

## Al-Si ordering and twinning in edingtonite

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### ABSTRACT

An edingtonite crystal from Ice River, British Columbia, Canada, has a clear, euhedral rim and whitish, anhedral core. The rim shows the  $m\{110\}$ ,  $o\{111\}$ ,  $p\{1\bar{1}1\}$ , and  $c\{001\}$  sectors and a small  $2V$  value (about  $-22^\circ$ ) with some exceptions in the  $\{1\bar{1}1\}$  sector, and the core shows twinning without sectors and a large  $2V$  value (about  $-52^\circ$ ). X-ray diffraction analysis indicated that both the core and the rim are orthorhombic. However, optical observation leads to a different conclusion: the core is orthorhombic and consists of an ordered Al-Si structure, whereas the rim, especially the  $\{110\}$  sector, is evidently triclinic and has a partly ordered structure.

### INTRODUCTION

Edingtonite, a rare barium zeolite ( $\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 8\text{H}_2\text{O}$ ), has two polymorphs—orthorhombic, space group  $P2_12_12$  (Galli, 1976), and tetragonal, space group  $P4_2m$  (Mazzi et al., 1984). According to Hey (1934), orthorhombic edingtonite from the Böhlet mine, Sweden, shows  $2V = -54^\circ$ , and tetragonal edingtonite from Kilpatrick Hill, Scotland, shows  $-15^\circ < 2V < -20^\circ$ . Grice et al. (1984) described orthorhombic edingtonite ( $2V = -62^\circ$ ) from Ice River, British Columbia, Canada, and Mazzi et al. (1984) refined the crystal structure as tetragonal and disordered.

On the basis of studies of the relationship between surface features and internal textures of some zeolites and other minerals, Akizuki (1981a, 1981b, 1984, 1985) and Akizuki and Konno (1985) interpreted their optical properties and internal textures as being produced by atomic ordering on side faces of growth steps; furthermore, Akizuki suggested a general mechanism for the formation of growth sectors. These concepts are applied in this paper to edingtonite.

### OPTICAL OBSERVATION

Figure 1 shows the crystal form and faces of edingtonite from Ice River, Canada. The crystal is bounded by the  $p\{1\bar{1}1\}$ ,  $o\{111\}$ ,  $c\{001\}$ , and  $m\{110\}$  forms, and each face has growth hillocks or kinks. The crystal has a whitish core and a clear rim. The surface microtopography of the crystal faces was studied with reflection-type interference optical microscopy. Thin sections cut in various planes and observed between crossed polars on a universal stage allowed determination of  $2V$ , which varies with Al-Si ordering. The  $2V$  values range from  $-10^\circ$  to  $-54^\circ$ , but  $2V$  values at  $-22^\circ$  and  $-52^\circ$  are dominant.

Figure 2 shows the internal texture in a thin section cut near the crystal center and inclined slightly to the  $(110)$  face. The crystal consists of an anhedral core and a euhedral rim. According to a microprobe analysis by Grice et al. (1984),  $\text{K}_2\text{O}$  is more abundant in the rim than in

the core. The core is characterized by its white color, which is due to mineral inclusions, and by a large  $2V$  ( $-52^\circ$ ) and multiple twinning approximately parallel to the growth direction. The rim is transparent and shows a small  $2V$  ( $-22^\circ$ ) with some exceptions in the  $\{1\bar{1}1\}$  sectors. A sector is an area that was produced by crystal growth on each face, whereas a domain is produced by crystal growth on the vicinal face of the growth hillock or striation; thus, a sector consists of many domains.

Figure 3 shows the internal texture in the  $(001)$  thin section crosscutting the clear top portion of the crystal. The section consists of the  $p\{1\bar{1}1\}$ ,  $o\{111\}$ , and  $m\{110\}$  sectors, which are more or less heterogeneous between crossed polars. The light areas show large  $2V$  values ( $-52^\circ$ ), whereas dark areas show  $2V$  values as small as  $-22^\circ$ . The optic vibration direction  $Z$  is parallel to the  $a$  axis in the  $\{1\bar{1}1\}$  and  $\{001\}$  sectors with some exceptions, whereas the  $Z$  direction is variously inclined to the  $[110]$  in the  $\{110\}$  and  $\{111\}$  sectors with some exceptions in the  $\{110\}$  sector.

