

CLINOPTILOLITE FROM PATAGONIA
THE RELATIONSHIP BETWEEN CLINOPTILOLITE
AND HEULANDITE

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ABSTRACT

Clinoptilolite occurs as a layer 6-8 cm. thick interbedded with bentonitic clays of the Sarmiento formation (Eocene-Oligocene) in the Cañadón Hondo in Argentine Patagonia. Physical and optical data are given for the mineral; its density is 2.11, mean refractive index 1.478, birefringence about 0.001. A chemical analysis indicates a unit cell content of $(\text{Na}, \text{K})_{4.86}(\text{Ca}, \text{Mg})_{0.31}\text{Al}_5.49\text{Si}_{30.50}\text{O}_{72} \cdot 19\text{H}_2\text{O}$. The mineral has been formed by diagenetic alteration of volcanic glass in a non-marine environment.

Comparison of this material with other clinoptilolites, including the original material described by Pirsson (1890) and named by Schaller (1923), and with heulandite, shows that clinoptilolite is a distinct species. Clinoptilolite and heulandite have the same structure, but heulandite is essentially a calcium zeolite and clinoptilolite a sodium-potassium zeolite; analyses of the minerals indicate that there is a compositional gap between them.

INTRODUCTION

The material described in this paper was collected by Dr. G. G. Simpson in February 1931 during the Scarritt Patagonian Expedition of the American Museum of Natural History. Descriptions of some of the rock specimens were published by McCartney (1933), but he did not include any from the Cañadón Hondo. His paper, however, contains a sketch map showing the location of the Cañadón Hondo, which is a tributary of the Rio Chico some 40 miles northwest of Comodoro Rivadavia, in Argentine Patagonia.

A description of the geology in the Cañadón Hondo had not been published, but Dr. Simpson has permitted us to quote the following from his field notes:

"Cañadón Hondo is remarkably confusing and no clear idea of its geology can be obtained short of a detailed survey. Its great size, very complex and obscure structure with numerous faults and folds, the discontinuity of exposures or structures at critical points, the lenticular nature of the beds, the strangeness of their facies, and the general paucity of fossils make any very definite conclusions impossible.

Aside from the Patagoniano (late Oligocene-early Miocene) which is always readily recognizable and usually confined to the higher rim, the following types of sediments occur:

1. More or less massive white, pink, or rarely yellowish tuffs, with some tuffaceous clay.
2. Pale green, occasionally highly silicified and often very concretionary tuffs intercalated with bright green clay.
3. Green clay with spots and poorly sorted pebbles, associated with bright green sands and, rarely white sands.
4. Pale clays, massive, grey, pinkish, greenish, and fine to coarse crossbedded sands,

usually white or grey, but often greenish or pink to red. Although physically similar and not separable at present, these include two parts probably quite distinct in age:

- a. An upper series in which the pillar bed and mammal sandstone are intercalated.
- b. A lower series including true Banco negro.

In (2), probably in its lower part only, are also seen two very special types: thin widespread white beds supposed in the field to be diatomaceous earth, and finely laminated shales with local plants and fish."

From subsequent study, Dr. Simpson now adds the following observations:

"At least 1-2 of the above lithological units, and perhaps also 3, are unusual rock facies within the predominantly volcanic Eocene-Oligocene mass of sediments now sometimes lumped as the Sarmiento group or (less correctly) formation. Casamayoran fossils were found in beds included in facies 2 of the field notes, and that is the probable age of the clinoptilolite. 4a is definitely older and was later made the type of the Rio Chico formation and Riochican age and stage. The dating of these provincial ages in terms of the world scale is quite uncertain, but most vertebrate paleontologists now consider the Riochican as approximately late Paleocene and the Casamayoran as approximately early Eocene.

In 1-3, at least, the 'clay' of the field notes is bentonite. All these beds are continental. They are bounded above by the marine Patagonia formation ('Patagoniano') of latest Oligocene or early Miocene age and below by the marine Salamanca formation, probably of early Paleocene age."

In the last sentence of the quotation from the field notes there is a reference to thin widespread white beds supposed in the field to be diatomaceous earth. In 1956 a chance-taken α -ray powder photograph of one of these samples revealed that it was a zeolite with the heulandite structure, subsequently identified as clinoptilolite.

