

INTERFACIAL INTERACTION OF WATER
AND SILICATE MINERALS

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ABSTRACT

This program has relation to the categories of the nature of water and water cycle. In particular, the study deals with the basic interactions of water with the surface of minerals. The program has direct application to the areas groundwater and water in soils in the category of water cycle. We have investigated the problems of bonding and migration of water molecules upon sheet structures of mineral samples. The minerals used in the program have surface structures that are similar and in some cases identical to those found in clays. This study focused upon the molecular level rather than on the bulk property level of capillarity and hydraulics.

The interlayer binding energy of selenite was measured. The measurements were made within a test chamber in which the temperature and atmospheric pressure of the sample could be controlled and monitored. There was found to be no significant difference in the IBE of selenite in air (716 ergs/cm^2) and in vacuum (704 ergs/cm^2). There was found to be a slight difference in the low temperature IBE (768 ergs/cm^2) and the high temperature IBE (720 ergs/cm^2); however, this was attributable to effects of cold on the mechanism. It was concluded that the IBE is independent of atmospheric and temperature effects within the range of temperature and pressure studied.

The IBE of ionic bound lamella of Muscovite Phlogopite, Margarite, and Xanthophyllite has been calculated.

Temperature dependence of water mobilities has been studies in the cleavage chamber and in the Varian-MAT SMI-B high resolution, double focus mass spectrometer.

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STATEMENT OF THE PROBLEM

The mechanism of water molecules bonding to and migration over interfacial boundaries is fundamental to problems of subsurface water flow and storage. While extensive efforts are being carried out on the basis of macroscopic mechanics and hydraulics, little has been attempted on the microscopic level of atomic mechanisms. It is recognized that the amount of water transport required to be of use in the area of water resources might well be in quantities large enough to allow the use of bulk properties and macroscopic mechanics. However, until the degree of hydration reaches a level where capillary action, bulk diffusion, adsorption, and other macroscopic mechanisms are valid, initiating processes based upon the molecular parameters of the fluid and the crystal structure of the minerals involved ellipses -- must be employed for a complete understanding of the water-interface interaction. The major thrust of this investigation has been to extend the study of the transport and storage of subsurface water to the molecular level. The basic parameters of this study are molecular rather than bulk.

This program features a multi-disciplinary approach to fundamental problems in hydroscience. The general area of study is the physics and chemistry of water at a silicate sheet interface. In detailed terms, the study of the bond-

ing energies of ionic (muscovite) and hydrogen (selenite) bound lamellar solids, the quantitative influence of water vapor upon the bonding energies (specific surface energies), and the rate of surface diffusion of water across the surface of the lamellar sheets.

Applications of the information gathered in this study will be of assistance, if not necessary, to the hydroscientist in proposing or constructing models for subsurface water movement and storage. Here are listed some of the possible areas of application of the results of this study to the general problems of water resources.

- 1) The effect of monolayers on evaporative heat and mass transfer from clay surfaces.
- 2) Prediction of water movement in unsaturated soils.
- 3) The extent and strength of hydrogen bonding of interfacial soil water.
- 4) The effect of clay adsorbed water on the water flow characteristics of clay water system.
- 5) The physics and chemistry of soil water.
- 6) To establish realistic models for the reaction of water with soil.
- 7) The effect of clay type (crystal surface structure) upon capillary-diffusion of water in unsaturated soils.

- 8) The hydraulic movement of water through porous materials.
- 9) Shear strength of clay minerals for clay embankments.

SELENITE

Introduction

Selenite provides a convenient lamellar structure for the study of hydrogen bonding since its principal cleavage planes are believed to be hydrogen bound.1/ A measurement of the interlayer binding energy of selenite will give the value of the hydrogen bond strength.

The hydrogen atom has only one valence electron (1s), thus it should form chemical bonds with only one other atom. Under certain conditions a hydrogen atom is attracted by strong forces from two electronegative atoms. Thus, the hydrogen atom acts as a bond between the two atoms. This hydrogen bond is formed between only the most electronegative atoms and is believed to be largely ionic in nature.2/ The hydrogen bond in its most ionic form is formed by a bare proton which has lost its electron to another atom in the molecule. The proton then is attracted to negative atoms and forms hydrogen bonds with the atom. One common example of hydrogen bonding is in ice.2/

The hydrogen bond is relatively weak, only about 5 kilocalories per mole, however, it has a great importance in determining the properties of a substance. Hydrogen bonds have the effect of increasing the boiling and melting points of substances above what would normally be expected. It is the hydrogen bond that is responsible for the melting point of water to be higher than the value predicted by extrapolation from the values of similar compounds.2/

In a hydrogen bonded compound, the hydrogen atom generally is closer to one of the atoms than the other. Thus, the bond is stronger for one of the atoms in the arrangement. The weaker of the two bonds is generally referred to as the hydrogen bond.3/

Theoretical models for hydrogen bonds predict that the cleavage energy is not dependent upon the surrounding atmosphere.4/ The experiments performed will help evaluate this model. The model also predicts hydrogen bonds are possibly dependent upon temperature. If atmospheric effects do exist, the temperature experiments should be performed in high vacuum. Exposure of selenite to high vacuum for prolonged periods of time causes the sample to change its lamellar structure, thus altering the sample. If atmospheric effects can be shown to

be negligible, future studies of the thermal effects of hydrogen bonds would be greatly simplified. The samples could be cleaved in only moderate vacuum, which would increase the time available for performing the experiment, yet still insuring that water vapor does not cause frosting of the sample.

The energy required to produce new surfaces has been the topic of many experiments beginning with J.W. Obriemoff in 1930. Obriemoff observed that the energy required to cleave muscovite mica in vacuum was greater than the energy required in air. He measured the value of the IBE of mica in vacuum to be 11,500 ergs per square cm and the value in air to be 750 ergs per square cm.^{5/}

A.I. Bailey obtained a value of 620 ergs per square cm for the IBE of mica in air. This measurement was made by applying a force on each lamella.

M.S. Metsik used the method of driving a wedge between lamella to investigate charge structure on the lamella. He concluded that the charge structure was mosaic.^{6/}

Recent experiments by Phillips, Gutshall and Bryant have indicated that the decreased IBE of muscovite in vacuum may be due to the replacement of the ionic bonds

by weaker hydrogen bonds in the presence of water vapor.1/
The replacement of ionic bonds in the presence of water vapor by hydrogen bonds has been explained for muscovite and phlogopite by Phillips as a surface diffusion of water molecules into the crack tip. This model postulates that water dipoles enter the interlayer regions and clusters around the positive potassium ions. The water clusters have the hydrogen on the outer surface. The hydrogens are near the oxygen molecules, which form hydrogen bonds. The water molecules tend to neutralize the charge imbalance which formed the ionic bond. This neutralization results in a relaxation of the ionic bonds and replacement by the weaker hydrogen bond.1/

The IBE of muscovite mica in water atmosphere has been measured. This measurement can be compared with the measurement of the IBE of selenite. If the two values are similar this would suggest that the relaxation of the ionic bonds in water vapor truly is a hydrogen bond replacement process.

