

# Orientation and geometry of the thomsonite unit cell: a re-study

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**ABSTRACT.** New X-ray and optical studies show that thomsonite has  $a < b < c$  and its optical orientation is  $\alpha = b$ ,  $\beta = c$ , and  $\gamma = a$ . The refined cell dimensions of Old Kilpatrick thomsonite are  $a = 13.051$ ,  $b = 13.092$ , and  $c = 13.263$  Å. The systematic absences  $h+l$  odd for  $h0l$ ,  $h+k$  odd for  $hk0$ , and  $l$  odd for  $0kl$  uniquely determine the space group as  $Pcnn$  for which the arrangement of the alumino-silicate framework is suggested. The exceptions to the above absences are the 704 reflection (due to Renninger effect) and many weak  $hk0$  reflections which suggest that the space group might be  $Pcnm$  or  $Pcn2$ . The observed habit, cleavage, and parallel growth are discussed in the light of the proposed framework structure.

**THOMSONITE**  $4[\text{NaCa}_2\text{Al}_5\text{Si}_5\text{O}_{20} \cdot 6\text{H}_2\text{O}]$ , is a pseudo-tetragonal orthorhombic zeolite mineral. Its unit-cell dimensions, space group, and structure have appeared in the literature (see below) but these are either at variance with each other or are incomplete. This study is intended to remove the ambiguities that have persisted for a long time.

**Orientation.** All previous studies (Brewster, 1821; Brögger, 1878, 1889; Dana, 1892; Deer *et al.* 1963; Des Cloizeaux, 1862; Hahn, 1891; Hey and Bannister, 1932) agree that the  $c$  axis of thomsonite is longer than the other two axes and is parallel to  $\beta$ . The  $a$  and  $b$  axes, however, have essentially the same length and the previous morphological and single-crystal studies have failed to ascertain the identity of these two axes. Consequently there is ambiguity in the relationship between the optical and unit-cell orientations. A single-crystal study of thomsonite shows that  $\gamma$  is parallel to the shorter of these two axes. The relative lengths of the axes are  $a < b < c$ , and the optical orientation is  $\alpha = b$ ,  $\beta = c$ ,  $\gamma = a$ .

**Unit-cell dimensions.** Rotation, Weissenberg, and precession photographs gave for the Parkgate quarry thomsonite (UM No. I 8619),  $a = 13.05$ ,

$b = 13.08$ , and  $c = 13.22$  Å, and for the Old Kilpatrick thomsonite (UM No. I 1543)  $a = 12.996$ ,  $b = 13.009$ ,  $c = 13.235$  Å. The least-square refinement of a powder pattern of the latter (Table I) gave  $a = 13.051$ ,  $b = 13.092$ , and  $c = 13.263$  Å, axial ratio 0.9969:1:1.0131,  $D_x = 2.36$ .

The single-crystal photographs show pseudo-tetragonal symmetry and very few reflections have  $hkl$  and  $khl$  intensities different. For refinement, therefore, only the unambiguously indexed reflections were used. These are 110, 012, 112, 222, 040, 332. In indexing the rest of the pattern space-group extinctions and observed intensities were taken into consideration, although those omitted, unless forbidden by the space group, do contribute to the total intensity noted in Table I. The present indexing is better than the one so far available (JCPDS card No. 19-1344) and which is based on a wrong space group. The unit-cell dimensions and axial ratios are similar to those previously given (Brogger, 1978, 1889; Dana, 1892; Deer *et al.*, 1963; Hahn, 1891; Hey and Bannister, 1932; Taylor *et al.*, 1933; Wyart, 1931) but emphasis in the study is on identity of the  $a$  and  $b$  axes with the  $\gamma$  and  $\alpha$  vibration directions.

**Space Group.** The only restrictions on thomsonite spectra are on  $h0l$  when  $h+l$  is odd, on  $0kl$  when  $l$  is odd, and on  $hk0$  when  $h+k$  is odd, thus leading to the space group  $Pcnn$  ( $Pnna$  in standard setting). The 704 reflection, observed with Cu-K $\alpha$ , disappears with Mo-K $\alpha$  and must be due to Renninger effect. There are many weak  $hk0$  reflections with  $h+k$  odd and if they are not due to an impurity the space group must be  $Pcnm$  or  $Pcn2$ , or the symmetry may not be truly orthorhombic. Martin (1931) and Wooster (in Hey and Bannister, 1932) state that the mineral is pyroelectric with  $b$  as polar axis, but this is not compatible with either

*Pcnn* space group or with *Pcn2* which implies *c* as the polar axis. Space groups previously given are *Pcnn* (Gottardi, 1978), *Pnna* (Dal Negro *et al.* in Gottardi), *Pnma* (Deer *et al.*, 1963), and *Pnmm* or *Pn2n* based on systematic extinctions  $k+l$  odd for  $0kl$  and  $h+k$  odd for  $hk0$  (Taylor *et al.*, 1933; Wyatt, 1931), or *Pncn* based on additional absences  $l$  odd for  $h0l$  (Taylor *et al.*, 1933).

