

POLYMORPHISM AND CRYSTAL-CHEMISTRY OF HEULANDITES AND CLINOPTILOLITES

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ABSTRACT

A study of polymorphism conducted on 11 samples of the heulandite mineral group has confirmed the existence of two sub-groups: heulandite and clinoptilolite, with and without polymorphism respectively. The heat experiments on heulandite show the existence of a natural phase (*A*) and two collapsed phases (*B* and *I*). Furthermore, two types of heulandite (1 and 2) may be distinguished on account of their polymorphic behaviour and temperature of lattice destruction: type 1, heated to 400°C, reverts to phase *B* and the temperature of lattice destruction is lower than 550°C; type 2 heated to the same temperature, shows both *A* and *B* (or *I*) phases and its destruction temperature is higher than 550°. Examination of the chemical formulas of 21 minerals revealed that the results of the polymorphism test could be predicted on the basis of the Si/Al ratio and of the different content of bivalent cations; no significant correlations were noted, however, between cell dimensions and chemical composition investigated in 16 samples.

INTRODUCTION

Heulandite was introduced as a new zeolite mineral by Brooke (1822). Rinne (1923) seems to have been the first to describe its polymorphism: after heating a heulandite to about 350°C and cooling at room temperature, a new phase, called heulandite *B* by Slawson (1925), appears; it is distinctly different from the original phase, which can now be named heulandite *A*; Breger, Chandler, and Zubovic (1970), using the position of (020) reflection, gave evidence of 4 phases for heulandites, as follows: phase *A*-appearing at 8.92Å in the case of unheated minerals; phase *B*-appearing at 8.33Å in the case of minerals heated between 255°C and 330°C; phase *I* (intermediate)-appearing at 8.75Å in the case of minerals heated between 180°C and 318°C. BCZ identified a diffuse reflection at 8.62Å as another phase, occurring on cooling from 117°C to room temperature during the first heating cycle, and from 273°C during the third cycle.

Clinoptilolite was introduced as a new mineral by Schaller (1923); at that time clinoptilolite was considered similar to ptilolite (= mordenite). Later Hey and Bannister (1934) showed that clinoptilolite may be considered a silica-rich heulandite. The mineral is not polymorphic; Mumpton (1960) improved the nomenclature of this mineral family, introducing an experimental test to distinguish the

two minerals; if, after heating overnight at 450°C, the mineral no longer diffracted X-rays, it should be called heulandite; if, however, diffraction was maintained it should be called clinoptilolite. Obviously, the nomenclature of the majority of most so-called heulandites or clinoptilolites remained unaffected by Mumpton's test. Mumpton (1960) favored the hypothesis that the main reason for clinoptilolites being more heat-resistant was their higher silica content; Mason and Sand (1960) accepted Mumpton's test as useful, but favored the alternative hypothesis that their heat resistance was due to their cations (Na, K) being mainly monovalent as opposed to the bivalent cation (Ca) content of heulandite. Alietti (1967) gave evidence of the existence of zeolites of the heulandite family which, although all having a chemical composition with $Ca > (Na, K)$, could be divided into two groups by means of Mumpton's test: all those with clinoptilolite behaviour were a little richer in sodium and potassium; all those with heulandite behaviour were a little richer in calcium.

The author's data enabled him to trace a line in the triangle $Si_9O_{18}-Ca_{4.5}Al_9O_{18}-(Na, K)_9Al_9O_{18}$, separating the fields of heulandites and clinoptilolites. The minerals with a number of (Ca + Mg) ions between 1.05 (Ca-end member) and 0.75 plotted in the field of heulandites, while those with a (Ca + Mg) lesser than 0.75 fell in that of clinoptilolites. He grouped minor amounts of Mg with Ca, but Sr and Ba with (Na, K) because of ionic-radius similarities. Černý and Povondra (1969) and Passaglia (1969) later recognized the necessity for grouping all bivalent ions together, and I will do so in this paper. Kirov (1967) and Minato and Utada (1970) found calcium-rich clinoptilolites fairly similar to those of Alietti (1967).

Alietti's evidence therefore favored Mason's (1960) hypothesis, which was further supported by Shepard and Starkey (1964, 1966); who were able to show that a typical heulandite, if subjected to chemical treatment in order to substitute its calcium with potassium, exhibits a clinoptilolite heat behavior. Their evidence for the reverse transformation clinoptilolite to heulandite by chemical treatment was not so convincing, however, hence the problem cannot yet be considered entirely solved. The aim of this paper is to contribute to the solution of this problem.