Figure 4 shows the  $(001)$  thin section crossing the core. The core shows twins and a large  $2V$  value, whereas the rim ( $\{110\}$  sector) shows a small  $2V$  value and no twins. In the core, the optic vibration directions are in  $(110)$  reflection twin relation with each other, which is in accord with what has been known in edingtonite (Deer et al., 1963). In the rim, however, the  $Z$  direction is roughly parallel to the  $[110]$  rather than to the  $a$  axis, with variations from place to place. The  $X$  direction may be parallel or nearly parallel to the  $c$  axis in both the rim and core.

The internal textures in the sectors are compared with growth features on each face:

**The  $p\{1\bar{1}1\}$  face.** The surface is composed of thin steps with several growth centers (Fig. 5). Although the steps near the growth center are symmetrically inclined to the  $(110)$  plane, the direction of the steps varies with distance from the growth center, and the steps moving toward the bottom from the growth center are fine and irregular (Fig. 5).

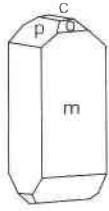


Fig. 1. Crystal form with the  $p\{1\bar{1}1\}$ ,  $o\{111\}$ ,  $c\{001\}$ , and  $m\{110\}$  faces of edingtonite from Ice River, Canada. From Grice et al. (1984).

**The  $\{1\bar{1}1\}$  sector.** A thin section was prepared parallel to the  $(1\bar{1}1)$  face. When conditions change abruptly during growth, Al-Si ordering and/or chemical composition vary at each growth step, and therefore microzoning corresponding to the growth steps is observed in the thin section parallel to the growth surface. In some minerals whose growth conditions changed abruptly at the latest stage of crystal growth, surface features are not correlated to in-

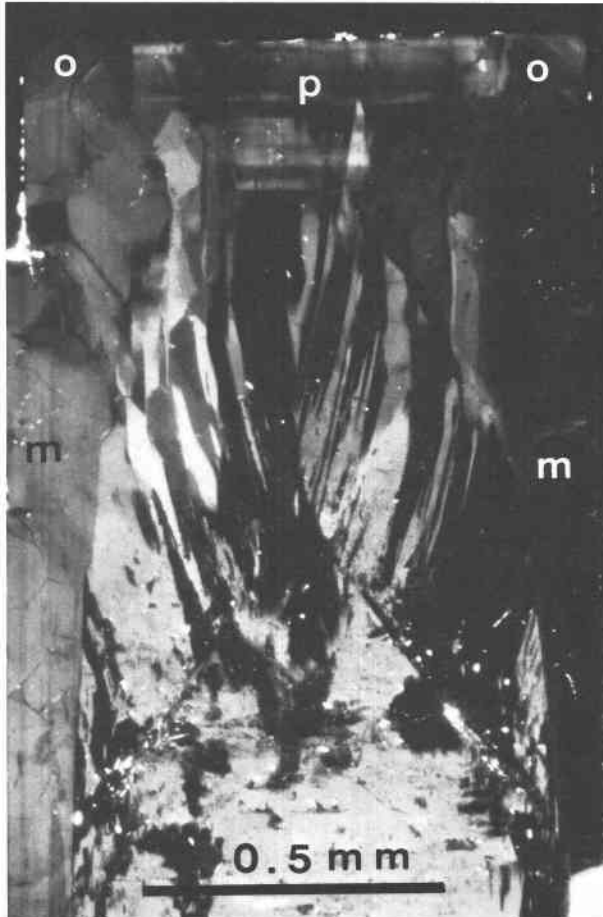


Fig. 2. Cross-polarized photomicrograph of the thin section inclined about  $10^\circ$  to  $(110)$  in the  $c$ -axis direction of edingtonite from Ice River. The crystal consists of an anhedronal core with twinning and a euhedral rim with  $m\{110\}$ ,  $o\{111\}$ , and  $p\{1\bar{1}1\}$  sectors.

