

The origin of sector twinning in harmotome

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Abstract

Harmotome from Strontian, Scotland and Korsnäs, Finland was studied from the standpoint of atomic ordering produced on the surface during growth. The (010) face has several rhombic growth hillocks consisting of four equivalent vicinal faces, and thin sections parallel to (010) show corresponding fourling texture. The thin section parallel to (001) shows some domains in which the extinction is inclined slightly to the *b*-axis, suggesting triclinic symmetry.

Deviation from orthorhombic to monoclinic symmetry can be explained by ordering of barium, as observed by structure refinement. Deviation from monoclinic to triclinic symmetry is attributed to Al/Si ordering, which was not shown by structure refinement. Both atomic orderings are produced on the side face of a growth step during growth. If the two side faces are symmetrical with respect to mirror planes in pseudo-orthorhombic harmotome, the two corresponding domains will be twinned. The space group of harmotome should thus be *P1*.

Introduction

The minerals of the harmotome-phillipsite series ($\text{Ba}_{\sim 2}\text{Ca}_{\sim 0.5}\text{Al}_{\sim 5}\text{Si}_{\sim 11}\text{O}_{32} \cdot 12\text{H}_2\text{O}$) have been described as orthorhombic, monoclinic and triclinic. Kalb and Klotsch (1944) suggested that phillipsite is orthorhombic, and Steinfink (1962) refined the crystal structure in the space group *B2mb*. Conversely, Sadanaga et al. (1961) refined the structure of harmotome in *P2₁/m*. Černý (1964) suggested that the orthorhombic symmetry exhibited by some members of this series is merely a geometric average produced by twinning a monoclinic structure. Subsequently, Rinaldi et al. (1974) refined the structures of both members in *P2₁/m*. Langeman (1886) reported harmotome with triclinic optics.

Single crystals invariably consist of complex sectoral twins, and Deer et al. (1962) suggest that the twinning may simulate single crystal forms, such as tetragonal and rhombic dodecahedra. Sahama and Lehtinen (1967) described sectoral twinning in harmotome from Finland. Akizuki (1981a, b, 1984) has interpreted sector twinning in some minerals in terms of atomic ordering of such cations as Al/Si and Fe^{3+} /Al produced during growth. The surface and internal textures of harmotome suggest that the sectorial twinning may originate by the same mechanism.

Optical observations

Crystal faces and internal textures are described in terms of an orthorhombic cell. The {101}, {010}, {111} and {001} forms in the pseudo-orthorhombic orientation correspond to the {100}, {010}, {110}, and {001} forms in the monoclinic orientation. Harmotome crystals from Strontian, Scotland and Korsnäs, Finland were used for the study. Both crystals were several millimeters in diameter and

showed {101}, {010}, {111} and {001} forms. The surface features and internal textures of harmotome from both localities are similar. All photographs reported in the present paper were obtained from harmotome crystals from Strontian. Sahama and Lehtinen (1967) showed that the Korsnäs crystal has one large growth hillock with four vicinal faces on the (010) face. The (010) faces of the present specimens have several rhombic growth hillocks, suggesting a spiral growth mechanism. The (001) face is divided into several blocks, elongated in the direction parallel to the *b*-axis, and each block has one spiral growth pattern. The block boundaries are slightly irregular. The (101) and (111) faces are finely striated parallel to the *c*-axis.

After surface features were observed by differential interference reflection optical microscopy, the surface was cemented to glass slide and a thin section was made. Figures 1 and 2 show growth features on the (010) face and Figure 3 represents the corresponding internal texture viewed in cross-polarized transmitted light. Figure 4 is a high-magnification photograph of the lower rectangle of Figure 3.

Growth hillocks, the centers of which are indicated by arrows in Figure 1, correlate with the internal fourling sectors shown in Figure 3. The optical orientations of the domains¹ showing white and black contrast are indicated by letters X and Y. The four domains corresponding to the growth hillock are in a twin relation. A high index face slightly inclined to (010) consists of closely-spaced kinks (Fig. 2), which correlate principally with the internal tex-

¹ A sector corresponding to a vicinal face on a hillock is called a domain to distinguish it from the sector corresponding to a face in the macrocrystal.

