

Origin of optical variation in analcime

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Abstract

Surface microtopography and internal textures of corresponding growth sectors of analcime from two localities in Japan were studied by means of polarizing and interference contrast microscopies. On the (211) face, a few large growth hillocks several mm in diameter and several hundred μm in thickness are noted. The hillocks are composed of flat surfaces with steps and also of rounded surfaces. The flat surfaces are almost parallel to the (211) face and the rounded surface is composed of high-index planes consisting of fine steps and kinks. Thin sections produced by cementing the growth surface on a glass slide show that most internal textures seen optically correlate well with growth patterns for both specimens.

These observations indicate that the characteristic internal textures seen on the optical micrographs are formed during the process of crystal growth, and that the symmetry of the sector grown on the vicinal faces $\{hll\}$ is ordered tetragonal, while that of the sector produced on the rounded vicinal faces consisting of various kinks and steps is disordered isometric. The two-dimensional atomic arrangements exposed on the vicinal faces and their symmetries control the Al/Si ordering in the process of crystal growth.

Introduction

Some natural minerals show sectoral textures whose optical symmetry is lower than that of the overall crystal form. Various hypotheses have been offered to explain the optical properties, including phase transitions, internal stress, or ordering of two kinds of atoms in the structure.

The optical variations in adularia were explained by differences in Al/Si ordering established during growth (Akizuki and Sunagawa, 1978), although Bambauer and Laves (1960) believed that they are produced in the process of phase transition. Ordered arrangement of Al/Si was found in chabazite by Smith et al. (1963, 1964). Takéuchi and Haga (1976) suggested that the cause for low symmetry in andradite-grossular garnet showing optical anomalies is due to the ordering of Fe^{3+}/Al . From X-ray analysis, Dollase and Hollister (1969) suggested that the {001} sector of staurolite is orthorhombic, while the {010} sector is monoclinic. From this observation, Hollister (1970) suggested that the distribution of aluminum and hydrogen ions is completely disordered in the {001} sector, in contrast with the {010} sector, and that the apparent disorder is a product of crystal growth.

Most natural analcimes exhibit distinct birefringence which has been variously attributed to loss of water (Náray-Szabó, 1938), to strain (Bannister, 1931) or to ordering of the Al/Si atoms in the structure (Coombs, 1955). Mazzi and Galli (1978) studied the relation between the optical character and the Al/Si ordering in analcime, and found that a trapezohedral analcime is composed of both isometric disordered and tetragonal ordered structures, causing the optical variation. Some optical observations suggested that the fine birefringent sectors in analcime are in twin relation (Stewart, 1941; Gottardi, 1978). Although the optics of analcime can be measured in thin section by means of the universal stage, it is very difficult to ascertain the three-dimensional distribution of some sectors in crystals under the optical microscope. Therefore, I studied the origin of the ordered and disordered sectors using a special thin section parallel to the {211} growth surfaces. In this paper, the origin of the optical variation in analcime is discussed in terms of a general model of order-disorder in growth sectors.

Observations

A thin section parallel to the growth surface was prepared from the specimen, whose as-grown face

was cemented on a glass slide, and was observed on the polarizing microscope with the universal stage in order to measure the optical orientations. The surface microtopography of crystal faces was studied by means of reflection-type interference contrast microscopy.

