

AN INFRARED STUDY OF WATER IN HEULANDITE AND CLINOPTILOLITE¹

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ABSTRACT

Infrared determinations have shown the water in heulandite and clinoptilolite to exist in two forms. The entire study has required only about 50 mg of each mineral.

When heulandite is slowly heated, part of its initial water is lost rapidly at first and then slowly up to $200^{\circ} \pm 3^{\circ}\text{C}$, at which temperature the mineral again begins to dehydrate very rapidly. The high ionic potential of the calcium in heulandite may be responsible for the strong retention of part of the water up to 200°C . An X-ray diffraction study in which the sample was heated in stages showed the heulandite-heulandite *B* transition to occur between 255° and 330°C . The structural transformation of heulandite, therefore, begins 55°C above the temperature at which loss of tightly bound water starts. This transition is in part accompanied by an irreversible structural change.

The dehydration curve for clinoptilolite was similar to that for heulandite except that loss of tightly bound water began at a somewhat lower temperature, namely, 185° to 190°C . At 500°C both heulandite and clinoptilolite each still retained about 20 percent of their initial tightly bound water.

This study has shown that published analytical data for the tightly bound water in heulandite and clinoptilolite are not correct; recently published crystallographic data confirm this conclusion for heulandite. Corrected values for the tightly bound water in both minerals are presented on the basis of the current study.

The infrared technique has proved to be effective for handling very small hygroscopic specimens in dehydration studies.

INTRODUCTION

The two zeolites, heulandite and clinoptilolite, have been studied in great detail by many mineralogists. Thanks to the excellent discussion of much of the early work by Mumpton (1960), it is not necessary to review the literature in detail in this paper. Although they are similar, heulandite has a higher calcium content, and clinoptilolite a higher content of sodium and potassium. Clinoptilolite also contains more silica, and at one time was actually called a high-silica form of heulandite. A major difference between the two zeolites is that heulandite undergoes a sluggish phase transition at about 230°C , whereas clinoptilolite does not invert (Mumpton, 1960).

As noted by Shepard and Starkey (1964), exhaustive study of the two minerals has been complicated because of difficulties in obtaining pure samples. For this and other reasons to be discussed, there has been considerable confusion regarding the composition of heulandite. Thus, the following empirical formulas have been proposed in the literature:

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- (1) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ (Imai, Otsuka, and Yoshimura, 1964).
- (2) $(\text{Ca}, \text{Na}_2)\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ (Dana, 1932).
- (3) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ (Koizumi and Roy, 1960).
- (4) $(\text{Ca}, \text{Na}_2)\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ (Merkle and Slaughter, 1968).
- (5) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ (Coombs *et al.*, 1959; Pécsi-Donáth, 1966).

It is clearly evident that there is disagreement both with respect to the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and to the number of molecules of tightly bound water. The first problem is related to the fact that aluminum may replace silicon in the tectosilicate; the problem related to water reflects, as will be shown in this paper, the analytical methods that have been used. Mumpton (1960) has lucidly illustrated these problems with statistical data showing the molar $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ratio to range from 4.5 to 6.5 with a maximum frequency at about 5.4, and the molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios to range from about 5.5 to 7.8 with a maximum frequency at about 5.9.

In this paper, we describe detailed X-ray diffraction and infrared absorption studies conducted in an attempt to relate the water content of heulandite to its thermal characteristics, namely, to its inversion at about 230°C as reported by Mumpton (1960) and others. We were, moreover, interested in the retention of water by the minerals.

The problem of how to label water in certain minerals is perennial, and there is a history of ambiguous usage, in the case of zeolites, for such adjectives as "zeolitic" or "structural." As will be shown below, the distinction customarily made between types of water retained by a mineral on the basis of its loss of water up to and then above 100°C may also be subject to error. To obviate an additional contribution to this confusion, the terms "loosely held" and "tightly bound" water are used in this work to describe the two relative degrees of retentivity of water noted for each mineral. As will be seen, differentiation of retentivities is based on dehydration studies at temperatures up to 500°C.

The need to characterize the water of certain minerals by methods other than conventional, empirical techniques has become particularly evident during this study of heulandite and clinoptilolite.

Samples used in this work were a heulandite from Berufjord, Iceland, and a clinoptilolite from the Pierre Shale, Buffalo County, South Dakota. Data for these samples have been published by Shepard and Starkey (1964). Additional analytical data for calcium, magnesium, potassium, sodium, and water for the two minerals are shown in Table 1. More complete analyses could not be obtained because of limited quantities of pure samples.

