The Canadian Mineralogist
Vol. 37, pp. 1307-1312 (1999)

GROWTH TEXTURE AND SYMMETRY OF HEULANDITE-Ca FROM POONA, INDIA

MIZUHIKO AKIZUKI[§], YASUHIRO KUDOH AND SETUKO NAKAMURA

Institute of Mineralogy, Petrology, and Economic Geology, Faculty of Science, Tohoku University, Sendai 980-8578, Japan

ABSTRACT

Heulandite-Ca specimens from Poona, India consist mainly of $\{\bar{1}11\}$, $\{001\}$, $\{100\}$ growth sectors. The growth sectors are optically triclinic, though the optical extinction angles relative to the *b* axis are larger in the $\{\bar{1}11\}$ and $\{001\}$ sectors than in the $\{100\}$ sector. All cell dimensions, determined by single-crystal X-ray methods, indicate that the $\{\bar{1}11\}$ and $\{001\}$ sectors are triclinic and the $\{100\}$ sector is monoclinic or nearly so. The triclinic structures are explained by the ordering of Al and Si on the crystal faces.

Keywords: heulandite-Ca, crystal growth, optical sectors, cell dimensions, chemical composition, Poona, India.

SOMMAIRE

Des échantillons de heulandite-Ca provenant de Poona, en Inde, montrent surtout les secteurs de croissance $\{\bar{1}11\}$, $\{001\}$ et $\{100\}$. Ceux-ci sont tricliniques d'après leurs propriétés optiques, quoique les angles d'extinction par rapport à l'axe *b* sont supérieurs dans les secteurs $\{\bar{1}11\}$ et $\{001\}$ que dans le secteur $\{100\}$. D'aprè les paramètres réticulaires, déterminés par diffraction X sur cristaux uniques, les secteurs $\{\bar{1}11\}$ et $\{001\}$ seraient tricliniques, tandis que le secteur $\{100\}$ serait monoclinique ou presque monoclinique. On explique les structures tricliniques par mise en ordre des atomes Al et Si sur les surfaces de croissance.

(Traduit par la Rédaction)

Mots-clés: heulandite-Ca, croissance cristalline, secteurs optiques, paramètres réticulaires, composition chimique, Poona, Inde.

INTRODUCTION

Most of the single crystals of zeolite-group minerals show a sectoral texture and optical anomalies if inspected with crossed polars. The macroscopic crystals consist of growth sectors corresponding to the crystal faces. Within a sector, the optical symmetry may be lower than the symmetry defined on the basis of morphology and X-ray diffraction (*e.g.*, Akizuki & Nishidoh 1988). However, recent studies have shown that for some zeolite minerals (*e.g.*, stilbite, brewsterite, and epistilbite), the symmetry obtained by X-ray diffraction may well correlate with the optical symmetry (Akizuki & Konno 1985, Akizuki *et al.* 1996, Yang & Armbruster 1996).

The purpose of the present study is to discuss a relation between the growth pattern and the symmetry of heulandite.

REVIEW OF THE PERTINENT LITERATURE

Stilbite has been considered to be monoclinic in X-ray-diffraction studies. However, Akizuki & Konno (1985) and Akizuki *et al.* (1993) found that the $\{001\}$ sector of stilbite is orthorhombic, and the $\{110\}$ sector is monoclinic in all samples studied by X-ray diffraction (powder and single-crystal methods), though the optical symmetry of both sectors is triclinic in detail. Also, the optical symmetry of many zeolites such as analcime, yugawaralite, harmotome, epistilbite and chabazite is lower than the symmetry determined by X-ray and morphological properties (*e.g.*, Akizuki 1985, Gaines *et al.* 1997). The property has been referred to as "optical anomaly". The optical anomaly of zeolites is probably due to Al, Si order, which is produced along growth steps on crystal faces (*i.e.*, Akizuki & Nishidoh 1988).