EXPERIMENTAL

The samples here studied are listed in Table 1, while the chemical analyses of new samples are reported in Table 2. Na, K, Ca, Mg, Ba, and Sr were analyzed by the atomic absorption method, Si by gravimetry, and Al by titration with EDTA-ZnSO₄.

Powder patterns were taken on a Philips diffractometer if enhancement of

TABLE 1. LIST OF SAMPLES

Locality	Reference	Note
1. Valle di Fassa (Italy)	Alietti (1967)	New data added
2. do.	do.	—
3. do.	do.	New data added
4. do.	do.	do.
5. Valle dei Zuccanti, (Vicenza) (Italy)	do.	—
6. Valle di Fassa (Italy)	do.	New data added
7. Valle dei Zuccanti, (Vicenza) (Italy)	do.	do.
8. Valle di Fassa (Italy)	do.	—
9. Eastern Rhodopes (Bulgarian)	Kirov (1967)	—
10. Kozakov Hill (Czechoslovakia)	Černý and Povondra (1969)	—
11. Agoura (California)	Wise (1969)	New data added
12. Albero Bassi, (Vicenza) (Italy)	Passaglia (1969)	do.
13. Summit, N. J.	Shepard and Starkey (1966)	—
14. Pierre Shale	do.	—
15. Giebelsbach (Switzerland)	Merkle and Slaughter (1969)	—
16. Col Aut, Buffaure, Trento (Italy)	—	All data are new
17. Masonade, Buffaure, Trento (Italy)	—	do.
18. Faroe Islands	Alberti (private communication)	New data added
19. Shizuma (Japan)	Minato and Utada (1970)	—
20. Hector (California)	Ames, Sand and Goldich (1958) from Mumpton (1960)	—
21. Patagonia	Mason and Sand (1960)	—

basal reflections by preferred orientation was desired; otherwise by a Guinier de Wolff camera. Some high-temperature diffractometer tracings were recorded on the GE diffractometer with the proper accessory; the samples were kept in vacuum at constant temperature for some minutes before the diffractometer tests using a scanning speed of 1°/min. Lattice constants were calculated by a least-squares program from indexed powder patterns.

POLYMORPHISM OF HEULANDITES AND CLINOPTILOLITES

The polymorphism of heulandite consists of a sharp contraction of the lattice when the mineral is heated to at least 230°C. The contraction investigated was determined by considering the position of the peak (020) in the diffractometer trace (copper radiation): data from literature concerning the amount of contraction are shown in Table 3.

Estimates of the temperature required if polymorphism is to be observed vary widely from author to author; the transformation rate itself is largely influenced by temperature; therefore if transformation starts at ~250°C it is readily observed only if the mineral is heated to ~350°C.

Here it must be pointed out that in my experiments the $d(020)$ spacings assumed three different values, thus indicating the existence of

three phases: besides the natural phase *A*, with $d(020) \sim 8.95 \text{ \AA}$, and the contracted phase *B*, with $d(020) \sim 8.25 \text{ \AA}$, there exists a third phase, for which I proposed the code letter *I* (intermediate) with $d(020) \sim 8.70 \text{ \AA}$ (Table 4).

This phase corresponds to the third phase identified by Breger, Chandler and Zubovic at about 8.75 \AA . I did not detect the high-temperature phase at 8.62 \AA reported by the same authors, which may be called *IH* (intermediate high temperature).

The phases that are present at the time of X-raying are influenced by three parameters:

- 1) temperature reached during heating,
- 2) length of time at high temperature,
- 3) time elapsed after cooling.

In what follows, by standard heat treatment I understand a 12-hour heating at 400°C followed by cooling, and X-raying after a delay of 15 minutes or so.