Weaker Van der Waals bonds exhibit the reverse effect. Substances which are bound with Van der Waals bonds become more tightly bound in the presence of water vapor. Phillips has explained this strengthening effect also

by the crack diffusion method. The weaker Van der Waals bonds are partially replaced by the stronger hydrogen bonding. This model could explain the higher friction measurements some Van der Waals bound materials have in the presence of water.1/

Thus it is obvious that a full understanding of ionic and Van der Waals bonding cannot be achieved until hydrogen bond strength is measured. The present investigation uses selenite to measure the hydrogen bond strength. The bond strength is measured in vacuum and in air to assure that hydrogen bonding exhibits no environmental effects.

By cleaving the selenite with great care, the cleavage will pass along a single crystalline plane. The surface obtained is nearly molecularly smooth and the energy of cleavage represents only the IBE; interplane stepping energies are not involved. Cleavage methods employed in this thesis are similar to those used by Bryant, Gutshall and Taylor.7/

EXPERIMENTAL TECHNIQUES

Experimental Method

Selenite was cleaved at a controlled environment. The method of cleaving was to attach one end of a partially cleaved piece of selenite to a rigid support. The other side of the cleaved portion of the specimen was attached to a calibrated quartz fiber. Displacement of the quartz fiber provided the force to cleave the specimen.

Sample Preparation

The selenite test specimens were rectangular with dimensions of approximately 1 cm x 7 cm and a thickness of approximately 1 mm. Specimens were cut from a large sample of natural selenite supplied by the University of Missouri-Kansas City Department of Geology. A great

amount of difficulty was encountered in obtaining a sample which was suitable for the experiments. The sample was chosen because of its clarity and lack of visible crystalline defects. Each prepared specimen was carefully examined to insure it contained no obvious defects in structure or in preparation.

Two methods of cutting the specimens were attempted. The first method used was to cut the selenite with a razor blade. The samples were prepared by a series of cuts using light pressure on the blade. This method proved to be unsatisfactory because the edges curled up around the cut. This curling seemed to be due to selenite dust from the cutting processes working its way between the layers. Blowing the dust away after each stroke with the razor blade decreased the edge curling effect, but the curling was still noticeable.

Using a hack saw blade to make the cuts was found to be more satisfactory. The blade was used without a blade holder. The weight of the blade was the only downward force on the blade. The cutting force of the saw blade was distributed over many points on selenite rather than one point as with the razor blade. The layers did not separate as easily and dust was not able to enter between

the layers. Thus, the cut edges did not curl.

The method using the hack saw was used because it produced less surface damage. Using the razor blade method, the selenite had an increased tendency to step between two layers or cleave on two planes.

During initial experimentation the selenite was found to be very brittle and it broke during cleavage. To prevent breaking the selenite was coated on the top surface with a clear plastic sheet. The plastic sheet was approximately .05mm thick and cut into a rectangle slightly larger than the selenite. Eastman 910 Adhesive was used to coat the selenite. The plastic sheet was placed on the adhesive coated surface of the selenite and carefully pressed down. Care was taken to prevent the adhesive from going onto the edges and causing edge locking.

After coating the selenite with the plastic sheet, the excess plastic was cut away. The sample was placed plastic side down on a piece of glass. The excess plastic was cut away using a razor blade. The blade caused the selenite to cleave inward from the edges about .2 cm on one cleavage plane. This slight cleavage minimized the edge effects during the experiments.

The sample was mounted on the sample support using Eastman 910 Adhesive with the plastic coated side up. One end of the sample was attached to the quartz fiber and the sample was cleaved in from that side about 1 cm. The sample and manipulator were then mounted in the test chamber.

Sample Chamber

The sample chamber consisted of a glass cylinder 15 cm long and 6.3 cm in diameter. The chamber was attached to a vacuum system by a metal flange. A metal bellows was placed between the sample chamber and the remainder of the vacuum. This method reduced the strain on the glass chamber and allowed more freedom in alignment.

A mechanical pump was used to reduce the chamber pressure to 10^{-3} torr. An oil diffusion pump was used to maintain a pressure below 10^{-5} torr. An ionization guage was used to monitor the pressure below 10^{-4} torr.

