

Sector growth and symmetry of (F,OH) apatite from the Asio mine, Japan

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Abstract

A study of apatite crystals from the Asio mine, Japan, showed sectoral texture related to the growth of the crystal, and with optically biaxial properties within the sectors. Wet chemical analysis gave a composition $\text{Ca}_5(\text{PO}_4)_3(\text{F}_{0.64}, \text{OH}_{0.38}, \text{Cl}_{0.01})_{1.03}$ for the specimen.

Additional diffraction spots were not observed in precession and oscillation X-ray photographs and electron diffraction photographs. Since the internal textures correlate with the surface growth features, it is suggested that the internal textures and the unusual optical properties were produced during non-equilibrium crystal growth. The fluorine/hydroxyl sites in hexagonal apatite are symmetrically equivalent in the solid crystal but, at a growth surface, this equivalence may be lost, resulting in a reduction of crystal symmetry. Heating of the apatite to about 850°C results in the almost complete disappearance of the optical anomalies due to disordering, which may be related to the loss of hydroxyl from the crystal.

KEYWORDS: apatite, sector growth, optical anomaly, atomic ordering.

Introduction

THE crystal structure of apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ has been described as belonging to the hexagonal centrosymmetric space group $P6_3/m$ (Beevers and McIntyre, 1946). Apatite is optically negative and normally uniaxial. However, Hounslow and Chao (1969) found monoclinic chlorapatite with space group $P2_1/a$ from Ontario, Canada, in the crystal structure, of which Cl atoms are ordered in orientation. They suggested that the monoclinic structure was produced by a phase transition in the solid state after crystal growth. Also, Mackie *et al.* (1972) and Elliott (1985) found monoclinic structures in both synthetic chlorapatite and

hydroxyapatite by single crystal analyses, and suggested that reduction of symmetry in monoclinic apatite results from the ordering of Cl and OH in the (0,0,z) anion columns. Hughes *et al.* (1989) discussed F, OH, Cl atomic orderings in the structure of the end-members of apatite.

Watanabe (1932) observed an optical anomaly in apatite crystals from the Asio copper mine, Japan, but did not observe the surface growth patterns and corresponding domains within the sectors. The crystals consist of many fine domains, and the extinction angles and 2V values vary from domain to domain. Takano and Takano (1959) studied specimens by X-ray diffractometry, and suggested that the internal texture and optical property were produced during hydrothermal

alteration after crystal growth, though no evidence for this was given.

Some low-temperature natural minerals such as zeolites show sector textures whose optical symmetry is lower than that of the overall crystal form. Based on studies of the relation between surface features and internal texture, Akizuki (1986) has explained the optically abnormal properties and internal textures of some minerals as atomic orderings produced on the side faces of growth steps, suggesting a general mechanism for sector growth. The objective of the present study is to describe the surface growth features, internal textures and crystal structure of biaxial apatite from the Asio mine and to discuss the origin of the optical sectors and the symmetry.

Experimental

Specimens. Apatite crystals occur in the druses of chalcopyrite veins, together with quartz and other sulphide minerals. Homogenization temperatures of quartz crystals are in the range of 200–350°C (Enjoji and Takenouti, 1976). Three kinds of apatite crystals were collected several decades ago. Apatite I is short prismatic and transparent variety, about 1 cm in diameter and 1–2 cm in length. Apatite II is translucent, because of fine solid and liquid inclusions and an overgrowth of fine quartz, and is about 5 mm in diameter and 1 mm thick. Apatite III consists of dendritic aggregates of thin foliated crystals (< 1 mm) and 5 mm in diameter.

Chemical analysis. Apatite I was used for the analysis because of the clear crystals. Material was carefully hand-picked, and the final purity was checked by polarized optical microscopy and X-ray powder diffractometry. Chemical zoning, even for chlorine, was not detected in microprobe analysis, though the microprobe would not detect small amounts of impurities. The powder sample was decomposed with a mixture of hydrochloric and nitric acids for the determination of calcium and phosphorus. Calcium was separated as calcium oxalate, and determined by the EDTA titration method. Phosphorus was determined colorimetrically with vanadomolybdc acid. The decomposition by fusion with sodium carbonate was done for the analyses of halogen. Fluorine was determined using an ion-selective electrode after separation by steam distillation. The determination of chlorine was made titrimetrically by Mohr's method. Orange elementary analysis was used for water and CO₂. The sample was mixed with anhydrous sodium tetraborate flux, and analysed on a YANACO MT-5 CHN recorder. The measurement errors are estimated as