In these standard conditions phase *I* is observed in only a few samples (Table 4). The heulandite group can be differentiated:

heulandite type 1—observed in samples 1, 4, 5, 12, 16, 17, 18: if the heating has reached a proper temperature ($\sim 400^\circ\text{C}$) only phase *B* appears. These samples do not exhibit any powder pattern after heating at 550°C . Sample 10 is described by Černý and Povondra (1969) as behaving in the same way. The same holds for sample 13 as de-

TABLE 2. CHEMICAL ANALYSES

	16	17	18(a)
SiO ₂	60.06	60.66	57.17
Al ₂ O ₃	13.65	13.87	17.03
Fe ₂ O ₃	1.16	0.97	0.04
MgO	0.38	0.23	0.02
CaO	4.44	4.74	7.13
SrO	1.35	1.59	0.19
BaO	0.75	0.59	0.31
Na ₂ O	1.07	1.27	1.39
K ₂ O	0.66	0.80	0.73
H ₂ O ⁺	12.43	12.59	16.71
H ₂ O ⁻	3.11	2.90	—
	99.06	100.21	100.72

(a) Analysis supplied by A. Alberti

Table 3. (020) spacings (Å) of heulandites

References	Heulandite A (natural)	Heulandite B (after heating)	Temperature (°C) needed to start the polymorphic inversion
Koizumi and Kiriyama (1953)	9.0	8.4	300°-400°
Mumpton (1960)	8.90	-	230° for a slow inversion
Shepard and Starkey (1964)	9.0	8.3	250° for a slow inversion 300°-350° for a fast inversion
Alietti (1967)	9.20 ^(a)	8.28	300°-400° for a fast inversion
Breger, Chandler and Zubovic (1970)	8.92	8.33	255°

(a) Value obtained with a Guinier camera, hence not precise at low angles.

scribed by Shepard and Starkey (1966), and for sample 2 (Alietti, 1967).

heulandite type 2—observed in samples 3, 6, 7. If heating has reached a proper temperature ($\sim 400^\circ\text{C}$) both the *A* and *B* (and/or *I*) phases appear. For these samples the powder pattern after heating at temperature as high as 550°C is still sharp. In my opinion, the same behavior is also exhibited by samples 9 and 19. The sample called “anomalous zeolites of heulandite-clinoptilolite structure” of Shepard and Starkey (1966) also belongs to this type; the same holds for specimens of Brown, Catt, and Weir (1969). It is a pity that Shepard and Starkey did not analyze their samples, and the analyses of Brown, Catt, and Weir give too high a balance error to be considered reliable.

clinoptilolite—observed in sample 11. Only phase *A* can be observed, no matter how high the heating temperature is. These samples have the highest resistance to heating (750°C). The same holds for sample 14 as described by Shepard and Starkey (1966) and for sample 20 (Mumpton, 1964).

If the samples which underwent standard heating are re-examined after 20 days without re-heating, heulandite type 1 does not exhibit any change, while heulandite type 2 exhibits patterns of phases *A* and *I*. These facts show that any previously formed phase *B* has been inverted to a phase *I*. I find that if the same samples are examined after six months, heulandites type 1 show an almost complete reversion to

phase *A*; while heulandites type 2 still contain some phase *I*, but probably there is a tendency to revert to phase *A*.

The significance of these different behavior patterns can be better understood if we consider some non-standard heat treatments and some high-temperature diffractometer tracings, obtained with six samples specially selected for this particular purpose, namely samples 4 and 16 (heulandite type 1); sample 3, 6, 7 (heulandite type 2) and sample 11 (clinoptilolite). First, it should be pointed out that *I* can distinguish *A* and *I* peaks only in diffractometer tracings at room temperature; with the high temperature attachment the peaks are rather poorly defined and, being indistinguishable from one another, are always called *A*.

If sample 4 (which after standard treatment gives peak *B* only) is heated for 10 min at 400°C and then allowed to cool it consists at first of phases *A* + *I* + *B*; after 48 hours at room temperature, however, phase *B* disappears in favor of phase *I*. High temperature diffraction reveals that the transformation *A* to *B* is slow, so at 400°C both phases

TABLE 4. THERMAL TREATMENTS

T°C	Type	1	3	4	5	6	7	11	12	16	17	18
230°C	A	vs	vs	vs	vs	vs	vs	vs	s	vs	s	vs
	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	B	nd	nd	nd	m	nd	nd	nd	nd	nd	nd	nd
280°C	A	s	vs	vs	vs	vs	vs	vs	s	vs	vs	nd
	I	vs	vs	m	nd	nd	nd	nd	nd	s	nd	w
	B	m	nd	m	vs	w	nd	nd	nd	m	s	m
400°C	A	nd	m	nd	nd	s	s	vs	w	nd	m	nd
	I	nd	vs	nd	nd	w	nd	nd	nd	nd	nd	nd
	B	s	w	s	vs	vs	s	nd	m	vs	vs	w
450°C	A	nd	vs	nd	nd	s	m	vs	nd	nd	nd	nd
	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	B	s	vs	w	vs	vs	m	nd	nd	m	vs	nd
500°C	A	nd	vs	nd	nd	vs	s	vs	nd	nd	nd	nd
	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	B	nd	s	nd	m	s	nd	nd	nd	m	m	nd
550°C	A	nd	vs	nd	nd	vs	s	vs	nd	nd	nd	nd
	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	B	nd	s	nd	nd	s	nd	nd	nd	nd	nd	nd

