A redetermination of the unit-cell geometry of scolecite

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SUMMARY. A re-examination of the mineral scolecite has shown that the previously published monoclinic (pseudo-orthorhombic) unit cell is face-centred and that the Hermann–Mauguin space-group symbol has been incorrectly assigned. The reduced monoclinic cell yields a 9·85 Å, b 18·98 Å, c 6·52 Å, β 110° 6ɪ ; space group Aa. New indexed powder data are included.

SCOLECITE ($Ca(Al_2Si_3O_{10}).3H_2O$) is a naturally occurring zeolite closely related to natrolite and mesolite. Hey and Bannister (1936) examined scolecite in detail and derived from Laue and rotation photographs a nearly orthogonal monoclinic cell with parameters a 18·48 Å, b 18·95 Å, c 6·54 Å, β 90° 31′. They noted that scolecite belonged to class m because of its pyro- and piezoelectric properties and concluded that its space group is C_s^4 with a close approximation to the orthorhombic space group C_{2v}^{19} ($Fdd2$), which is the space group possessed by natrolite. Their best determination of the crystal density was taken to be 2·274 g/cm³ although other reported values were in the range 2·24–2·31 g/cm³.

Taylor, Meek, and Jackson (1933) have discussed all three minerals and have proposed a structure for scolecite based upon their structure for natrolite whose orthorhombic cell (a 18·3 Å, b 18·6 Å, c 6·57 Å) is very close to Hey and Bannister's cell for scolecite.

We recently examined a specimen from Thailand consisting of radiating groups of white or colourless needles up to 10 mm long, whose optical properties (α 1·514, β 1·517, γ 1·519; $2V_\alpha$ 37°; a:[001]19°) suggested its identity with scolecite. The radiating needles enclose small fresh or limonitized crystals of pyrite and are associated with a wollastonite–diopside rock. The material was collected from a poorly exposed area underlain chiefly by quartz-veined sandstone of Triassic (?) age, some 15 km south-west of Surat Thani, at approximately 99° 15′ 0″ E, 9° 3′ 30″ N.

Single-crystal photographs taken about the needle axis revealed an axial repeat distance of about 6·53 Å whilst zero and upper layer equi-inclination Weissenberg photographs showed monoclinic symmetry with a β angle close to 90°. After mounting the crystal about the b axis a unit cell could be derived with parameters a 18·506 Å, b 18·978 Å, c 6·522 Å, β 90° 41′, which are in very good agreement with those reported by Hey and Bannister. The twinning across (100) was readily observed in these photographs.

However the lattice and space group absences were clearly those of a non-standard cell. The following presences were noted: hkl, all odd, all even; $hk0$, ($h = 2n$, $k = 2n$);

okl ($k = 2n$, $l = 2n$); hol, $h+l = 4n$; hoo ($h = 4n$); oko, ($k = 2n$); ool ($l = 4n$). These lead to the non-standard monoclinic space group Fd. A smaller cell exactly half the volume can be chosen by taking c^* along d^*_{202} for the orthogonal cell[1] and this yields the reduced monoclinic cell of a 9.848 ± 0.008 Å, b 18.978 ± 0.004 Å, c 6.522 ± 0.006 Å, β $110°\,6' \pm 6'$. The choice of the reduced cell was confirmed by taking rotation, zero, and upper layer equi-inclination Weissenberg photographs about all three axes and the a axis (18.48 Å) of the face-centred cell. The presences for the true cell are: hkl, $k+l = 2n$, and hol, $h = 2n$, $l = 2n$, which correspond to space group Aa. All the single-crystal photographs were taken with, and cell parameters measured, using Cu-$K\alpha$ radiation (mean $\lambda = 1.5418$ Å).

A mean density of ten determinations of our crystal, by flotation in a mixture of bromoform and carbon tetrachloride, gave D 2.243 g/cm³ ($\hat{\sigma} \pm 0.012$ g/cm³) indicating four formula units per cell. This value is lower than the theoretical density of 2.275 g/cm³ and that of Hey's best estimate, which may indicate a small deficiency of water molecules in the structure of the Thailand specimen.

As a final check that our sample was indeed scolecite, authenticated specimens were obtained from the British Museum (Natural History) and the Department of Mineralogy and Petrology, Cambridge. X-ray examination of crystals from both yielded the same lattice geometry, unit cell, and space group as those of the Thailand sample. The X-ray examination of the British Museum specimen (BM 33887) was made upon an untwinned fragment broken off the end of a large twinned prismatic crystal. The sample from Cambridge University (specimen no. 2865) was a small lath crystal, which upon examination proved to be a true single crystal. The c-axis photographs of this crystal revealed large-scale streaking of the reflections on all layers indicating considerable disorder.

There is no doubt that the great similarity between the X-ray photographs of natrolite and scolecite led initially to the choice of a nearly orthogonal cell for the latter. For scolecite, with its inherent high pseudo-symmetry, and with the crystal mounted about the c-axis, the projection of c^* on a^* is such that for even l layers there is a near coincidence of an hkl row with a central lattice line, i.e. $2lc^* \cos \beta^* \approx la^*$ (compare the lattice of cobalt molybdate; Smith, 1962). Thus even layer equi-inclination Weissenberg photographs show straight lines of hkl spots, which simulate an okl row of an orthorhombic lattice. Nevertheless, although the reduced cell of scolecite is smaller and more oblique, it may well be instructive to retain the pseudo-orthogonal cell to illustrate the structural similarities of natrolite and scolecite.