GENERAL DESCRIPTION

The material available for investigation consisted of two specimens, both evidently the full thickness of the clinoptilolite band, since they were bounded on two surfaces by bedding planes with adherent clay. One had a thickness of 6 cm. and the other of 8 cm. Since the thicker specimen was also the purer and more homogeneous, it was investigated in detail.

One bedding surface of the specimen was coated with a layer, 1 mm. thick, of translucent barite, to which was adhering some fragments of dense pale green bentonitic clay. The thin layer of barite was followed by 6 cm. of white chalky clinoptilolite, quite tough, with a conchoidal fracture. The succeeding 2 cm. showed streaks of pale green bentonitic clay interlayered with the clinoptilolite, and the clinoptilolite showed a granular instead of a dense compact structure. A thin section cut across this part of the specimen shows that the main part of the specimen (the dense compact material) is pure clinoptilolite, apparently formed by the alteration of fine-grained (less than 20 microns) volcanic glass; it has rare thin

veinlets of opal and montmorillonite. The granular material is a mixture of orthoclase and clinoptilolite, and the bentonitic clay consists essentially of montmorillonite.

A specimen of the clinoptilolite was analyzed in more detail by making size separations and studying the size fractions in order to detect small amounts of other phases. X-ray analysis of the size fractions showed a small amount of montmorillonite and opal (alpha-cristobalite) in the -8 micron size fractions. In thin section, the opal and montmorillonite were seen to be restricted to a few thin veins (less than 0.3 mm. thick) cutting the clinoptilolite and extending from the bordering montmorillonite. Unaltered volcanic glass was found in small amount ($<1\%$) only in the coarsest size fraction.

TABLE 1. X-RAY POWDER DIFFRACTION DATA ON CLINOPTILOLITE FROM PATAGONIA
(Relative intensities visually estimated)

d (Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
8.96	vs	3.55	w	2.54	w	1.701	vw
7.94	m	3.43	m	2.44	w	1.664	vw
6.80	w	3.33	vw	2.36	vw	1.597	vw
5.98	vw	3.18	w	2.19	vw	1.523	vw
5.13	m	3.10	vw	2.09	vw	1.488	vw
4.65	w	2.98	s	2.02	w	1.416	vw
4.35	w	2.81	m	1.955	w	1.350	vw
3.97	vs	2.74	w	1.829	vw	1.315	vw
3.72	w	2.68	vw	1.776	vw		

In immersion liquids under the microscope crushed fragments of the clinoptilolite show no sign of crystal form. The granules have a pale brownish turbidity. The mean refractive index is 1.478 and the birefringence very low, about 0.001.

An electron micrograph of dispersed clinoptilolite shows that part at least is present as well-formed plates or laths; these plates evidently reflect the development of the form (010), a prominent form and the single cleavage in heulandite. Because of the very small particle size, and the fact that the clinoptilolite is itself nearly isotropic, the texture of a fracture surface was examined in the electron microscope by the preshadowed carbon replica technique. The surface appeared very homogeneous and exhibited an irregular fracture pattern. No smooth areas with conchoidal fracture which would indicate the presence of unaltered glass were found.

An x-ray powder photograph was made of a -200 mesh size fraction of the clinoptilolite, and the d-spacings and intensities of the lines are given in Table 1. The powder photograph shows that the material is a well-crystallized clinoptilolite.

Coombs (1958) has compared powder photographs of clinoptilolite and heulandite and points out two main types of difference between them: (a) a tendency towards larger spacings in clinoptilolite, which he ascribes to the effect of the large potassium ion involved in the replacement of CaAl in heulandite by (Na, K) Si in clinoptilolite; (b) differences in relative intensities, resulting from the method of mounting combined with differences in crystallinity of the samples. The strong (020) reflection at about