*Geometry of the aluminosilicate framework.* Assuming that the  $h+k$  odd reflections are due to some impurity, the framework may be considered as based on *Pcnn*. Taylor *et al.* (1933) attempted to derive the structure based on the pseudo-cell ( $c = 6.61 \text{ \AA}$ ) but the result was the gonnardite structure as is now known (Amirov *et al.* 1972). Alberti and Gottardi (1975) have theoretically derived that the framework of thomsonite is based on the *Pcnn* space group. They figure the geometri-

cal arrangement of chains but it has proved impossible to derive a framework with symmetry *Pcnn* based on the chain heights suggested by them. Fig. 1 shows the framework based on space group *Pcnn* with origin on the centre of symmetry. The heights of diagonally opposed chains related by the centres of symmetry at  $\frac{1}{2}0$  and  $\frac{1}{2}\frac{1}{2}$ , are  $1/16$ ,  $-1/16$ , and  $7/16$ ,  $9/16$ . The distribution, approximate position, and absolute heights of the Si and Al atoms are also shown. The oxygen positions are not shown but their position is fixed because they occur in the (Si,Al) $O_4$  tetrahedra and are governed by the (Si,Al)-O-(Si,Al) bond lengths and bond angles.

The structure of thomsonite based on *Pnna* is stated (Alberti and Gottardi, 1975; Galli, 1976; Gottardi, 1978) to be 'in preparation' by Dal Negro *et al.* but to-date it has not appeared in press. It should be possible to test the hypothesis when this structure is published.

*Optical structure in relation to morphology.* The most interesting specimens for this purpose are comptonite (part of BM No. 1914, 1496) and Parkgate quarry thomsonite which respectively show that (001) and (100) as the best faces.

Thomsonite from Dunbartonshire (I 1543) and Bohemia (OUM 13693) are prismatic with poorly defined rectangular or hexagonal sections. The comptonite is tabular on (100) and has a six-sided (001) section (Brewster, 1821), showing striations parallel to (010). The (041) twinning (see below) can be discerned by re-entrant angles. The (001) face is composed of 2 vicinals with mutual angle of nearly  $180^\circ$ .

The Parkgate quarry thomsonite is platy on (100) and shows the (001) face composed of two vicinal faces with a mutual angle of  $177.1^\circ$ . These vicinals make angles of  $88.9^\circ$  and  $87.9-88.3^\circ$  with the (010) cleavage trace (fig. 2). The two main crystal parts associated with the vicinal faces are similar in plane polarized light but under crossed Nicols show different characteristics: whereas one contains blebs with a slightly different ( $3^\circ$ ) extinction angle from the main body, the other is virtually free of them. The two parts have the same refractive index but make an extinction angle of  $0.6^\circ$  with the (010) cleavage. The bleb-infested part has a 2V of  $54.5^\circ$  whereas the bleb-free part has a 2V of  $52-53.5^\circ$ .

The bleb-free part is separated from its twin on the left with the sharp (041) plane which makes an angle of  $76.8^\circ$  with the vicinal face and  $16.4^\circ$  with  $\beta$ . The (041) plane makes an angle of  $15.7^\circ$  with the (010) face of the twin and  $13.2^\circ$  with the  $\beta$  of the twin. The refringence of the twin is noticeably lower and 2V higher ( $60^\circ$ ) than that of the bleb-free thomsonite. The twin also shows very faint lamellae parallel to (001). These characteristics show that