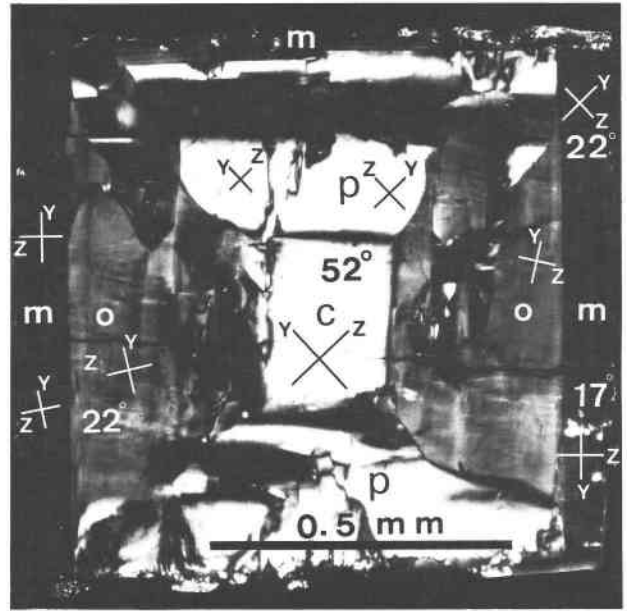


Fig. 3. Cross-polarized photomicrograph of the thin section normal to the  $c$  axis of edingtonite. The crystal consists of the  $m\{110\}$ ,  $p\{1\bar{1}1\}$ ,  $o\{111\}$ , and  $c\{001\}$  sectors. Optical vibration directions  $Z$  and  $Y$  are shown. The  $Z$  direction is variously inclined to  $[110]$  on the  $(001)$  plane in the  $m\{110\}$  and  $o\{111\}$  sectors.

ternal texture (Akizuki, 1981a). Figure 6 shows various domains in the  $\{1\bar{1}1\}$  sector; the arrow indicates the growth center, which corresponds to the summit of the growth hillock. Straight lamellae corresponding to the growth steps radiate from the growth center. The lattice pattern on the upper area suggests overlapping of lamellae. The optical extinction directions are in twin relation between the light and dark domains, as the black and white lines show. The

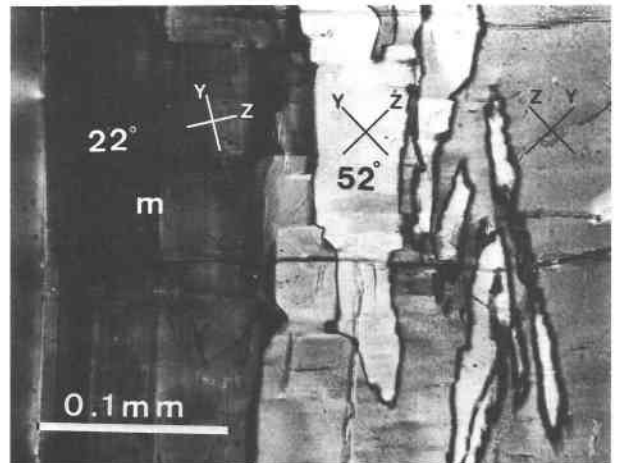


Fig. 4. Cross-polarized photomicrograph of the  $(001)$  thin section, which shows a dark rim ( $m\{110\}$  sector) with fine growth zoning and a light core with twinning of edingtonite. The optical vibration directions  $Z$  and  $Y$  are shown.

