THE AMERICAN MINERALOGIST, VOL. 45, MARCH–APRIL, 1960

CLINOPTILOLITE REDEFINED

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ABSTRACT

Since its introduction into the literature in 1923, clinoptilolite has been a subject of confusion within the zeolite group of minerals. A critical review is made of papers dealing with the original description of clinoptilolite, its occurrence in the groundmass of altered pyroclastics and of the arguments favoring its identity with "silica-rich" heulandite.

New experimental data on clinoptilolite from Hector, California, and on other samples from Tertiary sediments assist in the redefinition of this zeolite. Although the powder pattern of clinoptilolite is almost identical with that of heulandite, high temperature *x*-ray diffraction studies show that at about 230° C., heulandite transforms into "heulandite B," and at 350° C. becomes amorphous. Clinoptilolite, however, remains stable to about 700° C. without reaction at lower temperatures.

The data of chemical, optical and differential thermal analyses are also employed to redefine clinoptilolite as the high-silica member of the heulandite structural group usually containing monovalent rather than divalent cations, and to retain the name as a valid mineral species on equal status with heulandite.

The enrichment of silica in the clinoptilolite lattice as compared to heulandite is apparently correlatable with its increased thermal stability, and is probably a direct consequence of its origin from altered volcanic glass.

INTRODUCTION

The recent work of Ames, Sand and Goldich (1958) on the Hector, California bentonite deposit has disclosed the presence of a zeolite mineral in beds of altered pyroclastic material, closely associated with the montmorillonite, hectorite. This zeolite was identified by them as clinoptilolite, a mineral first named by Schaller in 1923. The exact distinction between clinoptilolite and heulandite, however, has been the subject of discussion for many years.

Hey and Bannister (1934) concluded from similarities in *x*-ray diffraction patterns that minerals previously reported as clinoptilolite were simply "silica-rich heulandites" and that there was little to justify use of the former name.

If the mineral first described by Pirsson in 1890 from the Hoodoo Mountains, Wyoming, and subsequently named clinoptilolite by Schaller (1933) were a unique occurrence, there would be little justification for a detailed redefinition of the species at this time. However, other occurrences of "heulandite-like" or "clinoptilolite-like" zeolites have been reported from the groundmass of altered pyroclastic beds and their lacustrine equivalents, not to mention the extensive heulandite-tuff horizons of South Island, New Zealand (Coombs, 1953). (See also Bramlette and Posnjak, 1933; Kerr, 1951; Kerr and Cameron, 1934; Regnier, 1958;

Deffeyes, 1958; Weeks, 1958; Weber, 1957, and Van Houten, 1959.) The relatively widespread distribution of heulandite-clinoptilolite zeolites would seem to necessitate a proper redefinition of such species and the properties by which one may readily distinguish them from each other.

The present study attempts to redefine the material clinoptilolite by first reviewing the published results of others and secondly by presenting new experimental data determined on heulandite and clinoptilolite samples. These data clearly indicate that clinoptilolite is a valid mineral species closely related to, but clearly distinct from, heulandite.

PREVIOUS WORK

In 1890 the second occurrence of "mordenite" was reported by L. V. Pirsson from the Hoodoo Mountains of northwestern Wyoming. This zeolite was found in the amygdules of a weathered basalt and, despite its platy habit, was identified with the mordenite from Nova Scotia described by How (1864), primarily on the basis of its chemical analysis. Pirsson's analysis of optically homogeneous material (see Table 1) yields a base:alumina:silica:water mole ratio of 1:1:10:6.6 which is close to the 1:1:9:6 reported by How and the 1:1:10:7 ratio reported for ptilolite (Cross and Eakins, 1886). It occurs as small, platy crystals (1×1×4 mm.) unlike the habit of either Nova Scotia mordenite or the fibrous ptilolite for Colorado (Cross and Eakins, 1886). Crystallographically this zeolite was reported by Pirsson to be identical with heulandite. Its optical properties, however, are not completely consistent with those of mordenite (Schaller, 1932).

In reviewing Pirsson's description, Schaller (1932) concluded from new optical determinations, its platy habit and monoclinic crystallography, that the Hoodoo Mountain zeolite should be classified as neither mordenite or ptilolite, and instead, proposed the new name "clinoptilolite" for this species, alluding to its compositional similarity with ptilolite and its rather large extinction angle.

The widespread distribution of materials answering the above descriptions was first noted by Bramlette and Posjnak (1933) who pointed out that clinoptilolite is a common alteration product in pyroclastics where alteration has not proceeded as far as the formation of montmorillonite. Samples of Tertiary bentonite from San Luis Obispo County, California, Dome, Arizona and Pedro, Wyoming, were examined and in each instance the small crystals and almost isotropic relic shards from the washed residues could be identified optically and crystallographically with the clinoptilolite of Schaller. An analysis of the Dome material is close to that of clinoptilolite if allowance is made for about 5% clay impurity. A pure sample was not available, however, and the presence of quartz, feldspar, montmorillonite and unaltered volcanic glass is likely. For the first time, *x*-ray diffraction patterns of clinoptilolite were taken and although no *d* spacings were reported, the patterns were described by Bramlette and Posjnak as distinct from that of mordenite, but practically indistinguishable from that of heulandite.

The *x*-ray similarity between clinoptilolite and heulandite was further expanded by Hey and Bannister (1934) who themselves took rotation photographs around the *a* axis of a single crystal of clinoptilolite from the type locality, No. 5268, in the Brush Collection at Yale University. The results were "completely identical" with the *a* axis rotation photograph of heulandite. They explained the wide differences in optical properties between clinoptilolite and heulandite as due to slight difference in chemical composition and concluded that these zeolites must be members of the same isomorphous series (*sic*) and the name clinoptilolite is unnecessary.