Heulandite-Ca is a common zeolite, with chemical composition $(K,Na)Ca_4Al_9Si_{27}O_{72}\cdot 24H_2O$, and has been considered to be monoclinic since the 19th century (Rinne 1887). Ventriglia (1953) reported heulandite to be piezoelectric, which suggests an acentric symmetry. Merkle & Slaughter (1968) determined the symmetry of heulandite as monoclinic, space group *Cm*. Also, Alberti (1972) suggested from X-ray analysis that the "most probable" space group is *Cm*, whereas it is

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[§] *E-mail address*: akizuki@mail.cc.tohoku.ac.jp

possible that the true symmetry of heulandite is lower, *i.e.*, $C1$. Armbruster & Gunter (1991) confirmed a centrosymmetric space-group by a missing second harmonic generation effect. Gunter *et al.* (1994) did not observe a deviation from $C2/m$ for Na-exchanged and non-exchanged heulandite, but found Cm diffraction symmetry for Pb-exchanged heulandite. Structure refinements on completely Cd-exchanged heulandite led also to Cm symmetry, and revealed highly significant deviation in degree of Si,Al order from the $C2/m$ model (Armbruster 1998). Cs-exchanged heulandite could only be refined in the triclinic space-group $C\bar{1}$ with significant Si,Al order deviating from the topological symmetry (Yang & Armbruster 1996). These examples indicate that the true symmetry of heulandite is probably triclinic $C1$. Armbruster (1998) reviewed the role of Si,Al order and assessed the true symmetry of heulandite.

EXPERIMENTAL

In several samples of heulandite-Ca from Poona, India, the surface growth-pattern with steps and the corresponding internal growth-sectors were observed by reflection interference and transmission polarized optical microscopy. Unit-cell dimensions were obtained by X-ray diffraction.

Optical observations

The transparent crystals are about 2 cm in a diameter and about 1 cm thick, and consist of parallel growth of thin (010) crystal plates. The macroscopic crystals show small $(\bar{1}11)$, (001), and (100) faces and large (010) faces (Fig. 1).

The $(\bar{1}11)$ face shows some elongate triangular growth hillocks with fine growth-steps that are symmetrically inclined to the (010) mirror plane. The corresponding two sectors, which are observed in a thin section normal to the (010) cleavage, are in a twin relationship with respect to the (010) plane. The direction of optical extinction is inclined about 3° to the (010) cleavage plane. This observation suggests that the $\{\bar{1}11\}$ sectors are triclinic.

Some growth hillocks with vicinal faces are observed on the (001) face (Fig. 2A). Although this face is normal to the morphological (010) mirror plane, the vicinal faces are symmetrically inclined to the (010) mirror plane. The (010) plane of symmetry of the growth hillock is indicated by black lines in Figure 2A. Fine growth-steps are nearly parallel to the zone between (001) and $(\bar{1}11)$ faces, though the steps are more or less curved.

Thin sections cut parallel to (001) were made through the {001} sector. With crossed polars, the sections show some symmetrically inclined growth-bands corresponding to the steps on the vicinal face (Fig. 2B). The direction of optical extinction of the bands is 2–3° inclined to the *b* axis on the (001) thin section, suggesting triclinic symmetry. Thus the plane of symmetry between the two kinds of bands changes into a twin plane.

The steps on the (100) face are nearly normal or nearly parallel to the morphological (010) mirror plane (Fig. 3). The (100) thin section of the {100} sector shows wavy extinction between crossed polars. The extinction angle with respect to the *b* axis is smaller than that in the $\{\bar{1}11\}$ and {001} sectors, suggesting that the symmetry is monoclinic or nearly so.

Many minute euhedral crystals of heulandite, which are parallel to each other, are observed on the (010) growth face. The (010) section of the {010} growth sector shows a complicated growth-induced texture that correlates with the growth pattern on the (010) face. The thin section normal to (010) shows narrow growth-induced bands in the {010} growth sector. The optical extinction angles of the sectors vary from band to band and from place to place in the band. Thus it was not possible to extract an optically homogeneous fragment from the {010} sector for a single-crystal X-ray experiment.

