

THE CRYSTAL STRUCTURE OF STAUROLITE

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ABSTRACT

Staurolite (a 7.8713(24), b 16.6204(26) c 5.6560(11), β 90°, $C2/m$) is pseudo-orthorhombic. Although the structure (alternating layers of kyanite and $AlFe_2O_3(OH)$) given by Náray-Szabó and Sasvári (1958) is basically correct, the details are more complex. Two new octahedral sites U(1) and U(2) at (0.5, 0, 0) and (0.5, 0, 0.5) are weakly occupied in a specimen from St. Gotthard; the U(1) and U(2) octahedra share faces with the Fe tetrahedron, and the indicated low occupancy of the latter might be explained by prohibition of simultaneous occupancy of the octahedra. Assignment of atoms is not unique: chemical and Mössbauer data in association with crystal-chemical speculation suggest the following for the St. Gotthard specimen:—Fe site—0.6 Fe, 0.3 Mg or Al, 0.04 Ti; Si site—0.93 Si, 0.06 Al; U sites—0.04 Fe, 0.02 Mn; Al sites—some Mg and Fe substituting for Al. Suggested substitution of $(OH)_4$ for SiO_4 is not substantiated. A generalized formula for staurolite is $(7 \text{ octahedral sites, principally Al})_{\sim 18}(1 \text{ tetrahedral site, principally Fe})_{\leq 4}(1 \text{ tetrahedral site, principally Si})_8O_{48}H_{\sim 4}$. Protons were not located from the X-ray data: a complex distribution of OH ions is likely in view of the extensive cation substitution; probably the protons are associated principally with O(1) to provide a better charge balance (Hanisch, 1966). It is suggested that the presence of these protons is essential to the stability of the staurolite structure, and that the complex substitutions are caused in part by the requirements of an overall charge balance and in part by exchange relations with other minerals. Submicroscopic twinning on (010) may have reduced the observed deviation from orthorhombic symmetry. Octahedral distortions are determined partly by shortening of shared edges: however, the unshared edges O(1A)—O(1B) of the A1(2) octahedron and Fe tetrahedron are short because of packing problems down the z -axis.

INTRODUCTION

Staurolite has been a chemical and crystallographic enigma for many years. Careful chemical analyses by Juurinen (1956) clarified the chemical contents of several typical specimens, but the derived formula $H_4Fe_4Al_{18}Si_8O_{48}$ is too idealized; moreover it balances electrostatically only if half the iron is in the ferric state, which conflicts with the experimental finding that the iron is mostly ferrous. Although the proposal by Náray-Szabó (1929) that staurolite is built up of alternating kyanite and iron-aluminum hydroxide layers was a reasonable first approximation, the optical and X-ray evidence for monoclinic symmetry obtained by Hurst, Donnay and Donnay (1956) made necessary a modification by Náray-Szabó and Sasvári (1958) in which two extra Al ions were added in octahedral sites. The formula given by Náray-Szabó and Sasvári, $H_2Fe_4Al_{18}Si_8O_{48}$, balances electrostatically if iron is entirely ferrous but conflicts with the higher water contents in analyses made by Juurinen and others. Schreyer and Chinner (1966) have proposed recently the substitution of $4H^+$ for Si^{4+} . The present investigation was begun to

attempt a resolution of these problems. Hanisch (1966) has published a note on a parallel investigation of a Zn-rich staurolite in which orthorhombic symmetry was assumed in the refinement. Although the principal conclusions are similar to those found here, there are some important differences which may be caused in part by the different chemical compositions of the samples.

EXPERIMENTAL

Specimen #1558 from the University of Chicago Mineralogy Collection was selected for study. The locality is given as St. Gotthard, Switzerland and the assemblage of staurolite, kyanite and mica is typical of specimens from this locality found in most mineralogy collections. Juurinen's specimen no. 2 comes from Pizzo Forno, Switzerland, about 25 km SE of St. Gotthard.

The microprobe analysis of the Chicago specimen is quite close to the chemical analysis given by Juurinen (Table 1). Corrections to the microprobe analysis were made by the procedure listed by Smith (1965) using the following reference standards: for Si-sillimanite, synthetic pyrope and E21 orthopyroxene; for Al-sillimanite; for Fe and Mg-E21 orthopyroxene; for Ti-Y5, Y16 and H39 clinopyroxenes; for Mn-H37 and H39 clinopyroxenes. Analyses were made at 15KV and $0.1\mu\text{A}$. The staurolite was spatially uniform in composition. No elements between Na and U besides those listed in Table 1 were detected. In making the corrections the H_2O content found by Juurinen for specimen no. 2 was added to the assumed composition. Since the microprobe and chemical analyses are similar it was decided to carry out the X-ray diffraction analysis on the basis of the microprobe data assuming the iron oxidation ratio and water content given by Juurinen's analysis. Table 1 shows the analysis recalculated to 48 oxygen atoms.

The cell dimensions were determined from a diffractometer powder pattern using $\text{FeK}\alpha$ radiation and an internal silicon standard ($a = 5.4306 \text{ \AA}$). Ambiguities in indexing were resolved by comparison of intensities from single crystal patterns. All lines were sharp and consistent with orthorhombic geometry yielding a 7.8713(24), b 16.6204(26), c 5.6560(11) \AA . The standard errors in brackets were obtained from a least-squares fit of sixteen $1/d^2$ values. Juurinen obtained a 7.872 b 16.605 c 5.654 \AA . Weissenberg photographs confirmed the presence of $0kl$ reflections forbidden by C_{2mm} ; in addition, careful visual inspection revealed the absence of symmetry planes normal to x and z .

The data were consistent with $C2/m$, $C2$ or Cm . It was not necessary in the diffraction analysis to postulate lack of a center of symmetry in conformity with absence of a pyroelectric effect (as reported by Hurst, Donnay and Donnay).