Maze analcime

The transparent trapezohedral crystals found in cavities of basalt from Maze, Niigata Prefecture, Japan are as much as 1 cm in diameter. A thin section cut perpendicular to a growth plane (211) shows zonal growth texture parallel to the surface. Both optically isotropic and anisotropic domains coexist in one crystal. The optically uniaxial anisotropic domains are tetragonal according to Mazzi and Galli (1978). Sharp boundary traces between the isometric and non-isometric domains cross the zonal texture. This indicates that both domains coexisted at the same stage of crystal growth. The (211) growth surface is characterized by the development of growth hillocks (Fig. 1). Figure 2 shows a schematic cross-section of a growth hillock on the (211) face of analcime. Figure 2 is normal to Figure 1 and is parallel to both the tetrad and triad axes. The growth hillock is composed of two kinds of vicinal faces; one is the (*hll*) face which consists of flat planes and steps. The flat plane is almost parallel to (211) which is a stable face in analcime, and the side plane of the steps corresponds to the high-index plane (*h'l'l'*). The other is a rounded surface which is composed of a high-index plane (*hkl*) consisting of fine steps and kinks. A spiral dislocation may pass through the summit of the hillock, but the distance between the steps on the rounded vicinal surface is so narrow that the spiral growth pattern cannot be found.

Figure 1b shows a photomicrograph under crossed polars of the same area as in Figure 1a. The sectors in the thin section (Fig. 1b) are clearly related to the different types of growth surface and this indicates that they are produced during the growth of the crystal. The uniaxial sectors correspond to the surface with flat planes and steps, and the isometric sectors correspond to the rounded surfaces. The sectors have sharp boundary traces parallel or nearly parallel to the edge of the (211) face. The optic axis of the anisotropic areas is parallel to the *a* axis of isometric analcime. This fact is consistent with the idea that the uniaxial analcime in these crystals is tetragonal. An electron microprobe study of the crystal showed that chemical composition is the same in both sectors.

Irakawa analcime

The specimens occur as well-developed crystals, sometimes as large as 3 cm in diameter, in cavities of dolerite from Irakawa, Yamagata Prefecture, Japan. The crystals are transparent except at their contact with the country rock where they are whitish and include acicular natrolite crystals. A thin section normal to the growth surface shows a complicated pattern similar to that of the Maze analcime. The growth pattern on the (211) surface (Fig. 3a) differs distinctly from that for the Maze analcime (Fig. 1a). For the Maze analcime, one-third of the vicinal face on the growth hillock is composed of flat faces and steps and the remaining two-thirds is rounded. However, the corresponding vicinal face of Irakawa analcime, which consists of flat faces and steps, is much narrower than that of Maze analcime and the boundaries between the two kinds of vicinal faces are not distinct. Figure 3b shows a photomicrograph of a thin section between crossed polars of the same area as in Figure 3a. One-to-one correlation is not clear as compared with Maze analcime. The growth hillocks centered at P and Q are partially mantled by the growth hillock S made at the latest stage of crystal growth. Since the growth hillock S is very thin in contrast with the growth hillocks P and Q, the corresponding sector S is very faint in Figure 3b, while the corresponding thick sectors P and Q are distinct in the thin section. The rim of the thin growth hillock S consisting of irregular steps is isotropic, whereas the area with flat faces and steps along the crystal edge is anisotropic. The boundary trace is shown by an arrow in Figure 3b. The isotropic sector of growth hillock P shown by two dashed lines is in contact with the growth hillock Q under the hillock S (Fig. 3a). One hillock with growth center R is found in the square of Figure 3a. Although the boundary between the flat face with straight steps and the irregular face shown by a fine line is curved in Figure 3a, the corresponding boundary is vertical in Figure 3b. Figure 4 shows a large magnified photomicrograph of the growth sector R. Since this section is thinner than that of Figure 3b, one-to-one correlation is better between the surface feature and the inner texture, as compared with the case of Figures 3a and 3b. The near-surface growth sectors differ distinctly from those produced at earlier stages of growth, the latter resembling the growth sectors of Maze analcime. Evidently, growth conditions changed abruptly at the latest stage of crystal growth of the Irakawa analcime.

Discussion

General mechanism of formation of the order-disorder growth sectors

From my studies of sectoral textures and optical properties of adularia, chabazite, stilbite, topaz, and other minerals (Akizuki and Sunagawa, 1978; Akizuki *et al.*, 1979; Akizuki, 1980, 1981), a general mechanism of formation of the order-disorder growth sectors of minerals is suggested.