Since the work of Bramlette and Posjnak (1933), zeolites resembling the clinoptilolite of Schaller have been described from numerous localities as alteration products of volcanic ash and pyroclastic beds. Kerr (1931) described rhyolitic glass from Ventura, California showing alteration to a weakly birefringent, platy zeolite whose indices of refraction matched closely those of heulandite. In a bentonite from Tehachapi, California, Kerr and Cameron (1936) noted a clear, colorless, platy zeolite in amounts up to ten per cent, also with low birefrigence and a mean index of refraction around 1.475. *X*-ray diffraction patterns of this material gave lines which could be identified with those of heulandite.

Also of significance is the heulandite reported by Fenner (1936) as groundmass cement in drill cores from Yellowstone, and by Steiner (1953) at the Hotsprings of Wairakei, New Zealand. Gilbert and McAndrews (1948) described an authigenic zeolite resembling either heulandite or clinoptilolite from a marine arkose in Santa Cruz County, California. They report that this material is unaffected by boiling 20 per cent HCl and has optical properties more closely approximating those of clinoptilolite than the literature values for heulandite. In addition they reported a significant difference in the effect of heating on the optical axis of their authigenic zeolite compared with normal heulandite.

Coombs (1954) has studied in detail the thick sequence of altered volcanic tuff near Southland, New Zealand of Triassic age and reports the presence of considerable amounts of zeolite minerals including a heulandite-like species. His chemical analysis of slightly impure material gives rise to a mole ratio of 1:1:6.2:5. This mineral occures in fibers or lamellae replacing volcanic glass shards. Coombs concludes that this mineral is "essentially a normal heulandite and not the silica-rich variety, clinoptilolite . . . which has been frequently reported in tuffs."

On the basis of chemical and optical data Ames, Sand and Goldich (1958) concluded that the tabular zeolite associated with hectorite at Hector, California, was identical with the clinoptilolite of Schaller. The "silica-rich heulandite" argument of Hey and Bannister (1934) was not considered by them even though the *x*-ray pattern of the Hector material matches well that of heulandite. Although the present author has noted the presence of up to 10 per cent fine-grained quartz and feldspar in the clinoptilolite samples kindly supplied by Drs. Ames and Sand from this locality, the above authors reported a mole ratio of 1:1:10:6 for this zeolite, as calculated from their chemical analyses. The mean index refraction of this material is 1.480, compared with 1.500 for heulandite.

In addition to the several dozen pyroclastic beds of the Western states sampled by the author, unpublished data kindly supplied by Drs. F. B. Van Houton, K. Deffeyes, J. Regnier and G. C. Kennedy, have led to the realization that clinoptilolite is not an uncommon alteration product of volcanic pyroclastics, and that a clear distinction between clinoptilolite and heulandite is imperative at this time.

EXPERIMENTAL RESULTS

During the course of a broad mineralogical study of natural and synthetic zeolites, a number of samples of heulandite and clinoptilolite have been examined. It should be especially noted that most of the samples referred to as clinoptilolite are actually clinoptilolite-rich rocks. Pure fractions of clinoptilolite are extremely difficult to separate and consequently much of the work on this mineral has been carried out on unbeneficiated samples, containing up to 25% quartz, feldspar and montmorillonite impurities. The samples from Hector, California, Fish Creek Mountains, Nevada and Patagonia are all at least 90% pure; the last sample appears to be 99% clinoptilolite. *X*-ray diffraction studies, optical examinations and thermal treatments, are, of course, little affected by small amounts of impurities. In addition, many significant trends may be ascertained from chemical analyses of slightly impure material even though exact empirical formulas may be calculated only from analyses of pure minerals.

X-Ray Diffraction and Optical Data

A sample labeled as Pirsson's type mordenite from Hoodoo Mountains, Wyoming, was borrowed from the Brush Mineral Collection of Yale University, No. 5268. The prominent phase of this specimen occurs as pink, radiating needles and showed the characteristic *x*-ray diffraction pattern of well-crystallized mordenite. The friable white matrix consisted of quartz and feldspar. Evidently, this specimen is not the same material examined by Hey and Bannister (1934) (*vide supra*). If no additional Hoodoo Mountain type material can be located, it is indeed difficult to interpret data previously determined on Pirsson's original material.

Drs. L. B. Sand and Lloyd Ames kindly supplied several samples of the material described by Ames, Sand and Goldich (1958) as clinoptilolite from Hector, California. In thin section the rock consists of about 20% cavities or voids (plainly visible in hand specimens) about 1–2 mm. in diameter, 70–75% weakly birefringent platy crystals less than 2 microns in size and about 10–15% quartz, feldspar, and montmorillonitic impurities (see Fig. 1). The major component occurs as tiny, shredded plates or laths, replacing the glass shards, relicts of which are abundant in the section. In many places the clinoptilolite can be seen projecting out into cavities from the edges. The crystalline impurities are about .1–.5 mm. in size.