Approximately 9,000 diffractions were measured on a PAILRED single crystal diffractometer using monochromatized $\text{MoK}\alpha$ radiation. The crystal was mounted with the z -axis along the principal axis of the equi-angle geometrical configuration. After collection of diffractions in a quarter-sphere, the crystal was rotated through 180° about z and the second quarter-sphere examined. The minimum spacing was 0.4 \AA . Comparison of the diffraction intensities showed that the Laue group was $C2/m$ in conformity with the conclusion from visual examination. There was no need to invoke triclinic symmetry. Intensities were averaged in pairs according to $C2/m$: very strong and very weak intensities were omitted from the structural refinement and about 3200 intermediate intensities were inserted into the least squares refinement using the ORFLS program. The crystal was a small prism about 0.4 mm in mean dimensions: a trivial absorption correction was applied using program ABSRP written by C. W. Burnham. Velocity and polarization corrections were made.

TABLE 1. MICROPROBE AND CHEMICAL ANALYSES
Weight percent

	1 Microprobe	2 Chemical	Microprobe analysis calculated to 48 oxygen atoms
SiO ₂	26.97	27.46	7.46
TiO ₂	0.72	0.58	.15
Al ₂ O ₃	54.53	53.94	17.77
Fe ₂ O ₃	1.12 ^a	1.16	.23
FeO	11.81 ^a	12.22	2.73
MgO	1.91	2.24	.79
MnO	0.27	0.18	.06
H ₂ O	(2.37)	2.37	(4.39)
Total	99.70	100.15	

1. Analysis of U. of Chicago specimen #1558 from St. Gotthard, Switzerland. C. R. Knowles and J. V. Smith, analysts.

2. Analysis of Juurinen specimen #2 from Pizzo Forno, Switzerland probably from same locality.

^a Assuming same oxidation ratio as found by chemical analysis.

In the first stage of the refinement, the intensities were averaged according to Laue symmetry Cmmm and an isotropic refinement carried out starting from the coordinates given by Náray-Szabó and Sasvári. An arbitrary assignment of cations to the various sites was made in the expectation that the population factors would tend to compensate for incorrect assignments. Because of the large number of observed intensities it was possible to obtain successful refinements of both the population factor and the temperature factor for the densely populated sites: for the weakly populated sites Al(1A), Al(1B), U(1) and U(2) the temperature factor was locked at a reasonable value and only the population factor was refined. The positional parameters are close to those given by Hanisch for the zincian staurolite. Using the signs from the isotropic refinement, Fourier syntheses were calculated. Initially the deviation from orthorhombic symmetry was examined by using the difference in the observed amplitudes F_{hkl} and $F_{\bar{h}k\bar{l}}$. Clear indications were obtained of atomic displacements and rapid refinement was obtained from least squares adjustment of observed and calculated amplitudes using monoclinic symmetry. Difference maps were then calculated using the output of the monoclinic refinements. Two new sites, U(1) and U(2), listed neither by Náray-Szabó and Sasvári, nor by Hanisch, were found to be weakly populated. Substitution of larger cations such as Fe and Mn will be proposed for these sites. The final F_o-F_c synthesis showed trivial peaks around all but one of the cations and anions indicating only small, near-isotropic atomic displacements: for the exception, the Fe site, there were weak but clearly defined peaks (Fig. 1) which to a first approximation could be represented by three positive and two negative lobes. The positive lobes lie at 0.3₁ and 0.3₆ Å from the center. Because of the strong deviation from an ellipsoidal distribution of electron density, it is supposed that the Fe site consists of at least three separate centers of displacements occupied either spatially, temporally or both. Independent sites in the monoclinic cell related by a pseudo mirror plane at $z=1/4$ are labelled A and B except for the U sites which are labelled U(1) and U(2), respectively.

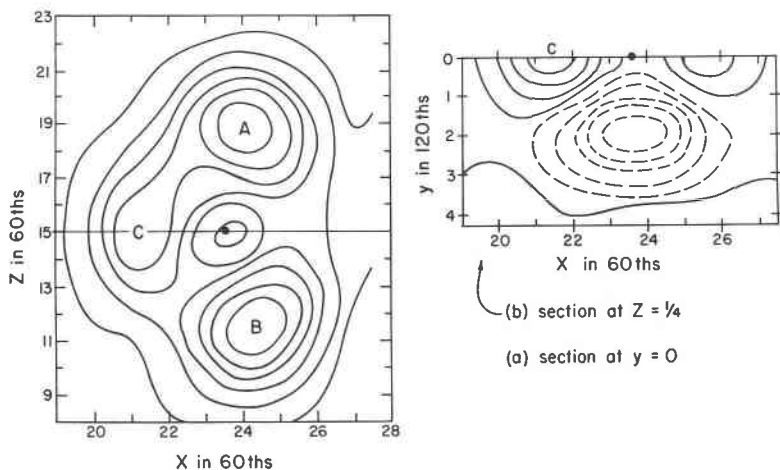


FIG. 1. Two sections through the $(F_0 - F_c)$ synthesis in the vicinity of the Fe site which is marked by a dot. A, B and C are referred to in the text.

As the analysis proceeded it became possible to think about assignment of cations to the nine possible sites with octahedral or tetrahedral coordination. At the outset it must be admitted frankly that the problem is incapable of a unique solution, and that the proposed assignments are based on a horrendous mixture of experimental data and crystal-chemical speculation. One important clue to the distribution of the Fe atoms was obtained from a gamma-ray resonance pattern (Fig. 2) of the Fe^{57} atoms, kindly prepared by S. Hafner. Substitution of Al in the Si site seems to be well established, but the distribution of the Mg atoms could not be established because of the similar scattering factors of Mg and Al and because their crystal chemical properties are not sufficiently distinctive. Because the arguments concerning the atomic assignments are so complex they are discussed separately in the next section.

Table 2 shows the results of a refinement in which the atoms are assigned according to one of the possibilities discussed in the next section. Readers should note that this is only one of an infinite number of ways in which atoms may be assigned to give a satisfactory fit with the observed X-ray intensities. If the site occupancies are changed, the refined B -values will change. For example, change of the content of Al(3A) from 0.85 Al, 0.10 Ti, 0.06 Fe to 0.55 Al, 0.28 Fe caused B to increase from 0.30 to 0.43. Consequently the errors attached to the B -values have no absolute significance. The errors attached to the atomic positional parameters, however, are meaningful since these parameters are essentially immune to changes in the site occupancies. Table 3 shows the important interatomic distances and Table 4 the interatomic angles.