EXPERIMENTAL

An infrared absorption technique for the determination of fixed water (designated as H_2O^+) in rocks has recently been published (Breger and Chandler, 1969). With modifica-

tions, as noted below, to suit the needs of the current study, the method was applied to the determination of water in samples of heulandite and clinoptilolite that were dehydrated at various temperatures. Briefly, the determination of water was carried out as follows: the sample (50 mg of heulandite or clinoptilolite) was ground for 3 minutes in a Wig-L-Bug vibratory mill. Grinding was conducted in a stainless steel mortar with a stainless steel hammer for 30-second periods with 1-minute intervals to eliminate any possible loss of water as a result of heating. The ground sample (3 mg) was mixed with 297 mg of potassium bromide, and the 1 percent mixture was milled, as before, for two 30-second periods with a 1-minute interval. The hammer was next removed, and the mixture was vibrated for 30 seconds to assure homogeneity.

The 300-mg mixture was placed in a cool furnace and heated to the desired dehydration temperature (110°, 150°, etc.). This temperature was maintained for one-half hour, the mixture was removed from the furnace and cooled in a desiccator, and 100 mg was then weighed and compressed into a 13-mm disk. The disk was slowly heated to 110°C, main-

 TABLE 1. PARTIAL ANALYSES FOR HEULANDITE AND CLINOPTILOLITE^a

	Heulandite	Clinoptilolite
CaO	8.4 ^c %	2.3%
MgO	0.30	1.0
K ₂ O	2.1	3.0
Na ₂ O	0.80	2.4
H ₂ O+	12.88 ^b	7.57 ^e
H ₂ O-	2.74 ^b	6.00 ^e

^a Analyses by L. Shapiro and staff, U.S. Geological Survey, Washington, D. C., using rapid rock analysis methods. The heulandite, from Berufjord, Iceland, and clinoptilolite, from the Pierre Shale, Buffalo County, South Dakota, were both made available by Anna Shepard of the U. S. Geological Survey.

^b Analyses by B. Ingram, U. S. Geological Survey, written communication, 1968.

^c From Shepard and Starkey (1966)

tained at that temperature overnight (about 16 hours), and scanned at 110°C with a 100-mg potassium bromide disk, also at 110°C, in the reference beam. A Perkin-Elmer Model 21 double beam infrared spectrophotometer with sodium chloride optics was used. Baseline absorbances at 2.96 μ m, measured as illustrated in Figure 5, were recorded.

The original analytical technique (Breger and Chandler, 1969) was based on 2-mg samples. Inasmuch as the current study was conducted on 1-mg samples, it was necessary to obtain calibration curves for absorbance vs sample size. To do this, disks were prepared as above but having varying amounts of heulandite or clinoptilolite. These were heated to 110°C, and scanned at that temperature. The calibration curves, shown in Figure 1, are linear and consistent with the Beer-Lambert law. Each point of Figure 1 represents the average of two analyses.

The points of Figure 2 illustrate water contents of samples of heulandite that were dehydrated and analyzed as described above at temperatures ranging from 110° to 500°C; similar data for clinoptilolite are recorded on Figure 3.

Conventional infrared absorption curves for heulandite and clinoptilolite are shown in Figures 4 and 5. These are general spectral scans in which the minerals were milled with

Nujol or Fluorolube (Figure 4), or in which potassium bromide disks containing 1 percent of sample were heated to 110°C for 16 hours and the absorption spectra were obtained while the disks were maintained at that temperature (Figure 5).

Inasmuch as determinations of water were to be made on statically heated samples, it was desirable to obtain X-ray diffraction data, for use in establishing inversions or structural changes, under similar conditions. Adaptation of the method used by Shepard and Starkey in their earlier work was employed using a diffractometer heating stage designed

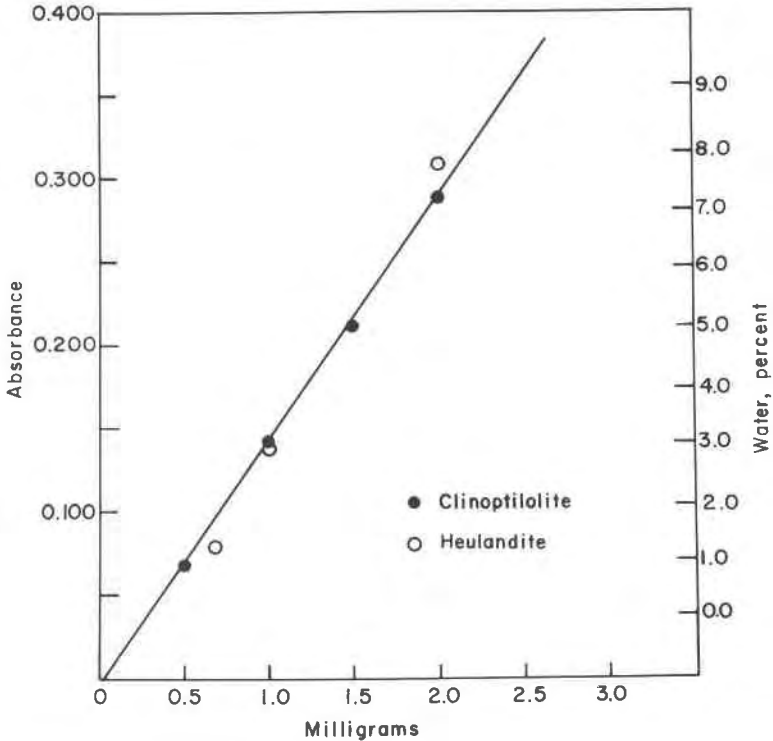


FIG. 1. Calibration curve showing base-line infrared absorbance at 2.96 μm for disks containing varying amounts of heulandite and clinoptilolite.