When a crystal grows in a solution with low supersaturation, a three-dimensional lattice is produced by the stacking of two-dimensional lattices. The two-dimensional atomic arrangements exposed on the side planes of the growth step and their symmetry affect the degree of ordering produced during growth. Therefore, the two-dimensionally ordered structure produced on the surface during growth is not always the same as the three-dimensionally ordered structure which occurs by a phase transition after growth.

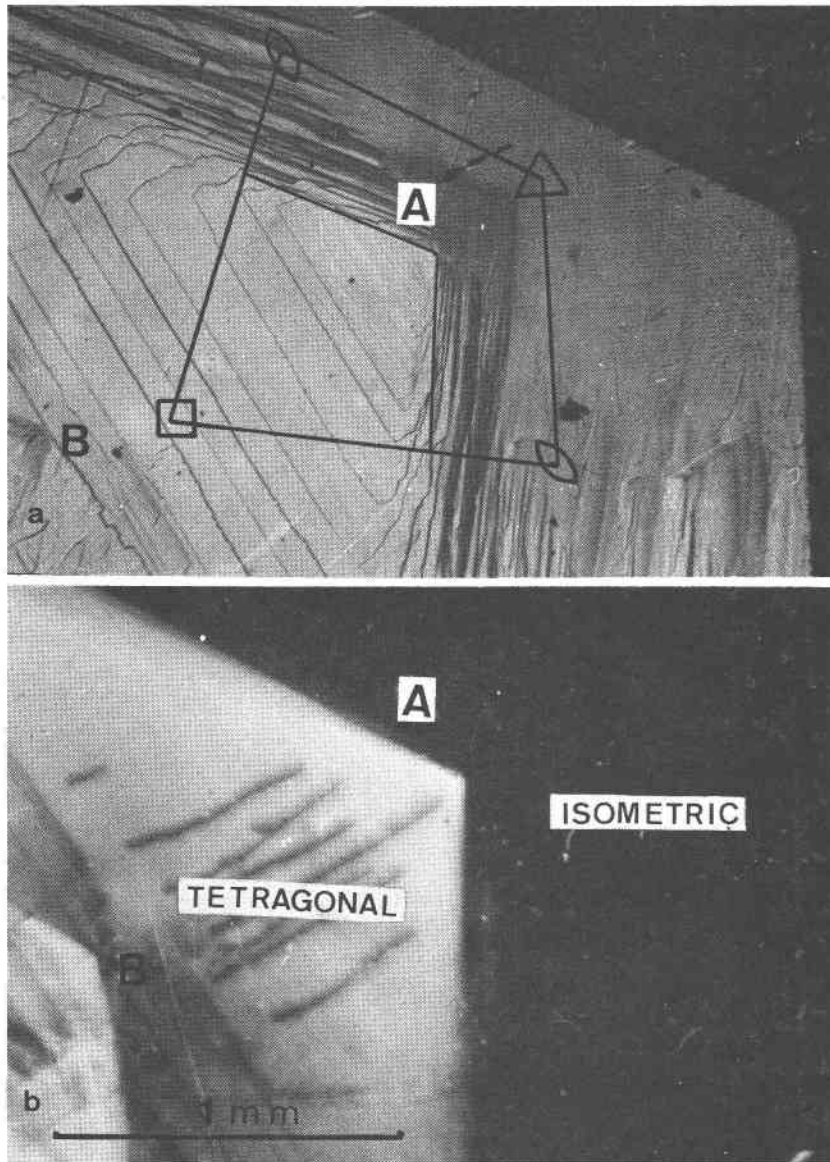


Fig. 1. Corresponding reflection interference-contrast (a) and polarized (b) photomicrographs of (211) of analcime from Maze. Ideal form of (211) face and symmetrical axes inclined to the face, by which the crystal orientation can be recognized are drawn on the surface. The symbols \square , \triangle , and \circ show tetrad, triad, and diad axes respectively. The letter A shows the corresponding growth center of growth hillocks. Some striations on the tetragonal area are due to cracks.