Figure 3 is a projection down z of the crystal structure. The immediate neighbors of one atom of each type are shown. No attempt was made to prepare a polyhedral diagram since the U and Fe polyhedra would interpenetrate each other in a confusing way.

Table 5¹ lists the observed and calculated structure amplitudes for all measured dif-

¹ Table 5 has been deposited as Document No. 9900 with the American Documentation Institute, Library of Congress, Washington, D.C. 20540. Copies may be secured by citing the document number and remitting in advance \$5.00 for photoprints or \$2.25 for microfilm.

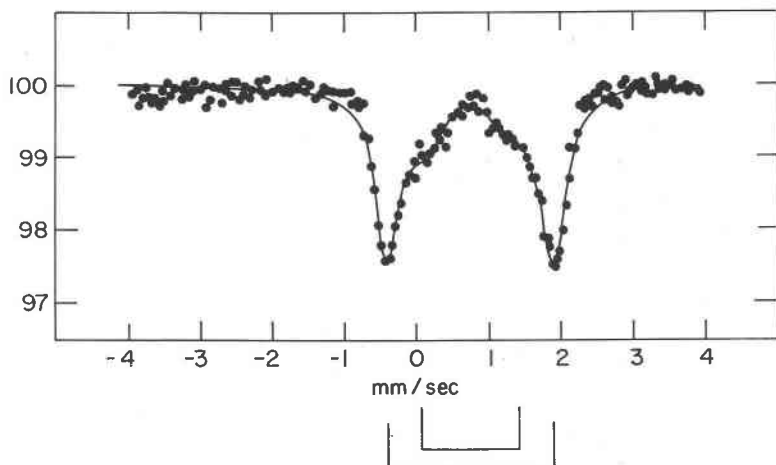


FIG. 2. The Mössbauer gamma-ray spectrum of Fe^{57} atoms in staurolite. The spectrum has been fitted with two doublets specified by the following parameters:

isomer shift (vs. Co^{57} in Cu)	$IS_1=0.74$ mm/sec; $IS_2=0.76$ mm/sec
electric quadrupole splitting	$\Delta_1=2.33$ mm/sec; $\Delta_2=1.53$ mm/sec
half width	$w_1=0.36$ mm/sec; $w_2=0.65$ mm/sec

fractions. Because of cost only 3160 diffractions were used at one time in the least-squares refinements, though all observed intensities were checked against calculated amplitudes. Only a dozen diffractions were significantly affected by extinction, and these were omitted in the final refinement. The data for Table 2 were obtained for a refinement in which the strongest and weakest intensities were omitted. Results of the refinements were essentially independent of weighting schemes, and to save space the weights which varied only from 1 to 2 are omitted from Table 5. Form factors for half-ionized atoms were interpolated from Volume III of *International Tables for X-ray Crystallography*. No correction was made for anomalous dispersion. The final unweighted R -factor for the 3160 selected reflections used in the final refinement was 0.08. Addition of the other reflections raises the value to 0.12, but many of these reflections were below the limit of detection at diffraction angles higher than those used in most structure analyses.

The gamma-ray resonance pattern for Fe^{57} atomic nuclei is shown in Figure 2. Because the pattern shows a pair of principal absorptions associated with ill-defined shoulders of smaller separation it is clear that the iron atoms in staurolite are distributed in more than one structural site; furthermore the shoulders are so broad that they must result from more than one site. Earlier X-ray workers have assigned all the Fe to the site labelled Fe because of the high electron density and because of the inter-atomic distances. The pair of principal absorptions in the Mössbauer pattern is assigned to Fe^{2+} atoms in site Fe. From a computer fit using Lorentzian line shapes, the assumption of two Fe sites leads to 77 percent of Fe in the Fe site and 23 percent elsewhere. It is not possible to proportion the 23 percent between the indicated multiple sites because of incomplete resolution and because of lack of knowledge of the relation between line splitting and atomic environment. Ferric iron has been assigned arbitrarily to the Fe site but there are no convincing arguments why it should not go into an octahedral site. Indeed it is possible that the ferric iron results merely from oxidation during chemical analysis (Schreyer and Chinner, 1966), since no

TABLE 2. ATOMIC PARAMETERS AND SITE CONTENTS

Atom	x	y	z	B	Assumed site content	Observed occupancy	Number of atoms
Fe	0.39281 (11)	0.0	0.24815 (16)	1.01 (1)	0.64 Fe, .32 Al, .04 Ti	0.916 (6)	2.35 Fe, 1.17 Al, .15 Ti
Si	.13414 (8)	.16612 (4)	.24902 (12)	.25 (1)	.936 Si, .064 Al	.991 (6)	7.42 Si, .51 Al
Al(1A)	.5	.17511 (6)	.0	.29 (2)	.95 Al, .05 Mg	.975 (8)	3.71 Al, .19 Mg
Al(1B)	.5	.17477 (7)	.5	.31 (2)	.95 Al, .05 Mg	.978 (8)	3.71 Al, .20 Mg
Al(2)	.26356 (9)	.41042 (5)	.25122 (14)	.36 (1)	.95 Al, .05 Mg	.982 (6)	7.47 Al, .39 Mg
Al(3A)	.0	.0	.0	.43 (4)	.67 Al, .33 Fe	.415 (8)	.55 Al, .28 Fe
Al(3B)	.0	.0	.5	.41 (6)	.67 Al, .33 Fe	.282 (8)	.37 Al, .19 Fe
U(1)	.5	.0	.0	.4	.68 Fe, .32 Mn	.080 (4)	.11 Fe, .05 Mn
U(2)	.5	.0	.5	.4	.68 Fe, .32 Mn	.038 (4)	.06 Fe, .02 Mn
O(1A)	.23274 (33)	.0	.96313 (49)	.68 (3)	1.00 O		
O(1B)	.23438 (33)	.0	.53428 (49)	.69 (3)	1.00 O		
O(2A)	.25569 (21)	.16153 (10)	.01527 (31)	.49 (2)	1.00 O		
O(2B)	.25519 (21)	.16127 (10)	.48391 (31)	.49 (2)	1.00 O		
O(3)	.00143 (22)	.08917 (11)	.24702 (32)	.59 (2)	1.00 O		
O(4)	.02156 (20)	.24925 (10)	.25002 (31)	.45 (2)	1.00 O		
O(5)	.52741 (20)	.10004 (10)	.24944 (30)	.42 (2)	1.00 O		

Notes: 1. Random error from ORFLS program listed in brackets to same significance level as parameter.