approximately 0.05 wt.% each for water and CO₂. The analyses on the solution, prepared by fusing the sample with lithium metaborate, for Si, Al, Mn, Fe and Sr were performed by Inductive Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The ICP-AES analysis shows that the contents of the other elements are negligibly small, being < 100 p.p.m. Table 1 presents the analytical results and the chemical formula based on 13(O,OH,F,Cl); that is, Ca₁₀P₆O₂₄·(F_{0.64},OH_{0.38},Cl_{0.01})_{1.03}, in which CO₂ is not considered.

TABLE 1. Chemical composition of apatite from the Asio mine, Japan

P ₂ O ₅	41.83	P	2.99	} 3.01
SiO ₂	0.10	Si	0.01	
Al ₂ O ₃	0.06	Al	0.01	} 5.00
CaO	55.19	Ca	4.99	
MnO	0.10	Mn	0.01	} 1.03
FeO	0.04	F	0.64	
SrO	0.02	Cl	0.01	
F	2.38	OH	0.38	
Cl	0.05			
H ₂ O	1.34			
CO ₂	0.09			
Sum	101.20			
O = F,Cl	1.01			
Total	100.19			

Optical observations. The optical observations were of apatite I because of the clear crystals. The crystals consisted of (0001) and (10 $\bar{1}$ 0) faces, which were observed by interference-contrast microscopy. Special sections were prepared, in some cases parallel to or perpendicular to the as-grown face, in order to correlate surface growth features with internal textures as well as with optical properties. These sections were observed under the polarizing microscope with a universal stage to measure 2V values and optical orientations.

The {0001} sector. The (001) face is covered with many minute growth hillocks (50–100 μ m in diameter), suggesting high growth rates at the latest stage of crystal growth (Fig. 1). Population of the minute hillocks is $1 \times 10^4/\text{cm}^2$, which is abnormally high for natural crystals. Each growth hillock consists of six vicinal faces {10 $\bar{1}$ l} without (0001) face. A thin-section parallel to the (0001) face was prepared from a specimen whose grown face was pasted to a glass slide. The thin-section shows fine sixfold sectors between crossed polars,