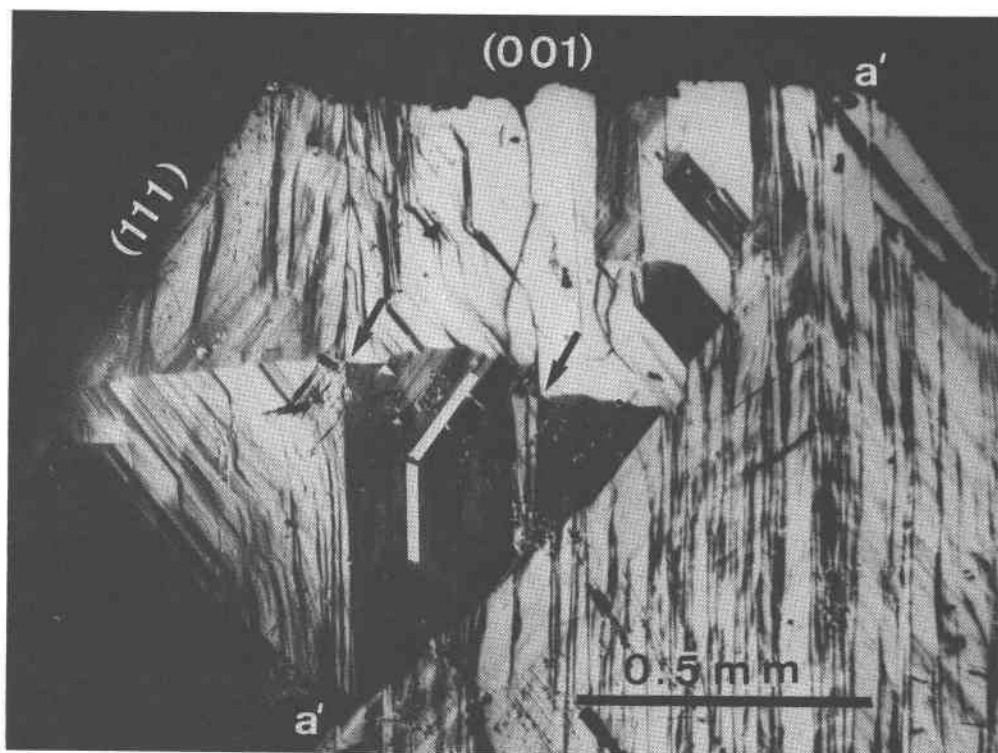


Fig. 1. Differential interference reflection photomicrograph showing growth feature on the (010) face of harmotome from Strontian, Scotland. Vicinal faces on the growth hillock consist of two kinds of steps as shown by two white lines. Two summits of growth hillocks are indicated by arrows; the pseudo-orthorhombic setting is used.

ture noted in Figure 4. In both areas showing black and white contrast in Figure 4, the extinction directions are symmetrically inclined to $[001]$, although the extinction direction in the area on which kinks are extremely dense is parallel to $[001]$, suggesting a optically orthorhombic structure.

In Figures 1 and 2, growth features are different on each side of the line $a'-a'$ and $a''-a''$ respectively, and in Figure 3, the internal texture varies at $b-b$. Frequently, different internal textures overlap in the section. Figure 2 indicates that the area with kinks (left side) is partially mantled by the area with straight steps parallel to $[001]$. The superstructure is thin compared to the substructure, and as the surface is polished slightly, the one to one correlation between Figures 2 and 3 is not always clear. The fine growth steps parallel to (110) occur between the $[001]$ steps or close to them. Corresponding $[001]$ straight lamellae, which were observed in the (010) thin section, show extinction inclined in the same direction as that of the substructure with the steps parallel to (101) , though the lamellae are not clear in Figure 3. Although the extinction angles between the $[001]$ lamellae and the substructure are slightly different, no twin relation is seen in the lamellae.

The four $\{111\}$ sectors corresponding to macrocrystal faces are observed at the crystal rim (Fig. 3). Two sectors are light and the other two are dark. The $\{111\}$ sectors and

the domains of the growth hillock, whose corresponding surfaces have growth steps parallel to each other, show the same optical orientation, with the optic axial planes of the $\{111\}$ sectors inclined symmetrically with respect to (100) and (001) , as well as to the optic axial planes of the fourling domains of the hillock shown in Figure 3. Their extinction directions are inclined at 2° to the b -axis on the (001) section. Thus, the eight $\{111\}$ sectors are triclinic, and are in a twin relation with respect to the (100) , (010) and (001) planes. In transmitted light, the $\{111\}$ sector shows only a few broad lamellae corresponding to the striations on the surface.