intensity: vs = very strong s = strong m = medium w = weak; nd = no diffraction

may be present for some time. Transformation is usually completed during cooling so that at room temperature only the *B* phase appears. The behavior of sample 16 is very similar to that of sample 4. If sample 3, which after standard treatment gives peaks *A + B + I*, is heated for 10 min at 400°C, it exhibits a peak of phase *A* only; if heated for 4 hours at 400°C it gives peaks *A + I* and a small peak *B* immediately after cooling, but after 24 hours the small peak disappears in favor of *I*. At high temperatures an alternating-temperature run was executed and peaks observed as follows: at 290°C, *A* and *B*; back to 20°C only *A*; back to 295°C, *A* and *B*; at 320°C and 350°C, only *B*; back to 20°C, only *A*; at 400°C, only *B*; on cooling to room temperature, only *A*. It was only after heating at 500°C that *A* and *B* were both present on cooling (as they are after standard treatment). Sample 7 has a thermal behavior similar to sample 3. If sample 6 (which after standard treatment gives peaks *A + I + B*) is heated for 10 min at 400°C, it gives the same three peaks immediately after cooling, but 24 hours thereafter *B* completely disappears in favor of *I*. At high temperatures the *B*-peak appears at 350°C along with the *A*-peak and both persist to 400°C, but after cooling only *A* is present. The *IH* phase identified by Breger, Chandler and Zubovic was not confirmed, the *I* and *IH* being too close in my samples and not resolved with my high temperature apparatus.

On the whole, the polymorphic inversion can be summarized as follows:

- at high temperatures (400°C or more) heulandite type 1 exhibits a polymorphic inversion to the *B*-phase. The inversion is sometimes slow, but once the *B*-phase appears it persists at room temperature;
- heulandite type 2 show a typical *A*→*B* inversion at high temperatures, but when cooled to room temperature phase *B* tends to revert again to *A* (or *I*). The high temperature inversion *A* to *B* is also sometimes incomplete. Prolonged heating stabilizes phase *B* sufficiently to enable it to be observed at room temperature as well;
- clinoptilolite does not exhibit any polymorphism.

One more point should be raised here: the constant presence of two or more phases in samples of heulandite type 2 after a standard treatment might cast doubt on the chemical homogeneity of these samples and lead one to suspect that heulandite type 2 is a mixture of a mineral of type 1 with clinoptilolite. Such a possibility can be rejected, however, for the high-temperature tracing showed that, at high temperatures, heulandite type 2 samples reverted to the *B*-phase; if some heulandite type-1 were present, *B* should persist during cooling

to room temperature, but this does not occur. If clinoptilolite were present, it should not revert completely to the *B*-phase, as sample No. 3 does at high temperatures. In sample 6 the presence of *A* + *B* + *I* after brief heating and the persistence at high temperature of both *A* and *B* phases could imply that this sample is indeed such a mixture; if it is, the presence of a peak of phase *B* at temperatures higher than 550°C testifies to the presence of a mineral with a typical behavior different from that of heulandite type 1 and clinoptilolite. J. V. Smith kindly tested samples 6 and 16 with the microprobe and no major heterogeneity was revealed. It is possible that some samples with behavior of heulandite type 2 are actually mixtures, but there is sufficient evidence to show that some at least are not.

From this short description of the polymorphism it is clear that there is a sharp distinction between heulandites type 1 and 2 on the one hand and clinoptilolites on the other, for the latter do not show any kind of polymorphism, unlike the former. The distinction between heulandites type 1 and type 2 is less sharp. According to our results, Mumpton's test may be expanded into a more complete tool of classification:

1. The temperature of 450°C proposed by Mumpton for the heat resistance test must be raised to 550°C, because an overnight heating at 450°C is insufficient to destroy completely the lattice of most typical heulandites.
2. The preceding test must be completed with a test for the existence of polymorphism: (a) Using a high-temperature (~400°C) diffractometer tracing; or (b) Using a room temperature diffractometer tracing immediately after an overnight heating at 400°C. In either kind of pattern the presence of the *B* peak (with or without an *A* peak) is evidence of polymorphism.