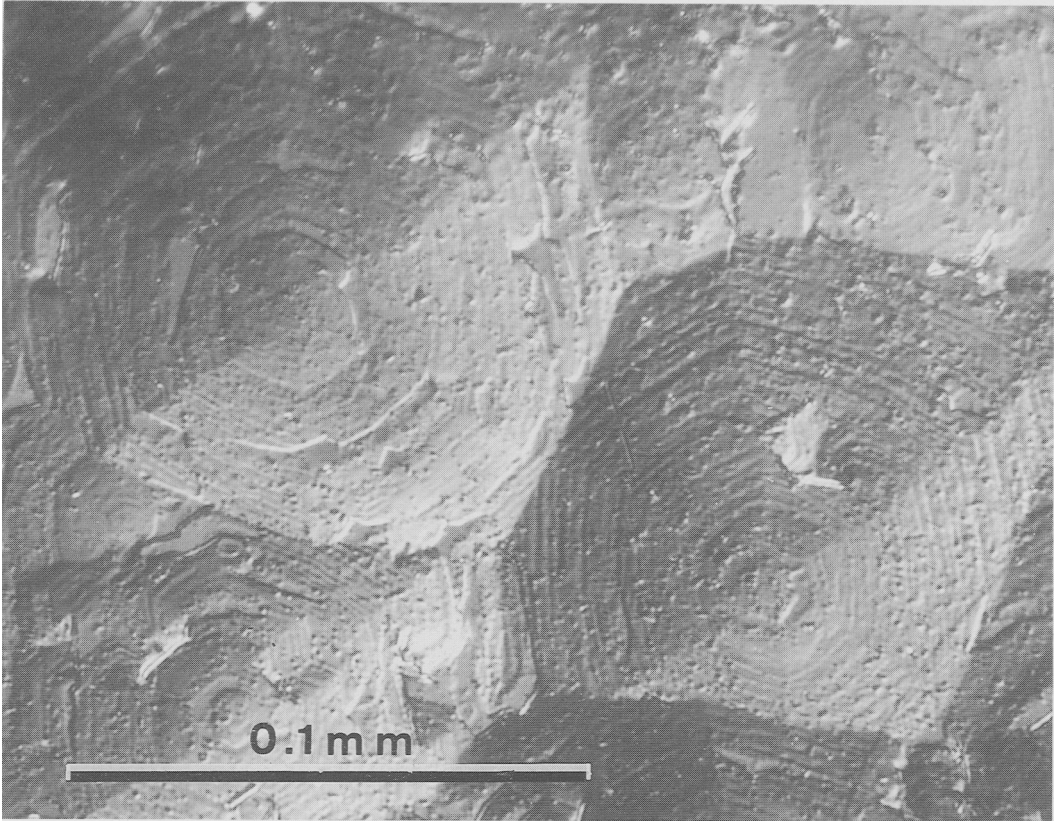


FIG. 1. Reflection interference-contrast optical photomicrograph of (0001) surface of the apatite crystal. The growth hillock consists of six vicinal faces with a growth centre.

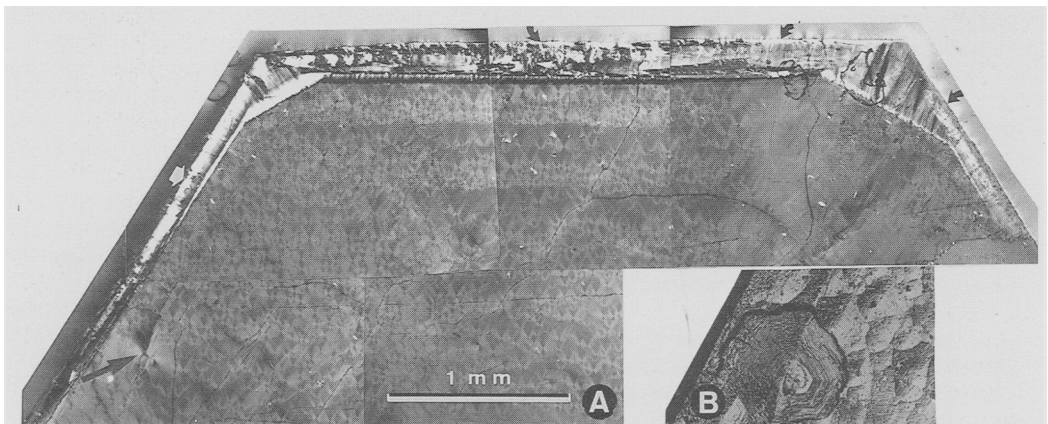


FIG. 2. (A) {0001} sector (core) and $\{10\bar{1}0\}$ sector (thin rim) in the section parallel to the (0001) face. The {0001} sector consists of many minute sixfold sectors, and the $\{10\bar{1}0\}$ sector shows a complicated internal texture. (B) The corresponding growth pattern on the (0001) face, which consists of one large hill and several hillocks with growth summits. The large hill corresponds to the internal texture shown by the black arrow in (A). Small black and white arrows indicate the crystal edge. (Crossed polarized light.)

whose form is similar to that of growth hillocks on the surface (Figs. 2A, 2B). One-to-one correlation is not clearly observed between the surface growth features and internal texture, because the hillocks are too fine and overlap each other. The large growth hill, however, corresponds to the internal sixfold sectors in the section (Fig. 2A and B). Therefore, it is suggested that the internal texture was produced during crystal growth, and not by the alteration or transition in solid state after growth.

Figure 3 shows sixfold sectorial twins in the (0001) thin-section between crossed polars. The sectoral boundaries are sharp near the centre. The large sectors consist of finer sectors overlapped with each other. The optical vibration direction Z is parallel to the boundary of sixfold sectors in general. However, in Fig. 3, the direction Z is inclined from the sector boundary, as shown by a

black line, because of the overlapping of the finer sectors. The $2V\alpha$ values are smaller than 20° through the sections. The optic vibration direction X , which was measured in the section normal to the (0001) face, is inclined at an angle within 2° to the c -axis, suggesting triclinic symmetry.