A calibrated quartz fiber attached to a manipulator

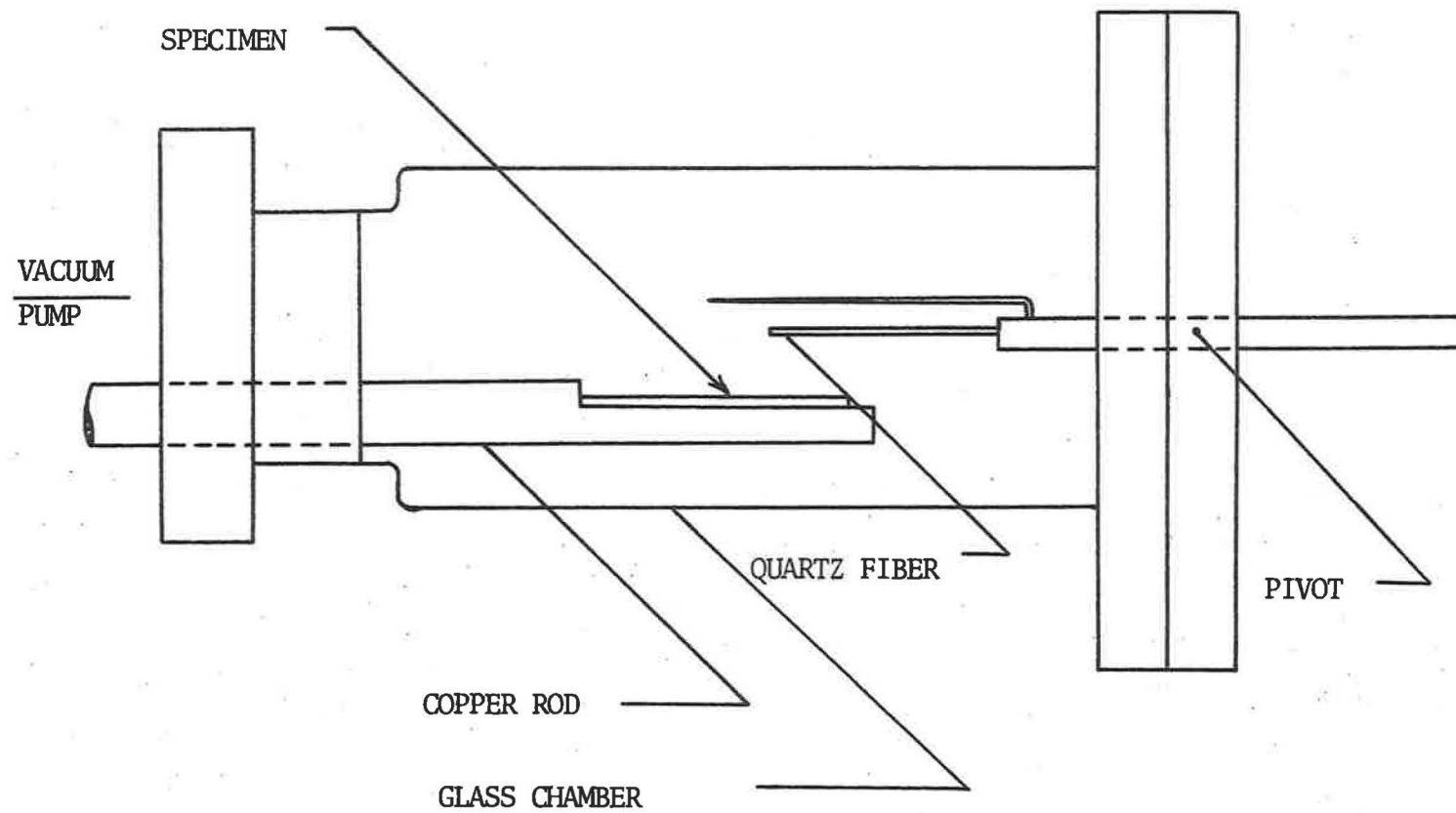


Figure 1. Schematic diagram of test chamber used for cleavage measurements.

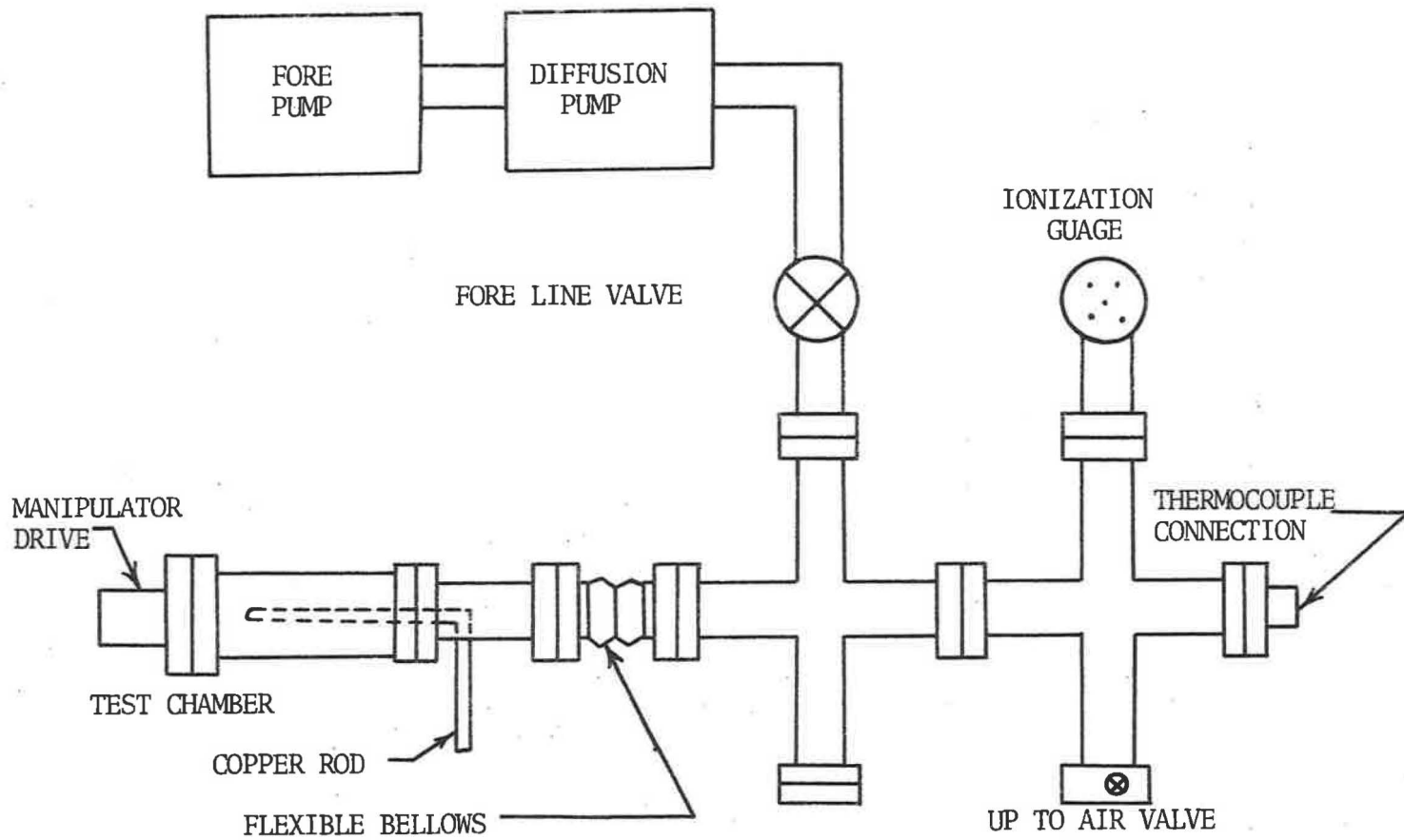


Figure 2. Schematic diagram of vacuum system used for cleavage experiment.

rod was used to cleave the specimen. Two cameras were to record data. One camera mounted to photograph horizontally was used to record the deflection of the quartz fiber and the distance through which the force moved. The second camera was mounted vertically to photograph the area which was being cleaved. Photographs were taken simultaneously using the two cameras.

The selenite was cleaved by driving the manipulator rod with a synchronous motor and a rack and pinion. This method allowed the selenite to be cleaved at a uniform rate which was repeatable in each trial measurement. This method also maintained a constantly increasing cleaving motion thus not allowing relaxation of the sample and rehealing of the cleaved area.

Sample Holder

The sample holder was a rectangular metal rod supported by a 15 cm flange. The sample was mounted on the end of the sample holder and the hook was mounted on the top of the sample and attached to the

quartz fiber. The quartz fiber was mounted on the metal manipulator rod. The manipulator rod was introduced into the specimen chamber by means of a metal bellows. The manipulator rod was mounted to the flange in a manner which allowed it to be pivoted in the vertical plane. The specimen and manipulator were mounted into the glass test chamber and connected to a mating flange.