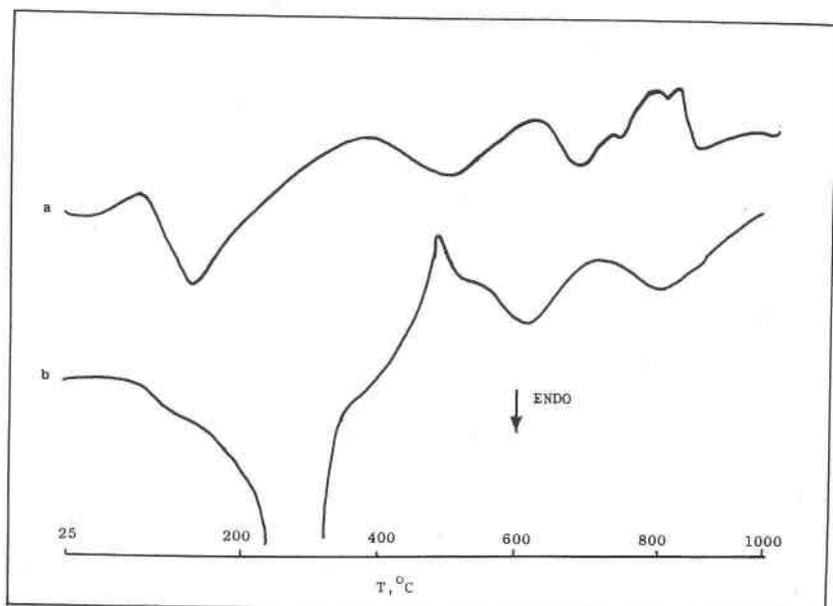


FIG. 1. Differential thermograms of *a*) clinoptilolite, Patagonia; *b*) heulandite, Paterson, New Jersey.

9 Å is enhanced by preferred orientation of (010) cleavage flakes in macroscopically crystallized material.

The differential thermal analysis curves for the clinoptilolite and for a heulandite are given in Fig. 1. The differences are marked and characteristic. Mumpton (1958) states that at about 230° C. heulandite transforms to "heulandite B" and at 350° C. becomes amorphous, whereas clinoptilolite remains stable to about 700° C. without reaction at lower temperatures. However, the endothermic reaction just below 200° C. on our D.T.A. curve for clinoptilolite presumably reflects the loss of at least part of the constitutional water.

The determination of the true density of the clinoptilolite presents some problems, on account of the fine-grained and porous nature of the material. A number of small fragments were broken from the purest part

of the specimen, placed in a glass cylinder, and covered with a bell jar. The bell jar was thoroughly pumped out with a vacuum pump, and a mixture of methylene iodide and acetone ($D = 2.20$) was then run into the cylinder with the fragments. All the fragments floated. Acetone was added in small amounts until the fragments were in suspended equilibrium, and the density of the liquid then determined. In this way the density of the clinoptilolite was found to be 2.11 ± 0.02 .

ORIGIN OF THE CLINOPTILOLITE

The occurrence of this thin bed of clinoptilolite in a thick sequence of bentonitic clays presents an interesting problem of origin. The geological evidence indicates that both the clinoptilolite bed and the bentonitic clays are the products of diagenesis of volcanic glass tuffs laid down in a non-marine environment. Two hypotheses, not mutually exclusive, may be suggested:

- (1) The clinoptilolite bed was formed from a volcanic glass of composition rather similar to that of the clinoptilolite, and different from the volcanic glass from which the bentonitic clays were derived.
- (2) The initial composition of the volcanic glass was similar throughout, but special conditions of diagenesis led to the formation of the clinoptilolite.

For the first hypothesis, a rhyolitic glass practically lacking in iron, magnesium, and calcium would be a satisfactory parent material for the clinoptilolite, whereas the bentonitic clays would be derived from material of dacitic or andesitic composition. This hypothesis is supported by the occurrence, at another locality in the Cañadón Hondo, of a thin white chalk-like layer interbedded with bentonitic clays. This white layer was identified on sight as clinoptilolite also, but proved to consist of colorless volcanic glass containing numerous small orthoclase crystals—the type of parent material postulated above for clinoptilolite.

The second hypothesis envisages a difference in composition and circulation of the diagenetic waters acting on volcanic glass of fairly uniform composition. Clinoptilolite would be formed when the volcanic glass was acted on by waters rich in sodium and potassium—possibly an alkaline lake water similar to those of the alkaline lakes of Nevada and California. Montmorillonite would form where circulating waters removed some silica and most of the alkalis. This hypothesis suggests that the clinoptilolite formed during a short-lived episode when the volcanic glass was being deposited in an evanescent alkaline lake.

We have discussed these hypotheses with Dr. Simpson, who makes the following comment:

“I see no objection to either hypothesis, and I know nothing that would really help to choose between them.