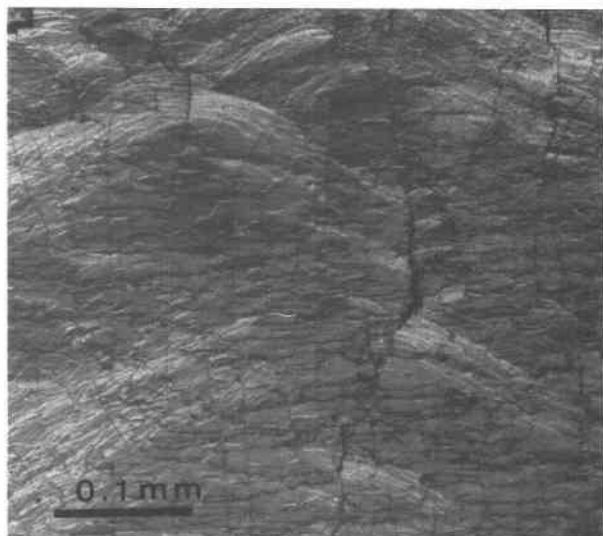


Fig. 5. Reflection interference photomicrograph showing growth features on the  $\{1\bar{1}1\}$  face of edingtonite. The  $[110]$  direction is horizontal.

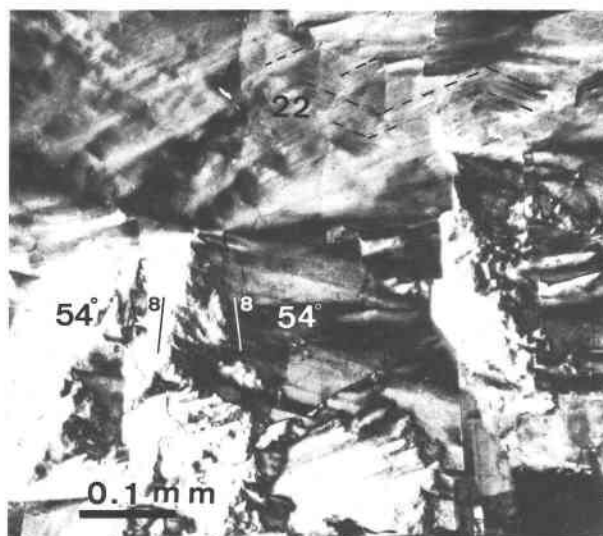


Fig. 7. Cross-polarized photomicrograph of the  $\{1\bar{1}1\}$  sector in the  $(1\bar{1}1)$  section of edingtonite. Dashed lines show fine lamellae corresponding to the growth steps. Extinction angles from the vertical direction and  $2V$  values are shown. Crystal orientation is the same with that of Fig. 6.

optic vibration directions  $Z$  and  $Y$  are parallel to the  $a$  and  $b$  axes with some exceptions, and the  $2V$  values vary from about  $-20^\circ$  to about  $-50^\circ$ .

Figure 7 shows internal texture in another thin section parallel to the  $(1\bar{1}1)$  face. Domains showing large  $2V$  values correspond to the growth hillocks, and the extinction angles ( $8^\circ$ ) are symmetrically inclined with respect to the vertical  $(110)$ , a pattern that suggests twinning. Fine lamellae with kinks, which are shown by dashed lines in