Quartz Fiber Calibration

To cleave the selenite a quartz fiber was used as a cantilever beam. The spring constant of a quartz fiber remains constant over a large range of displacement. The spring constant allows the fiber to be calibrated for any deflection.

To calibrate the fiber, it was mounted in the proper position in the manipulator of the sample holding flange. The flange was then locked into a vise which held it rigidly in place. Weights were suspended from the fiber at approximately the same position where the sample hook was to be placed. Weights were added and the displacement of the fiber was recorded photographically in the same manner that the fiber displacements were recorded during a cleavage experiment. Weights were added in increments of increasing mass and removed in the same way. Each deflection was recorded.

The slope of a line of force in dynes verses displacement in cm gives the spring constant in dynes per cm. Two trials of each measurement was made, and an average value for the slope was taken.

DATA ANALYSIS

Photographic Method

Data was recorded using two simultaneously activated cameras. Photographs were taken approximately every ten seconds during cleavage. Data measurements were then made from the series of photographs of the cleavage process.

The side view photograph was used to record the quartz fiber deflection and the distance through which that deflection occurred. The force necessary to cleave a specimen was then given by

$$F=kx$$

where F was the force in dynes, k is the quartz fiber constant given in dynes per cm, and x is the deflection of the quartz fiber in cm.

The energy required to cleave the specimen was the scalar product of the force and the distance through which it was applied. This product was found by measuring the area under the curve of force versus distance

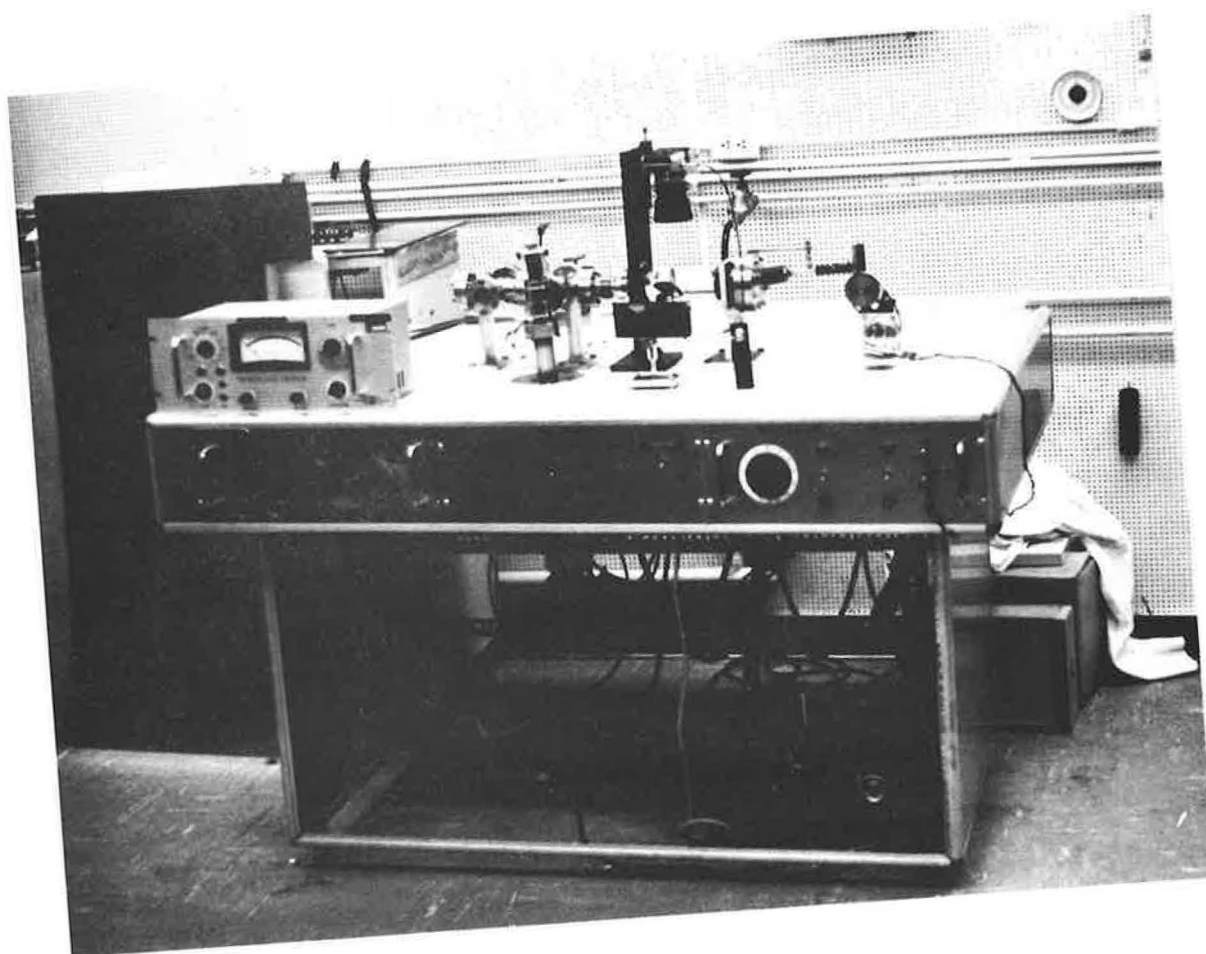


Figure 3. Controlled environmental test system used for determining the IBE of selenite.