TABLE 2. CHEMICAL ANALYSIS OF CLINOPTILOLITE FROM PATAGONIA
ANALYST: H. B. WIJK

	1	2		3	4
SiO ₂	69.07	69.41	Si	30.91	30.50
TiO ₂	0.04	0.04	Al	5.57	5.49
Al ₂ O ₃	10.88	10.59	Mg	0.13	0.12
Fe ₂ O ₃	0.08	0.08	Ca	0.20	0.19
FeO	0.00	0.00	Na	3.83	3.78
MnO	0.01	0.01	K	1.10	1.08
MgO	0.18	0.19	H ₂ O±	19.27	19.01
CaO	0.39	0.41	O	72.96	72.00
Na ₂ O	4.23	4.42			
K ₂ O	2.52	1.92			
P ₂ O ₅	0.00	0.00			
H ₂ O+110°	6.56	6.85			
H ₂ O-110°	5.82	6.08			
CO ₂	0.00	0.00			
	99.78	100.00			

1. Weight per cent
2. Recalculated to 100, after deducting 4% KAlSi₃O₈.
3. Atoms per unit cell.
4. Atoms per unit cell, recalculated on the basis of O=72.

Simply on speculative weighing of possibilities, (1) seems to me somewhat more likely. One can easily imagine that a nearly unique weather event (some very unusual air movement) could once or twice carry a thin deposit of ash from a distant rhyolitic source into a momentarily quiescent area of long-continued dacitic or andesitic vulcanism. It seems (still speculatively) a little less likely that formation of an alkaline lake would be so nearly unique. If the climatic conditions were right, one would expect that other such deposits would occur in so thick a series over so large an area, through so long a time. Lake deposits are known elsewhere in Patagonia during this time, and in them the ash is bentonitic. The faunas suggest a fairly warm to humid climate throughout this time. The floras are very poorly known but are at least consistent with the humid climate. So this one alkaline lake would be extremely exceptional, but of course not impossible."

CHEMICAL COMPOSITION

A sample of the clinoptilolite was taken for chemical analysis from the purest middle section of the band, and was selected to avoid any of the small veinlets of opal in the material. When crushed and examined in immersion mounts under the microscope the only foreign material seen was occasional grains of orthoclase; a grain count indicated an amount of 4%.

The sample was analyzed by Dr. H. B. Wiik. The results are given in Table 2.

In order to correct for the presence of the small amount of orthoclase, amounts of K_2O , Al_2O_3 , and SiO_2 corresponding to 4% $KAlSi_3O_8$ have been deducted from the analysis figures, and the analysis then recalculated to 100. Since the orthoclase probably contains some sodium replacing potassium, this procedure results in a distortion of the relative amounts of sodium and potassium in the clinoptilolite. However, the distortion is certainly small, and does not affect the total molecular proportion of sodium plus potassium.

Hey and Bannister (1934) have shown that the unit cell formula for heulandite (and clinoptilolite) is $Na_xCa_yAl_{x+2y}Si_{36-(x+2y)}O_{72} \cdot 24H_2O$, where $(x+y)$, the number of large cations per unit cell, is variable, ranging from 4 to 6. The corrected analysis of the Patagonia clinoptilolite (omitting those components present in amounts less than 0.1%) has been recalculated into atoms per unit cell, using the cell dimensions $a=7.46$, $b=17.84$, $c=15.88$, $\beta=91^\circ 26'$ given for heulandite by Strunz and Tennyson (1956), and the measured density of 2.11. When this is done the oxygen content is 72.96, slightly higher than the true value of 72. On recalculation to $O=72$, $Si+Al$ becomes 35.99, very close to the true value of 36; the total $Ca+Mg+Na+K$ is 5.17; H_2O^\pm is 19.01, instead of the ideal value of 24. The low figure for water in the Patagonia clinoptilolite is probably due to its having been stored in a warm dry museum for twenty-seven years prior to analysis, with the consequent loss of weakly bonded water.