by Skinner, Stewart, and Morgenstern (1962). Two thermocouples were cemented to the plate upon which the sample was spread, and the sample was confined to as small an area as possible in order both to minimize and monitor temperature gradients, which never exceeded 4°C in the sample during the analysis. Copper $K\alpha$ radiation and a nickel filter were used; X-ray scans were carried out at normal pressure and room humidity.

Three consecutive heating-cooling cycles were carried out with the heulandite. In the first, the heulandite was heated (Table 2, heating cycle I) in 5° to 10° increments and was maintained at each temperature for periods up to 16 hours. Above 240°C, the temperature was raised very slowly to 255°C over a period of 20 hours. Numerous X-ray diffraction scans were recorded during the three heating-cooling cycles recorded in Table 2.

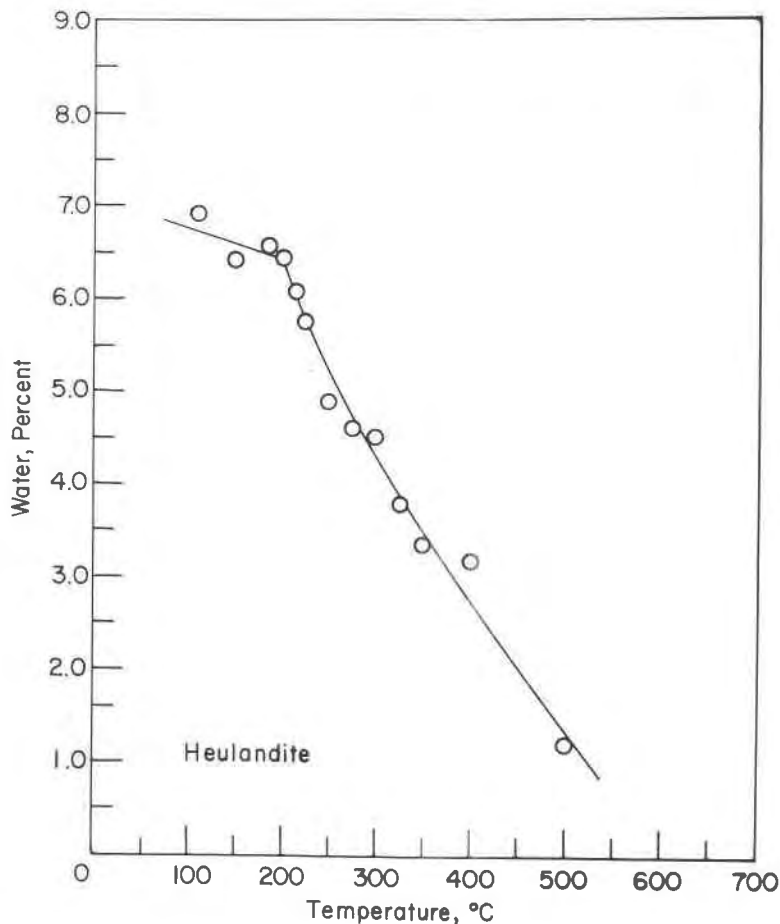


FIG. 2. Water content of heulandite after heating to various temperatures.

DISCUSSION

Mumpton (1960) reported that thermal gravimetric analysis (TGA) of heulandite, when heating is conducted at 40°C per minute, shows a sharply accelerated rate of loss of weight at about 250°C. This temperature is undoubtedly too high in view of the very rapid heating rate. Milligan and Weiser (1937) obtained the equivalent of a TGA curve for heulandite and reported two major losses of weight: one between 110° to 120°C, and the other between 200° to 220°C. The loss of weight at 110° to 120°C has not generally been reported by others and, again, there is no indication as to the conditions under which the curve was obtained.