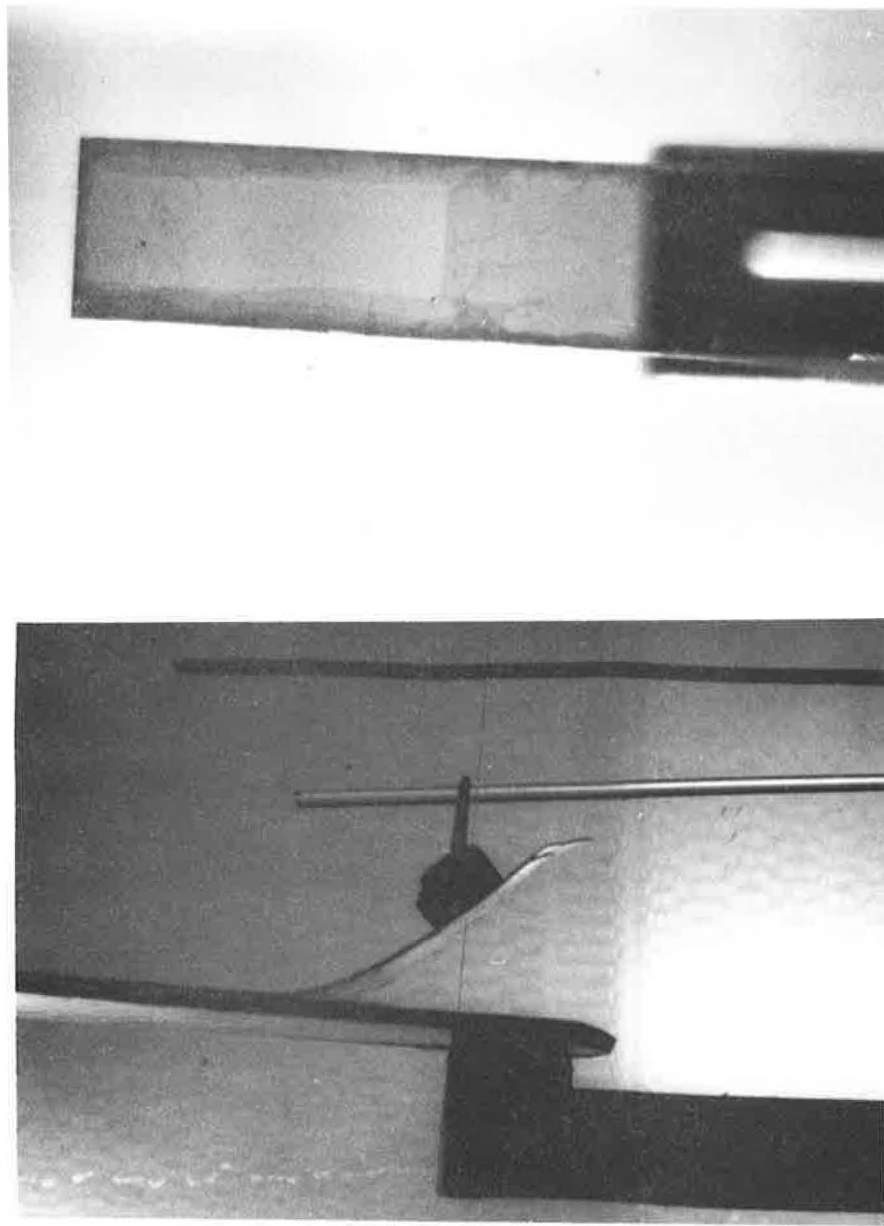


Figure 4. Simultaneous photographs necessary during cleavage to determine the IBE of selenite in various environments.

through which it was applied. This product was found by measuring the area under the curve of force versus distance. The force plotted in dynes and distance plotted in cm gave the energy required for cleavage of the specimen in ergs.

Measurement of Cleaved Area

The top view camera was used to record the area cleaved. This area was measured directly from the photographs by using a polar planimeter. The camera was set to record the bifurcation line which bounded the cleaved area. The area from the edge of the specimen to the bifurcation line of the first photograph was compared with the area from the last photograph. Subtraction gave the area cleaved.

Evaluation of IBE

The IBE was determined by the graphical technique of plotting force versus distance. The area under the curve which represented energy was measured using a polar planimeter. This energy was normalized to give the IBE by dividing by the area cleaved. Thus the IBE was found in terms of ergs per square cm.

TEMPERATURE DEPENDENCE EXPERIMENTS

Experiment Equipment

The system for cooling or heating the sample was made by removing the sample holder and replacing it with a copper holder. The copper holder was fabricated from a three fourths inch copper rod. The rod was miter cut to form a 90 degree angle.

Entry into the sample chamber was made through the side opposite the manipulator rod. A three fourths inch hole was made in the wall of a stainless steel extension to the vacuum chamber. One section of the copper rod was inserted vertically into the hole and soldered into place to form an air tight seal. About eight inches of this rod protruded from the bottom wall of the vacuum system.

Inside the system the second section of the rod was soldered on the first at a 90 degree angle. This copper section went horizontally into the glass sample chamber. The last two inches of the section were

milled to form a flat horizontal area upon which the sample was to be mounted. Below the flat area a small hole was drilled to be used for a thermocouple.

One face of the sample was glued to the copper rod with Eastman 910 Adhesive. The other face was plastic coated and a hook was attached to one end of the plastic. The sample was then partially cleaved and the sample chamber placed around it. The manipulator rod was attached to the hook.

Temperature was controlled by simultaneously using heater tape and liquid nitrogen. A dewar was placed around the bottom of the vertical section of copper rod and heater tape was wrapped around the top part of the rod. The heater tape was controlled by means of a variable transformer. This method allowed the copper rod to be brought to an equilibrium temperature easily in the range of -150 degrees Celsius to 100 degrees Celsius. The temperature was monitored by the thermocouple below the sample platform. Experiments were performed in vacuum to prevent condensation of water vapor at cold temperature.

Alterations of Sample Preparation

When the sample was cooled below -25 degrees Celsius, the plastic coating began to curl. This was found to be due to the difference in expansion coefficients of selenite and the plastic coating.

To prevent this curling cellophane tape was used as a coating. Three layers of tape were used directly on the top of the selenite. The three layers provided the desired rigidity for effective cleavage. The adhesive of the cellophane tape did not become brittle or hard at temperatures used in the experiment. Thus, some degree of freedom was available to allow thermal expansion between the tape and the selenite. The tape coating could only be used at temperatures below room temperature because at room temperature it did not have the necessary rigidity. At temperatures above room temperature it began to melt.

ERROR ANALYSIS

Number of Trials

Three trials were taken for each experiment. This number was believed to be sufficient for two reasons. Previous experiments on muscovite performed in the same manner and had given very small errors. Also, the selenite experiments gave little deviation from the mean IBE with only three trials. Three was chosen for the number because it was believed that any pinning or stepping errors would be noticeable by comparing one trial with two others.

Pinning and Stepping

Selenite was found to be very hard to cleave without noticeable pinning or stepping. All trials in which there was obvious pinning or stepping were stopped and no calculations were made. Because the number of aborted trials was so large the microscopic pinning and stepping was studied qualitatively as a possible source of error.

Sample surfaces from the cleavage experiments were replicated by carbon coating the surfaces. The surface replicas were examined in the electron microscope to determine if microscopic stepping existed. A total of twenty grids were examined from two samples. One sample was cleaved in air and the other sample cleaved in vacuum.