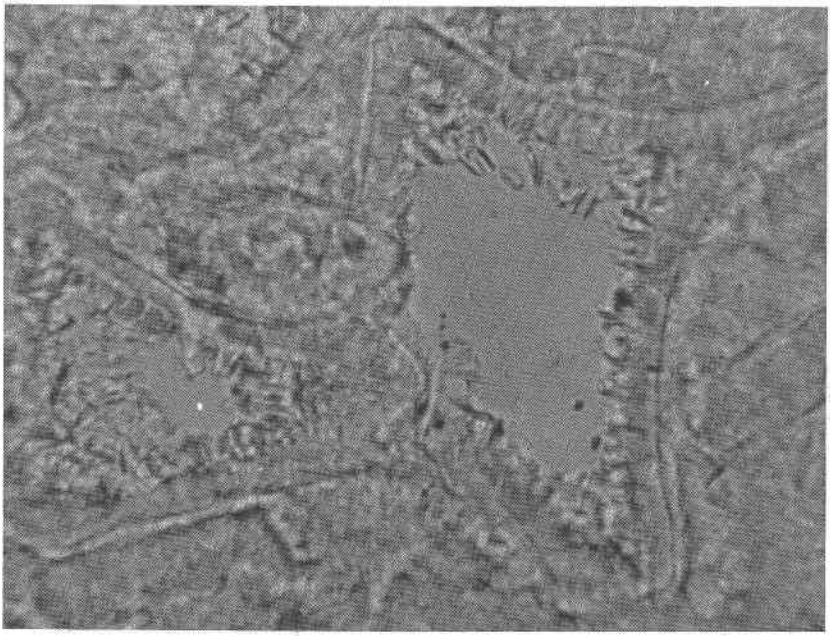

FIG. 1. Photomicrograph of altered volcanic tuff, Hector, California. ×700.

The *x*-ray diffractometer trace (Table 1, Fig. 2) is similar to that reported by Ames, Sand and Goldich (1958), both being very similar to heulandite. No feldspar peaks were observed and only a broad, diffuse peak could be measured at low angles, to indicate montmorillonite. The

TABLE 1. LATTICE SPACING FOR CLINOPTILOLITE AND HEULANDITE

Hector, California Clinoptilolite		Prospect Park, New Jersey Heulandite	
d	I/I$_0$	d	I/I$_0$
9.00	10	8.90	10
7.94	4	7.94	2
6.77	3	6.80	1
6.64	2	6.63	1
5.91	1	5.92	1
—	—	5.58	1
5.24	3	5.24	1
5.11	1	5.09	1
—	—	4.89	1
4.69	2	4.69	2
4.48	2	4.45	2
4.34	2	4.36	1
3.96	10	3.97	2
3.90	8	3.89	3
3.83	1	3.83	1
3.73	1	3.71	1
3.55	2	3.56	1
3.46	2	3.47	1
3.42	6	3.40	2
3.12	3	3.12	1
3.07	2	3.07	1
3.04	2	3.03	1
2.97	5	2.97	4
2.87	1	—	—
2.82	3	—	—
2.80	1	2.80	1
2.73	1	2.72	1
2.72	1	—	—
2.68	1	2.67	1
2.44	1	2.48	1
2.42	1	2.43	1
2.38	1	2.35	1
2.29	1	2.28	2

intense peak at 3.34 Å is coincident with the major quartz line. High temperature *x*-ray diffraction data given below prove conclusively that this is a quartz peak. Several fractions of the powdered sample were prepared by means of simple water sedimentations. Aside from an increase in the intensity of the montmorillonite peak in the lightest fraction, no other changes were observed.

In Fig. 2 are shown the *x*-ray diffractometer traces of heulandite from

Prospect Park, New Jersey, and clinoptilolite from Hector, California. These tracings are typical of many other samples examined by the author and the corresponding *d* spacings and intensities are listed in Table 1. The *x*-ray diffraction tracings of 7 typical heulandite and 8 clinoptilolite specimens are shown schematically in Fig. 3. The peaks of clinoptilolite are consistently much stronger than those of heulandite, and somewhat broader. Many of the weak peaks present in clinoptilolite tracings are absent in those of heulandites. The (020) reflection of heulandite at 9.9°2θ is always far more intense than the remaining lines of the pattern, while this same reflection in *x*-ray tracings of clinoptilolite is, in many samples, exceeded in intensity by the (004) peak at about 22.3°2θ. The many differences between diffractometer tracings of clinoptilolite and heulandite have proved quite adequate for the identification and differentiation between these two similar zeolites. From the spacing differences listed in Table 1, the unit cell of clinoptilolite appears to be slightly larger in the *b* dimension than heulandite (using the structural scheme of Ventriglia, 1955, for heulandite).

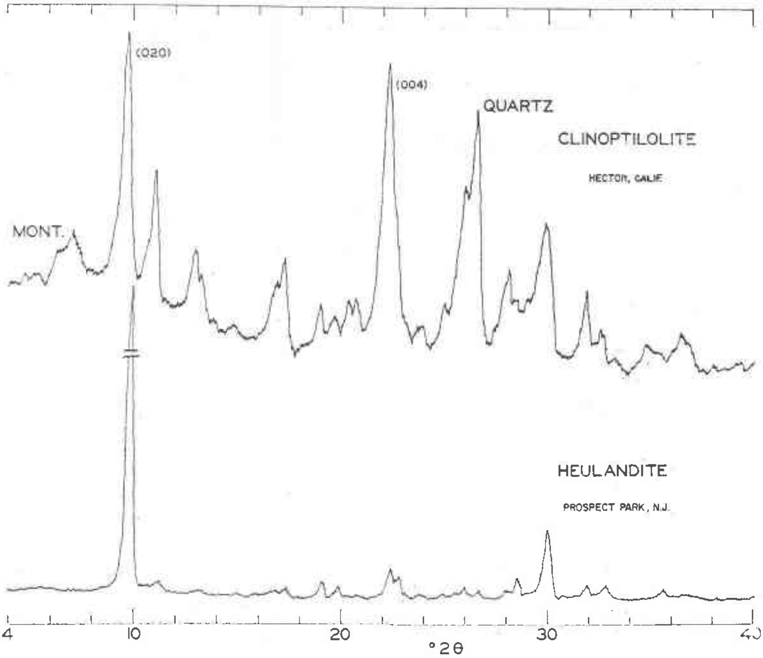

FIG. 2. *X*-ray diffraction tracings of heulandite and clinoptilolite.

