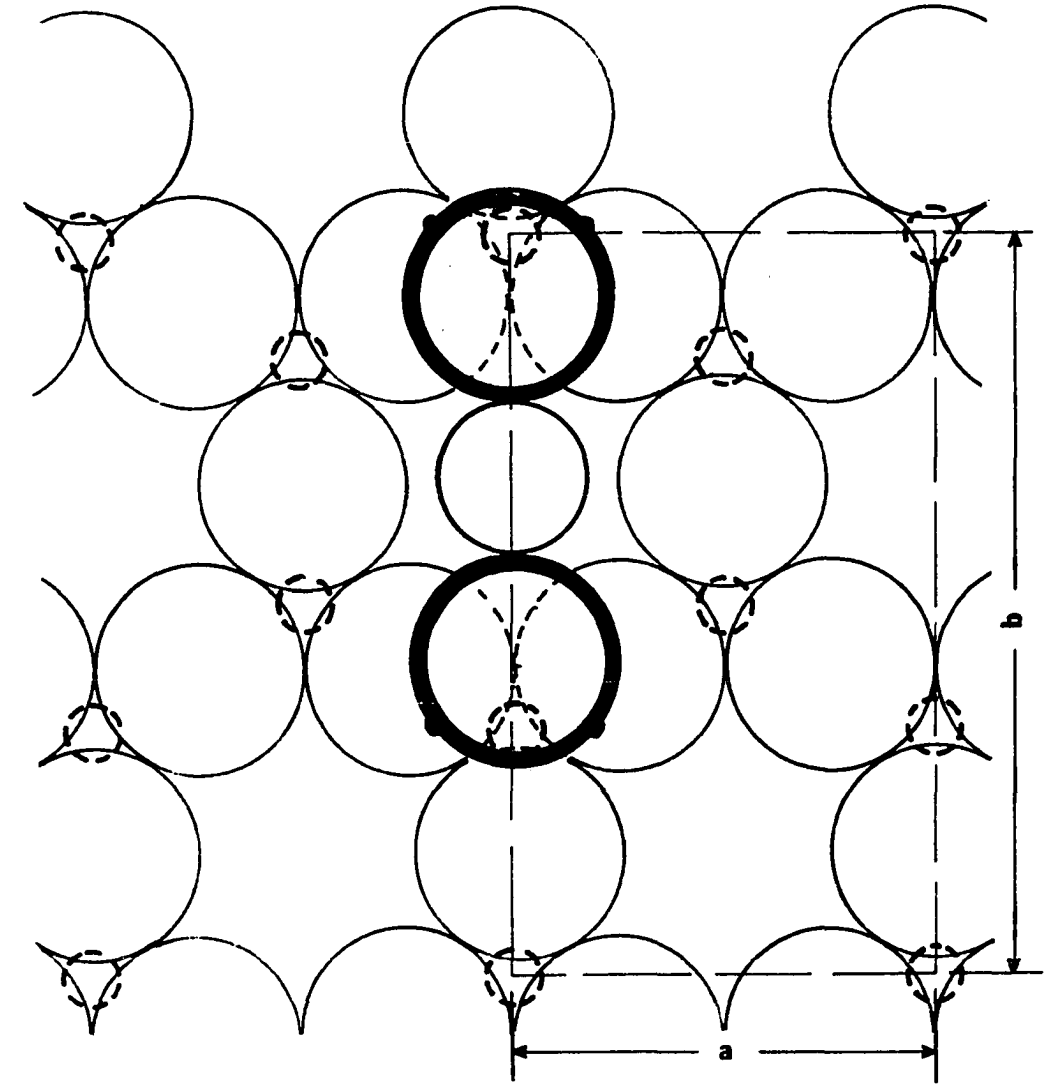
The water structure suggested in this study is that of water molecules bonded both to the clay structure and to the interlayer cation. In this the two negative poles of the water oxygen, which are more or less tetrahedrally-disposed with respect to the hydrogens, are bonded to the interlayer cation and to the silicon of the hexagonal ring of silicon-oxygen tetrahedra surrounding the cation (see Figure 29).