The average behavior of the three subgroups is as follows: *Clinoptilolites* have a high heat resistance (heating at 750°C does not normally destroy their lattice) and can be clearly distinguished from the heulandites by means of the proposed tests. *Heulandites of the two types*, on the other hand, are not readily distinguished for not only do they both exhibit polymorphism but also their lattice-destruction temperature is difficult to assess, being very close to the limit of 550°C in some cases. However, it should be borne in mind that, although heulandites of both types invert to the *B* phase at proper temperature, in the case of heulandites type 1 phase *B* lasts for some months at room temperature, whereas in type 2 there is a partial inversion to

the *I* phase immediately on cooling, the process being completed within a week or so. Phase *I* shows the tendency to revert to phase *A*.

CRYSTAL CHEMISTRY

Table 5 lists the coefficients of the chemical formulas of 21 minerals of the heulandite group. Where possible each sample has been classified according to the test described in the preceding chapter, from either my own data or data reported in references. For some samples the result of the test is not known, hence only the probable subdivision is reported in Table 6. The formulas of Table 5 have been inserted as points in the diagram of Figure 1. A general examination of this diagram gives a good idea of the wide variation of chemical composition in this mineral group. The area occupied consists of a strip rising from lower left to upper right. Points occurring to the left correspond to heulandites type 1, those in the middle to heulandites type 2, those the right to clinoptilolites.

The boundary heulandites type 1/heulandites type 2 can be traced with some confidence, whereas the boundary heulandites type 2/c clinoptilolites is less certain. The silica coefficients of clinoptilolites are higher than 7.30, while their bivalent cation coefficients are lower than 0.4. The silica coefficients of heulandites type 1 are lower than 71.0, while their bivalent cation coefficients are higher than 0.7. Heulandites type 2 have intermediate coefficients.

The preceding description refers to natural samples only. Shepard and Starkey (1964, 1966) have clearly demonstrated that:

- 1) A K-exchanged heulandite behaves like a typical clinoptilolite in its absence of polymorphism and high temperature of destruction, which is but a little lower ($\sim 50^{\circ}\text{C}$) than for a natural clinoptilolite;
- 2) A Na-exchanged heulandite behaves in a particular way, differently from both heulandites and clinoptilolites;
- 3) A Ca-exchanged clinoptilolite is less temperature resistant than natural clinoptilolite, but more so than heulandites type 1. At high temperature it shows the lattice contraction typical of heulandites, behaving like an heulandite type 2.

If one grants that the boundaries are traced correctly in the diagram of Figure 1, one can see that it is impossible to shift samples 11, 14, and 21 by an ion exchange process into the heulandite type 1 area, because of their high silica content; the same probably holds for sample 20 as well.

Table 5

Coefficients in the chemical formulae													
Sample no.	K	Na	Σ mon	Mg	Ca	Sr	Ba	Σ biv	Fe ^m	Al	Si	O	H ₂ O
1	0.08	0.32	0.40	0.10	0.70	0.01	0.01	0.82	0.01	2.00	6.97	18	6.75
2	0.05	0.39	0.44	0.10	0.74	0.01	0.01	0.86	0.02	2.06	6.90	18	6.14
3	0.06	0.27	0.33	0.05	0.59	0.02	0.02	0.68	0.04	1.73	7.24	18	6.03
4	0.21	0.18	0.39	0.17	0.78	0.01	0.01	0.97	0.18	1.86	6.89	18	5.61
5	0.25	0.01	0.26	0.34	0.60	0.01	0.01	0.96	0.08	1.87	6.98	18	6.18
6	0.14	0.72	0.86	0.03	0.56	0.01	0.03	0.63	0.04	1.74	7.12	18	6.30
7	0.62	0.28	0.90	0.22	0.42	0.01	0.02	0.67	0.01	2.01	6.93	18	6.06
8	0.27	0.07	0.34	0.09	0.54	0.01	0.06	0.70	0.07	1.67	7.26	18	7.06
9	0.26	0.08	0.34	0.08	0.53	-	-	0.61	0.02	1.61	7.39	18	5.57
10	0.21	0.36	0.57	0.01	0.39	0.31	0.11	0.82	-	2.26	6.74	18	6.25
11	0.41	0.52	0.93	0.05	0.12	-	-	0.17	-	1.45	7.54	18	6.00
12	0.60	0.24	0.84	0.16	0.41	0.14	0.03	0.74	0.14	2.27	6.62	18	6.46
13	0.20	0.14	0.34	0.06	0.85	-	-	0.91	-	2.04	6.92	18	6.47
14	0.34	0.53	0.87	0.14	0.18	-	-	0.32	-	1.57	7.44	18	5.38
15	0.22	0.02	0.24	-	0.87	0.10	-	0.97	-	2.32	6.70	18	6.52
16	0.10	0.24	0.34	0.07	0.56	0.09	0.03	0.75	0.10	1.89	7.05	18	6.08
17	0.12	0.29	0.41	0.04	0.59	0.11	0.03	0.77	0.08	1.90	7.03	18	5.98
18	0.11	0.31	0.42	-	0.89	0.01	0.01	0.91	-	2.34	6.67	18	6.50
19	0.40	0.35	0.75	0.09	0.38	-	-	0.47	0.09	1.74	7.20	18	4.21
20	0.15	1.26	1.41	0.06	0.16	-	-	0.22	0.07	1.45	7.39	18	4.38
21	0.27	0.94	1.21	0.03	0.05	-	-	0.08	-	1.37	7.62	18	4.74