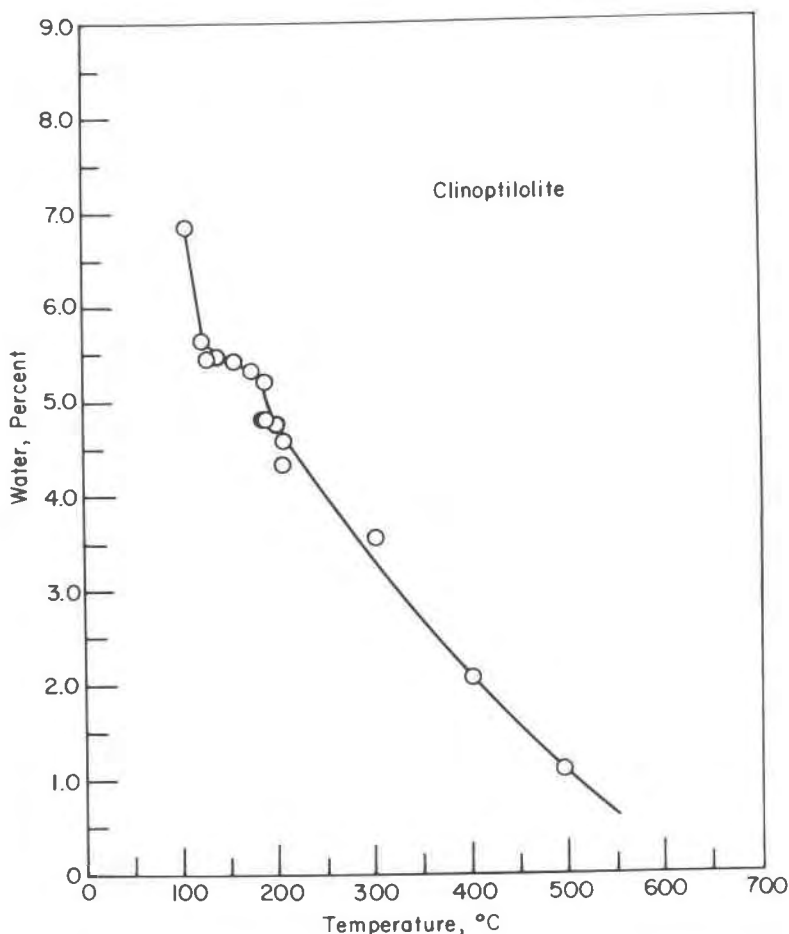


FIG. 3. Water content of clinoptilolite after heating to various temperatures.

Differential thermal analysis (DTA) curves for heulandite published by Mason and Sand (1960) and by Mumpton (1960) indicate major endothermic peaks at about 250° and 350°C, respectively. These curves, however, are difficult to interpret without information regarding the heating rates. Logvinenko, Kulesko, and Shumenko (1962) conducted DTA and TGA analyses on two samples of heulandite and reported endothermic peaks at 205° and 350°C, presumably when the samples were heated at 20°C per minute. As a footnote, they pointed out that static heating led to temperatures lower by 110° to 150°C. The TGA curves published by Logvinenko and co-workers are difficult to evaluate,

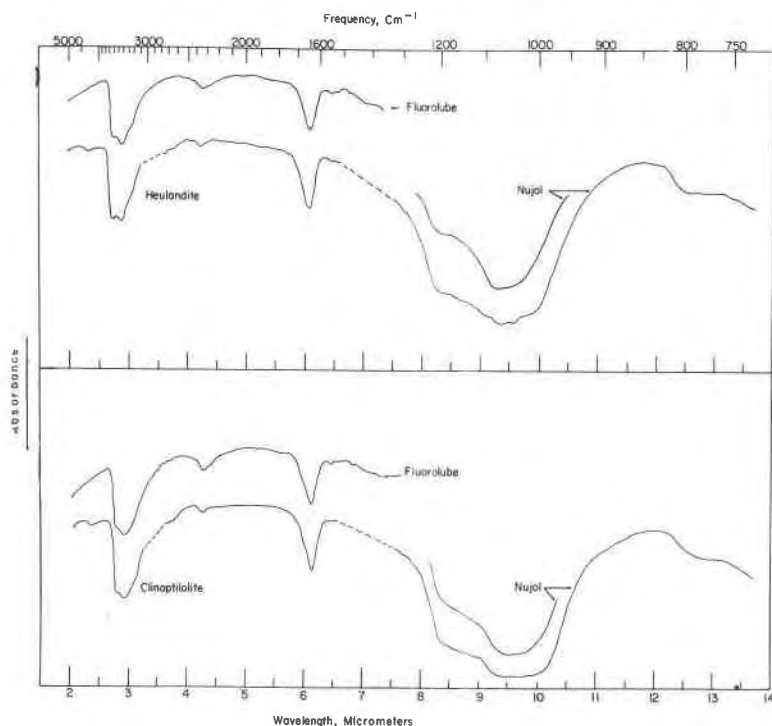


FIG. 4. Absorption spectra of heulandite and clinoptilolite in Nujol and Fluorolube mulls. Dashed lines indicate regions where Nujol absorbs; Fluorolube absorbs extensively at wavelengths greater than $7 \mu\text{m}$.

but there appears to be no sudden loss of weight that would correspond to either of the peaks noted in the DTA curves.