2. The assumed site content was used to determine the atomic scattering factor; all values for half-ionization.

3. The observed occupancy was obtained from ORFLS program by simultaneous refinement of occupancy and B factors of cations. For U(1) and U(2) only the occupancy was refined assuming $B=0.4$. For the oxygen atoms only B was refined.

TABLE 3. INTERATOMIC DISTANCES (Å)

Fe—tetrahedron		Al(1B)—octahedron		Al(3A)—octahedron	
Fe-O(1A)	2.046(3)	2 Al(1B)—O(2B)	1.942(2)	2 Al(3A)—O(1A)	1.844(3)
Fe-O(1B)	2.043(3)	2 Al(1B)—O(4)	1.903(2)	4 Al(3A)—O(3)	2.037(2)
2 Fe-O(5)	1.972(2)	2 Al(1B)—O(5)	1.897(2)	Mean	1.972
Mean	2.020	Mean	1.914	4 O(1A)—O(3)	2.844(3)
O(1A)—O(1B)	3.230(4)	2 O(2B)—O(4)	2.891(2)	4 O(1A)—O(3)	2.647(3) ⁱ
2 O(1A)—O(5)	3.281(3)	2 O(2B)—O(4)	2.750(2)	2 O(3)—O(3)	2.794(4)
2 O(1B)—O(5)	2.268(3)	2 O(2B)—O(5)	2.717(2)	2 O(3)—O(3)	2.964(3) ^g
O(5)—O(5)	3.325(3)	2 O(2B)—O(5)	2.498(2) ^d	Mean	1.790
Mean	3.257	O(4)—O(4)	2.848(3)	Al(3B)—octahedron	
Si—tetrahedron		2 O(4)—O(5)	2.505(2) ^b	2 Al(3B)—O(1B)	1.855(3)
Si-O(2A)	1.634(2)	O(5)—O(5)	2.867(3) ^e	4 Al(3B)—O(3)	2.060(2)
Si-O(2B)	1.637(2)	Mean	2.703	Mean	1.992
Si-O(3)	1.651(2)	Al(2)—octahedron		4 O(1B)—O(3)	2.863(3)
Si-O(4)	1.641(2)	Al(2)—O(1A)	1.920(2)	4 O(1B)—O(3)	2.678(3) ^j
Mean	1.641	Al(2)—O(1B)	1.921(2)	2 O(3)—O(3)	2.862(4)
O(2A)—O(2B)	2.651(2)	Al(2)—O(2A)	1.930(2)	2 O(3)—O(3)	2.964(3) ^g
O(2A)—O(3)	2.678(2)	Al(2)—O(2B)	1.920(2)	Mean	2.816
O(2A)—O(4)	2.699(3)	Al(2)—O(3)	1.872(2)	U(1)—octahedron	
O(2B)—O(3)	2.687(2)	Al(2)—O(5)	1.867(2)	2 U(1)—O(1A)	2.114(3)
O(2B)—O(4)	2.696(2)	Mean	1.907	4 U(1)—O(5)	2.191(2)
O(3)—O(4)	2.665(2)	O(1A)—O(1B)	2.426(4) ^f	Mean	2.165
Mean	2.679	O(1A)—O(2A)	2.707(2)	4 O(1A)—O(5)	2.788(3)
Al(1A)—octahedron		O(1A)—O(3)	2.647(3) ⁱ	4 O(1A)—O(5)	3.281(3)
2 Al(1A)—O(2A)	1.938(2)	O(1A)—O(5)	2.788(3)	2 O(5)—O(5)	2.854(3) ^c
2 Al(1A)—O(4)	1.900(2)	O(1B)—O(2B)	2.700(2)	2 O(5)—O(5)	3.325(3) ^h
2 Al(1A)—O(5)	1.896(2)	O(1B)—O(3)	2.678(3) ^j	Mean	3.057
Mean	1.911	O(1B)—O(5)	2.789(3)	U(2)—octahedron	
2 O(2A)—O(4)	2.888(2)	O(2A)—O(2B)	3.005(2)	2 U(2)—O(1B)	2.100(3)
2 O(2A)—O(4)	2.743(2)	O(2A)—O(3)	2.783(2)	4 U(2)—O(5)	2.195(2)
2 O(2A)—O(5)	2.715(2)	O(2A)—O(5)	2.490(2) ^a	Mean	2.163
2 O(2A)—O(5)	2.490(2) ^a	O(2B)—O(3)	2.799(2)	4 O(1B)—O(5)	2.789(2)
O(4)—O(4)	2.849(3)	O(2B)—O(5)	2.498(2) ^d	4 O(1B)—O(5)	3.268(3)
2 O(4)—O(5)	2.505(2) ^b	Mean	2.692	2 O(5)—O(5)	2.867(3) ^e
O(5)—O(5)	2.854(3) ^c			2 O(5)—O(5)	3.325(3) ^h
Mean	2.699			Mean	2.060

^a shared edge between Al(1A) and Al(2) octahedra^b shared edge between Al(1A) and Al(1B) octahedra^c shared edge between Al(1A) and U(1) octahedra^d shared edge between Al(1B) and Al(2) octahedra^e shared edge between Al(1B) and U(2) octahedra^f shared edge between Al(2) and Al(2) octahedra^g shared edge between Al(3A) and Al(3B) octahedra^h shared edge between U(1) and U(2) octahedraⁱ shared edge between Al(2) and Al(3A) octahedra^j shared edge between Al(2) and Al(3B) octahedron

peaks attributable to ferric iron are seen in the Mössbauer pattern. The present conclusions are consistent with those reached by G. M. Bancroft, R. G. Burns and A. G. Maddock in a Mössbauer study of two staurolites, one of which is similar to the specimen used in the present work. I am indebted to Dr. Burns for sending a copy of a manuscript submitted to *Geochimica et Cosmochimica Acta*.