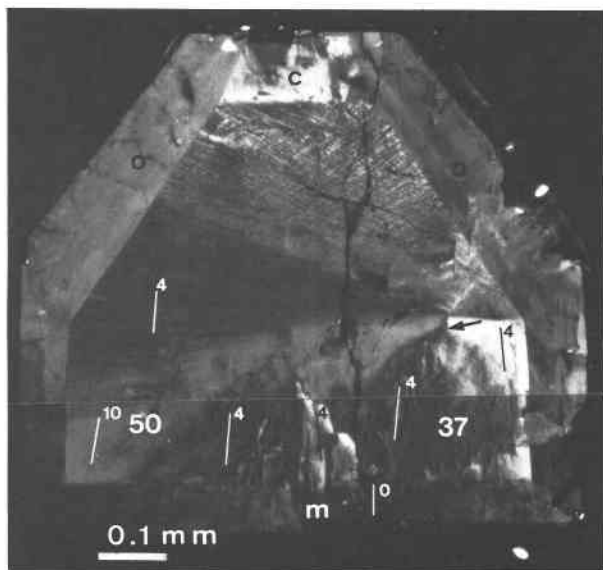


Fig. 6. Cross-polarized photomicrograph of the  $\{1\bar{1}1\}$  sector in the  $(1\bar{1}1)$  section of edingtonite. The rim shows the  $o\{111\}$ ,  $c\{001\}$ , and  $m\{110\}$  sectors. Extinction angles from the vertical direction and  $2V$  values are shown.

the upper part of Figure 7, show small  $2V$  values. The extinction directions are inclined from  $10^\circ$  to vertical. The optic vibration directions  $Z$  and  $X$  are parallel to the  $a$  and  $c$  axes, respectively, with some exceptions, and are in twin relation between both the light and dark domains.

**The  $o\{111\}$  face.** The  $(111)$  face is rough, because it consists of numerous, fine kinks.

**The  $o\{111\}$  sector.** The  $2V$  value is about  $-22^\circ$ , and the  $Z$  direction is roughly parallel to the  $[110]$ . No lamellae were observed in the sector, though it is finely heterogeneous.

**The  $m\{110\}$  face.** The  $(110)$  face is composed of many small edingtonite crystals grown parallel to the  $(110)$  face. Steps, without a growth center, lie parallel or normal to the  $c$  axis on the face of parallel-grown crystals, though no growth steps are observable in some areas.

**The  $m\{110\}$  sector.** The thin section normal to the  $c$  axis revealed fine growth zoning with  $2V = -22^\circ$  (Figs. 3 and 4). The optic vibration direction  $Z$  changes from the  $[110]$  to the  $a$ -axis direction in the  $(001)$  section, a situation that suggests monoclinic or triclinic symmetry. The section parallel to the  $(110)$  face represents some domains corresponding to the parallel-grown crystals. The extinction angles vary from place to place in the  $(110)$  section, though the angles are small. The optic vibration direction  $X$  is inclined about  $1^\circ$  to the  $c$  axis in some domains, resulting in sectorial twinning. These domains are triclinic.

#### X-RAY ANALYSES

Areas showing small  $2V$  values are abundant in the upper (transparent) part of the crystal, whereas areas showing large  $2V$  values are dominant in the lower part.

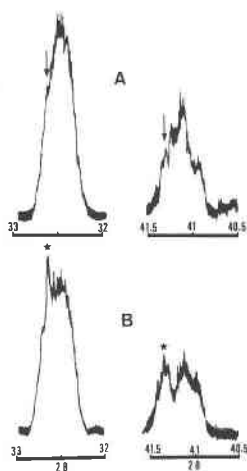


Fig. 8. X-ray diffraction peaks of (A) the upper portion (transparent) and (B) the lower portion (whitish) of the edingtonite crystal. The two peaks, which are shown by the arrows, correspond to those indicated by stars.

These parts were separated, and two diffraction patterns from 32 to 33° and from 40.5 to 41.5°  $2\theta$  were recorded by X-ray diffractometer using  $\text{CuK}\alpha$  radiation, a scanning speed of  $\frac{1}{6}^\circ$  per minute, and a chart speed 1 cm per degree. The two scans covered the intervals for the 131 and 311 and the 141 and 411, respectively, which are unequivocally indexable pairs (Fig. 8). The peaks split into four, except for a broad peak (A) between 32 and 33°  $2\theta$ . The weak peaks with arrows in the upper portion (A) correspond to the strong peaks with stars in the lower portion (B).

