

## CRYSTAL-STRUCTURE REFINEMENT OF A HIGHLY ORDERED STAUROLITE

ROBERTA OBERTI, FRANK C. HAWTHORNE\*, ALBERTO ZANETTI AND LUISA OTTOLINI

CNR Centro di Studio per la Cristallografia e la Cristallografia, via Abbiategrosso 209, I-27100 Pavia, Italy

JUAN I. SOTO

Departamento de Geodinámica, C.S.I.C. – Universidad de Granada, Ave. Fuentenueva s/n, E-18071 Granada, Spain

### ABSTRACT

The crystal structure of zinc-rich staurolite,  $\text{Zn}_{2.40}\text{Fe}_{1.41}\text{Mg}_{1.27}\text{Mn}_{0.01}\text{Ni}_{0.01}\text{Ti}_{0.09}\text{Li}_{0.01}\text{Cr}_{0.02}\text{Al}_{16.80}\text{Si}_{7.99}\text{O}_{45}(\text{OH})_3$ ,  $a$  7.877(3),  $b$  16.609(5),  $c$  5.665(1) Å,  $\beta$  90.68(2)°,  $V$  741.0 Å<sup>3</sup>,  $Z = 1$ , from the Nevado-Filábride complex, Lubrin, Almería province, Spain, has been refined to an  $R$  index of 2.0% based on 986 observed reflections collected with MoK $\alpha$  X-radiation. This crystal is poor in Al, as reflected in the high Si content and the large amount of [6]-coordinated Mg. The  $\beta$  value is the largest yet measured for staurolite, and is slightly larger than the maximum  $\beta$ -angle predicted for staurolite (Hawthorne *et al.* 1993b). Site-scattering refinement shows that the  $M(3)$  cations are highly, but not completely, ordered:  $Q_{M(3)} [= (X_{M(3A)} - X_{M(3B)}) / (X_{M(3A)} + X_{M(3B)})]$  is equal to 0.89, rather than to the value of 1.0 expected for the  $\beta$  angle of this crystal. However, the refined  $M(3A)$  and  $M(3B)$  site-scattering values are compatible with complete order of Al at  $M(3A)$  but disorder of Mg over  $M(3A)$  and  $M(3B)$ . The results of this work quantitatively support the order-disorder model for staurolite proposed by Hawthorne *et al.* (1993b), but suggest that the quantitative details can be affected by the presence of [6]-coordinated Mg because it behaves differently from [6]-coordinated Al.

**Keywords:** staurolite, crystal structure, chemical analysis, cation order.

### SOMMAIRE

La structure cristalline d'un échantillon de staurolite zincifère, de composition  $\text{Zn}_{2.40}\text{Fe}_{1.41}\text{Mg}_{1.27}\text{Mn}_{0.01}\text{Ni}_{0.01}\text{Ti}_{0.09}\text{Li}_{0.01}\text{Cr}_{0.02}\text{Al}_{16.80}\text{Si}_{7.99}\text{O}_{45}(\text{OH})_3$ ,  $a$  7.877(3),  $b$  16.609(5),  $c$  5.665(1) Å,  $\beta$  90.68(2)°,  $V$  741.0 Å<sup>3</sup>,  $Z = 1$ , provenant du complexe de Nevado-Filábride, à Lubrin, dans la province d'Almería, en Espagne, a été affinée jusqu'à un résidu  $R$  de 2.0% en utilisant 986 réflexions observées avec rayonnement MoK $\alpha$ . Ce cristal a une faible teneur en Al, comme le témoigne la teneur élevée en Si et en <sup>6</sup>Mg. L'angle  $\beta$  est le plus grand qui soit connu pour la staurolite, et dépasse même la valeur maximum prédite (Hawthorne *et al.* 1993b). L'affinement du pouvoir de dispersion montre que les cations au site  $M(3)$  sont fortement ordonnés, mais ne le sont pas complètement;  $Q_{M(3)} [= (X_{M(3A)} - X_{M(3B)}) / (X_{M(3A)} + X_{M(3B)})]$  est égal à 0.89, plutôt qu'à la valeur attendue selon l'angle  $\beta$  de ce cristal, 1.0. Toutefois, les valeurs affinées de la dispersion aux sites  $M(3A)$  et  $M(3B)$  sont compatibles avec une mise en ordre complète de Al au site  $M(3A)$ , et un désordre complet des atomes Mg sur les sites  $M(3A)$  et  $M(3B)$ . Nos résultats concordent avec le modèle ordre-désordre proposé par Hawthorne *et al.* (1993b), mais ils semblent indiquer que la présence de <sup>6</sup>Mg peut en affecter les détails quantitatifs, vu son comportement distinct de celui de <sup>6</sup>Al.