TABLE 4. INTERATOMIC ANGLES

Fe—tetrahedron		Al (2)—octahedron	
O(1A)-Fe-O(1B)	104.37(11)	O(1A)-Al(2)-O(1B)	78.33(9)
2 O(1A)-Fe-O(5)	109.50(6)	O(1A)-Al(2)-O(2A)	89.34(9)
2 O(1B)-Fe-O(5)	108.97(7)	O(1A)-Al(2)-O(3)	88.51(10)
O(5)-Fe-O(5)	114.99(10)	O(1A)-Al(2)-O(5)	94.81(10)
		O(1B)-Al(2)-O(2B)	89.36(9)
Si—tetrahedron		O(1B)-Al(2)-O(3)	89.82(10)
O(2A)-Si-O(2B)	108.27(9)	O(1B)-Al(2)-O(5)	94.82(10)
O(2A)-Si-O(3)	109.20(9)	O(2A)-Al(2)-O(2B)	102.64(8)
O(2A)-Si-O(4)	111.00(9)	O(2A)-Al(2)-O(3)	94.06(8)
O(2B)-Si-O(3)	109.61(9)	O(2A)-Al(2)-O(5)	81.95(8)
O(2B)-Si-O(4)	110.66(9)	O(2B)-Al(2)-O(3)	95.11(8)
O(3)-Si-O(4)	108.08(9)	O(2B)-Al(2)-O(5)	82.52(8)
Al(1A)—octahedron		Al(3A)—octahedron	
2 O(2A)-Al(1A)-O(4)	97.62(7)	4 O(1A)-Al(3A)-O(3)	85.87(8)
2 O(2A)-Al(1A)-O(4)	91.24(7)	4 O(1A)-Al(3A)-O(3)	94.13(8)
2 O(2A)-Al(1A)-O(5)	90.17(7)	2 O(3)-Al(3A)-O(3)	86.62(10)
2 O(2A)-Al(1A)-O(5)	82.61(7)	2 O(3)-Al(3A)-O(3)	93.38(10)
O(4)-Al(1A)-O(4)	97.14(11)		
2 O(4)-Al(1A)-O(5)	82.61(7)	Al(3B)—octahedron	
O(5)-Al(1A)-O(5)	97.68(11)	4 O(1B)-Al(3B)-O(3)	86.15(8)
		4 O(1B)-Al(3B)-O(3)	93.85(8)
Al(1B)—octahedron		2 O(3)-Al(3B)-O(3)	87.99(10)
2 O(2B)-Al(1B)-O(4)	97.49(7)	2 O(3)-Al(3B)-O(3)	92.01(10)
2 O(2B)-Al(1B)-O(4)	91.32(7)		
2 O(2B)-Al(1B)-O(5)	90.12(7)	U(1)—octahedron	
2 O(2B)-Al(1B)-O(5)	81.17(7)	4 O(1A)-U(1)-O(5)	80.71(6)
O(4)-Al(1B)-O(4)	96.86(11)	4 O(1A)-U(1)-O(5)	99.29(6)
2 O(4)-Al(1B)-O(5)	82.49(7)	2 O(5)-U(1)-O(5)	81.28(9)
O(5)-Al(1B)-O(5)	98.18(11)	2 O(5)-U(1)-O(5)	98.72(9)
U(2)—octahedron			
4 O(1B)-U(2)-O(5)	80.94(6)		
4 O(1B)-U(2)-O(5)	90.06(6)		
2 O(5)-U(2)-O(5)	81.53(9)		
2 O(5)-U(2)-O(5)	98.47(9)		

ASSIGNMENT OF ATOMS TO SITES

In this section, the chemical, X-ray and gamma-ray resonance data will be combined with crystal-chemical theory to provide information on the assignment of atoms to the various sites. The arguments are tedious and the results only partly conclusive.

From the X-ray data, both population factors and interatomic distances were obtained. X-ray diffraction yields an electron density profile.