After cutting parallel to the (0001) face, a (0001) thin-section was prepared (Fig. 4). The section consists of core and rim, which correspond to {0001} and $\{10\bar{1}0\}$ sectors, respectively. The {0001} sector shows larger triangular domains than those near the (0001) face. The optic axial planes are parallel to the boundaries as shown by white arrows with $2V\alpha=35^\circ$ and 40° , whereas it rotates 60° from the sector boundary in the sector indicated by the black arrow with $2V\alpha=30^\circ$. The optic vibration directions X are inclined at an angle of up to 2° to the c -axis, which was measured in the section parallel to the $(10\bar{1}0)$ face.

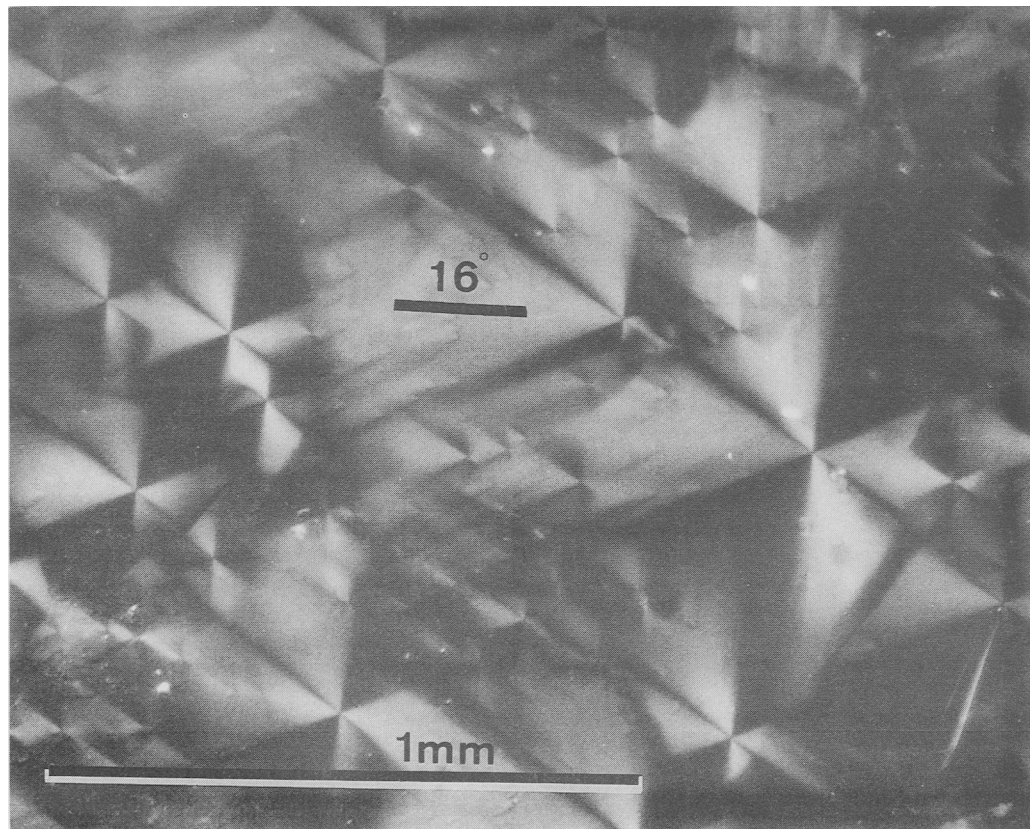


FIG. 3. The sixfold growth sectors in another (0001) thin-section near the surface. Large triangular sectors consist of smaller sectors. The optic axial plane is parallel to the black line, and the optic vibration direction X is approximately parallel to the c -axis. The $2V\alpha$ value is 16° . (Crossed polarized light.)