The (001) face (with spiral patterns shown in Figure 5) was very slightly polished, and a thin section was prepared. The section shows broad, long domains corresponding to the blocks on the surface, though the pattern corresponding to the spiral is not seen in cross-polarized light. The contrast is too weak for a clear photograph in the horizontal section. On a universal stage, the (001) section shows two kinds of domain whose optic axial planes are tilted symmetrically with respect to (100) . For the two areas whose growth directions are mutually opposed (Fig. 5), the optic axial planes are symmetrical. For the area in which the steps are normal or nearly normal to the b -axis, the section shows fine, short lamellae (about 0.2×0.03 mm) parallel to the b -axis, although corresponding patterns are

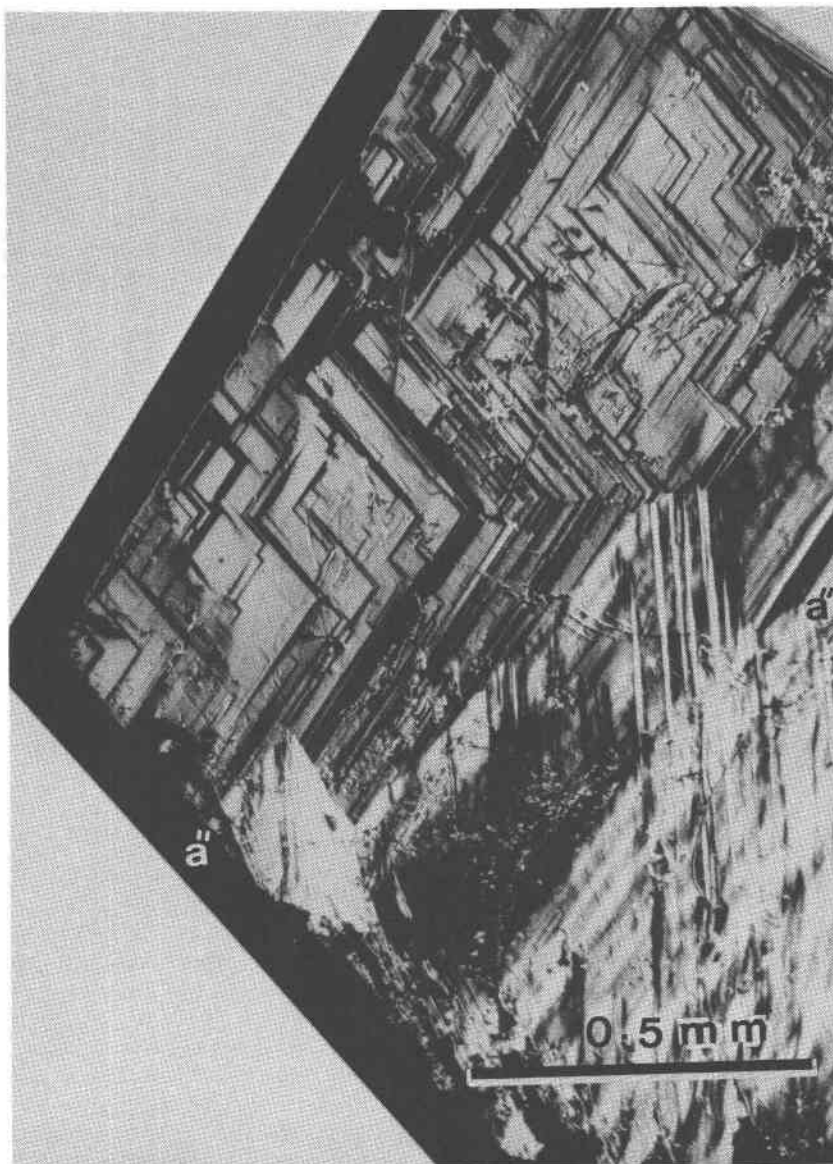


Fig. 2. Differential interference reflection photomicrograph showing growth kinks and $[001]$ striations on the (010) face of harmotome.

not observed on the surface; the optic axial planes of the lamellae are inclined symmetrically with respect to the b -axis, suggesting triclinic symmetry.