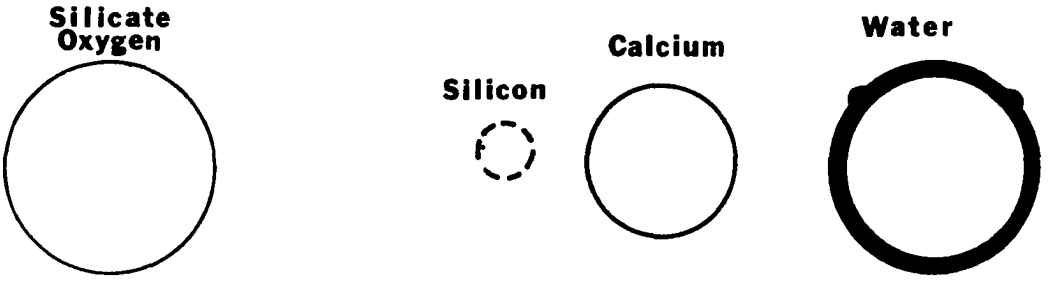
A structure of this nature requires explanation in terms of how it explains the previously-described observations and in terms of the bond configuration necessary for such a structure. The following discussion includes consideration of the observed b-axis change and the possible ways that it can be explained, the oxygen of the water molecule and the silicon of the surface tetrahedra and their possible bond configuration, and lastly supporting observations from infrared spectroscopy, nuclear magnetic resonance, and thermodynamic studies by others. Also discussed in terms of the proposed structure is the relative expandability of different cation substituted montmorillonites.

It is assumed that the change in b-dimension as a function of water content requires that the water be bonded in some manner to the silicate layer. This could be by hydrogen bonding to the silicate oxygens, by bonding of the cations to the silicate oxygens and to the water, or by linkage of the water oxygens and the silicons of the

Fig. 29

Suggested Structure for Interlayer Water on Calcium Montmorillonite





tetrahedra. The hydrogen bonding of water to the silicate oxygen surface could produce the b-axis shortening due to epitaxy between structured water and the silicate surface as suggested by Ravina and Low (1972). In the study by Ravina and Low the maximum b-dimension change is approximately 0.06 Å, whereas those of this study range from 0.0054 Å to 0.0396 Å. Since the determinations in this study were at water contents below those of Ravina and Low, where c-cell dimensions in excess of 200 Å were observed, it would appear that their suggested epitaxial structure could account for the higher values of change in b. That is, there is b-cell dimension change at very low pH_2O and there could be additional change at higher pH_2O. The air-dried clay used by Ravina and Low, which was in equilibrium with 10 percent relative humidity, at presumably 25°C, would be at a higher water content than that at which b-cell dimension change was observed in this study. An additional difference between this study and that of Ravina and Low is the return of the shortened b-dimension to higher values on complete dehydration. Since their study did not include water contents below about 2.3 torr this type of b-cell dimension change presumably would not be observed. If an epitaxial structure between the water and the silicate lattice results in increasing b-dimension with increasing water content as Ravina and Low indicate then b should not increase on the absence of water. Therefore the b-cell dimension change at low water content should not be due to water in epitaxial arrangement with the silicate layer. The epitaxy is probably between the water taken on at higher states of hydration and the water adsorbed initially in a different orientation. As was described in the section on previously-suggested water structures the