TABLE I. Powder diffraction pattern of Dunbartonshire thomsonite

$d(\text{\AA})$	$I$	$hkl$	$d(\text{\AA})$	$I$	$hkl$
9.205	20	110	1.811	30	640
6.566	70	020	1.777	5	552
5.901	60	012	1.755	10	{ 642
5.391	15	112			{ 624
4.625	100	220	1.714	15	730
4.377	30	212	1.676	5	516
4.133	30	130	1.653	5	008
3.960	5	131	1.634	15	{ Si
3.792	10	222			{ 080
3.504	70	312	1.613	10	554
3.273	5	040	1.587	5	{ 280
3.194	70	232			{ 082
3.138	70	Si	1.571	10	812
2.944	100	{ 240	1.535	10	507
		{ 042	1.508	5	626
2.857	100	412	1.463	30	{ 840
2.793	15	332			{ 636
2.674	100	{ 422	1.439	10	428
		{ 242	1.388	7	{ 922
2.579	30	150			{ 384
2.430	25	432	1.357	5	Si
2.252	30	{ 530	1.331	7	094
		{ 334	1.316	7	086
2.182	70	060	1.305	7	1000
2.122	15	532	1.282	5	509
2.088	15	206	1.271	5	
2.062	15	{ 620	1.259	5	
		{ 602	1.246	10	Si
1.952	15	542	1.213	10	
1.920	30	Si	1.1909	10	
1.882	10	326	1.1381	10	
1.824	5	064	1.1085	10	Si

Cu-K $\alpha$  radiation; camera dia. 114.85 mm;  $a = 13.051$ ,  $b = 13.092$ ,  $c = 13.263 \text{ \AA}$ .