THE RELATIONSHIP BETWEEN CLINOPTILOLITE AND HEULANDITE

Pirsson (1890) described as mordenite a crystalline mineral, isomorphous with heulandite, occurring in a highly weathered amygdaloidal basalt in the Hoodoo Mountain, Wyoming. Schaller (1923) recognized that Pirsson's mineral was not mordenite and regarded it as an independent species, naming it clinoptilolite. Hey and Bannister (1934) studied Pirsson's original material by x -rays, and could find no differences between it and heulandite. Chemical analyses of clinoptilolite and heulandite could be expressed by the same unit cell formula, given above. They pointed out that analyses of clinoptilolite were higher in SiO_2 and lower in Al_2O_3 than those of heulandite, and concluded that clinoptilolite . . . "are essentially high-silica heulandites . . . the name clinoptilolite is unsuitable and should not be used." Mumpton (1958) claims that the base:alumina:silica ratio for heulandite is 1:1:6 and for clinoptilolite 1:1:8, that no specimens of these minerals have been found with compositions or properties intermediate between the two end members, and therefore proposes to redefine clinoptilolite as the high-silica counterpart

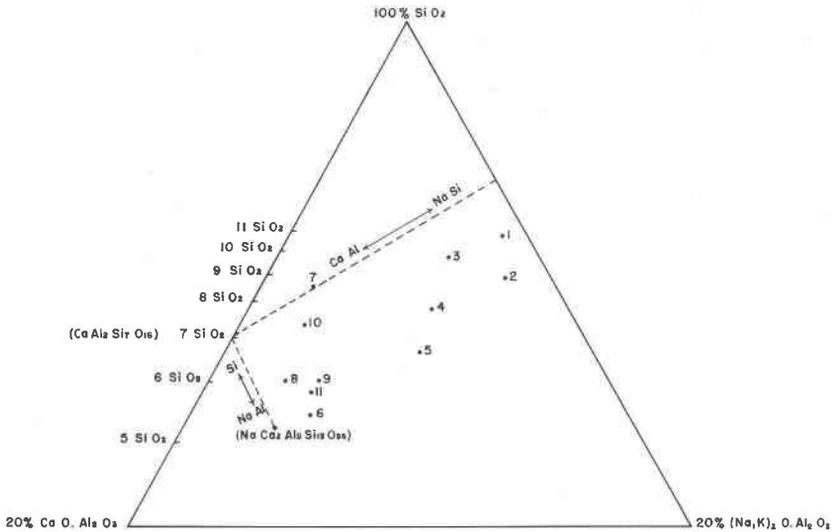


FIG. 2. Analyses of clinoptilolite and heulandite plotted in molecular percentages of the components $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $(\text{Na}, \text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3$ and SiO_2 . The dashed lines show the changes in composition produced by the substitution of NaAl for Si , and of NaSi for CaAl , in the ideal formula for heulandite, $\text{CaAl}_2\text{Si}_7\text{O}_{18}$.

1. Clinoptilolite, Patagonia. $n=1.478$, birefringence 0.001.
2. Clinoptilolite, Hector, California. *Econ. Geol.* **53**, 31 (1958), $n=1.480$.
3. Clinoptilolite, Hoodoo Mt., Wyoming. *Am. Jour. Sci.* **40**, 235 (1890), $\alpha=1.476$, $\gamma=1.479$.
4. Clinoptilolite, Dome, Arizona. *Am. Mineral.* **18**, 170 (1933).
5. Clinoptilolite, Challis, Idaho. *Proc. U. S. Nat. Mus.* **64**, Art. 19, 12 (1924), (described as heulandite). $\alpha=1.482$, $\beta=1.485$, $\gamma=1.489$.
6. Heulandite, Hawaii. *Am. Mineral.* **18**, 369 (1933), $\alpha=1.501$, $\beta=1.504$, $\gamma=1.509$.
7. Heulandite, Croatia. *Zentr. Mineral., Abt. A*, 227 (1940), $\beta=1.488$, birefringence 0.001.
8. Heulandite, Italy. *Rec. Accad. Sci. Torino* **64**, 105 (1929), $\beta=1.500$.
9. Heulandite, Sardinia. *Re. Accad. Lincei* **18**, 80 (1909).
10. Heulandite, Japan. *Zeits. Krist.* **52**, 513 (1913).
11. Heulandite, Iceland. *Zeits. Krist.* **49**, 201 (1911).

of heulandite and to retain the name as a valid mineral species, on equal status with heulandite.