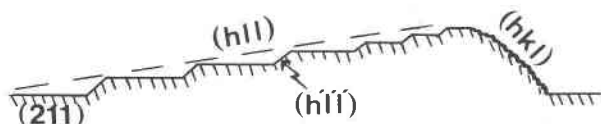


Fig. 2. Schematic cross-section of the growth hillock on the (211) growth surface. The (hll) plane shown in a dashed line consists of flat faces and steps. The flat face is almost parallel to the (211), and the step sides correspond to the high-index plane $(h'1'l')$. Because the step heights are very low, the surface seems to be a vicinal face under the optical microscope. The figure is enlarged in the direction normal to the (211) surface. Therefore, the surface is called the (hll) vicinal face in this paper. The other is the rounded surface which is composed of a high-index plane (hkl) consisting of fine steps and kinks.

It is possible for changes of the ordering to occur during crystal growth by the following mechanisms.

Figure 5 shows a schematic framework of a cubic crystal in which only two of the three sites a, b, and c are occupied. In a disordered cubic crystal all three sites are equivalent, and hence the two atoms must occupy at random two-thirds of them. Consider crystal growth on the (100) plane. Sites b and c are equivalent to each other but not equivalent to site a, because the framework of sites b and c are normal to the growth surface, while the framework of site a is

parallel to the surface. Therefore, the occupancies of sites b and c should be identical to each other, but may be different from that of site a. Thus, the (100) sector can be tetragonal and will probably have a c axis normal to the (100) plane. Since the same situation exists in the (010) and (001) sectors, six growth sectors in relation to the sectoral twinning may be formed in the cube during growth. An actual crystal will have various vicinal faces on the (100) growth surface and the corresponding sectors. The symmetry of such vicinal faces may be even lower than tetragonal.

Consider the following structure, $\dots T_1M T_2 T_1M T_2 T_1M T_2 \dots$. If the growth steps move in the vertical direction on the paper, the T_1 and T_2 sites which have identical configuration will be equivalent. If the steps move from left to right, the T_1 and T_2 sites will no longer be equivalent to each other, because T_1 is made before M and T_2 after M. Therefore, the symmetry in a growth sector will decrease to monoclinic or triclinic in some minerals. When a framework is monoclinic, the $\{h0l\}$ sectors, whose vicinal faces are parallel to the b axis, would be disordered and monoclinic, whereas the $\{hkl\}$ sectors would be ordered and triclinic. The sector made on a rough face consisting of various kinks will be disordered.