Table 1 shows lattice spacings of the peaks represented in Figure 8, which are compared with those of orthorhombic and tetragonal edingtonite crystals (Mazzi et al., 1984). The lattice spacings of the outside two peaks are consistent with those of orthorhombic edingtonite. Also, the inside two peaks suggest the orthorhombic symmetry, and their average lattice spacings are similar to those of tetragonal edingtonite. The upper portion showing dominantly small  $2V$  values has strong inside peaks, whereas the lower portion showing dominantly large  $2V$  values has strong outside peaks. The single-crystal X-ray precession method revealed no deviation from tetragonal symmetry in the crystals showing small  $2V$  values.

Table 1. Lattice spacings (Å) of edingtonite

A	B	Orthorhombic		Tetragonal <i>d</i>
		<i>hkl</i>	<i>d</i>	
	2.761	131	2.763	
2.754	2.755			2.753
	2.750			
	2.742	311	2.741	
2.203	2.203	141	2.201	
2.195	2.195			2.192
2.189	2.186			
2.183	2.183	411	2.181	

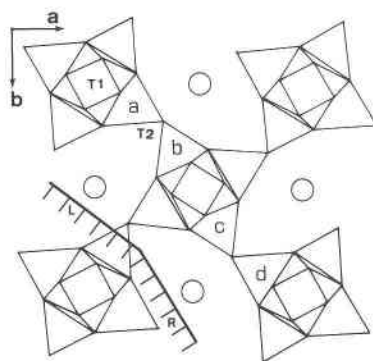


Fig. 9. Partial crystal structure projected along the *c* axis of edingtonite. Circles show Ba ions. Water molecules are omitted.

## DISCUSSION

X-ray analysis reveals that the area showing large  $2V$  values ( $-52^\circ$ ) consists of Al-Si ordered structure and that the area showing small  $2V$  values ( $-22^\circ$ ) has partly ordered structure. Through X-ray analysis, edingtonite from the Böhlet mine, Sweden, was interpreted as tetragonal by Taylor and Jackson (1933) but as orthorhombic by Galli (1976). Also, edingtonite from Ice River, Canada, was interpreted as orthorhombic by Grice et al. (1984) but as tetragonal by Mazzi et al. (1984). The edingtonite crystal discussed in this paper is interpreted as orthorhombic through X-ray analysis. However, the optical observations lead to a different conclusion. Although the core is orthorhombic and ordered, the rim, especially the  $\{110\}$  sector, evidently is triclinic, not tetragonal, in spite of its disordered structure, because no optical vibration directions are parallel to the crystal axes. This suggests that Al and Si occupancies are slightly different among the T2 tetrahedra (a, b, c, and d in Figs. 9 and 10). It should be noted that adularia shows a similar phenomenon, i.e., the  $\{110\}$  sector consists of a triclinic, disordered structure (Akizuki and Sunagawa, 1978).

Figure 9 shows a partial crystal structure of edingtonite.

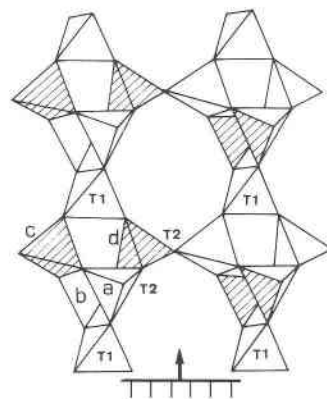


Fig. 10. A clinographic projection of the edingtonite tetrahedral chain, in which tetrahedra with Al atoms are shaded. Growth step is drawn at the bottom.

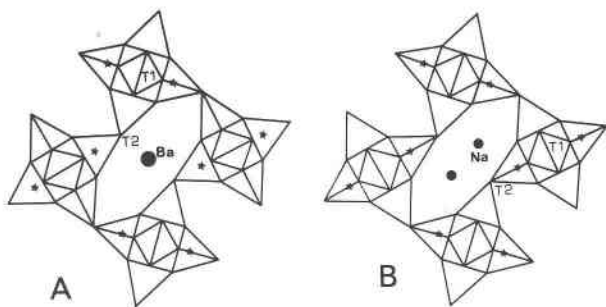


Fig. 11. Ordered crystal structures projected along the  $c$  axes of (A) edingtonite and (B) natrolite. Tetrahedra with stars are occupied by Al ions and other tetrahedra without stars have Si ions. Water molecules are omitted.