water structure suggested by Ravina and Low has one hydrogen of each water pointed down, toward the silicate surfaces. This does not agree well with the nuclear magnetic resonance work of Woessner and Snowden (1969) which indicates that the water molecules are oriented parallel to the clay surfaces. It also does not explain the high hydrogen ion activity at low water content (Woessner and Snowden, 1969; Durand et al., 1972; Fripiat et al., 1969), which was discussed in the section covering observations on the montmorillonite-water system, nor does it allow for any relationship between the interlayer cations and the structured water. The other two ways of affecting the b-cell dimension, bonding of the water to the cation and silicate oxygens or bonding of the water to the cation and silicate silicons, can be looked at from the standpoint of possible shortening forces. If water is bridging between either oxygen or silicon and the cation there is a misfit and a tendency to pull the cation toward one side of the ring of tetrahedra. For example if water bridges between a potassium cation and the silicons on opposite sides of the ring the Si-Si distance in the b-axis direction is 6.04 Å and the sum of one-half of two waters (one on each side of the potassium) plus a potassium ion is 5.42 Å to 5.66 Å depending on the assumed size of the water molecule (Franks, 1972). If such a bond does exist there is bond stretching and bond bending or both to accommodate it. Using an idealized model of six waters bonded to the cation and to each of the silicons of the tetrahedra in one ring the shortening components in the a and b directions can be calculated. In effect this is a calculation of the bond vectors with respect to the a- and b-axis directions that would be involved in bonding between the cation and six water molecules

located on the silicate ring. With six waters, the structure is in equilibrium with respect to stress on the ring of tetrahedra. Loss of water, presumably at random, would result in disequilibrium and allow distortion of the ring. Shortening due to loss of water from any of the tetrahedral silicons or shared ring oxygens would have an a- and b-axis component. For water bonded to the silicons the ratio of shortening components in the b and a direction is 8.000 to 6.928, a small but real tendency toward shortening in the b rather than the a direction. The same analysis for water bonded to the silicate oxygens yields a b to a shortening component ratio of 6.900 to 7.460, a tendency to shorten the a-axis rather than the b-axis. Since shortening in the b-axis direction is expected and observed the bridging from cation to silicate oxygen is unlikely. The idealized model assumes six molecules of water per ring which is more than is observed in some cases. The object of the model is to indicate that loss of water from random silica tetrahedra will result in shortening in the b-axis direction. There is no reason to assume and no evidence from this study that water is associated with preferred tetrahedra. Whatever association there is, therefore, should be random and the ratios indicated by the model are proportional to the relative tendency to b and a shortening.

If a structure like that proposed exists it requires a bond between water and the silicon of the tetrahedra. For this both oxygen and silicon must be compatible with such a bond. The suggested structure can be considered from either valence bond or molecular orbital theory. Molecular orbital theory is perhaps more applicable since interaction between molecules is involved.

The oxygen of water has a charge which is disposed more or less tetrahedrally around the atom. The angle between the two negative poles is not a tetrahedral angle of 109^{o} but is variable between about 111^{o} and 127^{o} depending on the compound in which it exists (Cotton and Wilkinson, 1967). The oxygen forms four sp^3 hybrid orbitals which may not be equivalent (Cotton and Wilkinson, 1967). The oxygen of the water in the proposed structure would have one electron lone pair pointed downward toward the silicon and the other pointed toward the interlayer cation. Oxygen can be four coordinate but it is uncommon as such and would be more likely to be three coordinate (Cotton and Wilkinson, 1967). If it is three coordinate one significant possibility is the loss of a hydrogen. This will be discussed later. Water can act as a bridge between two metal cations by bonding to the cations and losing a hydrogen (Cotton and Wilkinson, 1967). This could also be the source of OH in the interlayer that was mentioned in the discussion of the structure proposed by McConnell in which silica tetrahedrons were replaced by OH_4 tetrahedrons.

To bond to the silicon atom without completely disrupting the tetrahedral arrangement requires the use of a silicon d orbital. Silicon d orbitals can take part in bonding as can d orbitals for P, S, and Cl in SiO_4^{-4}, PO_4^{-3}, SO_4^{-2}, and ClO_4^{-} (Cotton and Wilkinson, 1967). In these compounds it is the overlap of the central atom d orbital with p orbitals of the coordinated atoms (Cruickshank, 1961). The d orbital is available for bonding as in trisilylamine, where the silicon d orbitals are of low enough energy to overlap with the nitrogen $2p_z$ orbitals (Cotton and Wilkinson, 1967). In this study the proposed silicon to oxygen bond, however, would be (p-d) σ bonding. It is difficult to say