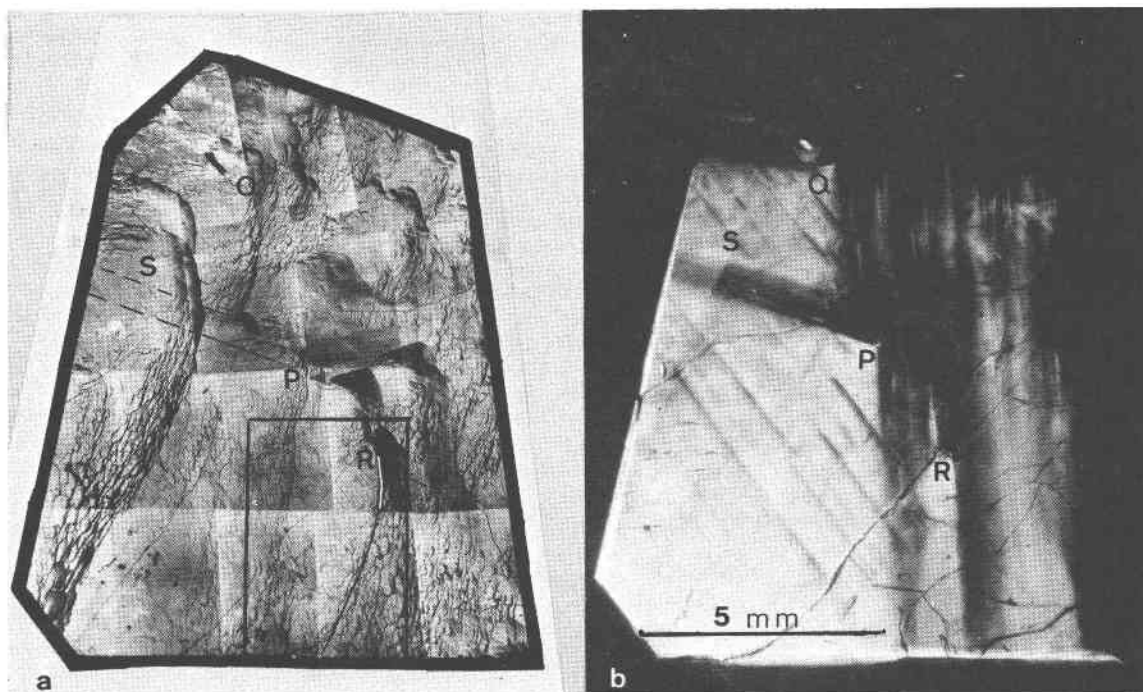


Fig. 3. Corresponding reflection interference-contrast (a) and polarized (b) photomicrographs of (211) of analcime from Irakawa, Japan. See text for details.

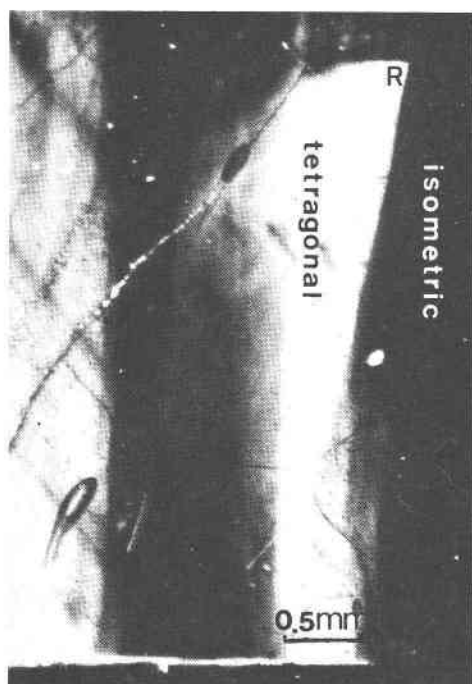


Fig. 4. Polarizing optical micrograph of the same sector as shown in the square of Fig. 3a. One-to-one correlation is better between the surface feature (Fig. 3a) and the internal texture as compared with Figs. 3a and 3b, due to thinner section.

Adularia (Akizuki and Sunagawa, 1978) and chabazite (Akizuki, 1981) are minerals typically showing both ordered and disordered growth sectors. In adularia, some growth hillocks consisting of $(10\bar{l})$ and $(11\bar{l})$ vicinal surfaces exist on the $(10\bar{1})$ face. The $\{10\bar{l}\}$ sectors corresponding to $(10\bar{l})$ vicinal surface parallel to the b axis are monoclinic, while the $\{11\bar{l}\}$ sectors corresponding to the $(11\bar{l})$ vicinal surface inclined to the b axis are triclinic. The $T_1(o)$ and $T_1(m)$ sites exposed on the side plane of growth step on the vicinal face $(10\bar{l})$ are equivalent with respect to K ion to each other and the structure is monoclinic. Both the sites on the vicinal face $(11\bar{l})$ are not equivalent with respect to K ion to each other, that is, since $T_1(o)$ site is in contact with K ion on the $(11\bar{l})$ face, Al ion will occupy the $T_1(o)$ site, because of a local charge balance, while $T_1(m)$ and two T_2 sites which are on the same sheet parallel to (110) will be occupied by Si ions, and it is triclinic. Chabazite, whose morphology is rhombohedral, is optically triclinic with the $2V$ value and optical orientation varying from place to place. Smith *et al.* (1963, 1964) suggested that the most probable cause for the decreased symmetry of chabazite is ordering of the Al/Si atoms. The directions of vicinal faces on the growth

surface explains why the crystal structure formed on the $\{10\bar{1}1\}$ surfaces is triclinic and ordered (Akizuki, 1981).