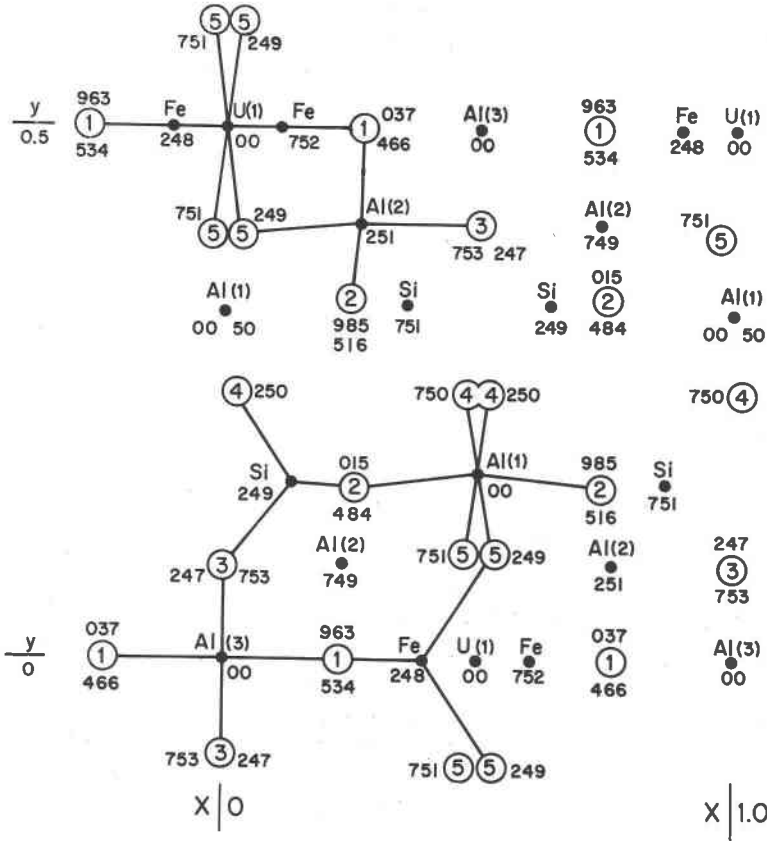


FIG. 3. The crystal structure of staurolite projected down the z -axis. The three-figure numbers give the heights of atoms as decimal fractions of the c -repeat. The cations are shown by large filled circles, and the oxygen atoms by open circles enclosing the sequence number. The structure can be considered to be formed approximately from alternating layers of kyanite (Al_2SiO_5) and $\text{AlFe}_2\text{O}_3(\text{OH})$ as shown by Naray-Szabó (1929). The oxygen neighbors of one of each type of cation are indicated by connecting lines. For clarity, no distinction is made between A and B pairs of oxygen atoms. The $U(2)$ sites are not shown, but are displaced $c/2$ from the $U(1)$ sites.

In a simple crystal structure such as quartz it is quite obvious which electron density peak corresponds to silicon and which one to oxygen. In staurolite assignment of cations is not obvious and the number of atoms obtained from the X-ray analysis *depends* on which type of atomic species is assigned. Roughly speaking the number of atoms is proportional to the inverse of its atomic number when the atomic numbers are fairly close. Thus 12 Al atoms would yield a similar electron density to 13 Mg atoms.

There are further technical complications base on the interaction in the mathematical refinement between the population factor and the "temperature" factor. The latter measures the mean displacement of an atom from its ideal crystallographic position either because of thermal vibration or because of positional differences caused by chemical substitution. Thus in staurolite the observed population factors were interpreted cautiously.

In using interatomic distances calculated from the centers of electron density profiles, it was borne in mind that these distances are dominated by the major chemical substituents. Thus care was taken in not excluding a potential minor substituent just on the basis of size. In addition coupled cation substitutions permitting favorable movements of oxygen atoms were thought to be possible.

Although there are only 7.46 atoms of Si for the 8-fold Si site, the structure refinement indicates nearly full occupancy when the scattering factor for Si^{2+} is used. Of the available cations, Al is the most reasonable substituent and has been assigned to fill the vacant Si sites. Such substitution would explain why the average Si-O distance in staurolite (1.641) is greater than the average in kyanite (1.628).

Since the U(1) and U(2) octahedra are so large it seems safe to assign the Mn here together with sufficient Fe to balance the observed population factor; however there is some uncertainty since the positions of the oxygen atoms are determined principally by bonding to other cations, and the true U-O distances may not be apparent. Since the Al(3A) and Al(3B) polyhedra are larger than the Al(1A), Al(1B) and Al(2) polyhedra, the remaining Fe was assigned to Al(3A) and Al(3B) sites. As the Al(3B) polyhedron is slightly larger than the Al(3A) polyhedron, one is tempted to assign Fe preferentially to Al(3B) sites: however, the difference is too small to justify this.

The assignment of the remaining Al and Mg is quite uncertain except for the obvious conclusion that sites Al(1A), Al(1B), and Al(2) are occupied principally by Al. The atomic scattering factors of Mg and Al are so similar that little guide is obtained from the population factors refined from the X-ray data. Mg occurs more frequently in octahedral environments but does occur in four-fold coordination (åkermanite) and in eight-fold coordination (pyrope); Al occurs in both octahedral and tetrahedral environments, the preference depending on the relation to the other structural units. From a size viewpoint, Mg should prefer the larger Fe tetrahedron to the smaller Al octahedra (the size comparison is based on the metal-oxygen distance corrected for coordination number according to Pauling's formula). However, the complex electron distribu-

tion at the Fe site and the unknown position of the protons may cause serious complications.

Since staurolite can be considered to be composed largely of alternating layers of kyanite and $\text{Fe}(\text{OH})_2$, it might seem legitimate to compare the average Al-O distances with those in kyanite to test for substitution of Mg. However when it is considered that Al-O octahedral distances in silicates range from 1.89 to 1.94 Å (see summary in Gibbs and Smith (1965)) and that the change of distance expected for substitution of 5 percent of the Al by Mg is so small (around 0.01 Å) it is obvious that no certain conclusions should be drawn from the sizes of the Al-octahedra. The kyanite used by Burnham (1963) can be regarded as having Al sites occupied entirely by Al atoms; the average distances for the four independent octahedra are Al-O 1.906, 1.918, 1.891 and 1.883 Å. The oxygen cation distances in staurolite: to Al(1A) 1.911, Al(1B) 1.914, Al(2) 1.907 are of comparable size.

It is unwise to draw conclusions from the size of the Fe tetrahedron. Further inconclusive evidence on the distribution of cations can be drawn from a subtle argument relating to simultaneous occupancy of Fe and the U(1) and U(2) sites. If sites Fe and U are occupied simultaneously, the tetrahedron and octahedron share faces. An alternate distribution in which faces are not shared would seem to be preferable. As 0.11 Fe and .05 Mn atoms have been assigned to U(1), and 0.06 Fe and 0.02 Mn to U(2), and each atom in a U site shares faces with two atoms in Fe sites, absence of face sharing implies a maximum occupancy of 3.52 atoms in the four-fold Fe site if U(1) and U(2) independently prohibit occupancy of the Fe site, and 3.68 atoms if U(2) prohibits only those atoms already prohibited by U(1).