Koizumi (1953) conducted DTA and TGA studies on a specimen of heulandite from Japan and reported the mineral to undergo continuous dehydration up to 260°C , at which temperature 65 percent of its water had been lost. We have similarly noted the loss of approximately 68 percent of its total original water content (15.62 percent, see Figure 3) when our sample was heated to 260°C . Koizumi reported rapid dehydration of part of the residual water to occur at 280°C , with the remaining water being gradually lost as the sample was heated to 600°C . He also noted that his observations did not confirm those made by previous workers.

Difficulties in interpreting and comparing DTA and TGA curves have long been recognized. McAdie (1967), reporting for a Committee on Standardization of these methods (organized in 1965 at the First International Conference on Thermal Analysis), recommended that each DTA

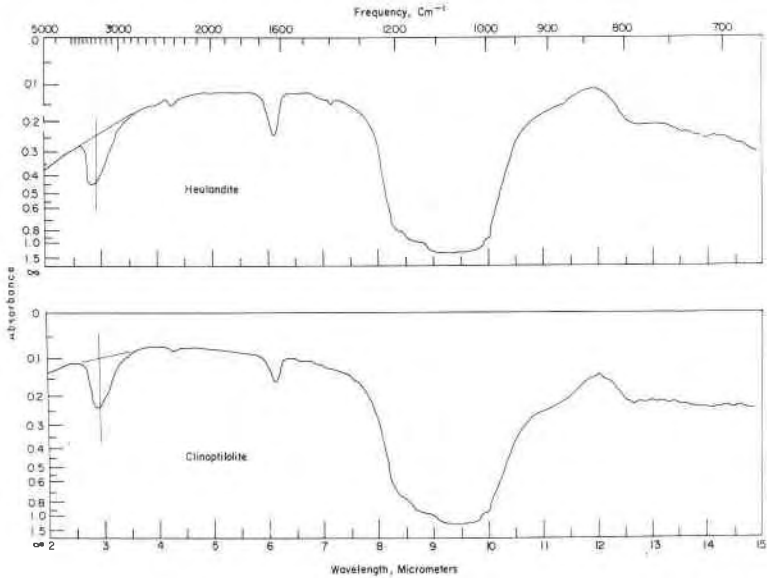


FIG. 5. Infrared absorption spectra of heulandite and clinoptilolite. Samples (1 mg) in potassium bromide disks (99 mg) heated to 110°C for 16 hours and scanned while at 110°C with reference to 100-mg disk of potassium bromide also at 110°C. Lines near 3 μm illustrate base-line technique for measuring absorbance for quantitative determination of water.

or TGA curve be accompanied by twelve informational parameters. Not one of the published curves for heulandite or clinoptilolite surveyed by us was properly referenced in this respect, making interpretation and comparison nearly impossible.

If present in a sample, hydroxyl groups are determined with, and reported as, water by the infrared technique that was used (Breger and Chandler, 1969). For compounds such as heulandite or clinoptilolite, where hydroxyl groups are absent, the method is specific for water.

The curve of Figure 2 shows the loss of water from heulandite to be slow between 110° and 200°C. At 200°C, however, a precipitous loss of water begins, and this rate of loss is nearly constant even up to 500°C, at which temperature the mineral still contains 1.20 percent water. Calibration of the furnace in which the samples were heated has shown the change in slope of the curve to occur at $200 \pm 3^\circ\text{C}$.

The inversion of heulandite on heating to a form known as heulandite B (Mumpton, 1960), as well as the partial re-inversion from heulandite B to heulandite when the temperature is lowered, have been described as sluggish. Shepard and Starkey (1964) reported the inversion to begin at 250°C and to reach its maximum intensity between 300° and 350°C; more recently (written communication, 1968) these same authors re-