Any two species of atoms which are capable of replacing each other in symmetry-equivalent sites must resemble each other in chemical properties but they need not have the same valences. Although the charge balance obviously must be maintained, this is done by a double set of substitutions at different sites. According to Pauling's second rule, the charge balance is maintained in a small area. The relations between alkali and aluminum atoms in some minerals such as feldspar and analcime were discussed by Ferguson (1979) and Mazzi and Galli (1978), who mentioned that aluminum atoms occupy the sites nearest to sodium atoms. This relation will be maintained for the two-dimensional atomic arrangement along a growth surface as well as for the three-dimensional structure. Thus, the Al/Si ordering produced during growth is explained within the concept of local charge balance, similar to Hollister's theory (1970) for the chemical sector of staurolite. This method of explaining the optical symmetry of some minerals is also similar to that of chemically sectoral textures suggested by Nakamura (1973) and Dowty (1976). Takéuchi and Haga (1976) discovered that grossular-andradite garnet exhibiting double refraction consists of the Fe^{3+}/Al -ordered structure. From the internal texture I assumed that the ordering was produced on the (110) surface during growth. Although the electrostatic charges are the same between the two cations, the ionic radii are different (0.57\AA for Al^{3+} , 0.67\AA for Fe^{3+}). The partitioning of the two ions may differ on the growth surface due to the different ionic radii. This concept is similar to that of the protosite

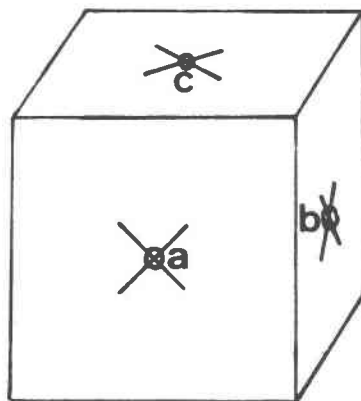


Fig. 5. Schematic diagram of cubic framework with three sites a, b, and c. See text for details.

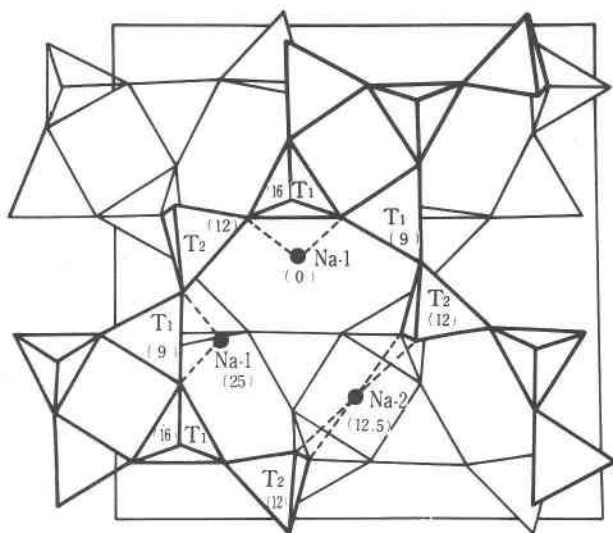


Fig. 6. Projection on (100) of the aluminosilicate framework of non-isometric analcime showing six- and four-membered rings of tetrahedra. Only the lower half of the unit cell content is shown. Numbers in parentheses denote X-coordinates in hundredths. (Modified from Deer et al., 1963 and Mazzi and Galli, 1978)

flexibility, which Nakamura (1973) used to interpret the chemical sectors of clinopyroxene. Ordering of F and OH may also occur on the growth surfaces of topaz, thereby explaining the optical anomaly (Akizuki et al., 1979), because the ionic radii (1.53Å for OH⁻ and 1.36Å for F⁻) are different from each other.

