MINERALOGICAL NOTES

THE CRYSTAL STRUCTURE OF HEULANDITE
$(Ca, Na_2)[Al_2Si_7O_{18}] \cdot 6H_2O$

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The zeolite heulandite has been reexamined in order to classify it structurally with other members of the zeolite group. An unrefined structure for heulandite has been determined from three-dimensional equi-inclination Weissenberg data. This new structure differs signifiantly from that proposed by Ventriglia (1955) and shows strong similarities with other closely related members of the zeolite family.

The single crystals used in this study are from a sample found at Giebelsback, near Fiesch, Wallis, Switzerland. A chemical analysis of the sample gives the following formula $(Ca,Sr,K_2)_{1.2}[Al_{2.4}Si_{6.6}O_{18}] \cdot (H_2O)_{6.5}$. There are four formula weights per unit cell. The parameters of the monoclinic cell are $a = 17.73$, $b = 17.82$, $c = 7.43$ Å, and $\beta = 116°20'$. Systematic absences and the zero moment centricity test indicated space group Cm or $C2$.

Three-dimensional Patterson maps were made at intervals of 0.05 along the b-crystallographic axis. From these maps the minimum function retrieved three independent silicon atoms forming an eight-member ring lying in the bc plane and perpendicular to a mirror, and indicated space group Cm. Successive three-dimensional Fourier syntheses based on these atoms, and the vector checking of new atomic sites with the Patterson maps led to the determination of the remaining framework atoms. Subsequent Fourier maps indicated calcium distributed over three positions on the mirror, and the locations of most water molecules in the structure.

The crystal structure of heulandite is characterized by large intersecting channels composed of 12-, 10-, and 8-member rings open across the mirrors and tied together by layers of 6-, 5-, 4-member ring groups located at heights of about $\frac{1}{4}$ and $\frac{3}{4}$ along b. The bc crystallographic plane is composed of 8-member rings held together by 4- and 6-member ring groups. Figure 3 shows the general arrangement of the silica atoms in this plane. The ab crystallographic plane is composed of a combination of 8- and 12-member rings held by a complex arrangement of 6-, 5-, and 4-member groups (Fig. 1). Heulandite's excellent cleavage (010) is shown by the presence of the open channels at heights of 0 and $\frac{1}{2}$ on the b axis. The calcium atoms lie on special positions in the open channels near the intersection of the 8- and 12-member rings, and they are surrounded
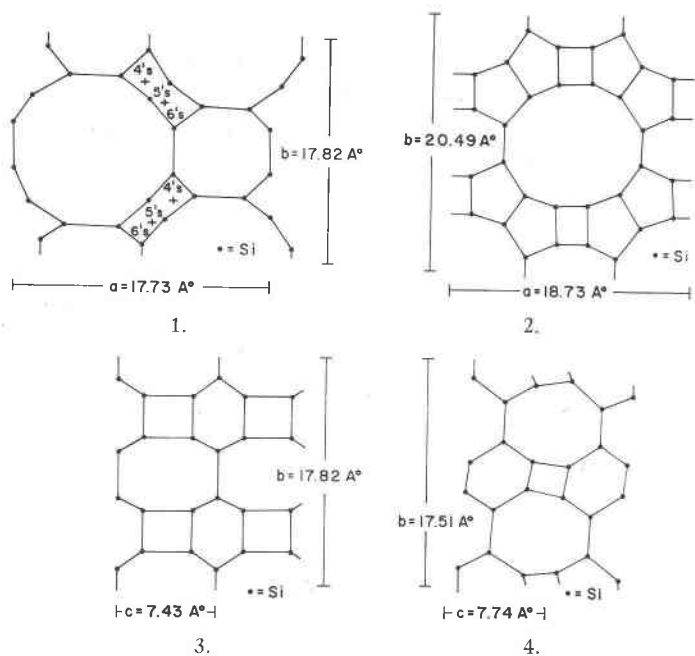
FIG. 1. The arrangement of silica atoms in the ab crystallographic plane of heulandite showing open channels of 12- and 8-member rings held by a complex of 6-, 5-, and 4-member ring groups.

FIG. 2. The arrangement of silica atoms in the ab crystallographic plane of mordenite (adapted from Meier, 1961).

FIG. 3. The arrangement of silica atoms in the bc crystallographic plane of heulandite showing open channels of 8-member rings held by 6- and 4-member ring groups.