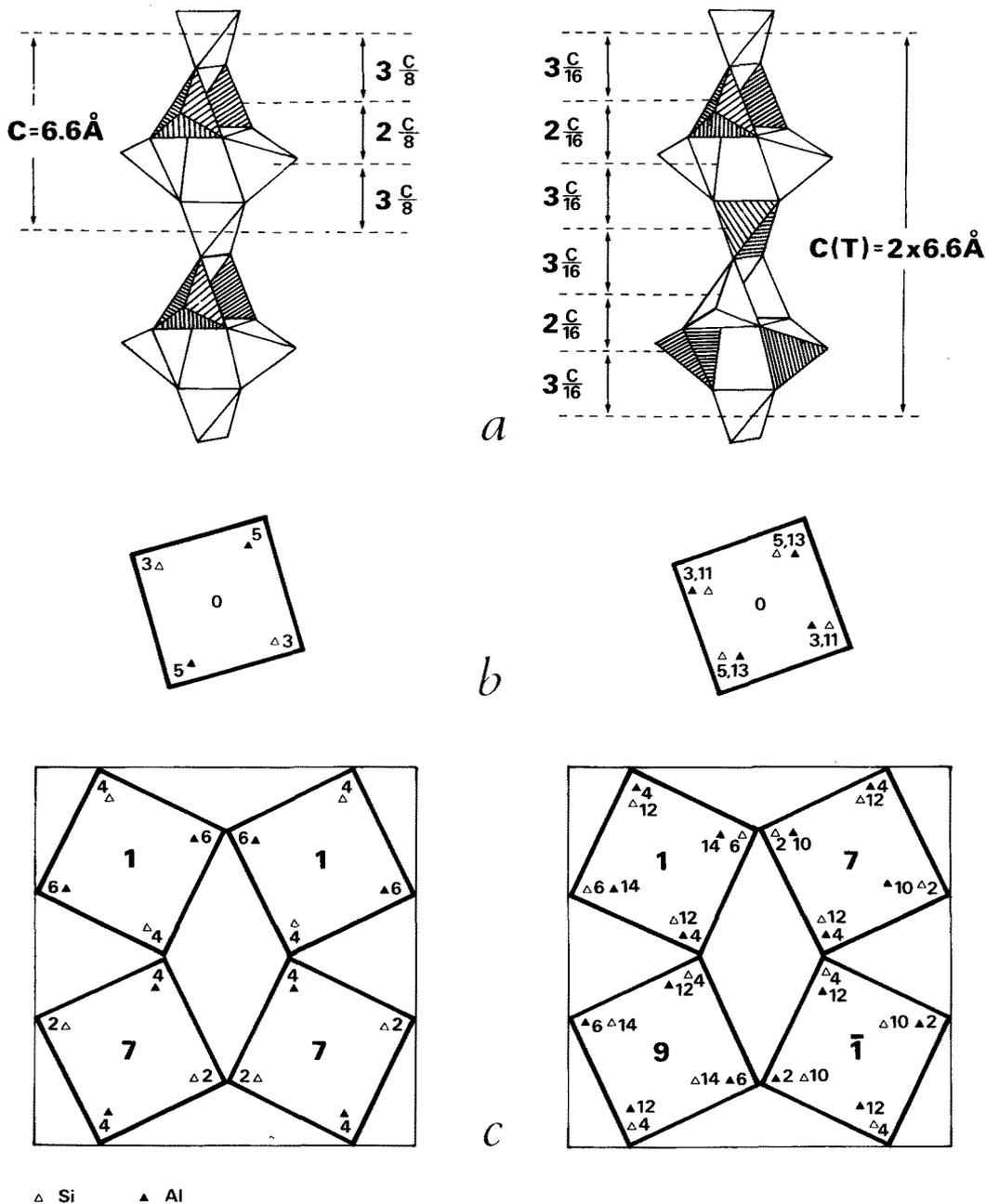


FIG. 1. (a) Disposition in ordered chains of  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra (shaded) (after Alberti and Gottardi, 1975). Left—zeolites with  $6.6 \text{ \AA}$   $c$ -axis repeat: natrolite, gonnardite tetranatrolite, paranatrolite, mesolite, scolecite, and edingtonite. Right—zeolites with  $13.2 \text{ \AA}$   $c$ -axis repeat: thomsonite, Rb-D and probably  $\text{Na}^{\text{ex}}$  K-F (Galli, 1976). (b) View down the  $c$ -axis of the chains. The heights of coupled  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra in fractions of the  $c$ -axis repeat relative to the zero height of the basal, uncoupled  $[\text{SiO}_4]$  tetrahedron. (c) Left—view down the  $c$ -axis of gonnardite (from Taylor *et al.*, 1933; Amirov *et al.*, 1972) and right—thomsonite. The heights of the basal  $[\text{SiO}_4]$  tetrahedra appear in the centre of the squares whereas the heights of the  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra connecting one chain to the others appear in the corners of the squares.

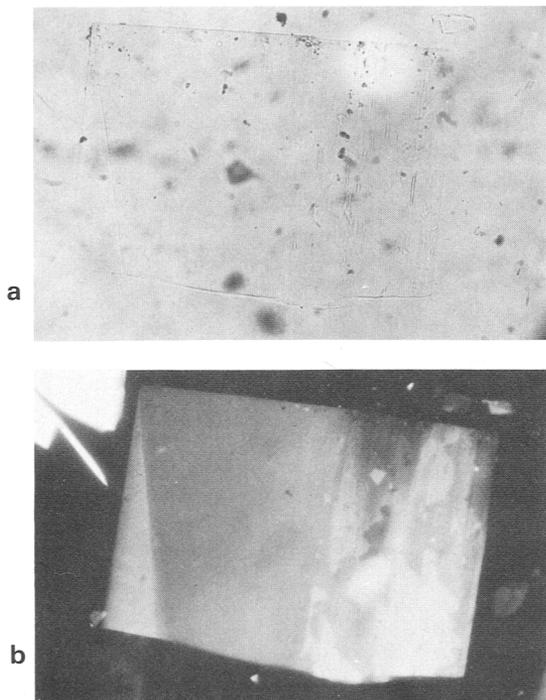


FIG. 2. The (100) plate of Parkgate quarry thomsonite showing vicinal faces (top), 010 cleavage, twinning (left), and composite structure (middle). The width of the crystal is 0.75 mm. (a) Plane polarized light; (b) crossed polars.

thomsonite may have a symmetry lower than orthorhombic found by the X-ray study.

*Morphology against structure.* Previous morphological studies (Brewster, 1821; Brögger, 1878, 1889; Dana, 1892; Deer *et al.*, 1963; Gregg and Lettsom, 1858; Hahn, 1891; Hey and Bannister, 1932; Hedde, 1901) do not unequivocally distinguish between the two horizontal axes and hence morphology and habit descriptions are open to question. The present study takes into account the previous work and establishes the following account consistent with the possible structure.

Thomsonite is either fibrous, elongation [001]; platy on (100); or somewhat tabular on (100) elongation [001]; cleavage (100) perfect, (010) good, twinning (110) and (041), parallel growth on (010). The (100) planes contain Si-O-Al bonds which are perhaps weaker than the Si-O-Si and Al-O-Al bond combination in the (010) planes and hence the superior cleavage and tabularity noticed on (100). The adjacent Al and Si atoms across the (010)

planes occur at different heights and it could explain the parallel growth on (010) by 180° rotation of the chain pairs about [010].

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