The *x*-ray diffraction pattern published by Coombs (1958) of a cli-

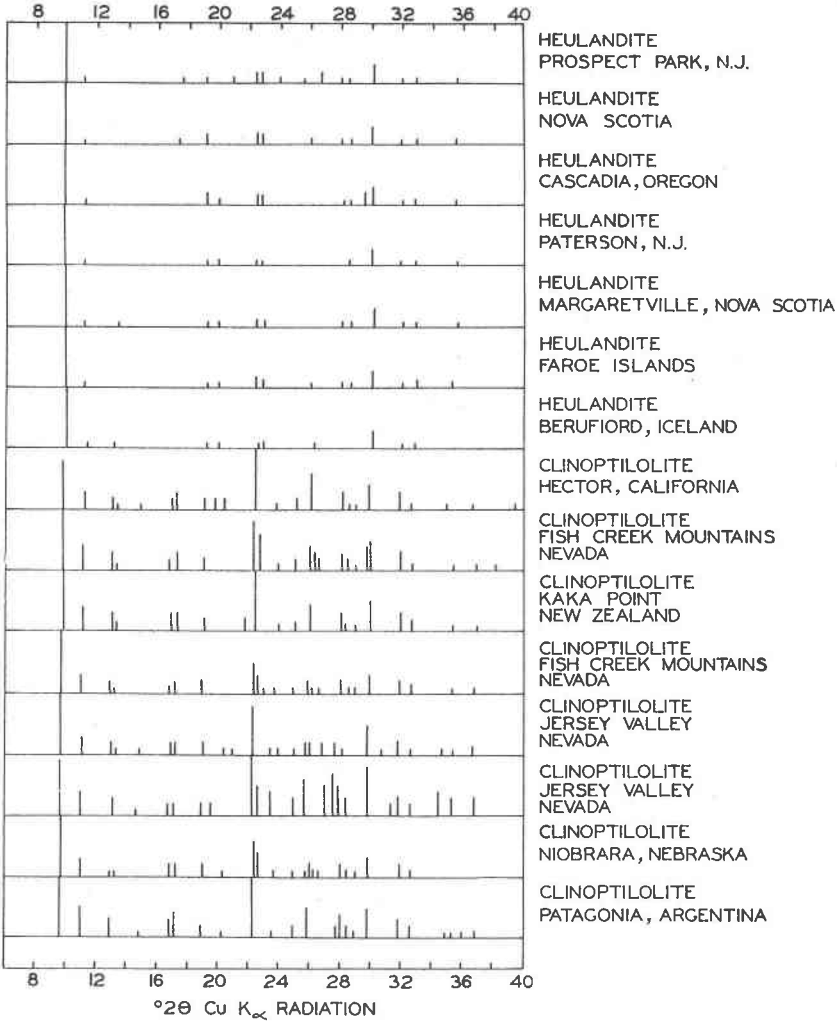

FIG. 3. Typical *x*-ray diffractometer patterns of heulandite and clinoptilolite (schematic).

noptilolite sample from Seaham, New South Wales also shows slightly greater *d* spacing unit cell and the typical clinoptilolite peak intensities, compared with heulandite.

Film patterns of heulandites and clinoptilolites are very similar and only with precise measurements can spacing differences between the two minerals be noted. The line intensities are also very similar, indicating that the packing of the sample for a spectrometer trace has resulted in a preferred orientation of heulandite grains. Most clinoptilolite grains are normally less than 1 micron in diameter and thus little orientation takes place when the sample holder is packed.

Thermal Data

Perhaps the strongest data supporting clinoptilolite as a valid mineral species, distinct from heulandite, are those determined by high temperature *x*-ray diffraction techniques, differential thermal analyses and thermal gravimetry. A heulandite from Prospect Park, New Jersey, and a clinoptilolite from Hector, California, were studied by the first of these methods in the following manner. The samples were powdered and packed into a platinum holder, which was then placed vertically in the *x*-ray beam of a Norelco 90° Diffractometer. A platinum-wound resistance furnace was placed around the sample holder and the temperature raised at intervals to 1200° C. The temperature was measured by chromel-alumel thermocouples, changed at frequent intervals, and could be controlled at ±5° C. for several hours and at ±10° C. overnight, at temperatures below 900° C. The results of the thermal *x*-ray study readily distinguish between heulandite and clinoptilolite.

No transitions or reactions were observed in clinoptilolite up to about 750° C. At this temperature the structure began to collapse after heating for 4 hours. Heating at higher temperatures resulted in the complete disappearance of the *x*-ray diffraction pattern and the formation of an amorphous product, resembling a glass. The prolonged stability of the peak at 3.34 Å, however, long after the clinoptilolite pattern had disappeared, indicates that this peak is the major quartz peak, an initial contaminant of the sample. Many quartz-free samples of clinoptilolite have been found whose *x*-ray tracings do not show this peak.

Heulandite, on the other hand, is far less stable to thermal treatment and undergoes a reaction at about 230±10° C. Above this temperature the phase present has been identified with the "heulandite B" of Slawson (1925) and Milligan and Weiser (1937) and Koizumi (1953).