The growth steps on the $(\bar{1}11)$ and (001) crystal faces are largely inclined to the morphological mirror plane, and the corresponding growth-sectors are optically triclinic. The growth steps on the (100) face are finely irregular and nearly normal or nearly parallel to the (010) mirror plane, and the corresponding growth-sector is optically monoclinic or nearly so. The relations between morphological and optical symmetries of heulandite are similar to those in many other zeolites (*e.g.*, Akizuki 1985).

Chemical composition

Table 1 shows chemical compositions of the {001} and {100} sectors, as determined by an electron-probe micro-analyzer. The chemical compositions are slightly different between the two sectors.

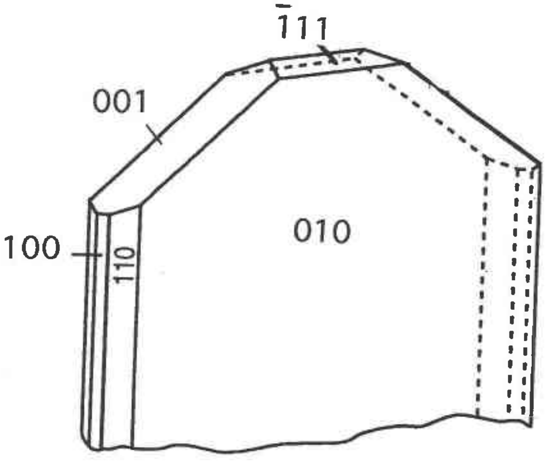

FIG. 1. Morphology of the heulandite specimen.