(Traduit par la Rédaction)

**Mots-clés:** staurolite, structure cristalline, analyse chimique, degré d'ordre des cations.

### INTRODUCTION

It is now well established that staurolite is monoclinic at room temperature and pressure (Hurst *et al.* 1956, Smith 1968, Tagai & Joswig 1985, Bringham &

Griffen 1986, Ståhl *et al.* 1988, Alexander 1989, Hawthorne *et al.* 1993a, b). Hawthorne *et al.* (1993a) refined the crystal structure of forty-two crystals of staurolite with  $\beta$  angles in the range 90.00–90.45°, and Hawthorne *et al.* (1993b) showed that all displacements of atomic positions [except the  $x$  coordinate of the O(4) atom] from the ideal values for orthorhombic  $C_{2mm}$  symmetry are continuous linear functions of the  $\beta$  angle. In addition, the degrees of Al-□ (vacancy), (Fe,Mg)-□ and (Fe,Zn...)-□ order over the

\* Now condemned to the Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2.  
E-mail address: fchawthorn@bldgwall.lan1.umanitoba.ca

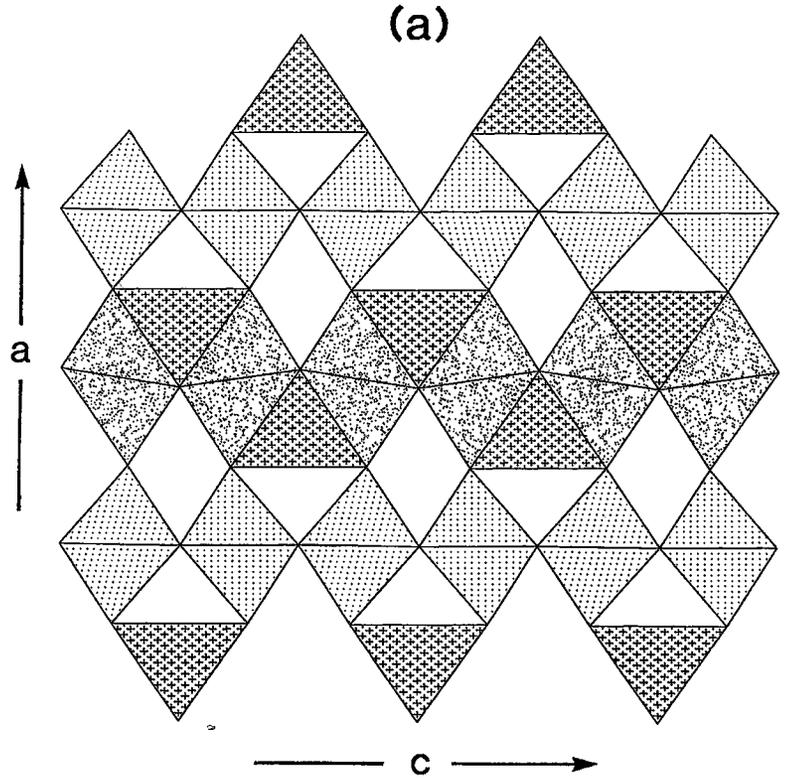
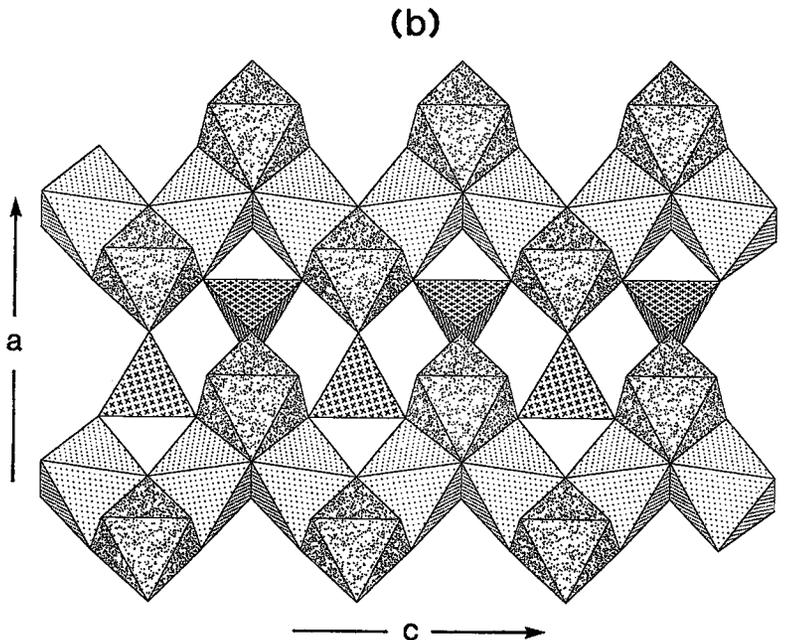