In replicating the samples it was decided that microscopic stepping would take place in a manner similar to macroscopic stepping. For this reason, the surfaces were shadowed in the direction in which cleavage occurred. Grid samples were taken from the center line of the replica proceeding in the direction of cleavage. By taking grid samples in this manner,

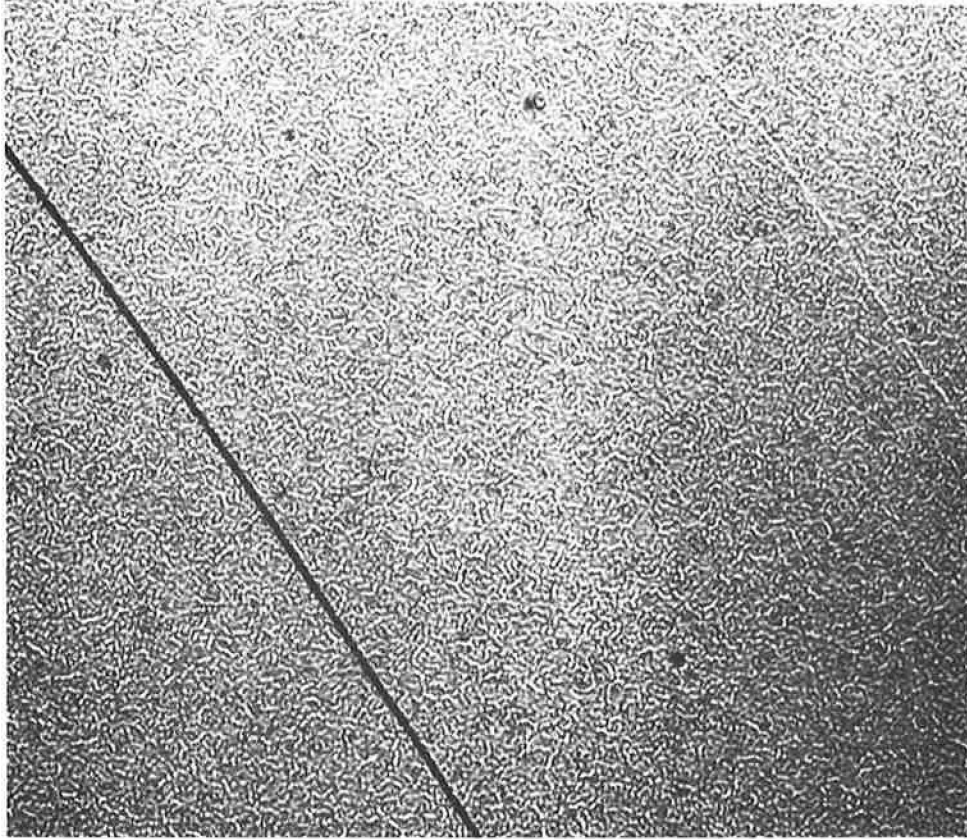


Figure 5. Electron micrograph of selenite stepping.
X88,000

the chance of double counting steps was minimized.

An actual quantitative effect of stepping on the total IBE could not be calculated since the energy to produce a step is not known. However, it is significant to know that there is stepping and it is occurring at a regular rate. It is also important to note that all steps were the same height, approximately 13 angstroms. The steps were also found to be at about a 20 degree angle with the direction of cleavage. Thus, several steps could be occurring simultaneously. This regular stepping phenomenon suggests that the whole IBE curve is shifted rather than just a few points.

The steps showed no preference for up or down stepping. Each direction occurred approximately the same number of times. One significant observation is that rarely did more than two steps in the same direction occur without being followed with at least one in the opposite direction.

Error in Measurement

The actual error in measurements were determined to be one half of the smallest calibration on the instruments. The largest error in measurement was in the direct measurement of the force deflection and cleavage distance from the photographs. The error was $\pm .005$ cm.

The error of the measurements taken from the photographs were reduced from the $\pm .005$ cm value due to the magnification of the camera and enlarger. However, the measurement of magnification had about a $\pm .02$ error due to the multiple errors of the two measurements taken to obtain the enlargement.

The measurement of the area cleaved on the photograph was $\pm .005$ square cm. This measurement was also effected by the $\pm .02$ error in magnification. The error in quartz fiber calibration was similar to the error for the force deflection error.

When combined the errors give a total error in the IBE of less than 5%, which is well within the standard deviation found in the experiments.

EXPERIMENTAL RESULTS

The mean values of the IBE of selenite are given in table 1. The mean values were obtained by performing three trials for each set of experimental conditions. The conditions under which selenite was cleaved were room temperature and pressure, room temperature and low pressure, low temperature and low pressure, high temperature and low pressure.

The pressure in the test chamber was monitored by the use of a ionization guage. The temperature was monitored by the use of a thermocouple imbedded in the copper rod beneath the sample.

The IBE values for selenite are: room temperature and pressure, 716; room temperature and low pressure, 704; low temperature and low pressure, 768; high temperature and low pressure, 720. Thus, no temperature or pressure effect was observed in the range of temperature and pressure studied.

TABLE I
MEAN
INTERLAYER BINDING ENERGY VALUES MEASURED
FOR SELENITE IN VARIOUS CONDITIONS

Temperature (degrees C)	Pressure (Torr)	IBE (ergs/cm ²)
25	760	716
25	10 ⁻⁵	704
-35	10 ⁻⁶	768
65	10 ⁻⁵	720

CONCLUSIONS

J.W. Obriemoff obtained the value of the IBE of muscovite mica in air to be 750 ergs per square cm.^{5/} The IBE value measured by Gutshall, Bryant and Cole was 700 ergs per square cm for muscovite mica in air.^{9/} I.A. Bailey obtained a value of 620 ergs per cm for muscovite mica in air. The measured IBE of selenite was 716 ergs/cm². This value is in close agreement with the values of the IBE of muscovite mica in air.

Selenite shows no environmental effects, the IBE measured in air, 716 ergs/cm² was approximately the same as that measured in vacuum, 704 ergs/cm². Thus, these experiments show air to be a non-interacting environment.

The high temperature experiments gave a value of 720 for the IBE of selenite in the range of 65 to 75 degrees Celsius. This value shows no substantial difference between the high temperature measurements and room temperature measurements of the IBE of selenite.

Low temperature measurements gave 768 ergs/cm^2 to be the IBE at -35 degrees Celsius. This value is slightly higher than the room temperature measurements. This difference could be due to the permanent deformation of the tape coating during cleavage at low temperature. This deformation was present during cleavage at room temperature, however, the coating returned to its original flat shape as the crystal cleaved out to near the end. Thus, the energy was returned to the cleavage system at room temperature and above but was retained as deformation at low temperature.

These experiments show the mean value of all IBE measurements to be 727 ergs/cm^2 for selenite. This value is within the range of values found in previous experiments for muscovite in air. Although these experiments do not prove the hydrogen bonds replace ionic bonds in the presence of water vapor they do lend some validity to the theory.