The (001) thin section, obtained from close to the crystal center, consists of $\{010\}$, $\{111\}$ and $\{110\}$ sectors with growth bands. Figure 6 shows the $\{010\}$ sector with two kinds of domains (white and black) crossing fine growth bands in the (001) section. The optic axial planes of both domains are tilted and mutually symmetrical with respect to (010) ; thus the white and black domains correspond to those in Figure 3. Figure 6 also shows that features on the (010) surface vary during growth, e.g., the white domain marked by a star extends on the other vicinal face (black

domain) during growth. The difference in extinction angles between the two domains is 4° on the (001) section, that is, the extinction angle is 2° to the b -axis, suggesting triclinic symmetry. The optical orientations and $2V$ values, which were measured on the same section, are slightly different between the $\{010\}$ and $\{110\}$ sectors, i.e., $2V_z = 85^\circ$ in $\{010\}$ sector, and $2V_x = 84^\circ$ in the $\{110\}$ sector of the Strontian specimen.

Discussion

Harmotome from Andreasberg, Hartz, Germany is pseudo-orthorhombic, and the crystal structure has been refined in the monoclinic space group $P2_1/m$ (Sadanaga et

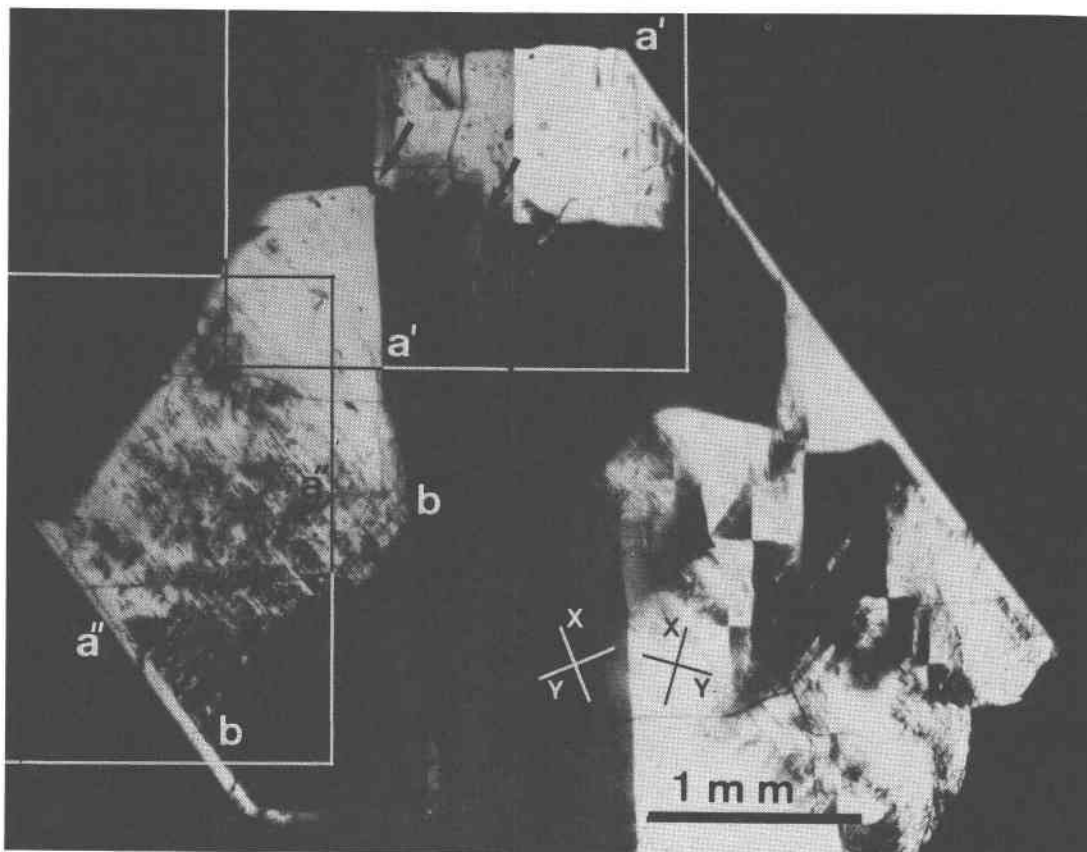


Fig. 3. Cross-polarized photomicrograph of harmotome, showing the internal texture just below the crystal surface in the (010) section. Two arrows show centers of fourlings, which correspond to the summits of the growth hillocks shown by arrows in Fig. 1. The textures in the two rectangles correspond to the surface features shown in Figs. 1 and 2. The positions of letters a' and a'' correspond to a' and a'' in Figs. 1 and 2. Optical vibration directions X and Y are represented in the two kinds of domains.