FIG. 1. a. Polyhedral representation of the oxide-hydroxide layer in staurolite. The  $M(3A)$  and  $M(3B)$  octahedra are regularly dot-shaded, the  $M(4A)$  and  $M(4B)$  octahedra are irregularly dot-shaded, and the  $T(2)$  tetrahedron is shaded with crosses. Octahedra adjacent along  $[001]$  share edges, and  $T(2)$  tetrahedra share faces with  $M(4A)$  and  $M(4B)$  octahedra. b. The crystal structure of staurolite, showing the kyanite-like part of the structure viewed  $15^\circ$  away in the  $(001)$  plane from  $[010]$ . The  $M(1A)$  and  $M(1B)$  octahedra are regularly dot-shaded, the  $M(2)$  octahedron is irregularly dot-shaded, and the  $T(1)$  tetrahedron is shaded with crosses.



$M(3A)$ – $M(3B)$ ,  $M(4A)$ – $M(4B)$  and  $T(2)$  subsites (Fig. 1), respectively, are linear functions of the  $\beta$  angle. Staurolite is an order–disorder series (Smith 1968, Dollase & Hollister 1969) between a completely disordered orthorhombic end-member [ $Ccmm$ ,  $\beta = 90^\circ$ ,  $M(3A) = M(3B) = 0.5Al + 0.5\Box$ ] and an ordered monoclinic end-member [ $C2/m$ ,  $\beta = 90.64^\circ$ ,  $M(3A) = Al$ ,  $M(3B) = \Box$ ] (Hawthorne *et al.* 1993b). Here, we report the characterization of a sample of highly ordered monoclinic staurolite, and show that it has a pattern of order and  $\beta$  angle close to the values predicted by Hawthorne *et al.* (1993b).

## EXPERIMENTAL

The staurolite sample examined here (number 524–36) is from a metapelite of the Nevado–Filábride complex, Lubrin, Almeria province, Spain (Soto & Muñoz 1993, Soto & Azafón 1993, 1994). A crystal [S(56)] was selected for crystallographic measurement and collection of intensity data on the basis of optical quality, lack of inclusions, and equant shape. The crystal was mounted on a Philips PW 1100 automated four-circle diffractometer equipped with  $MoK\alpha$  X-radiation. Unit-cell dimensions (Table 1) and intensity data were measured according to the procedure of Hawthorne *et al.* (1993a). Data reduction and refinement (Hawthorne *et al.* 1993a) converged to an  $R$  index of 2.0% for reflections with  $I > 5\sigma I$ . Atomic coordinates are listed in Table 2, refined site-scattering values are listed in Table 3, and selected interatomic distances are listed in Table 4. Structure factors and anisotropic-displacement parameters may be obtained from the Depository of Unpublished Data, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

The crystal used in the collection of the intensity data was subsequently mounted in epoxy, ground and polished, carbon-coated, and analyzed with a Cameca SX–50 electron microprobe according to the procedure of Hawthorne *et al.* (1993a) and a Cameca IMS 4F ion microprobe according to the method of Ottolini *et al.* (1993). For the determination of Li, we used staurolite