which d orbital would be employed in such a bond. The most likely appears to be the d_z^2 orbital which is along the z axis of the tetrahedral sp^3 Si hybrid in the Si-O tetrahedra. This orbital can overlap the water oxygen reducing the symmetry of the Si-O moiety from Td (tetrahedral) to C_{3_v} (3-fold rotation axis). That is, the bond angles in the Si-O tetrahedra would be expected to change little due to the relatively weak linkage. However, the formal symmetry would be reduced by coordination of the fifth oxygen to the silicon. This would likely yield the dsp^3 hybrid which is a trigonal bipyramid formed of five non-equivalent orbitals, the s, p_x, p_y, p_z, and d_z^2.

If such a structure exists there should be observable consequences other than the effect on the b-axis. One result would be stronger bonding of the water to the clay than can be accounted for by hydrogen bonding. Water has been observed to be retained on montmorillonite under vacuum at 100°C (Serratosa, 1968) and at temperatures in excess of 300°C (Low and White, 1970) where, if hydrogen bonding were the lone mechanism, evaporation and loss of interlayer water should have resulted. An additional ramification of this structure would be an increase in hydrogen ion activity with respect to liquid water through weaker bonding of water oxygen to the water hydrogens or loss of hydrogen and formation of a bridging OH. Durand et al. (1972), Low and White (1970), Fripiat et al. (1969), and Farmer (1968) have indicated weaker bonds between oxygen and hydrogen or increased hydrogen ion activity through infrared absorption work. There are also many indications that hydrogenation of organic molecules takes place in the interlayer space (Jang and Condrate, 1972; Durand et al., 1972; Fripiat et al., 1969; Farmer,

1968). It is pertinent to note, since the proposed structure is that of the last water lost and not of interlayer water in general, that, as mentioned previously, in the study by Durand et al., the transalkylation $NH_3 \rightarrow NH_4^+$ takes place only at low water content. That is, low water content is required for protonation. At higher water contents there would be water other than the initially adsorbed water. Serratosa (1968) showed that the amount of hydrogen bonding observed by infrared absorption decreased on evacuation and that the new bands observed represented water coordinated to the cations. It appears that the water in the interlayer exhibits hydrogen bonding, perhaps overshadowing other types, but that on evacuation and loss of most of the water the bond between water and cation becomes visible.

Another observable consequence of this structure would be the orientation of the water molecules. With the two lone pairs of the water oxygen bonded to the cation and silicon, and if the cation is not immersed in the hole in the tetrahedral sheet, the water molecule is tilted away from the cation and the two hydrogens of the water oxygen approach parallelism with the clay sheet. As was mentioned previously the nuclear magnetic resonance work of Woessner and Snowden (1969) indicates that the water molecules are parallel to the clay sheet. This work, as with the previously-mentioned infrared work, also indicates that there is a highly-ionized network of protons undergoing rapid exchange on the clay (Woessner and Snowden, 1969).

Another observable consequence of relatively strongly bonded water should be an entropy decrease of the water as compared to liquid water. As water is bonded to the clay interlayer cations and silicate