In Fig. 4 are the typical differential thermal analysis patterns of heulandite and clinoptilolite. The patterns of a dozen other samples were all quite similar. Although the temperatures of the reactions are slightly greater than those determined by high temperature *x*-ray diffraction, they represent the same phenomena described above. Aside from the broad endothermic peak, clinoptilolite exhibits no further thermal reaction up to 1000° C. Heulandite, however, shows an additional very sharp endotherm at approximately 300° C. which undoubtedly corresponds to the sluggish heulandite-"heulandite B" reaction, shown to take place at 230° C. by the high temperature *x*-ray diffraction study.

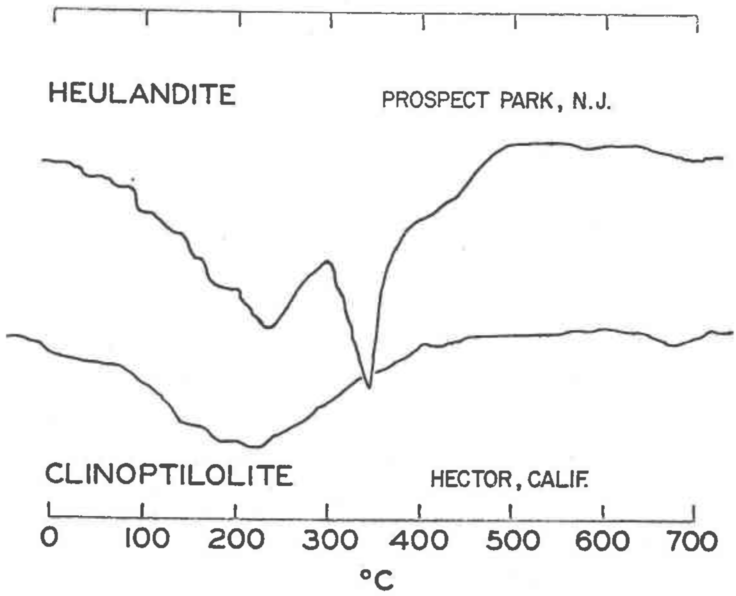

Fig. 4. DTA patterns of heulandite and clinoptilolite.

Thermal gravimetric analyses of heulandite at a heating rate of 40° per hour show a sharp steepening of the weight loss curve also in the region of 250° C. No break in the weight loss curve was noted for clinoptilolite.

Other authors have indicated thermal reactions for heulandite close to 120° C., but no evidence of such phenomena could be found in this study (see Milligan and Weiser, 1937).

If the differences in thermal stability between heulandite and clinoptilolite are due solely to the nature of the exchange cation in each species (*vide infra*) one might expect a calcium-exchanged clinoptilolite to exhibit the low temperature reactions and low thermal stability of heulandite. Conversely, a sodium-exchanged heulandite should be more thermally stable than the calcium variety. Such is not the case. Clinoptilolite from Hector, California, was almost completely exchanged to the calcium form by repeated slurrying with a large excess of a 1 Normal calcium chloride solution. A chemical analysis of the washed product gave 6.4 wt-% CaO, 0.2 wt-% Na_2O. If it is assumed that no exchange of the potassium and magnesium occurred, the clinoptilolite product is greater than 90% calcium exchanged. The *d* spacings and intensities of the peaks are virtually identical with those of the original clinoptilolite. A sodium-rich form of heulandite could not be prepared by the above methods even when boiling sodium chloride solutions were used.

Differential thermal analysis of the calcium exchanged clinoptilolite resulted in a pattern insignificantly different from that of the original sodium-potassium form, indicating that Ca-clinoptilolite does not transform to a "B" phase at low temperatures and is thermally stable well above the decomposition temperature of Ca-heulandite. This material was heated overnight at 450° C. and examined by *x*-ray diffraction methods. Only slight, if any, loss of structure was noted from the diffraction tracing.

At 550° C., after 24 hours, most of the structure of the Ca-clinoptilolite was destroyed although the main *x*-ray diffraction peaks were still discernible.

These data indicate that, although the calcium form of clinoptilolite is somewhat less stable than the sodium-potassium form, Ca-clinoptilolite does not resemble heulandite in its *x*-ray diffraction pattern nor in its low thermal stability. The presence of additional "structural" silica in the clinoptilolite lattice, compared with heulandite, appears to be more responsible for its increased stability than the nature of the exchange cation.

Chemical Composition

According to Pirsson's original analysis of the Hoodoo Mountain material, clinoptilolite has the molecular formula 1:1:9:6.8, base:alumina:silica:water, considerably more silica than most heulandites. In addition the dominant cation in heulandites is calcium, while this analysis listed almost equal parts of lime, soda and potash.

Due to both the fine grain character of almost every other clinoptilolite sample collected from sediments of pyroclastic origin, and the intimate association of the zeolite with admixed montmorillonite, opal and volcanic glass fragments, it has been almost impossible to separate a pure fraction of the zeolite for chemical analysis. It has been equally difficult to determine the purity of such a mixture after a particular separation attempt, since both optical and *x*-ray diffraction methods are of little use. Little confidence, therefore, can be placed on empirical formulas derived from the literature analyses of clinoptilolite, since the purity of the samples is uncertain. The analysis of "pure" clinoptilolite sample has recently been reported by Ames, Sand and Goldich, although the *x*-ray diffraction pattern of this material indicates the presence of several per cent quartz. In thin sections of Hector clinoptilolite, about 10 per cent quartz can be distinguished.

Mason (personal communication) reports chemical data for a clinoptilolite sample from Patagonia which lead to the empirical formula, $(.04\ MgO\ .07\ CaO\ .64\ Na_2O\ .25\ K_2O)Al_2O_3\ 10.8\ SiO_2\ 6.5\ H_2O$. By *x*-ray diffraction and optical examinations, this material appears quite pure, probably containing less than 1% impurities. Electron microscopy, however, reveals the presence of trace amounts of a foreign phase.