One important point arises to which we would like to draw attention. In the original publication by Hey and Bannister, the space group extinctions were not published with the result that the Schoenflies symbol C_s^4, which is not dependent upon unit-cell orientation, has been directly translated into the Hermann–Mauguin notation, which is orientation dependent, as Cc. This error has been compounded by later workers and the incorrect space-group symbol is now to be found in standard reference works, e.g. Bragg and Claringbull (1965, p. 356) and *Crystal Data* (1963). The propagation

[1] Because the β angle of the face-centred cell is nearly $90°$, c^* could equally be chosen to be along $d^*_{20\bar{2}}$.

TABLE I. *X-ray powder data for scolecite. Camera diameter 114·6 mm. Radiation Cr-Kα. λ = 2·29092 Å. Intensities visually estimated B = Broad)*

d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl	I
6·590 Å	6·626 Å	120	90	2·204 Å	2·209 Å	$26\bar{2}$	40
5·848	5·870	$11\bar{1}$	100		2·209	360	
	5·830	011			2·200	062	
4·722	4·745	040	60	2·191	2·193	$42\bar{2}$	< 5
4·608	4·628	200	50	2·169	2·168	222	5
4·387	4·386	$21\bar{1}$	90	2·143	2·147	$21\bar{3}$	< 5
4·208	4·222	140	30		2·141	$11\bar{3}$	
4·144	4·159	220	20	2·106	2·111	280	< 5
3·633	3·642	131	20	2·076	2·080	440	5
3·304	3·313	240	< 5		2·078	$37\bar{1}$	
3·221	3·227	051	30	2·039	2·040	$13\bar{3}$	5
3·181	3·190	$31\bar{1}$	30	2·030	2·031	162	5
3·151	3·158	211	30		2·030	013	
3·078	3·086	$20\bar{2}$	B 20	1·991	1·996	$19\bar{1}$	5
	3·083	122			1·994	091	
3·071	3·063	002	10	1·954	1·958	$51\bar{1}$	10
2·987	2·993	160	10		1·957	$33\bar{3}$	
2·929	2·935	$22\bar{2}$	60	1·943	1·944	411	< 5
	2·934	320			1·943	033	
2·900	2·904	$25\bar{1}$	10	1·904	1·906	191	5
2·882	2·881	$33\bar{1}$	100	1·899	1·898	0.10.0	< 5
2·851	2·857	231	70	1·877	1·876	082	B 10
2·684	2·687	$14\bar{2}$	< 5		1·875	$41\bar{3}$	
2·608	2·611	260	< 5		1·874	$15\bar{3}$	
2·578	2·579	$32\bar{2}$	15	1·866	1·867	431	10
	2·573	042			1·867	460	
2·549	2·552	122	< 5	1·855	1·855	113	10
2·474	2·479	071	15	1·839	1·839	$46\bar{2}$	10
2·440	2·440	$41\bar{1}$	10	1·814	1·817	520	B 15
2·416	2·420	310	15		1·814	371	
2·366	2·373	080	< 5	1·804	1·806	$43\bar{3}$	15
2·315	2·316	171	B 10	1·765	1·768	182	10
	2·314	400			1·767	$39\bar{1}$	
	2·314	142			1·762	$54\bar{2}$	
2·291	2·298	180	10		1·761	291	
	2·293	$43\bar{1}$		1·754	1·756	2.10.0	10
2·267	2·270	$16\bar{2}$	10	1·746	1·747	$55\bar{1}$	10
2·248	2·254	$40\bar{2}$	10		1·745	342	
	2·248	420		1·723	1·725	540	10

of this error has no doubt been aided by the goniometric measurements such as those reported by Winchell and Winchell (1951) where the axial ratios and β angle are clearly related to Bannister's choice of cell.

There is a further point of interest worthy of note. In the zero layer Weissenberg photograph about the *c* axis, the forbidden reflection 100 is clearly visible. As no other odd orders of *h*oo are present in this photograph or in the zero layer photograph taken about the *b* axis, the cause of the 100 reflection lies in the double diffraction effect (Renninger, 1937). In this instance, the 100 spot is shown to be derived by double diffraction between the $\bar{3}\bar{4}$0 and 540 reflections.

The powder data for scolecite are also suspect. Peng (1955) published powder data for scolecite (ASTM card 11–171) that are not in good agreement with the powder data from our sample, nor with those obtained from the University of Cambridge and the British Museum specimens, both of which gave identical patterns to that of the Thailand specimen. Table I lists the observed and calculated d spacings from our specimen. The data were collected in a Debye-Scherrer camera, Straumanis film mounting, using Cr-$K\alpha$ radiation for greatest dispersion of the reflections. Starting from the single-crystal unit cell parameters, the powder data were used in a refinement program due to Lindquist and Wengelin (1967). The following refined parameters were obtained: a 9·850 Å, $\hat{\sigma}\pm$0·005 Å, b 18·980 Å, $\hat{\sigma}\pm$0·010 Å, c 6·520 Å, $\hat{\sigma}\pm$0·004 Å, β 110·02°, $\hat{\sigma}\pm$0·04°.

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