Since the crystallization mechanism of order-disorder growth sectors is similar to that of chemical sectors, the sectors are not only different in the degree of ordering but also in chemical composition in some minerals (Hollister, 1970; Akizuki et al., 1979).

Mechanism of optical variation in analcime

Figure 6 shows the lower half of the unit cell of analcime projected onto (100). The framework contains six-membered rings and four-membered rings of tetrahedra that are normal to the triad and tetrad axes, respectively. All 48 tetrahedra are symmetrically equivalent and the 16 aluminum atoms must randomly occupy one-third of them in isometric analcime. The framework contains a set of 16 large vacancies of the six-membered rings at 1/8, 1/8, 1/8 etc., and 24 small vacancies of the four-membered rings at 0, 1/4, 1/8 etc. The large vacancies are occupied by water molecules and 16 of the 24 small vacancies are occupied by sodium atoms.

Eight of the four-membered rings in the unit cell are parallel to (100), and the remaining 16 four-

membered rings are parallel to (010) or (001) normal to (100). Therefore, the 8 four-membered rings parallel to the (100) are not equivalent to the 16 four-membered rings parallel to the (010) or (001) at the growth surface of (211), though they are equivalent in the three-dimensional structure. The Na-1 sites exist in the vacancies of the four-membered rings normal to Figure 6, while the Na-2 sites exist in the four-membered rings parallel to the figure. Therefore, the Na-1 and Na-2 sites are not equivalent on the (211) growth surface.

The differences in the two-dimensional atomic arrangements exposed on the growth surface affects the ordering in a non-equilibrium crystal growth condition. When the crystal grows on the (hll) vicinal face, the 16 Na atoms occupy the 16 Na-1 sites rather than the Na-2 sites (Mazzi and Galli, 1978). Mazzi and Galli also suggested that the Na occupancy of an octahedron depends only on the Al fraction in the nearest tetrahedron which shares one edge with that of the Na octahedron. The T₁ and T₂ sites of aluminum and silicon atoms shown in Figure 6 are the sites nearest to Na-1 and Na-2 respectively. Therefore, Al and Si occupancies at the T₁ and T₂ sites will not be equivalent to each other on the (211) surface and the tetragonal ordered analcime structure is produced during growth on the {211} surfaces. The Al/Si ordering in analcime is explained by the concept of local charge balance. The c axis of tetragonal analcime should be parallel to [100] of isometric analcime at the eight {211} sectors. The c axis of tetragonal analcime should also be parallel to [010] at the eight {121}, and [001] at the eight {112} sectors. Although the orientations of tetragonal analcimes differ between the three sector groups {211}, {121}, and {112}, they remain the same in one sector group and are not in twin relation with each other. Tetragonal ordered analcime grows on the flat surface parallel to the {211} on the hillock. Conversely, a disordered structure is produced on the rounded vicinal faces due to the fact that they consist of fine steps and/or kinks on which the orientations of growth differ from place to place.

A possible effect of growth rate on the degree of Al/Si ordering in K-feldspar was suggested by Laves (1952), who mentioned that when the rate of growth is high enough the ordering force is overwhelmed during crystallization, thus forming a more or less disordered framework. Hydrothermally synthesized isometric analcime apparently grows in this way (Saha, 1959). The growth rate of analcime in a natural hydrothermal vein is lower than the growth rate

of a synthetic analcime, and the degree of Al/Si ordering varies from sector to sector due to the difference in the two-dimensional atomic arrangements exposed on the growth surface.

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