The temperature dependant experiments yielded null results. This outcome could have been due to three factors: 1) The effect was too small for detection by the equipment; 2) There were opposing effects which nullify the temperature dependence; or 3) There

actually is no temperature dependence. J.M. Phillips has proposed that the second factor is the cause of the null results.^{10/}

The model proposed by Phillips uses the fact that the bonds are at an acute angle with the surface of the crystal. Phillips proposes that as the temperature increases the bond strength decreases, however, the angle of the bond with the surface is also altered by the increased thermal activity. The component of force in the breaking direction is increased by an amount nearly equal to the decrease caused by the reduced bond strength. Thus, the bond strength is less, but the component in the breaking direction remains the same, and the IBE remains the same.

SURFACE DIFFUSION OF WATER ON MUSCOVITE

Previous work by the authors has shown that the presence of water will reduce the interlayer binding energy of lamellar minerals.^{1/} The mechanism by which the water vapor moves to the crack tip of a partially cleaved sample, such as muscovite, was not determined in earlier studies. At least two possible methods are available, that is, by diffusion of a liquid layer along the surface, or by gas diffusion directly into the crack tip. Certainly, both of the above mechanisms probably provide water necessary to reduce the interlayer binding energy of lamellar minerals. However, in order to determine if water can migrate along a clean surface of muscovite, as well as to measure the diffusion rate, the following experiment was performed.

A. Experimental Details

The experimental techniques for measuring the interlayer binding energy of lamellar minerals has been described in detail above, thus only a brief description will be repeated herein. A sample, 1 cm by 5 cm and .5 cm thick is partially cleaved along the 5 cm direction. The partially cleaved sample is then mounted in a vacuum chamber on a rigid copper block. The sample is then cleaved, using a calibrated quartz fiber and the energy required for cleavage is measured. The area cleaved is also determined, thus allowing one to calculate the interlayer binding energy.

The above technique was modified in order to determine whether surface diffusion of the water could occur.

The sample was mounted on the copper block with Eastman 910 adhesive. The temperature of the block could be controlled from 183° K to 300° K. After the pressure of the chamber was reduced to 1×10^{-6} Torr, the muscovite sample was cleaved, thus exposing a clean surface. Water vapor was then admitted into the chamber, via a leak valve, raising the pressure to 50 Torr. At that pressure, all surfaces were coated with water. The copper block and sample were then cooled to 183° K, thus forming an ice layer. While maintaining the block and sample at the reduced temperature, the system was again evacuated to a pressure of 8×10^{-5} Torr. The pressure of the vacuum system was limited by the presence of the 183° K ice (Vapor pressure of ice at 183° K is approximately 7×10^{-5} Torr). The sample was cleaved further by the quartz fiber, thus exposing a clean portion of surface between the new crack tip and the ice layer. At this point, the temperature of the sample was increased. The interlayer binding energy of muscovite in vacuum is 9200 ergs/cm^2 and only 700 ergs/cm^2 in the presence of 1 torr of water vapor. Thus, when the water reaches the tip of the crack, further cleavage would occur. The sample temperature was increased until further cleavage of the sample resulted.

B. Experimental Results

Using the technique described above, the following results were obtained. A sample was coated with water and slowly warmed toward room temperature. At a temperature of 248° K, relaxation of the sample occurred. Thus, we know that water had moved to the crack tip. Since the vapor pressure of ice at 248° K is 0.5 Torr, it is believed that the water reached the crack tip by surface diffusion. This opinion is based on earlier observations that showed that at least 1 Torr of water vapor was necessary to reduce the interlayer binding energy. Furthermore, during the warming of the sample, the chamber pressure remained below 0.1 Torr, indicating that the partial pressure of water vapor was considerably below the necessary 1 Torr level.

The above results indicate that one should be able to obtain the necessary data to determine the surface diffusion rate of water on a muscovite sheet. These experiments are planned, but have not been done at this time.

APPENDIX I

In the high temperature experiments the newly cleaved surface became opaque white after cleavage. If left at the high temperature long enough the entire crystal turned opaque white.

The process involved in the clear to opaque transition was believed to be dehydration. To check this two experiments were performed; a crystal was weighed then heated until it was opaque then re-weighed; and a small crystal was placed in a mass spectrometer.

In the first experiment the crystals were weighed before and after heating to determine the percent change in mass. Each trial gave a definite loss of mass. However, there were no consistent quantitative results.

In the second experiment the crystal was heated in a mass spectrometer and the spectrum was scanned. A definite increase in the water peaks was observed. The 17 and 18 mass peaks remained in the same ratio throughout the heating process. This experiment showed that dehydration was taking place in the crystal and that

no other substances were being driven off the crystal in appreciable amounts from the heating process. The ratio of 17 to 18 mass indicated that the water was coming from the crystal in its complete form rather than coming off as a hydroxide ion and oxygen.

A graph of temperature versus peak height was made for the 17 and 18 mass peaks. The graphs show a sudden increase in the amount of water being given off at about 51 degrees celcius. No other conclusions were made on the experiments.