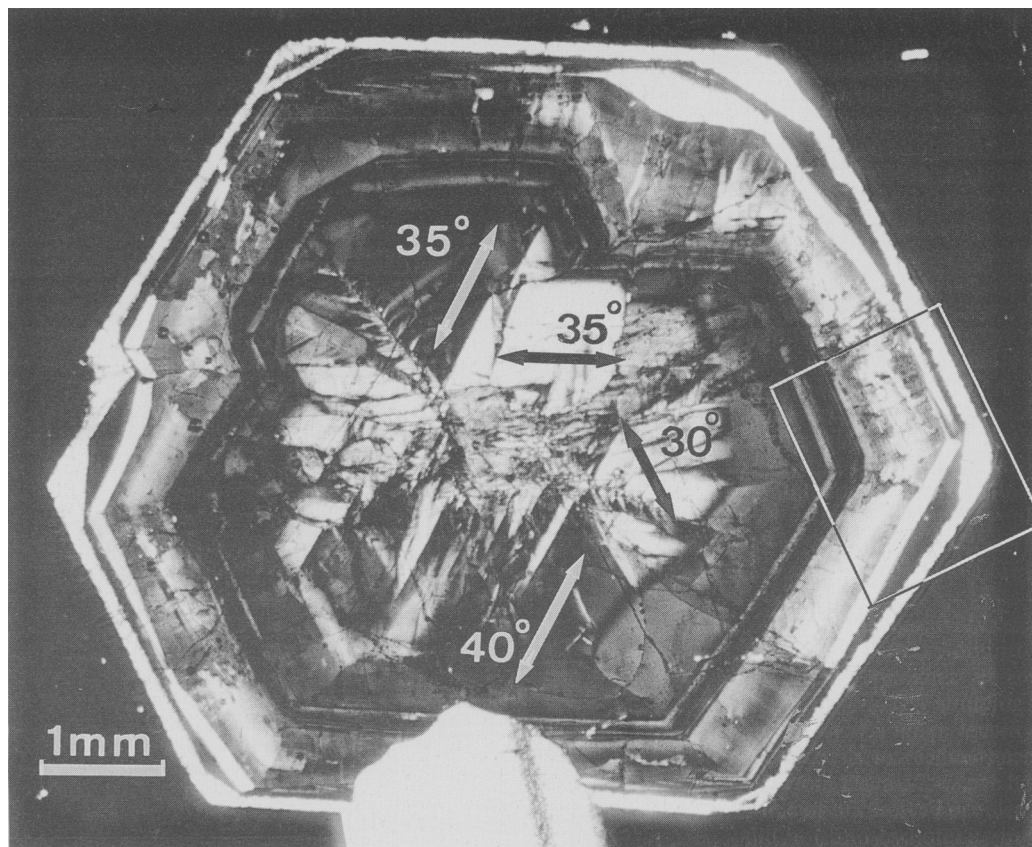


FIG. 4. The $\{0001\}$ sector (core) and $\{10\bar{1}0\}$ sector (rim) in the thin-section parallel to the (0001) face. The $\{0001\}$ sector consists of smaller triangular sectors. The optic axial planes are parallel to black and white arrows, and the optic vibration direction X is nearly parallel to the c axis. The $2V\alpha$ values vary from 30° to 40° . (Crossed polarized light.)

The $\{10\bar{1}0\}$ sector. Figure 5 shows a highly magnified photograph of the $\{10\bar{1}0\}$ sectors enclosed by the thin white line in Fig. 4. The sectors consist of growth bands parallel to the $(10\bar{1}0)$ face and isolated growth domains. The optic axial planes are approximately normal to the (0001) face, and the directions Z are parallel or inclined at an angle of about 60° to the growth bands as shown by thick black and white arrows. Therefore, the optic axial planes are symmetrically inclined with respect to the growth bands in some sectors, which indicates twinning, though this is not observed in Fig. 5. The outermost thin band consists of fine textures showing the biaxial optical property. The second black band is uniaxial ($2V\alpha=0^\circ$), i.e. hexagonal.

The $(10\bar{1}0)$ face shows parallel growth of fine prismatic crystals. The face was lightly polished

and a thin-section was produced through the outermost band of Fig. 5. The section shows small prismatic domains, which correspond to the surface growth feature (Fig. 6). The extinction direction X is inclined up to 3° to the c -axis, though they are parallel to this axis in some areas, suggesting triclinic and monoclinic symmetries.