al., 1961; Rinaldi et al., 1974). However, the oblique optical extinction shows that the harmotome crystals examined in this work are triclinic. Although a crystal is a three-dimensional structure, it is produced by superposition of a two-dimensional atomic arrangement. Although atomic sites may be equivalent in a three-dimensional structure, the sites are not always equivalent on a two-dimensional growth surface, because the immediate surroundings of the sites are not always the same with respect to the growth plane. Consequently, there is the potential for various degrees of atomic ordering to occur during growth. I propose that the non-orthorhombic character of harmotome is produced on the crystal faces during growth. The fundamental framework of harmotome is orthorhombic, but the barium ions have some flexibility with respect to their position in the channels (Rinaldi et al., 1974). Harmotome has three pseudo-mirror planes: (100), (010) and (001). Barium deviates slightly from the (100) mirror plane, reducing the symmetry from orthorhombic to monoclinic (Gottardi, 1978). This displacement of barium is in a direction defined

by the relation between barium and the framework tetrahedra in the two-dimensional atomic arrangement exposed on the side face of a growth step. Almost all growth steps on the (010) face are parallel to (101) or $(\bar{1}01)$. In Figure 7, both T4(1) and T4(2) coordinate to barium ions on the same side of the growth step parallel to (101) in the pseudo-orthorhombic setting, whereas barium and tetrahedra T2(1) and T2(2) do not exist on the same growth step. The immediate surroundings of the tetrahedra T2 and T4 are distinctly different with respect to the barium ion on the growth step, though both tetrahedra are equivalent in the three-dimensional orthorhombic structure. Consequently, barium ions are displaced towards one side of the mirror plane during growth, giving rise to monoclinic symmetry. If the growth steps are parallel to $(\bar{1}01)$, the situations of tetrahedra T2 and T4 will be reversed for barium ions on the way. The growth hillock on the (010) face consists of four vicinal faces $\{1k1\}$, and thus the corresponding sectors are in a fourling relation.

If the side face of a growth step is normal or parallel to



Fig. 4. An enlargement of the lower rectangular area shown in Fig. 3.