FIG. 4. The arrangement of silica atoms in the bc crystallographic plane of brewsterite (adapted from Perrotta and Smith, 1964).

by partially occupied water sites in both general and special positions. Table 1 is a listing of the unrefined coordinates for all atoms in the cell. Average isotropic temperature factors for the preliminary structure are: Si—0.88, O—2.02, Ca—1.00, and H_2O—4.08; the average bond lengths of the framework atoms are: Si—Si = 3.13, Si—O = 1.65, and O—O = 2.68 Å. The discrepancy index, R, for the preliminary structure is 0.20.

This new heulandite structure shows strong similarities to zeolite structures previously determined by other workers and classified by Smith (1963). The *ab* crystallographic planes of mordenite (Meier, 1961) and heulandite are similar. They differ only in that the four-member ring groups of mordenite are not present in the heulandite structure. These similarities are easily seen by comparing Figures 1 and 2. Absence of the four-member ring groups in heulandite is indicated by a smaller b_0

TABLE 1. HEULANDITE: UNREFINED ATOMIC COORDINATES

Atom	x	y	z
Si(1)	0.109	0.168	0.405
Si(2)	.002	.093	.000
Si(3)	.080	.184	.782
Si(4)	.342	.304	.909
Si(5)	.287	.216	.500
Si(6)	.495	.198	.216
Si(7)	.468	.173	.593
Si(8)	.216	.302	.086
Si(9)	.072	.415	.000
O(1)	.983	.000	.947
O(2)	.061	.130	.900
O(3)	.102	.143	.605
O(4)	.044	.122	.235
O(5)	.292	.338	.018
O(6)	.211	.167	.428
O(7)	.142	.256	.943
O(8)	.295	.259	.679
O(9)	.084	.247	.314
O(10)	.279	.283	.313
O(11)	.370	.151	.559
O(12)	.023	.404	.753
O(13)	.081	.500	.044
O(14)	.463	.162	.362
O(15)	.492	.263	.663
O(16)	.404	.376	.906
O(17)	.020	.380	.117
O(18)	.170	.383	.109
O(19)	.407	.233	.055
Ca(1)	.147	.000	.811
Ca(2)	.435	.000	.147
Ca(3)	.242	.500	.300
$H_2O(1)$	.006	.000	.528
$H_2O(2)$	.294	.500	.038
$H_2O(3)$	.296	.500	.767
$H_2O(4)$	.065	.500	.518
$H_2O(5)$	.386	.000	.772
$H_2O(6)$	.209	.000	.601
$H_2O(7)$	.256	.137	.005
$H_2O(8)$	.211	.423	.509
$H_2O(9)$	.360	.424	.469
$H_2O(10)$	.389	.000	.404
$H_2O(11)$	.379	.000	.291
$H_2O(12)$	.208	.000	.450
$H_2O(13)$	.375	.000	.520
$H_2O(14)$	.222	.172	.109

dimension, equal to 17.82 Å compared to a b_0 dimension of 20.49 Å in mordenite. Comparison of the bc crystallographic planes of heulandite and brewsterite Perrotta and Smith (1964), Figures 3 and 4 show similar arrangements of the 8-, 6-, and 4-member rings. This similarity is also seen by the nearly equal cell dimensions of heulandite ($b = 17.82$, $c = 7.43$ Å) and brewsterite ($b = 17.51$, $c = 7.74$ Å) in this crystallographic plane.

Full matrix least squares refinement of the structure is presently underway. A more detailed description, interpretation, and listing of data of the refined version of this structure is planned for publication at a later date in this journal.

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GROWTH OF SYNTHETIC CALCITE SINGLE CRYSTALS

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Calcite is an important optical material because of its high birefringence and availability as large, good quality, natural crystals. While sizeable quantities of natural calcite crystals are found in the earth's crust, at present all important sources of high quality crystals are foreign, and since the availability of these crystals at reasonable prices cannot be assured, we have undertaken a program to explore the possibility of producing large, high quality calcite crystals in the laboratory.

Growth from a stoichiometric melt is rendered very difficult by virtue of the high partial pressure of CO_2 over $CaCO_3$ at high temperatures (Smythe and Adams, 1923). Published data (Jamieson, 1960) indicates that the application of pressure tends to stabilize the aragonite structure of $CaCO_3$. On the other hand, most natural calcite is formed hydrothermally and small, synthetic crystals of unspecified quality have been prepared by this technique (Ikornikova, 1961). The low solubility of $CaCO_3$