X-ray and electron diffraction

An X-ray precession photograph was obtained from an apatite crystal showing a single crystal form ($0.4\text{mm} \times 0.4\text{mm} \times 0.3\text{mm}$) and consisting of six $\{10\bar{1}0\}$ and two $\{0001\}$ anisotropic sectors. The $h0l$ diffraction patterns, however, revealed no additional spots which would have the effect of decreasing crystal symmetry. Neither do the

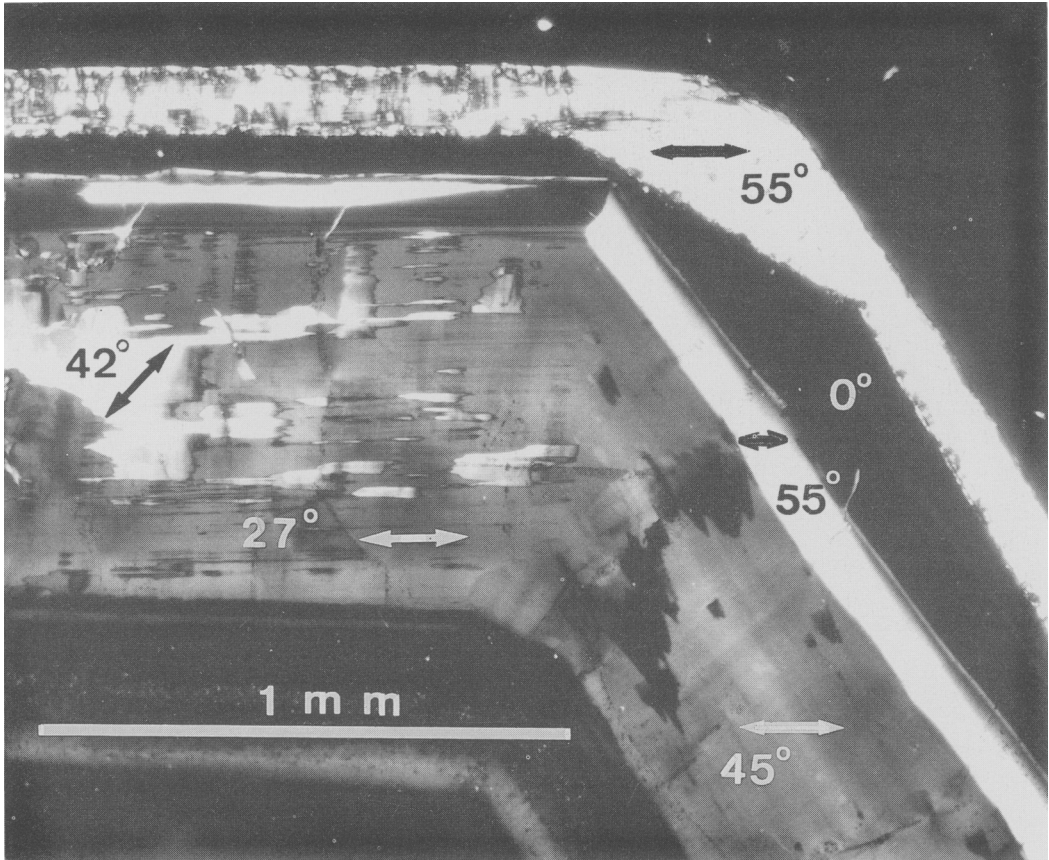


Fig. 5. Magnified photomicrograph of the $\{10\bar{1}0\}$ sector indicated by the square in Fig. 4. The left lower dark area with grey strip corresponds to the $\{0001\}$ sector. The optic axial planes are parallel to the black and white arrows, and the optic vibration direction X is nearly parallel to the c -axis. The $2V\alpha$ values are given.

electron diffraction films ($hk0$ and $hk1$) show any additional spots.

Differential thermal analysis

The D.T.A. curves of apatites are generally smooth and featureless. A basal (0001) slice of the specimen was heated in air at 850°C for 16 h, (a weight loss of about 1.5% being detected). The sectors of the heated crystal are uniaxial or biaxial with small $2V\alpha$ angle.