TABLE 2. FINAL ATOMIC PARAMETERS\* FOR Zn-RICH STAUROLITE CRYSTAL S(56)

	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
O(1A)	0.23322	0	0.95742	0.57
O(1B)	0.23857	0	0.52372	0.52
O(2A)	0.25648	0.16152	0.01521	0.41
O(2B)	0.25231	0.16101	0.48307	0.47
O(3)	0.00126	0.08935	0.23690	0.47
O(4)	0.02272	0.24946	0.24778	0.49
O(5)	0.52685	0.09893	0.24905	0.43
T(1)	0.13379	0.16615	0.24544	0.30
T(2)	0.38950	0	0.23730	0.64
M(1A)	1/2	0.17458	0	0.21
M(1B)	1/2	0.17502	1/2	0.30
M(2)	0.26292	0.41040	0.25527	0.38
M(3A)	0	0	0	0.42
M(3B)	0	0	1/2	1.69
M(4A)	1/2	0	0	0.87

\* standard deviations are  $<5$  in the last decimal place

TABLE 3. REFINED SITE-SCATTERING POWERS\* (epfu) IN Zn-RICH STAUROLITE CRYSTAL S(56)

	N**	S(56)	N**	S(56)	
M(1A)	4	50.7	M(3A)	2	24.5
M(1B)	4	51.3	M(3B)	2	1.4
M(2)	8	104.5	M(4A)	2	1.4
T(2)	4	106.6	M(4B)	2	–

\* esds are 0.1–0.4 epfu;

\*\* N is the number of sites corresponding to the structural formula

TABLE 4. SELECTED INTERATOMIC DISTANCES ( $\text{\AA}$ ) IN Zn-RICH STAUROLITE CRYSTAL S(56)

T(1)–O(2A)	1.634	T(2)–O(1A)	1.996
T(1)–O(2B)	1.631	T(2)–O(1B)	2.023
T(1)–O(3)	1.649	T(2)–O(5)	<u>1.968</u> $\times 2$
T(1)–O(4)	<u>1.637</u>	$<T(2)–O>$	1.989
$<T(1)–O>$	1.638		
M(1A)–O(2A)	1.933	M(1B)–O(2B)	1.966 $\times 2$
M(1A)–O(4)	1.894	M(1B)–O(4)	1.911 $\times 2$
M(1A)–O(5)	<u>1.899</u>	M(1B)–O(5)	<u>1.916</u> $\times 2$
$<M(1A)–O>$	1.909	$<M(1B)–O>$	1.931
M(2)–O(1A)	1.915	M(3A)–O(1A)	1.856 $\times 2$
M(2)–O(1B)	1.945	M(3A)–O(3)	<u>2.001</u> $\times 4$
M(2)–O(2A)	1.947	$<M(3A)–O>$	1.952
M(2)–O(2B)	1.903		
M(2)–O(3)	1.881	M(3B)–O(1B)	1.882 $\times 2$
M(2)–O(5)	<u>1.866</u>	M(3B)–O(3)	<u>2.103</u> $\times 4$
$<M(2)–O>$	1.910	$<M(3B)–O>$	2.030
M(4A)–O(1A)	2.112		
M(4A)–O(5)	<u>2.174</u>		
$<M(4A)–O>$	2.154		

TABLE 1. CELL DIMENSIONS AND STRUCTURE-REFINEMENT INFORMATION FOR STAUROLITE CRYSTAL S(56)

a ( $\text{\AA}$ )	7.877(3)	R(sym)	3.1
b	16.609(5)	N(all)*	1577
c	5.665(1)	N(obs)*	986
$\beta$ ( $^\circ$ )	90.68(2)	R(obs)	1.9 %
V ( $\text{\AA}^3$ )	741.1	R(all)	4.2 %

\* N = number of reflections

TABLE 5. CHEMICAL COMPOSITIONS AND UNIT FORMULA\* OF Zn-RICH STAUROLITE CRYSTAL S(56)