TABLE 2. DATA FOR X-RAY STUDY OF HEULANDITE

Heating Cycle	Heating Program ^a				Relative 2 θ Intensities				Notes	
	Temperature	Time at Temperature		Total Time		9.9°	10.1°	10.25°		10.6°
		°C	Hrs.	Mins.	Hrs.					
I	25	—	—	—	—	100 ^b	—	—	—	Original, unheated sample.
	180	16	—	18	30	—	160	—	—	Maximum intensity of reflection at 10.1°.
	248	—	30	24	10	—	200	—	—	
	255	1	30	44	—	—	175	—	10	First appearance of transition phase (heulandite <i>B</i>).
	318	1	30	162	—	—	8	—	70	Transition to heulandite <i>B</i> complete.
	330	2	30	164	30	—	—	—	70	
	188	4	—	188	30	—	—	—	57	No reverse transition.
	117	16	—	208	30	—	—	10	30	Diffuse reflections. First appearance of 10.25° peak.
	96	5	30	216	—	—	10	20	25	Diffuse reflections. Three phases present.
25	16	30	232	30	—	—	28	—	Only new phase present.	
II	25	—	—	—	—	—	—	28	—	Sample from end of heating cycle I.
	132	—	16	—	45	10	13	25	—	Broad, diffuse reflections.
	160	—	5	—	50	—	—	10	45	Rapid transition to heulandite <i>B</i> .
	200	—	10	1	—	—	—	—	48	Heulandite <i>B</i> only phase present.
	160	—	10	1	25	—	—	20	30	Diffuse reflections.
	150	—	10	1	40	—	10	12	25	Diffuse reflections.
123	—	25	2	35	—	—	27	—	10.25° reflection dominant.	
III	123	—	—	—	—	—	—	27	—	Sample from end of heating cycle II.
	155	—	30	1	—	—	—	30	—	New phase only.
	169	—	45	1	45	—	—	30	15	Note transition to heulandite <i>B</i> .
	191	—	20	2	40	—	22	37	20	Reflections diffuse. Three phases present.
	273	—	10	3	40	—	—	37	40	10.25° reflection diffuse; 10.6° reflection sharp.
	327	—	10	4	15	—	32	—	42	10.25° reflection replaced by sharp 10.1° reflection.
	335	—	40	4	55	—	28	—	47	Heulandite <i>B</i> and 10.1° reflection persist.
	25	—	30	5	25	27	—	25	22	Three reflections appear on saturation with water.
	25	141	—	146	—	45	—	60	—	Only new phase present in saturated sample after saturation with water.

^a The integrated times of Column 3 are always larger than the corresponding totals of Column 2 because many intermediate steps were not diagnostic and have not been included in the Table.

^b Relative intensities are based on the 9.9° reflection of heulandite at 25°C taken as 100.

examined the inversion using a diffractometer heating stage and heating the samples at 2°C per minute. Under these conditions, they noted inversion to begin between 220° and 240°C, and reported it to be complete at 260°C.

In our work, only a thermally induced lattice contraction was noted between 25° and 180°C. This was probably related to the loss of loosely held water, and was indicated by a gradual increase in 2θ from 9.9° to 10.1°. The onset of a phase change was first indicated at 255°C by the appearance of a 2θ reflection at 10.6°. The reflection of the original heulandite at 10.1° was, however, evident even up to about 330°C, thus confirming earlier reports (Shepard and Starkey, 1964) of a sluggish transformation.

As indicated in Table 2 (heating cycle I), the only changes in the diffraction pattern of heulandite *B* as it is cooled from 330° to about 120°C is a decrease in the intensity of the 10.6° reflection. At 117°C this reflection becomes rather diffuse and a new reflection appears at about 10.25°. The intermediate phase indicated by this reflection is probably the same as that at 10.16° noted by Shepard (written communication, 1968) and Hay (1963).

Transitory re-inversion of heulandite *B* to heulandite took place only below 100°C as indicated by the 10.1° reflection at 96°C. In addition to this weak reflection, a series of reflections of moderate intensity also appeared between 10.2° and 10.4° at this temperature. When the sample was finally cooled to 25°C and maintained at that temperature for 16 hours, only a fairly sharp peak at 10.25° was noted, indicating that an irreversible structural transformation to a new phase had occurred.

On reheating the previously heated sample (Table 2, heating cycle II), inversion to heulandite *B* occurred fairly rapidly over a much lower temperature range, 160° to 200°C, as indicated by the appearance of the reflection at 10.6°. On cooling, rapid re-inversion to heulandite began at about 160°C. When the temperature reached 123°C, however, only a reflection at 10.25° related to the intermediate phase remained. Formation of heulandite *B* between 160° and 200°C during heating cycle II, instead of between 255° and 330°C as in heating cycle I, may indicate that loss of water during the first cycle facilitated the transformation at a lower temperature during the second cycle.

When cooled to 25°C after a third heating cycle (Table 2), reflections were noted at 9.9°, 10.25°, and 10.6°, indicating that heulandite, the intermediate phase, and heulandite *B* were all present together. Saturation of the sample with water while it was maintained at 25°C for a week led to disappearance of the 10.6° reflection, whereas the peaks at 9.9° and 10.25° persisted and became more pronounced.

Clinoptilolite was similarly analyzed between 81° and 500°C over an integrated period of 243 hours; no reflections indicating any change in crystal structure were observed, confirming earlier published observations (Butuzova, 1964).

Inasmuch as inversion of heulandite, as indicated by X-ray diffraction data, first occurs at 255°C, it is clear that the inversion is not accompanied by sudden dehydration. It is possible, however, that transformation of heulandite into heulandite *B* can occur only after the water content of the mineral is reduced to a critical level. Information taken from Figure 2 indicated the water content to be 5.25 percent at 255°C, the temperature at which inversion is first noted. Further loss of water might be complicated and retarded by changes in the structure of the heulandite. If this were the case, then the retarded release of water from the mineral with increasing temperature would explain the observed sluggish transformation to heulandite *B*. This explanation would require a dependence of the inversion on the residual water content of the heulandite. It has been noted that neither water content nor X-ray reflection has been found to change on prolonged maintenance of a sample at the same elevated temperature. It appears, therefore, that inversion of heulandite cannot begin if it contains more than 5.25 percent water, and is essentially complete when the water content has dropped to 3.8 percent (at 330°C).