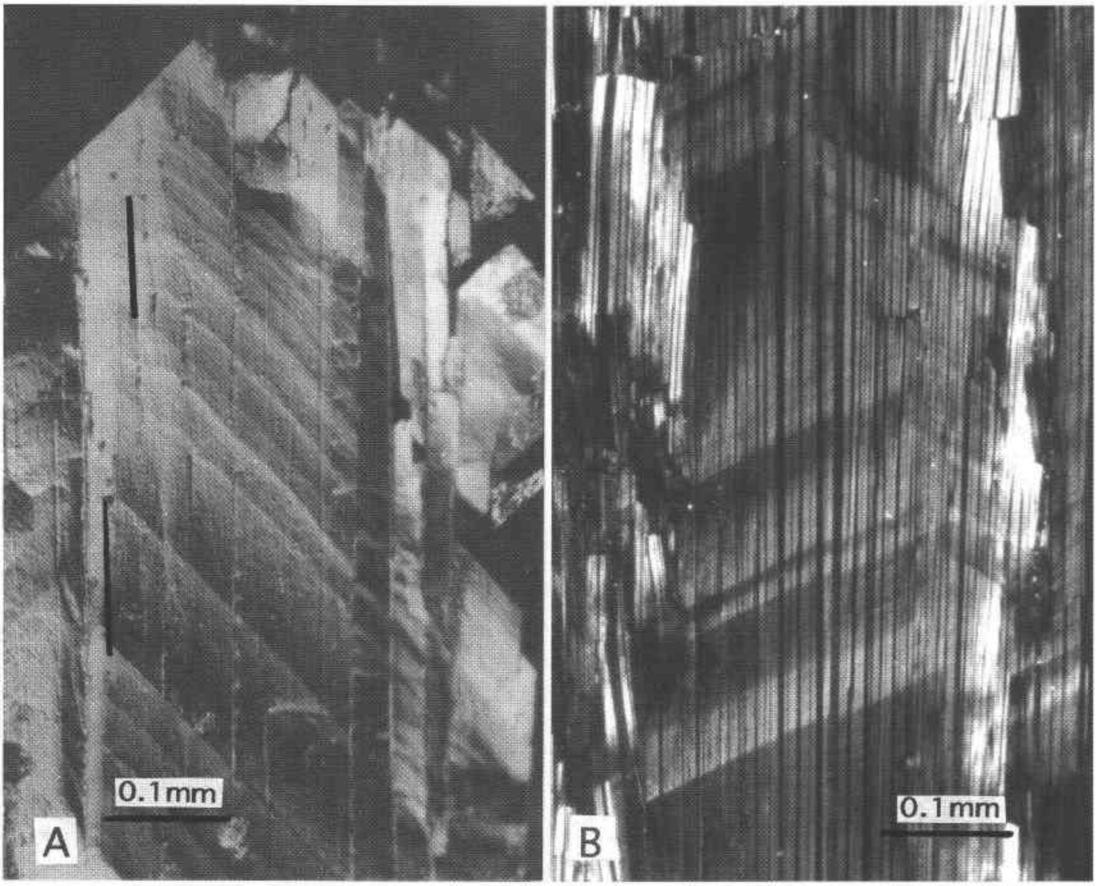

FIG. 2. A. Reflection photomicrograph of growth hillock with growth steps on the (001) face of heulandite. The *b* axis is horizontal. B. Photomicrograph of a (001) thin section of the {101} sector in crossed-polarized light. The broad bands correspond to growth steps on the (001) face shown in Figure 2A. The optical orientations of the bands are symmetrical with respect to the (010) plane, suggesting twinning. Vertical stripes are due to the (010) cleavage.

TABLE 1. CHEMICAL COMPOSITION OF TWO SECTORS OF HEULANDITE-Ca

	{001}	{100}		{001}	{100}
SiO_2 wt.%	60.40	58.25	Si *apfu*	27.73	27.27
Al_2O_3	15.25	15.85	Al	8.25	8.74
CaO	5.59	6.05	Ca	2.75	3.03
SrO	1.95	1.62	Sr	0.52	0.44
Na_2O	1.82	1.70	Na	1.62	1.54
K_2O	0.28	0.33	K	0.16	0.20
H_2O	----	----			
Total	85.29	83.80			

Structural formulae calculated on the basis of 72 atoms of oxygen.

X-ray analysis

The optically homogeneous specimens used for X-ray measurement were hand-picked from thin sections of the {$\bar{1}$11}, {001}, and {100} sectors of the same crystal. The dimensions of these specimens are (in mm): 0.09 × 0.08 × 0.19, 0.10 × 0.18 × 0.02, and 0.18 × 0.18 × 0.08, respectively. The X-ray measurements were conducted at room temperature with a Rigaku four-circle diffractometer (Rigaku AFC–7S) with graphite-monochromatized Mo$K\alpha$ radiation (λ 0.71069 Å). The unit-cell parameters in the three sectors were obtained by least-squares fitting of centered reflections (Table 2). The α and γ angles of the {$\bar{1}$11} and {001} sectors show significant deviation from 90° (approximately 0.1°), suggesting triclinic symmetry, whereas the {100} sector is nearly monoclinic.

TABLE 2. UNIT-CELL PARAMETERS, HEULANDITE-Ca, POONA, INDIA

	a (Å)	*b*(Å)	*c*(Å)	α(°)	β(°)	γ(°)	*V*(Å³)
(1)	17.733(5)	17.882(3)	7.418(2)	89.95(2)	116.45(2)	90.11(2)	2106.0(9)
(2)	17.702(3)	17.979(2)	7.416(1)	89.92(1)	116.48(1)	90.03(1)	2112.6(6)
(3)	17.712(3)	17.968(2)	7.420(1)	90.12(1)	116.49(1)	89.99(1)	2113.3(6)
(4)	17.700(3)	17.927(2)	7.422(1)	89.97(1)	116.51(1)	90.02(1)	2107.3(6)
(5)	17.694(2)	17.934(2)	7.422(1)	90.01(2)	116.51(1)	89.99(1)	2107.6(5)
(6)	17.671(1)	17.875(7)	7.421(3)	....	116.39(3)	....	2097.2

Estimated standard deviations are given in parentheses. The unit-cell parameters were obtained from: (1) 17 reflections between 18.52 and 24.58° ($\{\bar{1}11\}$ sector); (2) 23 reflections between 30.38 and 33.53° ({001} sector); (3) 24 reflections between 31.57 and 46.67° ({001} sector); (4) 25 reflections between 33.66 and 34.74° ({100} sector), and (5) 21 reflections between 31.63 and 46.68° ({100} sector). (6) Gunter *et al.* (1994).