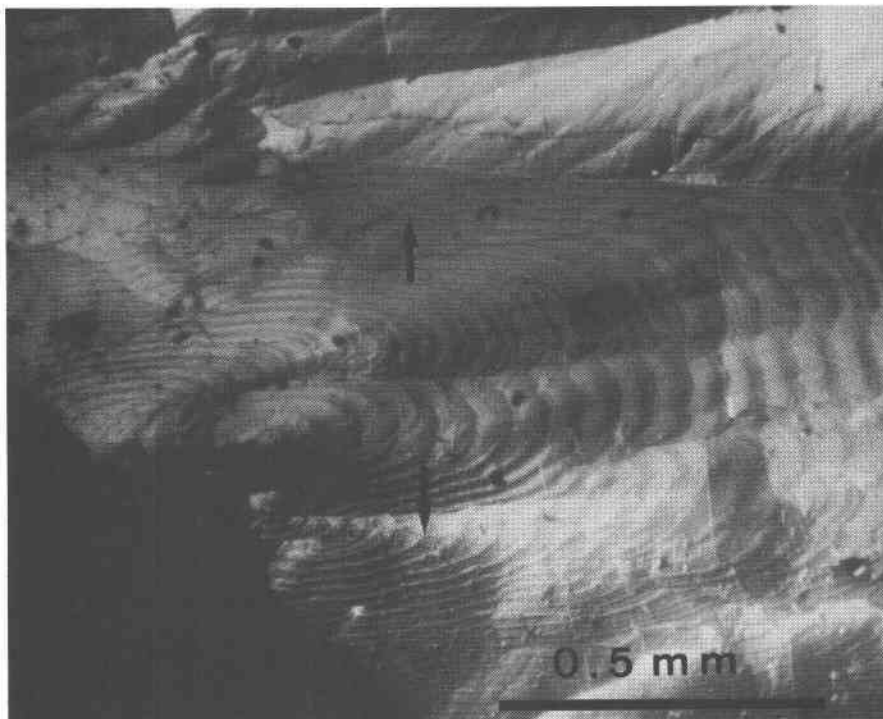


Fig. 5. Differential interference reflection photomicrograph of harmotome, showing a spiral growth feature on the (001) face; the **b**-axis is horizontal.

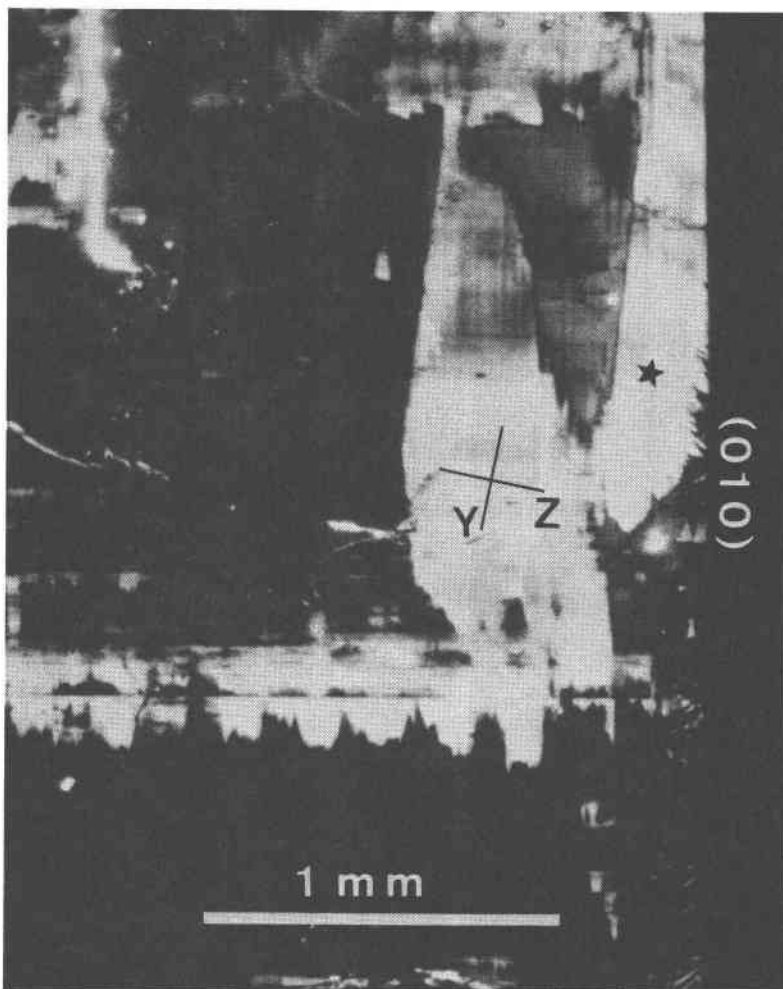


Fig. 6. Cross polarized photomicrograph of harmotome, showing the internal texture of the $\{010\}$ growth sector observed in the (001) section; the (010) face normal to the photograph is observed at the crystal rim.

the (100) pseudo-mirror plane, the barium ions will be disordered among the two sides in the channel, and the "1" and "3", and "8" and "9" oxygen sites will be statistically equivalent in the structure, resulting in orthorhombic symmetry. Although some straight steps on the (010) face are parallel to the (100) mirror plane, the crystal grows by the fine steps parallel to (101), which exist between the straight steps or close to them. Therefore, the structure is ordered and monoclinic.

The monoclinic symmetry may be reduced to triclinic by Al/Si ordering (Akizuki, 1981a). In many zeolites with an Al/Si ratio less than one, Al/Si ordering may be attributed to a kinetic relation between exchangeable cations and framework oxygens on the surface during growth. If the cations are isolated from direct contact with the framework oxygens by water molecules, the Al/Si structure is likely to be disordered. Such is the case in the stellerite structure, in which the calcium ions are completely surrounded by water molecules (Gall and Alberti, 1975). Exchangeable

cations in some zeolites, such as analcime, stilbite, epistilbite, yugawaralite and heulandite, bond to the framework oxygens that belong preferentially to Al-populated tetrahedra.