SiO <sub>2</sub>	27.38	Si	7.991
Al <sub>2</sub> O <sub>3</sub>	48.85	Al	<u>0.009</u>
TiO <sub>2</sub>	0.41	Sum	8.000
Cr <sub>2</sub> O <sub>3</sub>	0.08		
FeO	5.77	Al	16.795
MnO	0.04	Cr	0.018
ZnO	11.15	Ti	0.090
NiO	0.03	Fe	1.408
MgO	2.92	Mn	0.010
Li <sub>2</sub> O	<u>0.01</u>	Zn	2.403
Sum	<u>96.64</u>	Ni	0.007
		Mg	1.271
		Li	0.012
		CATSUM	30.014
		H	(3.00)

\* calculated on the basis of 48 anions with OH=3 *apfu* (Holdaway *et al.* 1986b, Hawthorne *et al.* 1993a)

ER-70 (Holdaway *et al.* 1986a, b) with the revised Li<sub>2</sub>O content of 0.08 wt% (Holdaway *et al.* 1991, R. Hergig, pers. comm., 1993, Ottolini *et al.* 1993). The results are given in Table 5.

#### SITE POPULATIONS

The site nomenclature follows that of Hawthorne *et al.* (1993a). The polyhedral geometry of the structure is shown in Figure 1.

##### *T(1) site*

Staurolite usually has a significant amount (>0.20 *apfu*, atoms per formula unit) of Al at the *T(1)* site. However, calculation of the unit formula of S(56) (Table 5) indicates 7.99 Si *apfu* and essentially no [4]-coordinated Al. This is in agreement with the <*T(1)*-O> distance of 1.638 Å (Table 4) according to the relationship between <*T(1)*-O> and <sup>141</sup>Al developed by Hawthorne *et al.* (1993a, Fig. 6).

##### *The M(1,2,3) sites*

The *M*-site populations were assigned according to the method described by Hawthorne *et al.* (1993a). The only significant minor component in S(56) is Ti<sup>4+</sup>, and this was assigned to the *M(2)* site following the results of Henderson *et al.* (1993). This leaves Al and Mg to assign to *M(1A)*, *M(1B)* and *M(2)*, Al, Mg and □ to assign to *M(3A)* and *M(3B)*, and Fe<sup>2+</sup> to *M(4A)* and *M(4B)*. We can assign Fe<sup>2+</sup> to *M(4A)* and *M(4B)* on the basis of the results of the site-scattering refinement (Table 6). As Al (*Z* = 13) and Mg (*Z* = 12) scatter X-rays in a very similar fashion, site-scattering refinement is not normally considered a reliable

method for the derivation of populations of these species. Instead, we must use mean bond-length considerations; this method can be both precise and accurate if consideration is given to inductive effects for the particular structure-type under examination.

The <*M(1A)*-O> and <*M(1B)*-O> distances are significantly different in S(56) (Table 4). However, Hawthorne *et al.* (1993a) showed that the difference between the <*M(1A)*-O> and <*M(1B)*-O> distances is a function of the β angle, and that the grand <*M(1)*-O> distance is affected by the Mg content of these two sites. The <*M(1A)*-O> and <*M(1B)*-O> distances for Zn-bearing staurolite [sample 117189 of Holdaway *et al.* 1986b, crystals S(11)–S(14) of Hawthorne *et al.* 1993a] diverge from nearly the same value at β = 90.03° to 0.014 Å apart at β = 90.45° (Fig. 2). If we extrapolate these curves to β = 90.68°, we obtain a difference of 0.021 Å (Fig. 2), almost equal to the difference of 0.022 Å observed for S(56). Thus the relative behavior of the *M(1A)* and *M(1B)* sites in S(56) is compatible with the model of Hawthorne *et al.* (1993a), and we can assign Mg to the aggregate *M(1)* site. Examination of the relationship between <*M(1)*-O> and total Mg content of the crystal (Hawthorne *et al.* 1993a, Fig. 7) shows that crystal S(56) departs significantly from the general trend for staurolite. The <*M(1)*-O> distance is considerably larger (1.920 Å) than that expected for an Mg content of 1.27 *apfu* (1.915 Å), suggesting that crystal S(56) has more Mg at the *M(1)* sites than the general relation indicates.