The meager chemical data in the literature indicate that clinoptilolite has a silica/alumina ratio of about 8.5 to 10.5 and contains predominantly monovalent over divalent cations.

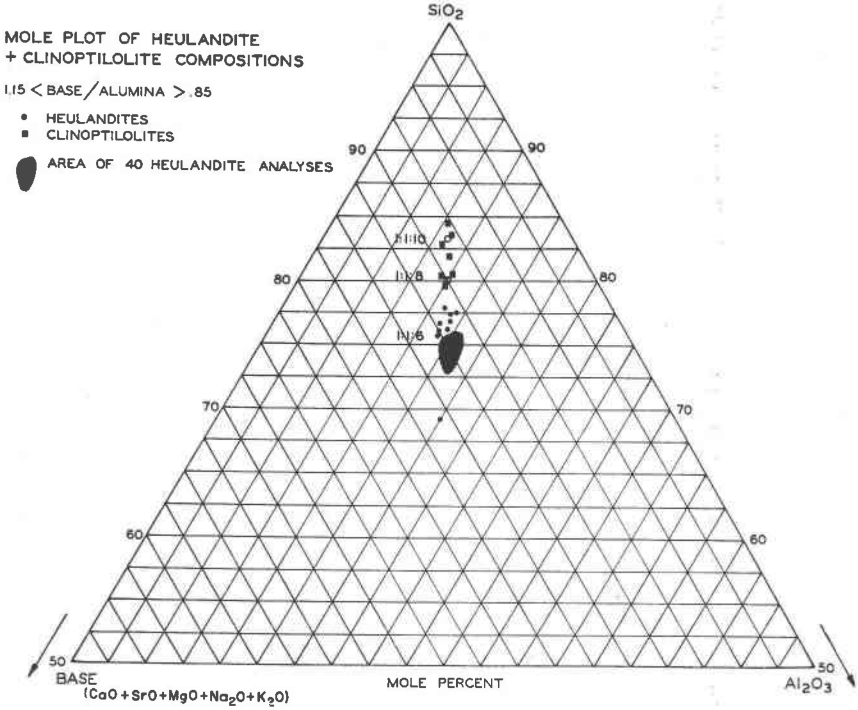

FIG. 5. Mole compositions of heulandites and clinoptilolites plotted on the ternary diagram base-alumina-silica.

The mole compositions of nearly 50 selected heulandite analyses are plotted in Fig. 5. The distribution of silica/alumina ratios for these literature analyses is shown in Fig. 6. From both figures it can be seen that the SiO_2/Al_2O_3 ratio of heulandites varies from 5.4 to 6.7, with only a few analyses greater than 6.7 (the accuracy of which are unknown).

Although not as conclusive as the differences in silica content, heulandites and clinoptilolites may also be differentiated on their water content. The number of moles of water per mole of alumina in heulandites varies between 5 and 6 while in clinoptilolite this ratio is usually between 6 and

7 (see Fig. 6). It is also interesting to note the difference in the so-called exchange cations of these two similar zeolites. In Fig. 7 are plotted the exchange cation compositions of heulandites and the few clinoptilolites available. It can be seen that heulandites are overwhelmingly calcium-rich while clinoptilolites contain major proportions of sodium and potassium. (Many heulandite analyses list considerable SrO, which has been added to the CaO for simpler calculations.)

At first glance it may seem plausible to distinguish these two minerals on the basis of the differences in their exchange cations. A distinction based solely on these grounds is, however, quite inadequate and can only be secondary to the much more significant difference in the silica content. The cation content of a zeolite is determined primarily by the cation environment at the time of crystallization and secondarily by the composition of the ground waters passing over it since that time. It is unlikely that ground waters could change the cation composition of heulandite although clinoptilolite might well be influenced by them. It is not unlikely that in the future a calcium form of clinoptilolite will be uncovered in nature, possibly in an environment much like the New Zealand hot springs locality described by Steiner (1953) and the tuffs described by Coombs (1954).

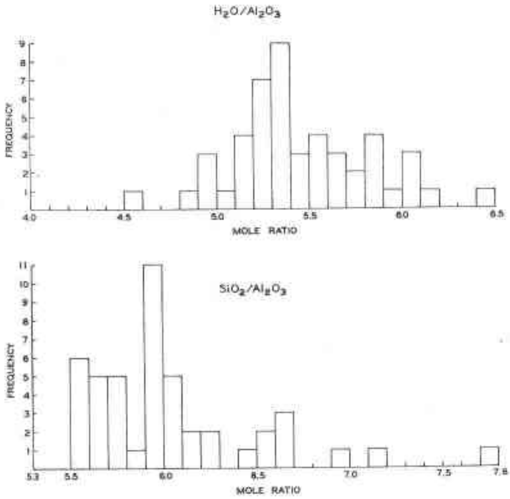

FIG. 6. Frequency distribution of mole ratios for heulandites. $(1.15 < \text{base/alumina} > 0.85)$

There is no precedent for naming two mineral species, which differ only on their exchangeable cation content. Individual names are not given to the many varieties of montmorillonite simply because the exchangeable cations are different from one specimen to another. Montmorillonoid minerals have been classified on the basis of the difference in nature of the so-called "structural" cations, that is, the ions of the tetrahedral and octahedral layers. It seems reasonable then to differentiate heulandite and clinoptilolite by the differences in their "structural" ions—the significant variation in the silica and alumina contents of their unit cells.