silicons it becomes highly ordered and should exhibit an exothermic reaction that is at least greater than the heat of wetting of the cations involved. Thermodynamic studies by Kittrick (1969b) indicate that the observed entropy decrease, going from liquid water to sorbed water, on hydration of vermiculite is greater than that attributable to hydration of the cation alone. For a sodium vermiculite the decrease is 13.2 k cal./mole of Na. The entropy of hydration of sodium is 6.2 k cal./mole. The difference, 7.0 k cal./mole is attributed by Kittrick (1969b) to hydration of negative charge sites. Since the hydration of negative charge sites is hypothetical, it does not seem unreasonable that some or all of this entropy decrease could be due to strong bonding of the water to silicon and the interlayer cation as is suggested for montmorillonite. The entropy decrease found on hydration of montmorillonite is not as great as that in vermiculite. Kijne (1969) discusses decrease in entropy for sorbed water compared to liquid water for sodium and calcium montmorillonites. In these, the water molecules with surface coverage of less than 0.1 for Ca- and 0.25 for Na-montmorillonites, the adsorbed water molecules had zero degrees of freedom. He also found that the entropy values for sorbed water were below that of liquid water for Ca, Na, and Li cations. Cs and Rb apparently increase the entropy. The largest entropy decrease is found at low partial pressure of water with entropy values increasing to near, but below, that of liquid water with increasing partial pressure of water. A large entropy decrease would be expected for the initially adsorbed water in the suggested structure. As more water is adsorbed with higher partial pressures of water the entropy would increase because the added water would be hydrogen bonded

to the initially adsorbed water rather than to the silicon and the interlayer cation. Kijne (1969) found that heat of wetting values were high at low water content and that they decreased with increasing water content. He also noted a marked discontinuity in heat of wetting vs. partial pressure of water, which were observed at low pressure. Such a discontinuity would be expected with the suggested structure. The initially adsorbed water will exhibit high heat of wetting as the cation and silicon become linked to the water oxygen. When this process is completed the additional water will be bonded by hydrogen bonding to the initially-adsorbed water or silicate oxygens or by additional hydration of the interlayer cations and will therefore exhibit a lower heat of wetting. There will be a discontinuity because the first process will go to completion or nearly so before the second can begin.

One observation that a structure for interlayer water must explain is the difference found in the maximum expansion of the clay as a function of the interlayer cation present. The expansion of Li and Na clays is essentially unlimited whereas the expansion of K, Ca, Mg, and Ba clays is limited to values less than about 16 Å. The ratio of charge to radius of the interlayer cation should be considered as a possible cause of the difference in expandability. Mg and Ca have a high value of charge/radius, 3.07, and 2.14 respectively, and are limited in expandability. Ba is limited in expandability but its value of charge/radius of 1.48 is less than that of Li, which has a charge/radius value of 1.66, and which is unlimited in expandability. K, with the smallest value of charge/radius, among the cations in this study, 0.74, is also limited in expandability. From another standpoint, if strength of cation

charge is limiting expansion then the cation with the highest value of charge/radius should limit expansion the most. Using two approximately size equivalent cations, Ca and Na, the Ca should limit expansion to a greater extent than Na. If Ca and Na clays are equilibrated at atmospheric moisture the Ca clay develops two "water layers" whereas the Na clay develops only one. This does not agree with Ca having a greater tendency to limit expansion and therefore it is felt that charge/radius value is not sufficient to account for the observations.

If the water associated with the interlayer cation is considered to be chemically bonded rather than water of hydration then the resulting structure can be looked at crystallographically rather than as ions in solution. The interlayer cations can be thought of as in coordination with oxygen, particularly if one of the water hydrogens is dissociated. In this case the Li, Na, and K can be considered to act as in Li_2O, Na_2O, and K_2O, all of which as crystals have the calcium fluoride structure. MgO, CaO, and BaO, however, crystallize in the sodium chloride structure (Fyfe, 1964). In the CaF_2 structure the univalent Na has four nearest neighbors whereas in the NaCl structure the divalent calcium has six nearest neighbors. This results in an electrostatic bond strength of 0.25 for Li, Na, and K, and 0.33 for Mg, Ca, and Ba. The attractive force for the coordinated water oxygens would be greater for calcium than for sodium by 32 percent. This is the least difference in electrostatic bond strength to be expected. It may be, however, that if the water molecule dissociates and gives up a hydrogen ion that the cations are bonded to essentially a large univalent anion. Since the coordination number of any ion is a function of