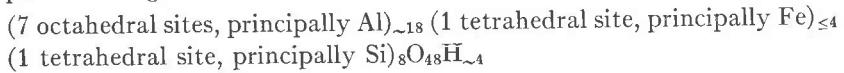
Table 2 shows the results of a refinement in which the Mg was assigned to Al(1A), Al(1B) and Al(2) and the remaining Al to the Fe site. From the population factors which were refined simultaneously with the temperature factors, the observed occupancy of the Fe site was deduced as 2.35 Fe, 1.17 Al and 0.15 Ti atoms giving a total of 3.67. The occupancies of the Al(1A), Al(1B) and Al(2) sites are slightly deficient by about 2 percent, with standard errors near 0.7 percent. Based on some early refinements in which it was found that observed population factors for Al average about 10 percent lower than those for Mg, it may be estimated that substitution of Mg into the Fe site would yield an occupancy near 2.35 Fe, 0.78 Mg, 0.46 Al and 0.15 Ti to give a total of 3.74 atoms in the Fe site, and deficiencies of about 3 percent in the Al content of the Al sites.

Another alternative is to assign all the Mg to the Al(3A) and Al(3B)

sites: however this can be rejected because the observed cation-oxygen distances of 1.972 and 1.992 are consistent with about one-third of the Al being replaced by Fe (expected distance about 1.97 Å) but not with the site being occupied solely by Mg and Fe (expected distance about 2.1 Å). In conclusion, there seem to be no convincing arguments for the location of the Mg atoms; nor did there seem any point in extensive refinement of different postulated populations.

THE CHEMICAL COMPOSITION OF STAUROLITE

In spite of the uncertainties in the foregoing discussion it seems reasonable to propose that existing chemical formulae for staurolite are too simple. Those formulae which separate the Fe from the Al with the implication that they occupy different sites are too naive, while the suggestion of deficiency in the Si site balanced by proton addition to the oxygens is definitely at variance with the X-ray data. It seems best to propose a more general formula:



with restrictions on the ranges of substitution.

At present there is incomplete evidence on the restriction in the ranges of substitution. The composition of natural staurolite is governed partly by exchange reactions with other minerals such as mica. Since staurolite appears to occur in a restricted range of metamorphic rocks both with regard to rock composition and metamorphic grade it cannot be expected that the potential range of substitution is represented fully by analyses now in the literature. For example, Juurinen's analyses nos. 1-5 for typical staurolites show Si between 7.5 and 7.9 atoms per cell, but the sixth analysis for an unusual zincian staurolite gives 8.1 atoms. More extreme values may be possible.

Syntheses of staurolites by Ganguly and Newton (1965) and Richardson (1966) show that Mg is not necessary in staurolite even though natural staurolites contain around 1 atom of Mg per cell. Although there seems no obvious structural reason why staurolite should not exist with the anhydrous composition $\text{Fe}_4\text{Al}_{18}\text{Si}_8\text{O}_{48}$ used by Richardson as a starting composition in syntheses of staurolite, the presence of quartz¹ in the product suggests that a silica-deficient staurolite is formed in preference (note that this composition requires both ferric and ferrous iron). Presumably the presence of protons is essential to the stability of staurolite, and this may be the key to the interpretation of the chemical analyses of natural staurolite. When protons enter the structure, ions of lower val-

¹ R. C. Newton pointed out that the formation of quartz might result from metastable vapor transport of SiO_2 .

ence (or vacancies) must replace ions of higher valence; Al replacing Si, and Mg replacing Al are convenient ways of balancing the charges. Since Mg is commonly available in the rocks from which staurolite crystallizes and since it can substitute for Fe and Al without major changes of bond length, it is not surprising to find significant amounts of Mg in natural staurolite.

Richardson has synthesized staurolites in which the Fe is replaced almost completely by Mg. Those bulk charges more ferroan than the 70 Fe/30 Mg atomic ratio produced quartz as well as staurolite showing that considerations other than simple substitution of Mg for Fe are important. The role of Al in these synthetic Mg-Fe staurolites is not clear though the absence of quartz in products of bulk charges more magnesian than the above ratio might suggest the absence of protons in the synthetic staurolite. However in view of the high water pressure used in the syntheses, and the known occurrence of protons in natural staurolites, it seems likely that protons enter the structure and that there are vacancies in some of the cation positions. It is of interest that the present work indicates a deficiency in the Fe site. Ganguly and Newton on the basis of the pressure variation of the dehydration curve of staurolite have also suggested a cation deficiency for their assumed composition $\text{Fe}_4\text{Al}_{17.48}\text{Si}_8\text{O}_{44.2}(\text{OH})_{3.6}$ for samples synthesized from mixes of composition $\text{Fe}_4\text{Al}_{18}\text{Si}_8\text{O}_{47} + \text{H}_2\text{O}$.

At the present time the content of H in staurolites must be regarded as uncertain because of the possibility of oxidation of Fe^{2+} to Fe^{3+} with concomitant emission of H_2 instead of water during the chemical analysis. It is difficult to see how analyses of H_2O could be too high (except for impure specimens): consequently it seems reasonable to take existing estimates of H as minimum values. Juurinen's values for carefully purified specimens range from 3.2 to 4.5 atoms per unit cell; other values from the literature tend to fall in the same general range though some are considerably lower. It seems likely that the H content of staurolite is well above the value of 2, assumed by Naray-Szabo and Sasvari, and closer to 4. Naray-Szabo and Sasvari proposed that the H atoms occupied the site (0,0,0.5) denoted Al(3B) in the present study. However their analogy with diaspore is untenable because Busing and Levy (1958) showed that the H atoms in diaspore lie 1.0  from the oxygens rather than at the center of the oxygen octahedron. Hanisch's suggestion that the protons in staurolite attach themselves to O(1) seems reasonable in view of the excess of negative charge over valence bonds for this oxygen. However, the complexity of the substitutions in staurolite may require other positions for protons in addition to this one. Careful study of the final (F_0 - F_c) map of staurolite failed to reveal evidence of protons. Particular care

was taken in examination of spherical shells 1 Å in radius about oxygen atoms. The complex peaks at the Fe site may result from interaction of the cations with protons. Peaks labelled *A* and *B* in Figure 1 might result from weaker bonding of the cation to one or other of the two O(1) atoms to which a proton may become attached. The peak labelled *C* might result from repulsion of the cation away from a U site occupied simultaneously with an Fe site, though this possibility of simultaneous occupancy has been downgraded earlier. There are other possibilities, of course;—substitution of Al or Mg on the Fe site might result in significant displacement from the position occupied by the dominant Fe atoms. Another possibility is anisotropic interaction of the outer electrons of Fe with the four oxygen atoms, a possibility made into a probability when protons are available. Since there are only about four H atoms to eight O(1) atoms, either a spatial or a temporal disorder of the protons would be expected. Careful analysis of the appropriate electromagnetic spectra should provide useful information on the protons, as would neutron diffraction data. Concerning the apparent need for protons in the staurolite structure, the most obvious explanation is simply the desirability of a better electrostatic charge balance in the structure than would be provided by cations alone. Calculations show that there is no simple way of adding cations of higher charge to a proton-free staurolite which does not leave a deficiency of valence bonds coming in to the O(1) atom. More sophisticated explanations involving electronic interactions with the transition metal Fe can be invoked, and may indeed have some role.