Discussion

As crystal optics are very sensitive for studying crystal symmetry, even if X-ray and electron diffraction show it as hexagonal, the crystal symmetry of this specimen may be monoclinic or

triclinic. Since the angle between the optic vibration direction X and the c -axis is small, the triclinicity will be small. The near-end-member apatite crystals are hexagonal or monoclinic: $P6_3/m$ synthetic and natural fluorapatite (e.g. Hughes *et al.*, 1989), $P2_1/b$ synthetic hydroxyapatite (Elliott *et al.*, 1973) and $P2_1/b$ synthetic chlorapatite (Mackie *et al.*, 1972). Although the F ions lie on the mirror plane, the Cl and OH ions are ordered above and below the (0,0,1/4) special positions in apatite, resulting in monoclinic symmetry. If both hydroxyapatite and chlorapatite grow at high growth rates under high-temperature conditions, the OH and Cl anions will be disordered above and below the mirror plane in both the end-member apatite structures, resulting in hexagonal symmetry. Also, Hughes *et al.* (1990) found monoclinic ternary apatite with

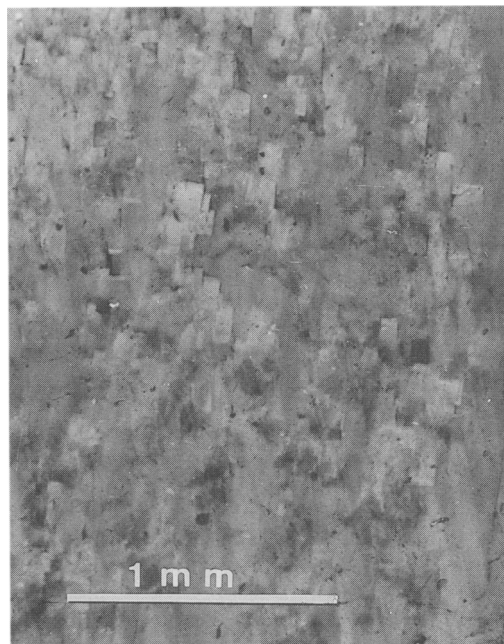


FIG. 6. The $\{10\bar{1}0\}$ growth sector in the thin-section parallel to the $(10\bar{1}0)$ face, which was produced through the outermost layer in Figs. 2A and 5. The c -axis is vertical. Short prismatic features correlate with the growth patterns on the $(10\bar{1}0)$ face. (Crossed polarized light.)

($F_{0.39}, Cl_{0.33}, OH_{0.28}$), and suggested that the reduction of symmetry in monoclinic ternary apatite results from the ordering of Cl and OH within the anion columns. Elliott *et al.* (1973) proposed that if F ions or vacancies are lower than 15% in (F,OH) apatite, monoclinic symmetry results. Although the fluorine content in the present ($F_{0.64}OH_{0.38}$) apatite is 63 at.wt.% the crystal symmetry is monoclinic or triclinic.

The F and OH ions may be ordered within the anion columns as well as Cl and OH ions. Many similarities are observed with respect to the crystal growth between the present apatite and brown coloured topaz from Brazil. The topaz crystals consist of optically orthorhombic, monoclinic and triclinic growth sectors (Akizuki *et al.*, 1979), and the F/OH ordering and triclinic symmetry were revealed in the structure by neutron diffraction (Parise *et al.*, 1980). The symmetry, however, was orthorhombic in X-ray diffraction and convergent beam electron diffraction (Neder, 1985). X-ray and electron diffraction may be insensitive to the ordering of light atoms of similar atomic number in the presence of heavier atoms (Neder, 1985).

Because of the very similar size and X-ray scattering power of OH and F ions, the additional X-ray and electron diffraction spots that might be expected to be produced by the ordered apatite would be very weak.

The optical symmetries and internal textures of the present specimens correlate with the growth directions of vicinal faces on the surface. Therefore, it is suggested that F/OH ordering was produced during non-equilibrium crystal growth on the side faces of growth steps, in the same way as Al/Si ordering occurs in adularia (Akizuki and Sunagawa, 1978) and zeolites (e.g. Akizuki, 1986).

The removal of some of the OH and F ions by heating could possibly result in vacancies in the structure, which would allow the diffusion of the large fluorine and hydroxyl ions required for disordering. The ordering of hydroxyl and fluorine on the various sites need not be complete in order to produce detectable optical effects because of the large difference in polarizability of the fluorine ion and the asymmetrical hydroxyl ion. Thus the degree of ordering and hence the extinction angles and $2V\alpha$ for corresponding growth sectors are likely to vary between the growth sectors that have grown under slightly different conditions, particularly with regard to the rate of growth of the side face of the step.

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