cation to anion radius ratio, changing the size of either can result in a change in the coordination number. These cations bonded to a large univalent anion would coordinate as LiF, NaF, KF, or KOH, all of which crystallize in the NaCl structure (Fyfe, 1964). They would then have six nearest neighbors possible and an electrostatic bond strength of 0.166, or 50 percent less than the divalent interlayer cations. This may be a sufficient difference to account for the 15.5 Å expansion maximum for Ca, Mg, and Ba as the interlayer cation and the effectively unlimited expansion of Li and Na clays. Potassium, presumably because of its size and proximity to the silicate oxygens, reacts differently and has limited expandability. There is an additional indication that coordination and resulting electrostatic bond strength may explain relative expandability. For Ca as the interlayer cation there would be a stronger attraction than with Na. For the expanded state "double layer" of water molecules there would be three above and three below the cation, coordinated to the cation and silicon of the clay structure. For less strongly bonded Na as the interlayer cation when hydration exceeds the "monolayer" state the Na should move closer to one clay plate than the other with water filling in with some other bonding configuration above or below. Lailach et al. (1968) and other workers have shown that the monovalent cations tend to be closely associated with the oxygen surface on hydration and that the divalent cations occupy positions between the layers. If this is the case then the amount of the last water to be lost should reflect the presence of water bonded primarily to one silicate layer or to two silicate layers depending on the cation charge. Table VI gives the number of water molecules lost per cation

during final collapse. Again, the number of molecules lost is not all that is lost during dehydration but only those responsible for collapse. For Li, Mg, and Na, Ca, almost size equivalent pairs the divalent cations are coordinated to approximately two times as much water as the monovalent. For K and Ba the relationship fails, presumably because of other interferences due to their large size and proximity to the silicate oxygens. From these data it is apparent that linkage of the monovalent cations to only one layer and linkage of the divalent cations to one layer above and one below is reasonable.

TABLE VI

WATER MOLECULES LOST PER CATION

Cation	Molecules Lost	Cation	Molecules Lost
Li	1.57	Mg	3.65
Na	2.14	Ca	5.57
K	10.95	Ba	11.27

The magnitude of d(001) change should be considered here. It might be assumed that the change in d(001) for divalent cations should be twice that of the monovalent cations. This would not be the case. Water coordinated to the interlayer cation would assume the most stable configuration. For this, in the case of six water molecules around the cation, three above and three below, the water molecules would be offset by 60^{o} alternating from top to bottom to reduce the mutual repulsion. In this case water bonded to two clay surfaces would take up no more

space in the d(001) direction than water bonded to monovalent cations. If the minimum d(001) attainable at higher temperatures or lower pressures than those used in this study is assumed to be 9.6 Å then the amount of allowable collapse observed in these samples is quite similar. There is some variability but the amount is reasonable in terms of the molecular size of water. Table VII gives the maximum allowable collapse for the six cation forms. This is not the observed collapse in that not all of the water could be removed from all of the samples at the temperatures and pressures employed. The d(001) decrease that would be caused

TABLE VII

MAXIMUM ALLOWABLE COLLAPSE ON LAST WATER LOSS IF 9.6 Å MINIMUM IS ASSUMED

Cation	Collapse	Cation	Collapse
Li	2.75	Mg	2.60
Na	2.55	Ca	2.65
K	2.60	Ba	2.40

by one thickness of water molecules, if the size of the water molecule is assumed to be 2.80 Å diameter, is less than 2.80 Å. This is due to the water oxygen being interstitial to the basal silicate oxygen triad. How much less than 2.80 Å the spacing should be is questionable since there may be some water present that is not interstitial to the silicate oxygens, causing a slight increase, and since the Si-O bond between clay and water may pull the water oxygen closer to the clay sheet, causing a decrease. The average of the values in Table VII is 2.59 Å which is

0.21 Å less than one water layer thickness. This would mean that the interstitial fit of water oxygens into the basal oxygen triad is roughly 0.1 Å which appears to be a reasonable value.