Table 6. List of the samples according to thermal tests.

Sample No.	Subdivision	Note on the thermal test of polymorphism
1	Heulandite type 1	T
2	Heulandite type 1	T
3	Heulandite type 2	T
4	Heulandite type 1	T
5	Heulandite type 1	T
6	Heulandite type 2	T
7	Heulandite type 2	T
8	Heulandite type 2	T
9	Heulandite type 2	NT
10	Heulandite type 1	TR
11	Clinoptilolite	T
12	Heulandite type 1	T
13	Heulandite type 1	TR
14	Clinoptilolite	TR
15	Heulandite type 1	NT
16	Heulandite type 1	T
17	Heulandite type 1	T
18	Heulandite type 1	T
19	Heulandite type 2	NT
20	Clinoptilolite	TR
21	Clinoptilolite	NT

Note: T = tested by author; NT = not tested by author, the classification here shown is the most probable; TR = not tested, but the result of the test can be deduced by thermal tests described in the reference paper.

The lattice constants of heulandites (*lato sensu*) are grouped in Table 7. It was impossible to find any correlation between chemical formulas and lattice dimensions. Shepard and Starkey (1966) demonstrated that exchangeable cations have considerable influence on lattice dimensions; the Si/Al in the lattice dimensions of samples 4 and 5,

having nearly the same composition but different lattice dimensions; this fact suggests the existence of a third influencing factor (Al/Si ordering?). The overlapping of the three effects probably prohibits any interpretation of these seemingly random variations.

CONCLUSIONS

The results presented here, in conjunction with the data contained in the literature (mainly those of Shepard and Starkey, 1964, 1966), enable one to conclude that heulandites (*lato sensu*) form a mineral group which is divided into two sub-groups: heulandite and clinoptilolite.