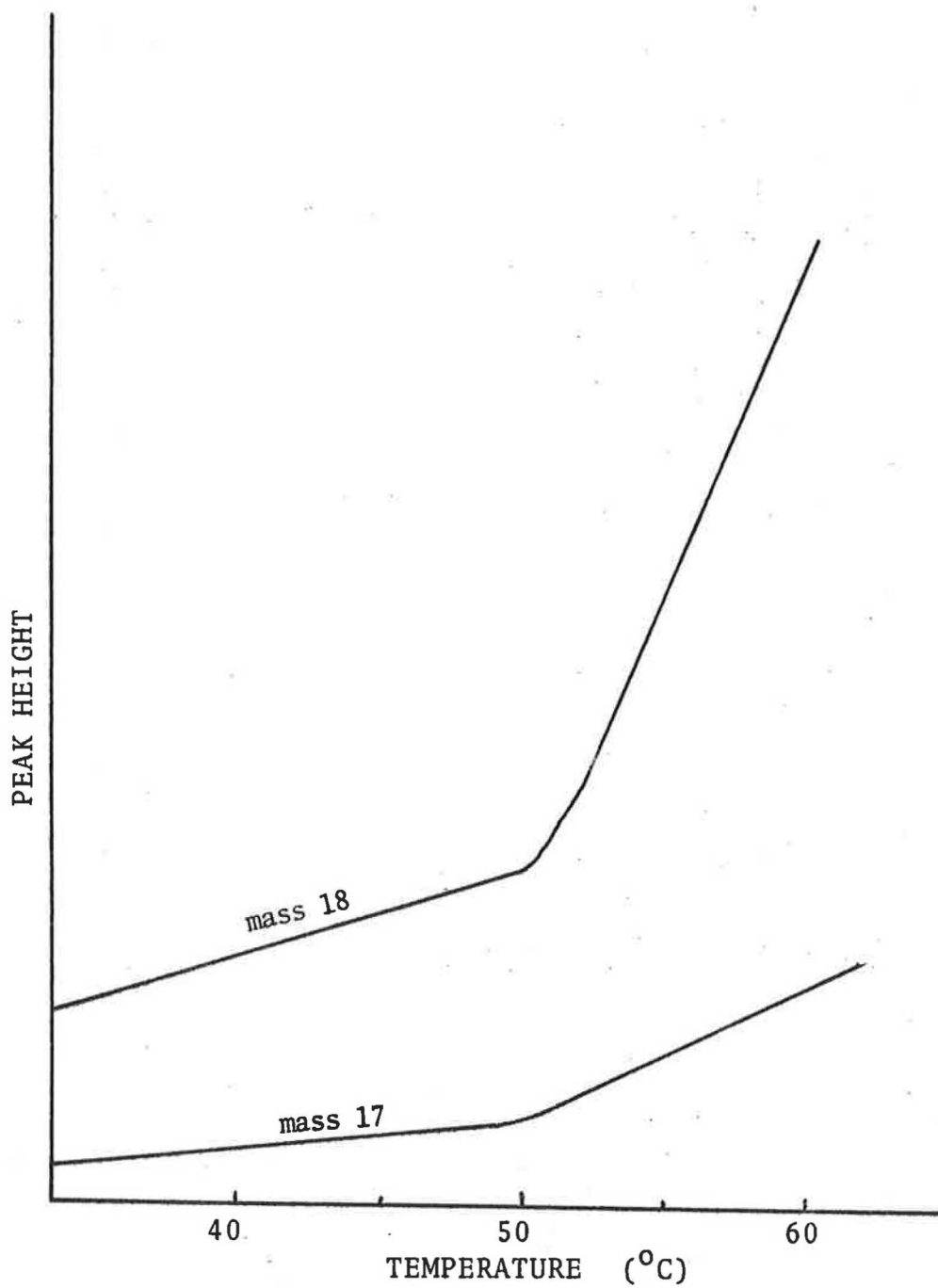


Figure 6. Graph of Peak height VS Temperature for 17 and 18 mass peaks.

APPENDIX II

Table 2

DATA ACCUMULATION FOR THE IBE OF SELENITE
IN VARIOUS ENVIRONMENTS

TRIAL	TEMPERATURE (Degrees celcius)	PRESSURE (Torr)	IBE (ergs/cm ²)
1	25	760	925*
2	25		628
3	25		790
4	25		729
5	25	10 ⁻⁵	710
6	25		715
7	25		686
8	-35	10 ⁻⁶	769
9	-35		780
10	-35		752
11	65	10 ⁻⁵	724
12	75		732
13	70		705

*Only four data points

APPENDIX III

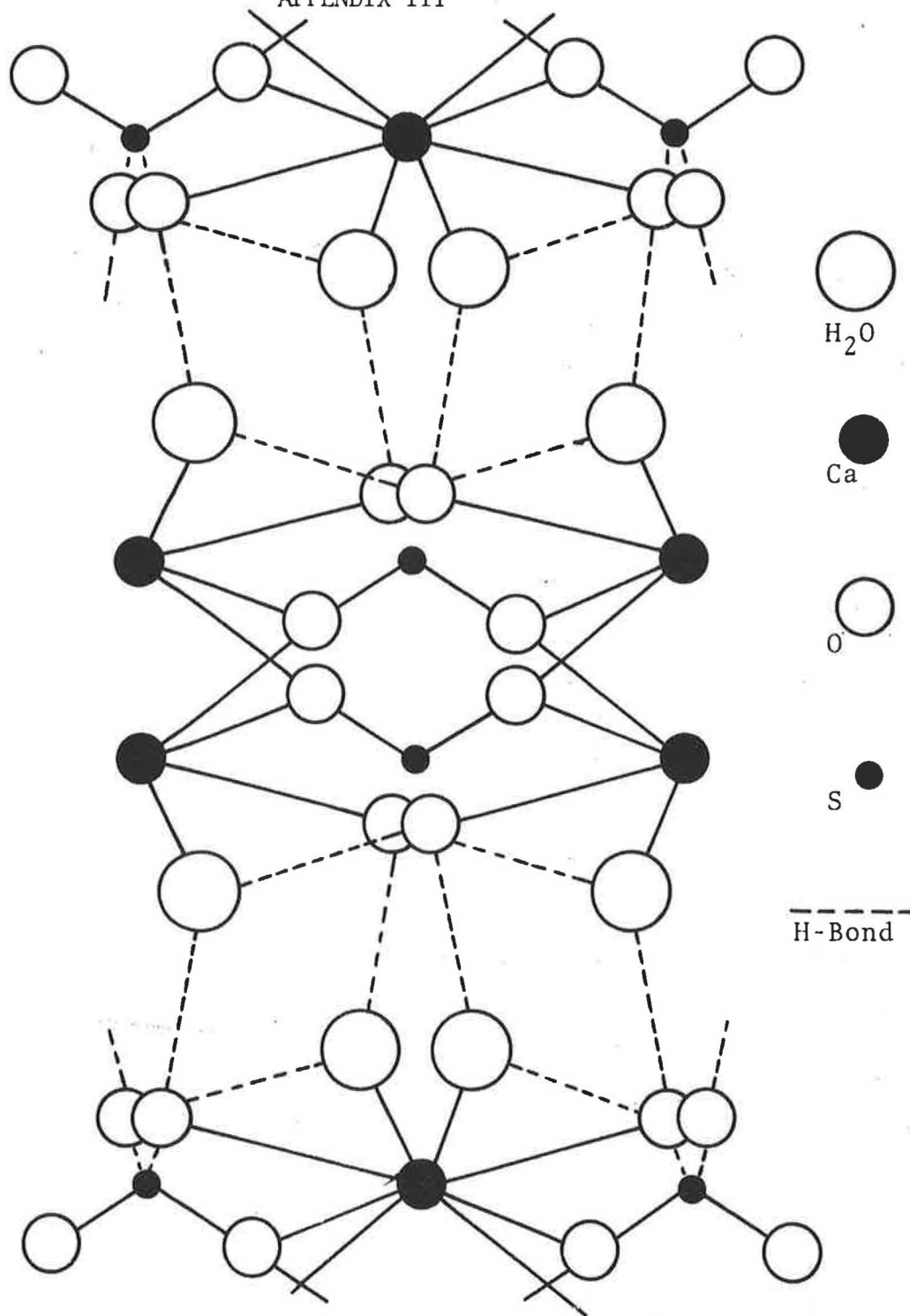


Figure 7. Structure of Selenite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The layers are seen edge-on.

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