CONCLUSIONS

The interlayer water in montmorillonite is held onto the clay by more than one type of bonding so that successive stages of loss are exhibited on dehydration. The first water to be lost is probably hydrogen bonded to either the silicate oxygens or to more strongly held water molecules, or is possibly water of hydration on the interlayer cations. The last water to be lost, that which is responsible for the final c-axis decrease, is bonded both to the interlayer cation and to the silicon of the tetrahedra. Random loss of this water distorts the silicate structure resulting in b-axis shortening until all of the silicon coordinated water has been lost. At complete dehydration the silica tetrahedral network resumes an undistorted configuration with the b-axis dimension returning to near its initial value. The bond between the silicon and the water oxygen is through an oxygen p orbital and the silicon d_z^2 orbital in a (d - p) σ configuration. The silica tetrahedron thereby becomes a trigonal bipyramid with dsp^3 hybrid orbital orientation. The water molecule, as a result of its bonding to the interlayer cation and the silicon of the clay structure has loosely bound hydrogens which result in high hydrogen ion activity and the availability of protons for hydrogenation of some materials, such as NH_3, adsorbed on the interlayer space.

The coordination of water oxygens around the cation results in a bond across the interlayer space from silicate sheet to water to cation to water to silicate sheet which serves to tie successive clay platelets together. The strength of the bond across the interlayer space as a function of cation type ranges from a minimum difference of 0.25 for monovalent to 0.33 for divalent, to a maximum difference of 0.16 for monovalent and 0.33 for divalent. The attractive forces between clay platelets with monovalent cations in the latter case would be 50 percent less than clay with divalent interlayer cations. The continued expansion on additional hydration of the clay is therefore more likely with monovalent cations than with divalent cations.

REFERENCES CITED

Barshad, I., 1949, The Nature of Lattice Expansion and its Relation to Hydration in Montmorillonite and Vermiculite: Am. Min., v. 34, p. 675-684.

Cotton, A. F., and Wilkinson, G., 1967, Advanced Inorganic Chemistry: New York; Interscience Publishers, p. 43, 361, 362, 410.

Cruickshank, D. W. J., 1961, The Role of 3d Orbitals in π Bonds Between (a) Silicon, Phosphorous, Sulphur, or Chlorine and (b) Oxygen or Nitrogen: J. Chem. Soc., v. 1961, p. 5486-5504.

Durand, B., Pelet, R., and Fripiat, J. J., 1972, Alkyl-ammonium Decomposition on Montmorillonite Surfaces in an Inert Atmosphere: Clays and Clay Minerals, v. 2, p. 21-34.

Farmer, V. C., 1968, Infrared Spectroscopy in Clay Mineral Studies: Clay Minerals, v. 7, #4, p. 373-384.

Franks, F., 1972, Water, A Comprehensive Treatise, Volume 1 the Physics and Physical Chemistry of Water: New York; Plenum Press, p. 101-102.

Fripiat, J. J., Pennequin, M., Poncelet, G., and Cloos, P., 1969, Influence of the Van Der Waals Force on the Infrared Spectra of Short Aliphatic Alkyl-ammonium Cations Held on Montmorillonite: Clay Minerals, v. 8, p. 119-134.

Fyfe, W. S., 1964, Geochemistry of Solids: New York, McGraw-Hill Book Company, p. 38, 42, 46.

Grim, R. E., 1953, Clay Mineralogy: New York, McGraw-Hill Book Company, p. 60, 61-62, 147-148, 165-174, 175-188, 220-230, 282-283.

Hendricks, S. B., and Jefferson, M. E., 1938, Structure of Kaolin and Talc-Pyrophyllite Hydrates and Their Bearing on Water Sorption of Clays: Am. Min., v. 23, p. 863-875.

Jang, S. D., and Condrate, R. A., 1972, The I. R. Spectra of Lysine Adsorbed on Several Cation-substituted Montmorillonites: Clays and Clay Minerals, v. 20, p. 79-82.

Kerns, R. L., 1967, Particle Size Separation of Clays: Oklahoma Geology Notes; v. 27, #9, p. 167-179.