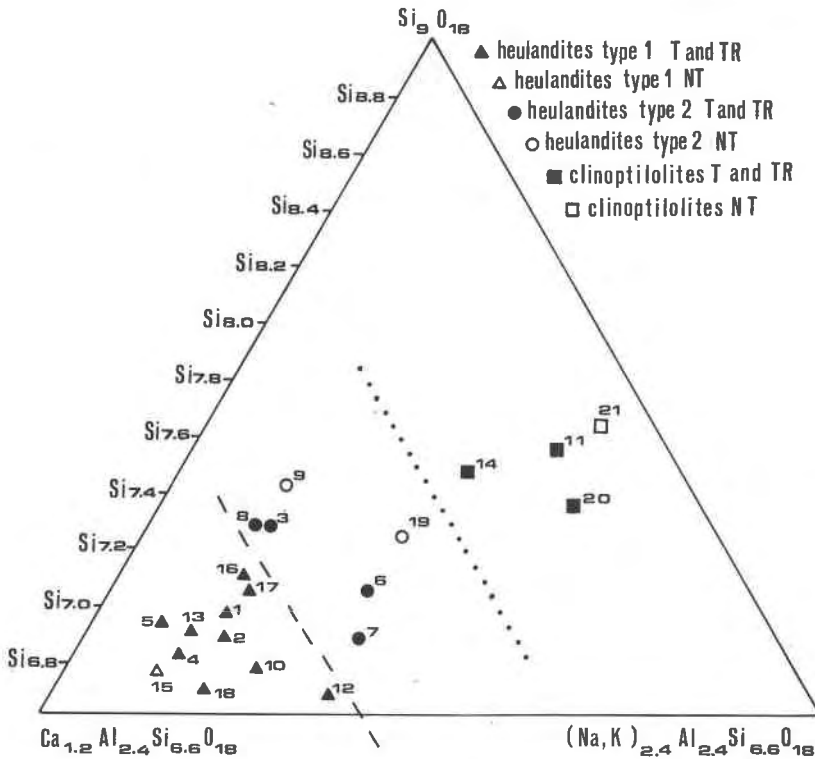


FIG. 1. Mole plot of minerals of the heulandites (*lato sensu*) in the upper part of the triangle $\text{Si}_9\text{O}_{18}\text{-Ca}_{4.5}\text{Al}_6\text{O}_{18}\text{-(Na, K)}_6\text{Al}_6\text{O}_{18}$. Some samples indicated by shaded symbols have either been tested by author (T) or test results are described in the references (TR) of Table 6. Some samples, indicated by unshaded symbols, were not tested (NT); the classification shown is the most probable one. The dashed line shows the approximate limit between the field of heulandites type 1 and that of heulandites type 2; the dotted line shows a possible limit between the field of clinoptilolites and that of heulandites type 2.

TABLE 7

sample	LATTICE CONSTANTS (Å) OF THE HEULANDITE-CLINOPTILOLITE SERIES					$V(\text{Å})^3$
	a	b	c	β		
1	17.691 ± 0.001	17.973 ± 0.002	7.407 ± 0.001	116°37' ± 1'	2105.486	
3	17.624 ± 0.002	18.021 ± 0.001	7.393 ± 0.001	116°25' ± 1'	2101.489	
4	17.619 ± 0.002	17.941 ± 0.002	7.376 ± 0.001	116° 4' ± 1'	2093.755	
5	17.702 ± 0.001	17.870 ± 0.001	7.412 ± 0.001	116°19' ± 1'	2103.174	
6	17.617 ± 0.001	17.960 ± 0.002	7.378 ± 0.001	116°32' ± 1'	2089.294	
7	17.735 ± 0.001	18.029 ± 0.001	7.419 ± 0.001	116°29' ± 1'	2120.491	
10	17.722 ± 0.012	17.856 ± 0.012	7.458 ± 0.007	116°37' ± 0.6'	2181.35	
11	17.658 ± 0.002	17.957 ± 0.001	7.399 ± 0.001	116°23' ± 1'	2102.116	
12	17.498 ± 0.004	17.816 ± 0.004	7.529 ± 0.001	116° 4' ± 1'	2107.715	
13	17.688 ± 0.02	17.810 ± 0.02	7.410 ± 0.01	116°29'	2093.885	
14	17.654 ± 0.02	17.929 ± 0.02	7.411 ± 0.01	116°15'	2104.113	
14 (Ca treated)	17.587 ± 0.02	17.808 ± 0.02	7.375 ± 0.01	116°28'	2067.243	
15	17.73	17.82	7.43	116°20'	2103.36	
16	17.651 ± 0.001	17.934 ± 0.002	7.393 ± 0.001	116°29' ± 1'	2094.547	
17	17.668 ± 0.001	17.970 ± 0.001	7.411 ± 0.001	116°24' ± 1'	2108.241	
18	17.720 ± 0.001	17.900 ± 0.001	7.431 ± 0.001	116°22' ± 1'	2111.894	

tilolite. The heat experiments on heulandites show the existence of a natural phase (called *A*) and two collapsed phases (called *B* and *I*). The heulandites can be divided into type 1 and type 2, which behave differently in their polymorphism and thermal stability. The difference in thermal behaviour is due both to a different Si/Al ratio and to a different content of bivalent cations. Thus, with a high Si/Al ratio only heulandite type 2 is possible, whereas with a low Si/Al ratio both types can exist. The higher the Si/Al ratio, the higher the respective temperatures necessary to start polymorphic inversion and destroy the lattice.

Natural clinoptilolites always have a high Si/Al ratio, while clinoptilolites obtained artificially by ion-exchanging heulandites can have a low Si/Al ratio.

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