It cannot be determined from these X-ray studies, or any other published studies, whether structural changes in the heulandite lead to the expression of part of its water, or whether loss of part of the water on heating results in structural changes, some of which are permanent. Pécsi-Donáth (1966) reported that heulandite begins to decompose into wairakite and silica at 330°C, but we have seen no evidence of quartz in our comparable X-ray patterns.

After the heulandite was heated and cooled through two cycles, further heating led to disappearance of the 10.25° X-ray reflection whereas the 10.1° and 10.6° peaks became more pronounced and persisted even to 335°C (Table 2). It must be remembered that the reflection at 10.1° is indicative of clinoptilolite and should not be present in the case of heulandite at this high temperature. It appears, therefore, that the heulandite may have undergone a transformation, such as exsolution, in which part was converted into heulandite *B*, and part into clinoptilolite. Additional experimental and analytical work would be necessary to confirm this suggestion.

Merkle and Slaughter (1968) have recently suggested that five molecules of water are coordinated about each calcium atom in heulandite, and that two of these water molecules are more tightly held than the

other three. Their structural conclusions were based on a chemical analysis, which indicated their sample to contain 13.67 percent of tightly bound water. On the basis of their analysis, they suggested the ideal formula:



for which the water content would be 15.1 percent. This formula is similar to that proposed by Pécsi-Donáth (1966), whose heulandite, from Fussa Valley, Tyrol, was reported to contain 15.39 percent *total* water. In both instances, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is 7/1. Wyart (1933) had previously suggested the same formula.

In view of the conclusion based on this formula that heulandite should contain about 15 percent of tightly bound water, it became essential to explain the fact that the water content of heulandite heated for 16 hours at 110°C in the current work contained only about 6.9 percent water (see Figure 3).

To examine this inconsistency, potassium bromide disks containing heulandite were made as before, and were analyzed at room temperature to determine the approximate total water content of the mineral; the average value obtained was 16.4 percent. On heating these disks to 110°C for one hour, the average water content of the mineral dropped to 12.9 percent, and the loss of water continued at a decreasing rate for the period of 45 hours during which measurements were taken. The rate of loss after 16 hours, at which time the water content had decreased to 7.2 percent, was relatively small. Chemical procedure for the determination of tightly bound water calls for the mineral specimen to be heated at 110°C for one hour, weighed, and then checked for "constant weight" in subsequent 15-minute intervals. Use of small samples and the hygroscopic character of substances such as heulandite make this determination difficult.

It is of extreme importance here to note that heulandite has been reported to contain about 13 percent of tightly bound water based on generally applied analytical techniques: Coombs *et al.* (1959), 12.45 percent; Merkle and Slaughter (1968), 13.67 percent; B. Ingram (Table 1), 12.88 percent. The value of 12.9 percent water found in this work by infrared analysis is consistent with these data. Development of an ideal formula for the mineral has been based on this value to a considerable extent, without recognition that this value for water is that for an undefinable intermediate for a sample as it is heated at 110°C for continuing intervals of time. In actuality, heulandite appears to contain only 6.9 percent water if heated for 16 hours at 110°C (Figure 2), and this value drops to 6.5 percent if the sample is heated for 16 hours at 200°C. This latter value, the point at which a break occurs in the dehydration

curve, should be taken as the true percentage of tightly bound water in the mineral, and all water above 6.5 percent should be considered to be loosely held water.

Merkle and Slaughter (1968) recognized the problem posed by water in heulandite and attempted to account for five of the six molecules of water in their ideal formula when determining the crystal structure of the mineral; the sixth molecule is presumably absent "because of unequal distribution of the calcium not all water sites have full occupancy. . . . in each calcium-water-framework relationship three of the five coordinated water molecules lie at a greater distance from the calcium than the other two, implying that two of the water molecules are more tightly held by the calcium than the other three."

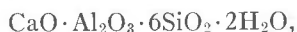
If the Merkle-Slaughter ideal formula were



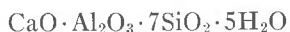
then the water content would be approximately 6 percent in accord with our observations.

As an additional note, Merkle and Slaughter attributed an endothermic peak at 350–400°C in their DTA curve of heulandite to the loss of the two molecules of water that are tightly bound in the structure. As shown in Figure 3, however, we have found that the loss of this water actually begins at $200 \pm 3^\circ\text{C}$ and is not complete even at 500°C, at which temperature heulandite still contains 1.2 percent water. Koizumi (1953) and Pécsi-Donáth (1966) also noted the presence of residual water in heulandite heated to 600°C.