Kerns, R. L., and Mankin, C. J., 1968, Structural Charge Site Influence on the Interlayer Hydration of Expandable Three Sheet Clay Minerals: Clays and Clay Minerals, v. 16, p. 73-80.

Kerr, P. F., 1959, Optical Mineralogy: New York; McGraw-Hill Book Company, p. 412-413.

Kerr, P. F., and Hamilton, P. K., 1950, Reference Clay Minerals, A.P.I. Proj. #49, Preliminary Reports 1-8; New York, Columbia Univ.

Kijne, J. W., 1969, On the Interaction of Water Molecules and Montmorillonite Surfaces; Soil Sci. Soc. Amer. Proc., v. 33, p. 539-542.

Kittrick, J. A., 1969a, Interlayer Forces in Montmorillonite and Vermiculite; Soil Sci. Soc. Amer. Proc., v. 33, p. 217-221.

_____, 1969b, Quantitative Evaluation of the Strong Force Model for Expansion and Contraction of Vermiculite; Soil Sci. Soc. Amer. Proc., v. 33, p. 222-225.

Lahav, N., and Bresler, E., 1973, Exchangeable Cation-structural Parameter Relationships in Montmorillonite: Clays and Clay Minerals, v. 21, #4, p. 249-255.

Lailach, G. E., Thompson, T. D., and Brindley, G. W., 1968, Absorption of Pyrimidines, Purines, and Nucleosides by Li-, Na-, Mg-, and Ca-Montmorillonites (Clay-Organic Studies XII): Clays and Clay Minerals, v. 16, p. 285-291.

Low, P. F., and White, J. L., 1970, Hydrogen Bonding and Polywater in Clay-Water Systems: Clays and Clay Minerals, v. 18, p. 63-65.

Low, P. F., Ravina, I. and White, J. L., 1970, Changes in b-Dimension of Na-Montmorillonite with Interlayer Swelling: Nature, v. 226, London, p. 445-446.

Macey, H. H., 1942, Clay-Water Relationships and the Internal Mechanism of Drying; Trans. Ceram. Soc, v. 41, p. 73-121.

Mackenzie, R. C., 1950, Some Notes on the Hydration of Montmorillonite: Min. Soc. Gr. Britain Clay Mineral Bull, v. 4, p. 115-120.

Mamy, J., 1968, Hydration of Montmorillonite, Dielectric Properties and Structure of the Water Film I and II: Annuls. Agron, v. 19, #2, p. 175-246.

Marshall, C. E., 1949, The Colloid Chemistry of the Silicate Minerals; New York; Academic Press, p. 41-48.

McConnell, D., 1950, The Crystal Chemistry of Montmorillonite: Am. Min., v. 35, p. 166-172.

McEwan, D. M. C., 1951, The Montmorillonite Minerals, "X-ray Identification and Structure of the Clay Minerals": Monograph, Min. Soc. of Gr. Britain, v. 86, p. 86-137.

Mehra, O. P., and Jackson, M. L., 1960, Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate: Clays and Clay Minerals, Monograph No. 5, New York, Pergamon Press, p. 317-327.

Mering, J., 1946, On the Hydration of Montmorillonite: Trans. Faraday Soc., v. 42B, p. 205-219.

Polyakov, V. E., 1968, Preparation of Cation-Substituted Types of Clay Minerals: Ukr. Khim. Zh., v. 34, #5, p. 526-528.

Ravina, I., and Low, P. F., 1972, Relation Between Swelling, Water Properties, and b-Dimension in Montmorillonite-Water System: Clays and Clay Minerals, v. 20, #3, p. 109-120.

Serratosa, J. M., 1968, Infrared Study of Benzonitrile (C_6H_5-CN)-Montmorillonite, the Montmorillonite Complexes: Am. Min., v. 53, p. 1244-1251.

Woessner, D. E., and Snowden, B. S., Jr., 1969, A Study of the Orientation of Adsorbed Water Molecules on Montmorillonite Clays by Pulsed N.M.R.: Jour. of Coll. and Interf. Sci., v. 30, #1, p. 54-68.