The degree of Al/Si ordering may vary because of differences in growth directions. If a tetrahedron is produced before the large cation site on the side face of the growth step is occupied, the tetrahedron is occupied by silicon rather than aluminum. Alternatively, if the tetrahedron is formed after the large cation site is occupied, the tetrahedron will be preferentially occupied by aluminum to satisfy the local charge balance. If the two tetrahedra are mutually equivalent with respect to the cation on the side face of a step, the Al/Si arrangement will be disordered between the two tetrahedra.

In harmotome, the four tetrahedra (T1, T2, T3 and T4) coordinated directly to the exchangeable barium ion are not equivalent on the side face of the step; therefore aluminum occupancy may be different among them. Fur-

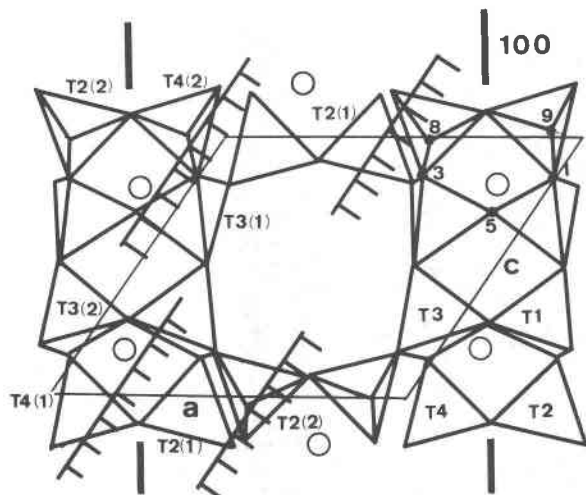


Fig. 7. Tetrahedra (T) and barium ions (circles) in the harmotome structure projected on (010); water molecules are omitted. Four growth steps parallel to (101) in the pseudo-orthorhombic cell and (100) pseudo-mirror planes are shown. The monoclinic cell is outlined. Modified from Sadanaga et al. (1961) and Rinaldi

thermore, the T2(1) and T2(2), and T3(1) and T3(2) sites may be nonequivalent with respect to aluminum occupancy on the side face of the growth steps shown in Figure 7, because the T2(1) and T3(1) tetrahedra are produced before barium ion is incorporated, whereas the T2(2) and T3(2) tetrahedra are produced after. Thus, aluminum occupancy may be higher at T2(2) and T3(2) than at T2(1) and T3(1), and the space group will then reduce to $P1$. Iitaka (1953) detected noncentrosymmetry in harmotome by the piezoelectric effect. Although no evidence of Al/Si ordering has been so far observed in harmotome, the structure may be locally ordered on a very fine scale.

If the growth steps (Fig. 7) are displaced in the other direction, symmetrical with respect to the (100) plane, a reversal relationship will occur among T-sites, resulting in twinning. The mirror and glide planes in a crystal of higher symmetry correspond to the twin plane in a sectorial crystal of lower symmetry. As the symmetry of an Al/Si ordered structure is triclinic, the twin planes occur parallel to (100), (010) and (001) of the pseudo-orthorhombic setting, corresponding to $(\bar{2}01)$, (010) and (001) in the monoclinic orientation. As the symmetry of the barium arrangement is $P2_1/m$, the twin planes with respect to the barium ions are (100) and (001). The (010) twinning will be due only to the Al/Si ordering. Hoffman et al. (1973) reported only the (100) and (001) twinning in so-called "morvenite" twin aggregate (their crystal setting differs from the present setting), but did not observe the (010) twinning.

Černý (1964) suggested that the orthorhombic symmetry of harmotome growth hillocks, which was observed by

Kalb and Klotsch (1944), can be explained by twinning of monoclinic individuals. The present observations confirm Černý's suggestion. The cruciform twins of harmotome are produced by penetration twinning. The fourling sectorial twinings are a result of crystal growth on hillocks having four vicinal faces. The number of twins correlates to the number of growth hillocks and kinks of growth steps, and no untwinned harmotome crystals are found in nature.

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