THE GEOMETRY OF STAUROLITE

Why is staurolite monoclinic and in what way does its structure deviate from orthorhombic symmetry? Perhaps staurolite is monoclinic because there are only four protons per unit cell and these attach themselves to half of the eight O(1) atoms which would otherwise be able to obey orthorhombic symmetry. But this merely changes the question because one then asks why are there only four protons and not eight? It would be possible to balance the extra charges by substitution of ions of lower valence. There is no obvious answer to the question of what causes the symmetry of staurolite, and it is necessary to proceed to the simpler question of how the structure deviates from orthorhombic symmetry.

(After completion of this paper, Hollister and Bence (1967) have obtained X-ray evidence for orthorhombic symmetry of some staurolite. If these results are confirmed, it will be necessary to determine the petrologic distribution of the two types of staurolite. Perhaps staurolite grows initially with orthorhombic symmetry, and subsequently inverts to monoclinic symmetry only under favorable conditions of annealing.)

Examination of Table 2 shows that the major deviations from orthorhombic symmetry are the relative occupancies of Al(3A) and Al(3B) and of U(1) and U(2). The maximum deviation from orthorhombic symmetry would be achieved if Al(3A) were occupied to the exclusion of Al(3B), and similarly for U(1) and U(2). It is possible that this does actually occur and that the occupancies result merely from twinning in (001) of two units each with complete occupancy of Al(3A). The apparent occupancies would then depend on the ratio of the twin volumes (if both sites are partly occupied the apparent occupancies would not be proportional to the twin volumes). One possible test concerns the apparent anisotropy of the electron density distribution. Twinning of atoms like Al(2) which lie near the pseudomirror plane at $z=1/4$ would cause an averaging of the mean coordinate and an elongation of the electron density along the z -axis. Thus the coordinate 0.25122 of Al(2) would result from the averaging of 60 percent of an atom at 0.2537 with 40 percent of atom at (0.50-0.2537) produced by the twin operation (assuming that the occupancies of Al(3A) and Al(3B) are proportional to the twin volumes). The deviation from the plane of symmetry is only 0.02 Å. O(3) has a larger displacement amounting to 0.06 Å. The pairs of atoms O(1A), O(1B) and O(2A), O(2B) would be related similarly. The present structure analysis which proceeded on the assumption that twinning had not occurred would produce an artificial elongation of the electron density along the z -axis. Examination of the final F_o-F_c maps shows positive peaks along the z -axis for Si, Al(2), O(1A), O(1B), and O(3). The peaks are near the noise level for Al(1A) and Al(1B), while there is no positive evidence for such peaks at O(2A), O(2B), O(4) and O(5). For Fe the five-peak pattern would obscure any anisotropic behavior from this cause. The decimal displacements from the $z=1/4$ plane of the positions listed in Table 2 are: Si, 0.00098; Al(1A), 0; Al(1B), 0; Al(2), 0.00122; O(1A) and O(1B), 0.00259; O(2A) and O(2B), 0.00082; O(3), 0.00298; O(4), 0.00002; O(5), 0.00056. Thus exactly those atoms for which major elongations of peaks would be expected do show this effect. However disordered arrays would probably yield similar displacements because the position of an atom is controlled primarily by its nearest neighbors: thus this agreement between prediction and observation is not conclusive evidence of twinning. Optical study of the single crystal used in the X-ray work revealed no evidence of twinning; the extinction was extremely sharp at all magnifications and at all angles of incidence. However the possibility of submicroscopic twinning still remains. The twin law suggested here is additional to those described by Hurst, Donnay and Donnay (1956) which apply to the typical simple contact twins.

Detailed discussion of the shapes of the coordination polyhedra is not

necessary since the relevant information is given in Tables 3 and 4. Briefly all edges shared between the strongly-occupied polyhedra are shortened about 0.2 Å with respect to the average edge. Edges shared between weakly-populated polyhedra are not drastically shortened. One edge is worth specific mention: the O(1A)–O(1B) edge of the Al(2) octahedron is very short (2.43 Å), but is not shared with another polyhedron. The reason seems to be that it together with the O(1A)–O(1B) edge of the Fe tetrahedron (3.23) account for the c repeat (5.66 Å). The latter edge is a little shorter than the average edge length 3.26 Å in the tetrahedron: presumably the c repeat is determined by the sum of many other distances, especially those in the columns of octahedra of type Al(1A) and Al(1B), while the Al(2) octahedron is more easily distorted than the Fe tetrahedron. A reverse situation occurs in olivine where the O(3)–O(3) edge of the M(2) octahedron is abnormally long (3.4 Å) because it plus the O(3)–O(3) edge shared by the M(2) octahedron and the Si tetrahedron (2.6 Å) account for the c repeat of 6.0 Å (Birle, Gibbs, Moore and Smith, in preparation).

Detailed study of the octahedral edges confirms the conclusion by Burnham (1963) that "the minimum-energy configuration of a structure is not primarily dictated by edge-sharing considerations," though these considerations must be of considerable importance.

Although some of the remaining problems such as the location of the protons should be resolved by the application of other techniques including neutron diffraction, there is no simple way apparent at this time for determining with certainty the structural position of the minor elements. Staurolite remains an enigma.

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