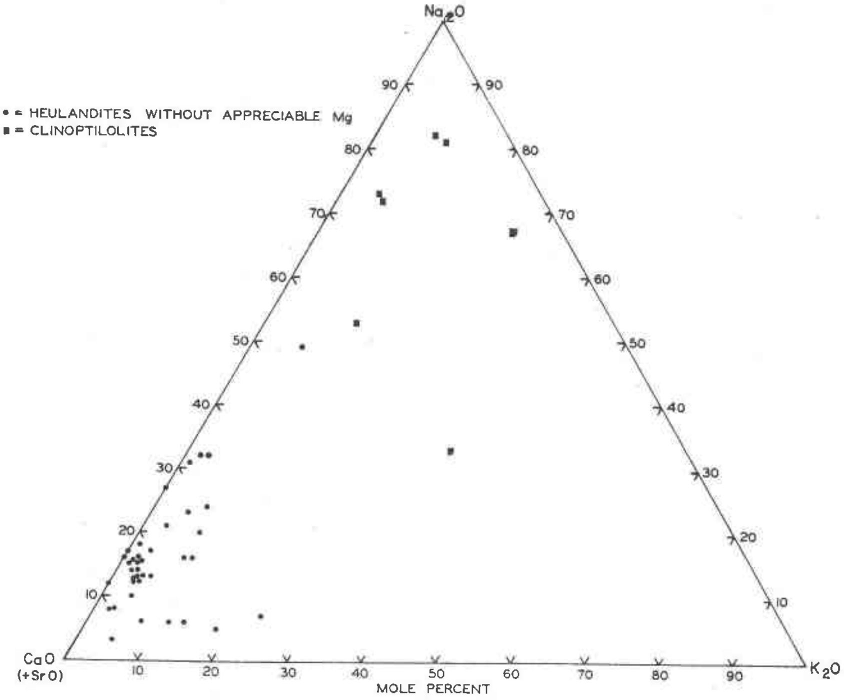

FIG. 7. Mole plot of base distribution in heulandites and clinoptilolites.

Despite the isomorphous relationship between the structures of heulandite and clinoptilolite there is little evidence to suggest the existence of complete solid solution between these two minerals. Chemical analyses and other properties indicate two distinct zeolite species.

To use the chemical analyses of minerals from the literature in support of a particular hypothesis is quite risky and only overwhelming evidence in favor of a proposed theory can be considered acceptable. If only a few scattered analyses of heulandites were to be presented, the existence of a continuous solid solution between the mole ratios 1:1:5 and a 1:1:10, base:alumina:silica, would appear plausible. If, however, many more analyses are calculated and plotted, as in Figs. 5 and 6, such a hypothesis cannot be accepted on the evidence available. Despite the so-called ideal unit cell ratio of 1:1:7, as determined by Wyart (1933), the analyses of natural minerals favor a range of 5.5 to 6.5 for the silica/alumina ratios of heulandites.

Clinoptilolite may, therefore, be defined chemically as the high silica member of the heulandite structural group usually containing more monovalent rather than divalent cations.

Such differences in the silica/alumina ratio of zeolites of the same structural type are, of course, quite significant and can be correlated directly with acid and thermal stabilities. Recent unpublished studies in this laboratory suggest that the silica content of certain zeolites is a direct function of the chemical environment from which these zeolites crystallized. Analcite, phillipsite, and erionite from igneous rocks all contain lesser amounts of silica in their structures than do their "sedimentary" equivalents. This may be due to the nature of their formation from volcanic glass particles by the action of ground waters. The availability of large amounts of silica in the glass combined with the presence of soda and potash in both the glass and the attacking waters may account for the subsequent high-silica, high-soda content of the zeolite.

TABLE 2. HYDROTHERMAL STABILITY OF CLINOPTILOLITE

Temperature ° C.	Pressure psi	Duration Days	Products
		*Clinoptilolite, Hector, California**	
300	20,000	8	Clinoptilolite+some Mordenite+Quartz
355	15,000	15	Mordenite+some Montmorillonite+Quartz
395	20,000	17	Montmorillonite+Albite+Quartz
		Clinoptilolite, Patagonia	
300	20,000	8	Clinoptilolite
355	15,000	15	Mordenite
445	20,000	7	Albite+Cristobalite+?

* Quartz and a small amount of montmorillonite are present in starting material.

*Hydrothermal Data**

According to Buckner (1958) clinoptilolite transforms to mordenite at 300° C. and 20,000 psi water vapor pressure. This reaction has been re-

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* Hydrothermal studies were carried out using standard methods and equipment previously described by Roy and Roy (1955) and Roy, Roy and Osborn (1953).

peated by the author on three samples of clinoptilolite, the results of which are listed in Table 2. All samples were reacted in sealed gold tubes containing a drop of distilled water. The samples did not react in identical manners under the same pressure-temperature conditions, possibly reflecting small differences in composition of the clinoptilolites. At 300° C., the Hector material begins to transform into mordenite and analcite while the Patagonia specimen remains stable after 8 days. At 355° C. both are almost completely converted to mordenite. Since the starting material contained an abundance of soda, sodium mordenite was produced, together with small amounts of silica. An envelope run at 300° C. of the Hector material resulted in the formation of analcite, quartz and some montmorillonite, indicating a possible leaching of silica from the starting material, which does not occur in the sealed tubes. Above 400° C. hydrothermal treatment of clinoptilolite resulted in the formation of alkali feldspars and silica. These data suggest that the upper limit of "stability" of clinoptilolite under hydrothermal conditions is probably about 300° C. or less.

Dr. M. Koizumi (personal communication) has found that heulandite decomposes to wairakite only, above 320° C. and under 15,000 psi water pressure.