The same situation occurs for the *M(2)* and *M(3)* sites. The reason for this is immediately apparent from Table 5. Crystal S(56) has a far lower Al-content than any of the staurolite crystals examined by Hawthorne *et al.* (1993a), and hence requires far more [6]-coordinated Mg to complete the occupancy requirements of the *M* sites. The problem of assigning Mg to the *M(1)*, *M(2)* and *M(3)* sites was resolved as follows. The total occupancy for these sites is 18.00 *apfu*, requiring 1.09 Mg *apfu* to be in [6]-coordination. Assume that this Mg is partitioned among the *M(1)*, *M(2)* and *M(3)* sites in the same fashion as for staurolite crystals S(1)–S(40); *i.e.*, in the proportion 23:6:10. This assignment should be reflected in the mean bond-lengths, as is the case. For example, Figure 3 shows the variation in grand <*M(1)*-O> bond-length for staurolite crystals S(1–3), S(11–14), S(4–6) and S(56). There is a linear increase in mean bond-length with increasing assigned Mg content at the *M(1)* site, which supports the assignment procedure used here. Note also that the site population and refined site-scattering at the *T(2)* site (see below) provides closure to this argument and supports the *M* site-population assignments.

There are two possibilities with regard to the relative ordering of Mg over the *M(1A)* and *M(1B)* sites: (1) Mg is disordered over *M(1A)* and *M(1B)* for β = 90°,

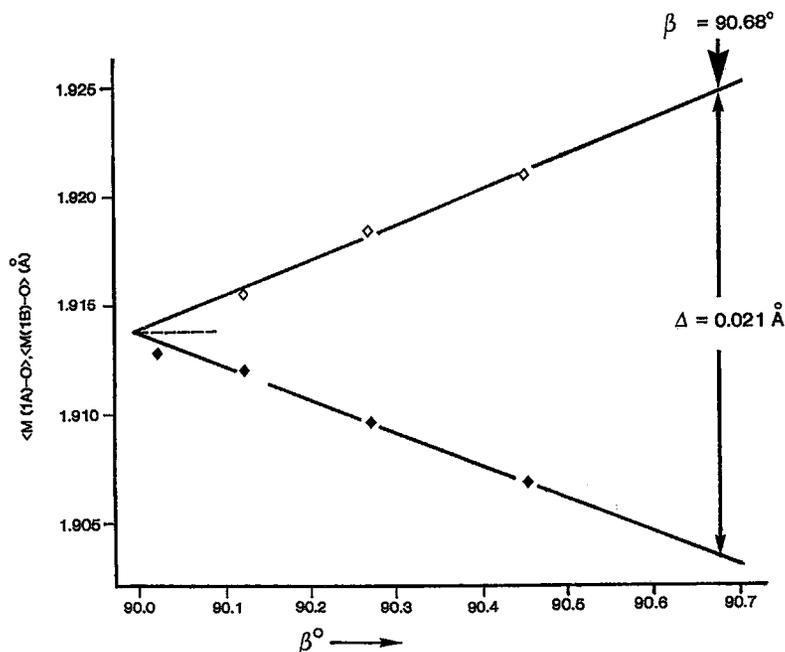


FIG. 2. The variation in  $\langle M(1A)-O \rangle$  and  $\langle M(1B)-O \rangle$  for staurolite crystals S(11–14) (Hawthorne *et al.* 1993a) as a function of  $\beta$  angle. The extrapolated difference in  $\langle M(1A)-O \rangle$  and  $\langle M(1B)-O \rangle$  for  $\beta = 90.68^\circ$  [corresponding to staurolite crystal S(56) of this study] is 0.021 Å.