A further observation is necessary with respect to the empirical formulas that have been proposed for heulandite. Most published analyses seem to indicate that the silica-alumina ratio is closer to 6 than to 7. If the true formula for the mineral were



the tightly bound water content would be exactly 6.5 percent, identical to that found in this work and shown in Figure 2. Koizumi and Roy (1960), who reported an "unequivocal" synthesis of heulandite based on the molar quantities of CaO, Al₂O₃, and 7SiO₂, reported the following empirical formula for the mineral:



Their suggestion, however, is not supported by an analysis of the product, nor can it be determined if the synthetic heulandite was accompanied by amorphous silica or other products that would tend to change the molar ratios of Al₂O₃, SiO₂, and water in the heulandite from those shown above.

In the current work, as in previously published studies, no change in the crystal structure of clinoptilolite was noted up to 500°C. The dehydration curve of Figure 3 is very similar to that for heulandite (Fig. 2), and indicates a very rapid loss of loosely held water to 125°C after which additional water of this nature is lost more gradually until a temperature of approximately 185°C is reached. At this temperature a sharp break in the dehydration curve reflects the initial loss of tightly bound water. This interpretation leads to the conclusion that clinoptilolite contains 5.2 percent of tightly bound water and, referring to Figure 3, that the mineral still contains about 20 percent of this water even when heated to 500°C.

The dehydration characteristics of heulandite and clinoptilolite are strikingly similar, except that the former begins to lose its tightly bound water at $200 \pm 3^\circ\text{C}$, and the latter at a somewhat lower temperature, namely, about 185° to 190°C. The difference between the higher ionic potential of calcium (2.0), the major cation of heulandite, and the lower ionic potentials of sodium (1.0) and potassium (0.75), the major cations of clinoptilolite, may result in the stronger retention of water in the former mineral. Piloyan and Novikova (1966) studied the dehydration kinetics of synthetic zeolites as well as of a natural heulandite. Their work led them to conclude that water is held more strongly in the natural product and, also as we suggest, that the higher the force field of the cation of the zeolite, the more tightly the water is bound in the structure of the mineral.

There appears to be no correspondence between the dehydration data obtained for heulandite and clinoptilolite in this work and that based on published DTA and TGA analyses. This discrepancy is difficult to evaluate because, as previously noted, of the absence of critical information regarding the techniques used for the DTA and TGA studies. As already mentioned, a critical factor is the heating rate. Thus, the slow loss of loosely held water followed by the incomplete loss of tightly bound water (Figs. 2 and 3) would tend to obscure both thermal and weight changes in the minerals unless proper analytical parameters were chosen. Failure to do so has undoubtedly led to the variety of published DTA and TGA curves, which contribute little or nothing to an understanding of how water is retained by heulandite and clinoptilolite. As noted by Pécsi-Donáth (1966) and by Piloyan and Novikova (1966), diffusion effects govern the rate at which water is lost when heulandite and other zeolites are heated.

Using published analyses for heulandite in which customary tightly bound water contents of about 13 percent are replaced by the value of 6.5 percent found in this work, the empirical, theoretical formula for the mineral of



can be calculated. The CaO may be replaced by (Ca, Na₂)O, and the SiO₂/Al₂O₃ ratio may be 6 or 7. These values depend upon the purity of the samples analyzed, the degree of replacement of Si by Al in the tectosilicate structure, and the degree of substitution for Ca by Na and other monovalent cations.

The analysis of clinoptilolite by Shepard and Starkey (1966) can be recalculated, using the value of 5.2 percent tightly bound water found in this work (Figure 3), to give



The cations (X) are primarily Na and K, with some Ca and Mg. Approximately 10 percent of the Si is replaced by Al in this particular sample.

The infrared absorption spectra for heulandite and clinoptilolite (Figure 4) are essentially identical between 2 and 14 μm , as has previously been observed by others (Kirov, 1967). Absorbances at 2.96 μm represent interactions between the potassium bromide and water (Breger and Chandler, 1969); those at 6.14 μm are related to molecular water. The broad absorption between 8 and 10 μm is related to silicate structure. The curves of Figure 4, obtained at room temperature, are very similar to those in Figure 5 except for the binodal absorbance in the former at 2.79 and 2.96 μm . Experience in the study of other minerals by the technique used in this work suggests that one of these peaks, that at 2.79 μm , be assigned to loosely held water (H₂O-), whereas the other, at 2.96 μm , be assigned to tightly held water (H₂O+). This designation of absorptions is contrary to that normally to be expected with the hydrogen bonding of water molecules where hydroxyl stretching frequencies normally decrease as bond strength increases. It is possible that at low water content the water molecules may be retained more tightly by the cations and that the hydrogen bonds between the water molecules are, therefore, lengthened.¹ It is quite clear that infrared absorption in the 2 to 14 μm region of the spectrum is of little value in distinguishing between heulandite and clinoptilolite. Moreover, differences in SiO₂/Al₂O₃ ratios in the two minerals cannot be recognized from these spectra.

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