Discussion and Conclusions

From the cursory descriptions and investigations on clinoptilolite available in the literature, it was not wholly inaccurate to label clinoptilolite as simply a silica-rich heulandite. Upon closer examination, however, there seems to be little doubt that clinoptilolite is a zeolite mineral closely related to, but distinct from, heulandite in composition, properties, stability and genesis. The occurrences of this zeolite in the groundmass of altered pyroclastic sediments will no doubt lead to speculations upon its genesis from the glass shards of volcanic ash and tuff. Because of the fact that monomineralic samples of clinoptilolite are almost impossible to obtain and that this zeolite usually occurs as laths about one micron or less in size, several of the standard mineralogical constants such as specific gravity or optical properties, cannot easily be determined with any degree of certainty.

The optical properties of zeolites in general are difficult to obtain since small variations in hydration, cation content or silica/alumina ratio all seem to affect the optical crystallography of the mineral. From the published data and the new samples studied in this investigation, clinoptilolite has a mean index of refraction of about 1.480 compared to 1.500 of most heulandites, slightly larger values for the optical angle and very low birefringence. Otherwise, the optics and crystallography of both minerals appear to be quite similar.

The similarity in optical properties and external crystallography suggest that the structures of clinoptilolite and heulandite are also closely related. The unit cell constants of clinoptilolite are only slightly larger than those of heulandite. Spectrometer traces of the two minerals are easily differentiated by the presence of many intense diffraction peaks for clinoptilolite and the somewhat larger *d* spacings of this mineral as compared with heulandite.

The most decisive criteria for distinguishing one phase from another are their reactions to thermal treatment. The low thermal stability and the reaction at 250° C. to a "B" modification clearly differentiates heulandite from clinoptilolite. The latter zeolite is thermally stable to well over 700° C. and goes through no low temperature reactions or transitions. That the higher thermal stability of clinoptilolite is not caused by the nature of the exchange cation is borne out by the stability of Ca-exchange clinoptilolite at 450° C., compared with the low temperature decomposition of Ca-heulandite. These conclusions are corroborated by both high temperature *x*-ray diffraction and differential thermal analysis data as well as by the results of thermal gravimetry. The high thermal stability of clinoptilolite more closely approximates those of the "rigid three-dimensional framework" zeolites such as analcite, mordenite, chabazite, and the Linde synthetic 4A and 13X zeolites all of which are thermally stable to at least 700° C. Heulandite, on the other hand, breaks down at relatively low temperatures, similar to the low thermal stability of "layered" and "fibrous" zeolites, natrolite, thomsonite, stilbite, and phillipsite. It is possible that the additional silica present in clinoptilolite has provided the "layered" structure of heulandite with additional structural linkages, thereby strengthening the framework.

Although analyses of heulandites are readily obtained, the difficulty in separating a pure clinoptilolite fraction from its host rock prohibits accurate chemical analyses. By correcting several analyses of clinoptilolite for the impurities present, silica/alumina ratios of about 9–10 can be calculated. The silica/alumina ratios of the heulandites studied in this investigation in addition to those compiled from the literature, group predominantly around 6.0. Essentially no heulandites or clinoptilolites have been found whose chemical compositions or physical properties approach what might be called a continuous solid solution series between the two end members, even if differences in their cation content are neglected.

Although the structures of these two zeolites are isomorphous, solid solution between heulandite, at a composition of 1:1:6:6 and clinoptilolite at 1:1:9–10:6, does not seem to be complete. It seems only proper, therefore, to classify clinoptilolite as a separate mineral species. On the other hand, it is likely that the silica content of clinoptilolite samples does vary between about 8.5 and 10.5.

Orginally the name clinoptilolite was coined to indicate its chemical similarity with ptilolite and its inclined extinction. Although chemical and physical properties are obviously much closer to heulandite than either ptilolite or mordenite, the name clinoptilolite already has been used on numerous occasions in the literature to represent the zeolite found in the groundmass of altered pyroclastics, and whose properties approximated those of heulandite. For this reason, it seems advisable to retain the name clinoptilolite despite the ambiguity of its origin.

In summary, clinoptilolite can be defined as a mineral of the zeolite group having a molecular composition close to $(Na_2O)_{.70}(CaO)_{.10}(K_2O)_{.15}(MgO)_{.05}\cdot Al_2O_3\cdot 8.5\text{–}10.5\ SiO_2\cdot 6\text{–}7\ H_2O$ and a structure similar to heulandite but which can be clearly distinguished from heulandite by optical, *x*-ray, thermal and chemical means.

Coupled with *x*-ray diffractometer traces, thermal treatment affords the best means by which heulandite and clinoptilolite may be clearly differentiated. *X*-ray film patterns are not suitable for differentiating between the two species. The DTA pattern of heulandite contains a sharp endotherm in the vicinity of 300° C. in addition to the zeolitic dehydration endotherm at lower temperatures. Clinoptilolite shows only the dehydration endotherm at low temperatures. If DTA equipment is not available, one need only place the sample in question in an oven at 450° C. overnight and examine the product by *x*-ray diffraction. Under these conditions the pattern of heulandite will have disappeared, and that of clinoptilolite will be essentially unaffected.

ACKNOWLEDGEMENTS

The author would like to express his appreciation for the many samples provided him by Drs. L. B. Sand, L. L. Ames, H. Winchell, B. Mason, and K. S. Deffeyes. His gratitude is also extended to Miss E. M. Flanigen, Drs. D. W. Breck, L. B. Sand, K. S. Deffeyes and B. Mason for the opportunity of discussing the clinoptilolite problem with them. Thanks are also due Miss Flanigen and Dr. Breck for critically reading the manuscript.

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Manuscript received July 2, 1959.