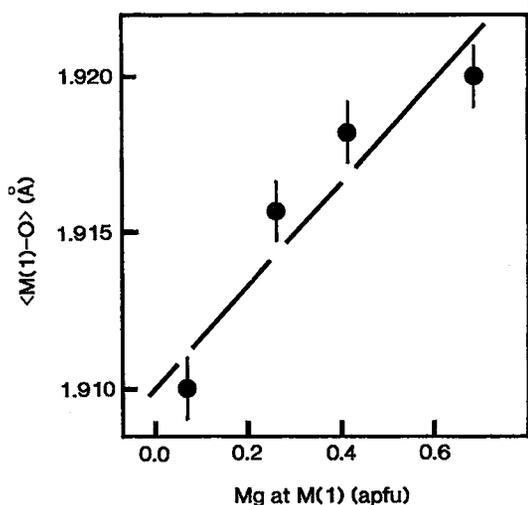


FIG. 3. Variation in grand  $\langle M(1)-O \rangle$  bond-length for staurolite crystals S(1–3), S(11–14), S(4–6) (Hawthorne *et al.* 1993a) and S(56) (this study) versus Mg assigned to the  $M(1)$  sites.

and increasing  $\beta$  correlates with increasing Mg–Al order over  $M(1A)$  and  $M(1B)$ , the difference between  $\langle M(1A)-O \rangle$  and  $\langle M(1B)-O \rangle$  here representing the effect of this ordering; (2) Mg is invariably disordered over  $M(1A)$  and  $M(1B)$ , and the difference between  $\langle M(1A)-O \rangle$  and  $\langle M(1B)-O \rangle$  represents spontaneous strain in the structure. We cannot distinguish between these two possibilities, and hence give the site population in terms of the aggregate  $M(1)$  site (Table 6).

For the  $M(2)$  and  $M(3)$  [ $\equiv M(3A) + M(3B)$ ] sites, Mg (6 and 10%, respectively) was assigned to each site as discussed above. The total scattering at the  $M(3)$  sites (Table 3) indicates exact half-occupancy by Al (including a small amount of Mg). Hawthorne *et al.* (1994) showed that the occupancy of the  $M(3)$  sites is strongly correlated with the H content in staurolite. The  $M(3)$  occupancy for S(56) is exactly 2.0 *apfu*, in accord with a H content of  $\sim 3$  *apfu*. The  $M(3A)$  and  $M(3B)$  site-populations can be derived directly from the refined scattering at these sites, as Al and  $\square$  dominate the constituent scattering (Table 6).

TABLE 6. SITE POPULATIONS IN STAUROLITE CRYSTAL S(56)

Site	Species	Population ( <i>apfu</i> )
<i>M</i> (1)	Al	7.31
	Mg	0.69
<i>M</i> (2)	Al	7.75
	Mg	0.14
	Ti + Cr	0.11
<i>M</i> (3)	Al	1.74
	Mg	0.26
	□	2.00
<i>M</i> (4)	Fe*	0.05
	□	3.95
<i>T</i> (1)	Si	7.99
	Al	0.01
<i>T</i> (2)	Fe*	1.36
	Zn	2.40
	Mg	0.22
	Li	0.01
	Al	—
Sum	<i>T</i> (2)	<u>3.99</u>
$\tau_{e}^{(2)}$ <sub>occ</sub>		107.3
$\tau_{e}^{(2)}$ <sub>ref</sub>		106.6

$\tau_{e}^{(2)}$  = site-scattering value of the *T*(2) cations; occ = as assigned; ref = from site-scattering refinement.  
 Fe\* = Fe<sup>2+</sup> + Mn + Cr + Ti + Fe<sup>3+</sup>

#### The *M*(4) sites

The *M*(4) sites are normally occupied by Fe<sup>2+</sup> (Smith 1968, Hawthorne *et al.* 1993a), and the variation in *M*(4) occupancy is strongly correlated with the H content of the crystal. The total scattering at *M*(4) (Table 3) indicates very low occupancy of these sites: 0.05 *apfu*. This, in turn, indicates that the H content of this crystal is ~3.0 *apfu*, and is the basis for use of this value in the calculation of the unit formula (Table 5).

#### The *T*(2) site

The *T*(2) site in staurolite is usually occupied by Fe<sup>2+</sup>, Zn, Mg, Li, □ and, in some cases, Al. For crystal S(56), all Zn, Fe and Mg (except that already assigned to other sites) was assigned to *T*(2), together with

minor amounts of Mn and Li. The resulting site-population is given in Table 6. First, it should be noted that the amounts of Fe and Mg assigned to *T*(2) are dependent solely on the assignments to the *M* sites, together with the unit formula calculated from the microprobe data. The total cations thus assigned are 3.99 *apfu*, in good agreement with the ideal value of 4.0 sites *pfu*. Second, the resultant effective scattering of 107.3 *epfu* (electrons per formula unit) (Table 6) is in close agreement with the refined value of 106.6 *epfu* (Table 3).