When, however, analyses of heulandite and clinoptilolite are examined, it appears that the differences lie not so much in the silica content, as Hey and Bannister and Mumpton maintain, but in the content of sodium and potassium. The compositional relationships and differences are illustrated in Fig. 2, in which analyses of clinoptilolite are plotted in terms of molecular percentages of the components SiO_2 , $\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $(\text{Na}, \text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3$. Since all the analyses when recalculated in this way contain more

than 80% SiO_2 and less than 20% of the other components, only this part of the three-component diagram $\text{SiO}_2\text{-CaO}\cdot\text{Al}_2\text{O}_3\text{-(Na,K)}_2\text{O}\cdot\text{Al}_2\text{O}_3$ is used in Fig. 2.

On Fig. 2 are also plotted six analyses of heulandite, selected as showing the highest values recorded for Na_2O and K_2O , and the greatest variation in SiO_2 content. The figure reveals a definite composition gap between heulandite and clinoptilolite, suggesting that although these two minerals have similar structures, a complete solid solution series between them does not occur.

We therefore believe that clinoptilolite is a distinct species, and should be defined as a zeolite with the heulandite structure in which $(\text{Na}+\text{K})$ in atoms per unit cell is predominant over Ca. The type material designated by Schaller, i.e., that described by Pirsson from Hoodoo Mountain, Wyoming, agrees with this definition.

Analysis 5 on Fig. 2 is particularly significant for discriminating between clinoptilolite and heulandite. Originally described as heulandite, it has a alumina:silica ratio of 1:6.7, and would therefore be classified by Mumpton as a heulandite. However, its molecular content of $\text{Na}+\text{K}$ exceeds that of $\text{Ca}+\text{Mg}$, and we consider it to be a clinoptilolite. We have obtained a sample of the original material described by Ross and Shannan through the courtesy of the U. S. National Museum. The differential thermogram corresponds to that of clinoptilolite. When tested as suggested by Mumpton (heated in an oven at 450°C . overnight and an x-ray powder photograph then run) it also behaved as a clinoptilolite, viz. a good powder photograph was obtained.

Wyart (1933), in a comprehensive study of heulandite, concluded that the ideal formula of this mineral is $\text{CaAl}_2\text{Si}_7\text{O}_{18}\cdot 6\text{H}_2\text{O}$, there being four of these formula units in the unit cell. He studied some twenty-six analyses of heulandite, and showed that the compositional variations could be largely explained by a replacement of Si by NaAl; natural heulandites he regarded as solid solutions in various proportions of the two components $\text{Ca}_2\text{Al}_4\text{Si}_{14}\text{O}_{36}\cdot 12\text{H}_2\text{O}$ and $\text{NaCa}_2\text{Al}_5\text{Si}_{13}\text{O}_{36}\cdot 12\text{H}_2\text{O}$. However, study of Fig. 2 shows that this is an over-simplification. Lines are drawn to indicate the variations in composition that can be produced by ionic substitutions of the type $\text{NaAl}\leftrightarrow\text{Si}$ and $\text{NaSi}\leftrightarrow\text{CaAl}$ in the ideal formula for heulandite. In terms of ionic substitution clinoptilolite bears a similar relationship to heulandite as albite does to anorthite.

On the $\text{CaO}\cdot\text{Al}_2\text{O}_3\text{—SiO}_2$ axis of Fig. 2 the points corresponding to integral values of x in $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2$ from 5 to 11 have been indicated. The purpose of this is to show that formulas written in this fashion are unsuitable for representing the compositions of these zeolites. In the analyses of the heulandites the molecular ratio of SiO_2 , to Al_2O_3 ranges

from about $5\frac{1}{2}$ (anal. 6) to $8\frac{1}{2}$ (anal. 7); in clinoptilolite this ratio ranges from about $6\frac{1}{2}$ (anal. 5) to nearly 11 (anal. 1). The compositions of these two minerals can only be expressed satisfactorily by formulas based on the unit cell content of 72 oxygen atoms.

Refractive indices for the analyzed heulandites and clinoptilolites, where available, are listed in the key to Fig. 2. These data indicate that refractive indices and birefringence decrease with increase in Si, both in heulandite and in clinoptilolite; substitution of Na and K for Ca results in a decrease of refractive index. Clinoptilolites have lower refractive indices than heulandites; from the available data no heulandite has a beta index lower than 1.488, and no clinoptilolite a beta index higher than 1.485. This provides a ready means for distinguishing the two minerals.

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