RESULTS AND DISCUSSION

The symmetry of heulandite has been considered to be monoclinic when studied with X-ray and optical methods. Since the (010) cleavage of heulandite is perfect, it was very difficult to produce a thin section normal to the cleavage. Therefore, in many previous studies, the optical properties of heulandite have only been observed in (010) thin sections (Slawson 1925, Hey 1930, Boles 1972, Gunter *et al.* 1994, Yang *et al.* 1997). However, the present optical and X-ray studies show that the $\{\bar{1}11\}$ and {001} are triclinic, and the {100} sectors are monoclinic or nearly so. The cell volume of the {001} sector is significantly larger than that of the {100} sector. The difference of volume and the departure from monoclinic character probably correlate with Al,Si order produced on the crystal surface during growth.

The symmetry is different from growth sector to growth sector in some zeolites such as stilbite (Akizuki & Konno 1985), brewsterite (Akizuki 1987) and scolecite (Akizuki & Harada 1988). Zeolites grow under non-equilibrium conditions in aqueous solutions, and the crystals show a heterogeneous growth-texture. Growth kinetics are important in crystal formation, resulting in a complicated shape and anomalous optical properties in growth sectors.

A three-dimensional crystal structure of a growth hillock is produced by the piling up of a two-dimensional atomic arrangement when the solution is below supersaturation. According to Pauling's second rule, the local charge-balance must be maintained in a three-dimensional structure. Thus tetrahedra in the zeolite's framework that are directly coordinated to alkali or alkaline earth ions are preferentially occupied by aluminum, because of charge balance on the crystal surface. The electrostatic charge on the growth surface, however, is not balanced in a direction perpendicular to the surface, and therefore an ionic crystal can grow continuously. The charge balance should be maintained along the two-dimensional structure exposed on the growth surface as well as within the crystal.

The two-dimensional atomic arrangements exposed on a growth-step surface of an aluminosilicate differ on each surface. If a tetrahedron is a favorably situated on the growth-step surface adjacent to a large cation in the channel, an aluminum ion will preferentially occupy the tetrahedron, whereas if the tetrahedron is situated prior to incorporation of the cation, a silicon ion will occupy the tetrahedral site. Thus, the degree of the Al/Si order may differ from sector to sector. If the vicinal surface consisting of growth steps is normal to a mirror or glide plane, the two symmetrically related sites will be equivalent on the step surface, resulting in a disordered arrangement. Conversely, if the vicinal surface is inclined to the mirror or the glide plane, the two symmetry-related sites in a crystal will not be equivalent on the surface. Thus ordering will occur, and the symmetry of the crystal will be reduced. The morphological mirror plane changes into a twin plane owing to the symmetrically ordered arrangements (*e.g.*, Akizuki & Sunagawa 1978, Akizuki & Nishidoh 1988).

Since the crystal face or the growth step on the ($\bar{1}$11) and (001) faces of heulandite is inclined to the morphological (010) mirror plane, the Al,Si occupancy is ordered with respect to the (010) mirror plane, and the corresponding sectors are triclinic. The (010) mirror plane of the growth hillock on the (001) face changes into twin plane. Since the finely irregular growth-steps on the (100) face are normal or parallel to the (010) mirror plane, the {100} sector consists of an Al,Si disordered structure, and the mirror plane is maintained, resulting in monoclinic symmetry.