#### MAXIMUM MONOCLINIC STAUROLITE

Hawthorne *et al.* (1993b) interpreted the patterns of order in the staurolite structure in terms of an order-disorder series between disordered orthorhombic *Ccmm* staurolite and ordered monoclinic *C2/m* staurolite. They predicted that ordered monoclinic staurolite should have a  $\beta$  angle of 90.64°, and that the *M*(3) cations should be completely ordered at the *M*(3A) site. Figure 4 shows the variation in  $Q_{M(3)}$  [= ( $X_{M(3A)} - X_{M(3B)}) / (X_{M(3A)} + X_{M(3B)})$ ], where  $X$  represents the relevant site-occupancies] as a function of  $\beta$  angle in staurolite crystals S(1–45). It is apparent that crystal S(56) is the most ordered staurolite crystal yet refined ( $Q_{M(3)} = 0.89$ ), and the  $\beta$  angle slightly exceeds the maximum possible  $\beta$  angle predicted by

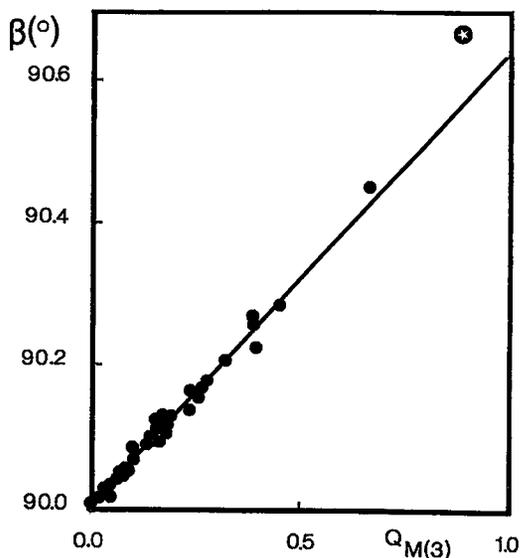


Fig. 4. Variation in  $Q_{M(3)}$  as a function of  $\beta$  angle in staurolite crystals S(1–45) (Hawthorne *et al.* 1993a, 1994) and S(56) (this study); S(56) is denoted by the star. Standard deviations are less than the size of the symbols.

Hawthorne *et al.* (1993b). The results for crystal S(56) support the general idea that staurolite is an order-disorder series involving  $Q_{M(3)}$  as the primary order-parameter. However, the details of crystal S(56) are not quite in accord with the predicted values. This lack of agreement provides us with another useful piece of information in the staurolite puzzle. The large value of the  $\beta$  angle originally suggested to us that the  $M(3)$  cations might be completely ordered at the  $M(3A)$  site. This is not the case (Table 3);  $Q_{M(3)}$  is actually equal to 0.89, significantly less than the ideal value of 1.0 for a completely ordered end-member. Crystal S(56) is very unusual from a compositional viewpoint. It has a very low Al content and an unusually high amount of Mg at the  $M(1)$ ,  $M(2)$  and  $M(3)$  sites. If the Al at  $M(3)$  were completely ordered at  $M(3A)$  and the Mg at  $M(3)$  were completely *disordered* over the  $M(3A)$  and  $M(3B)$  sites, the site-scattering values would be as follows:  $M(3A) = 24.2$ ,  $M(3B) = 1.6$  *epfu*, in very close agreement with the refined values. Of course, this argument does not *prove* that Mg at  $M(3)$  is disordered. However, the close agreement between the observed and calculated values, together with the large value of the  $\beta$  angle, does *suggest* that the model of Hawthorne *et al.* (1993b) is quantitatively correct, but may be perturbed by the presence of [6]-coordinated Mg that remains disordered over the  $M(3A)$  and  $M(3B)$  sites in the structure, irrespective of the degree of corresponding Al order.

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