The steps (L and R) of the vicinal faces on the  $(1\bar{1}1)$ , which are symmetrical with respect to the  $(110)$  plane, are projected on the  $(001)$  plane. In ordered edingtonite, T2 tetrahedra, whose oxygens are directly coordinated with Ba ions, are alternately occupied with Si and Al ions, because of the aluminum avoidance rule forbidding Al-O-Al bonds. On the contrary, T1 tetrahedra, whose oxygens are not directly coordinated by Ba ions, will preferentially be occupied with Si. The ordered structures that are produced on the L and R steps will be symmetrical with respect to the  $(110)$  plane. If the T2(b) and T2(c) tetrahedra are occupied by Al ions during growth on step R, the T2(a) and T2(d) tetrahedra will be occupied by Al ions on step L, and the result is twinning. In the orthorhombic, twinned crystals, the  $a$  axis of one component coincides with the  $b$  axis of the other, and vice versa; the  $c$  axis is common. Some domains in the  $\{1\bar{1}1\}$  sector are composed of the partially ordered structure, which may be due to a high growth rate or a rough step.

Also, a partially ordered structure occurs in the  $\{110\}$  sector. Figure 10 shows an ordered crystal structure of edingtonite. Growth steps normal to the  $c$  axis move from bottom to top in the structure. Although the T2(b) tetrahedron bonds with a tetrahedron under the paper and T1, the T2(a) tetrahedron coordinates with only the T1 on the growth step. If the T1 tetrahedron of the bottom is occupied by Si, the T2(a) tetrahedron can be occupied by Si or Al. If one of the T2(a) and T2(b) tetrahedra or both are occupied with Al, the T2(c) and T2(d) tetrahedra will be occupied with Si, though they are shown with Al in Figure 10. Thus, Al and Si are distributed randomly through the T2 tetrahedra, but Si will be more abundant than Al, because of the aluminum avoidance rule. Therefore, because of total charge balance, the T1 tetrahedra are occupied not only by Si but also by Al, and a disordered structure results (Mazzi et al., 1984). If the growth steps are symmetrically inclined to the  $c$  axis on the  $(110)$  face, a triclinic, twinned structure will occur in the  $\{110\}$  sector. The  $(111)$  face is very rough, and therefore the crystal structure has long-range disorder as well.

The twins in the  $\{1\bar{1}1\}$  sector are correlated with the growth hillock and vary as the growth patterns change on the surface. The twins in the core, however, result from

the same mechanism as those of growth twins in many minerals such as quartz and spinel. In the Ice River edingtonite, growth mechanisms differed in the core and rim, and the core might have dissolved slightly before the rim formed, as implied by the anhedral shape of the core.

Crystal structures of natrolite and edingtonite are similar. Since all the T2 tetrahedra are equivalent with respect to Al and Si on the pyramidal face of edingtonite (Fig. 11A), the twinning and disordering are easily produced by simple exchange of Al and Si on the growth surface of edingtonite. However, such exchange is difficult in natrolite during growth, because the orientations of T2 tetrahedra are not equivalent with respect to Al and Si on the growth surface (Fig. 11B), though they are equivalent in the three-dimensional structure. In twinned natrolite, the framework of one part is rotated about the normal to  $(110)$  with respect to the other (Pabst, 1971). Natrolite with a disordered structure may be produced during extremely high speed crystal growth. Thus, both ordered and disordered structures are commonly observed in natural edingtonite in spite of the mineral's rarity, whereas the disordered structure is rare in natural natrolite, which is a common zeolite.

#### ACKNOWLEDGMENTS

I would like to thank Professor Joseph R. Smyth, University of Colorado, for critical reading and corrections to the manuscript. Also, I am grateful to Professor Satoshi Kanisawa, Tohoku University, for his help with the X-ray work.

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