A crystal surface has many growth hillocks consisting of various vicinal faces with growth steps. If the straight growth-steps move in one direction on a crystal face, the Al,Si arrangement in the corresponding sector will be ordered and acentric. The steps move in one direction in the central area in Figure 2A, whereas the steps are slightly irregular in Figure 3. The growth steps move in the opposite directions with respect to a mirror plane (Fig. 2A), and the domain including the two growth-patterns must be centric in X-ray analysis. In general, the crystal face consists of a complicated growth-pattern, and the crystal has many faces. Thus, the average symmetry of a macroscopic crystal may be centrosymmetric, and such zeolites may reveal a higher diffraction-symmetry. For precise X-ray analysis, the specimen has to be carefully extracted from the heterogeneous zeolites.

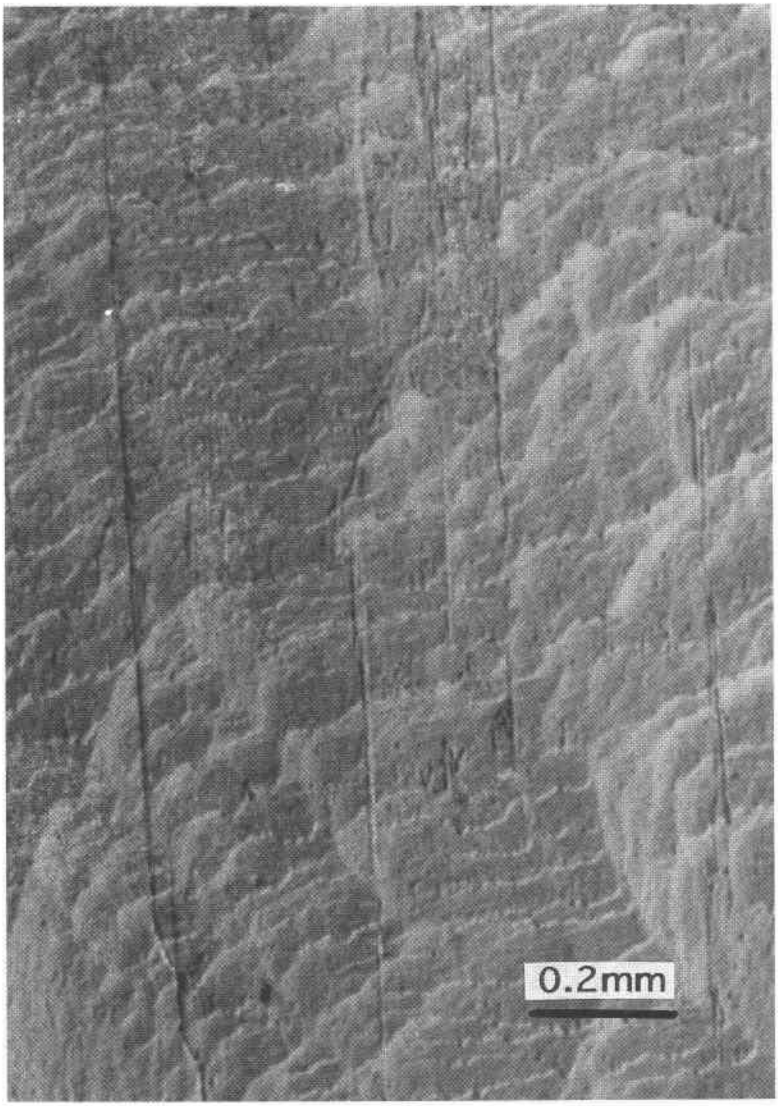

FIG. 3. Reflection photomicrograph of finely irregular growth steps on the (100) face. The *b* axis is horizontal.

ACKNOWLEDGEMENTS

We are grateful to Thomas Armbruster of Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, and one anonymous reviewer for useful comments on the manuscript.

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Received January 22, 1999, revised manuscript accepted September 8, 1999.