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The hydrogen locations and chemical composition of staurolite

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Auszug

Mittels Neutronenbeugung am Staurolith wurden aus *hk*0-Interferenzen die Lagen der Wasserstoff-Atome bestimmt. Aus Untersuchungen über kernmagnetische Resonanz, die Aufschluß über Wechselwirkungen zwischen Proton und Fe^{2+}-Ion vermittelt, folgt, daß die Protonen sich in den vierzähligen Lagen

$$P(1A),\quad x = 0{,}121_8,\quad y = 0,\quad z = 0{,}07_2,$$
$$P(1B),\quad x = 0{,}121_8,\quad y = 0,\quad z = 0{,}42_4$$

befinden. Beim untersuchten Kristall (mit drei H-Atomen in der Formeleinheit) sind somit je Elementarzelle drei Protonen statistisch über acht Plätze verteilt. Sie befinden sich in den Oktaedern um Al(3*A*) und Al(3*B*) in der Nähe der Oktaederflächen durch O(1) und zwei O(3)-Atome [in der Bezeichnung von Smith (1968)], zu denen sie eine schwache, gegabelte Wasserstoffbindung aufweisen.

Es wird versucht, die strukturellen und chemischen Eigenschaften des Stauroliths mit der Anzahl der H-Atome je Elementarzelle in eine allgemeine Beziehung zu bringen.

Abstract

A two-dimensional neutron-diffraction study of staurolite revealed the hydrogen locations in the *c*-axis projection. Hydrogen atoms are in the form of OH at the O(1*A*) and O(1*B*) positions according to the site notation given by Smith (1968), With the aid of nuclear-magnetic-resonance studies, which

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yield an effect of proton-to-Fe^{2+} interactions, and based upon Smith's positional parameters of Fe^{2+}, the hydrogen locations in space have been determined. They are in the two sets of four-fold sites:

$$P(1A),\quad x = 0.121_8,\quad y = 0,\quad z = 0.07_2$$

$$P(1B),\quad x = 0.121_8,\quad y = 0,\quad z = 0.42_4.$$

For the crystal we used, three protons per cell are statistically distributed over the eight positions. The locations are in the oxygen octahedra at the Al(3*A*) and Al(3*B*) sites, but they are nearly in the octahedral faces defined by O(1) and two O(3) atoms. The position of hydrogen atoms is such that a weak bifurcated hydrogen bond occurs between O(1) and two O(3) atoms.

An attempt is made to relate variations in the number of hydrogen atoms per cell to structural and chemical features of staurolite in general.

Introduction

The crystal structure of staurolite was originally determined by Náray-Szabó (1929) based upon an orthorhombic space group *Ccmm* and for $H_8Fe_4Al_{16}Si_8O_{48}$. The unit cell contains one formula unit. Later it became evident that the aluminum content per cell is closer to eighteen rather than the sixteen in the above formula (Skerl, Bannister and Groves, 1934; Juurinen, 1956). On the other hand, Hurst, Donnay and Donnay (1956) observed weak $0kl$ reflections with $l \neq 2n$, which rule out the above space group. Their optical study further revealed that the symmetry of staurolite is, in fact, not orthorhombic but monoclinic with $\beta = 90°$. The probable space group was found to be $C2/m$. In view of these contradictions, Náray-Szabó and Sasvári (1958) reinvestigated the structure by adopting the chemical formula $H_2Fe_4Al_{18}Si_8O_{48}$ and the new monoclinic space group. The result showed that the original structure proposed by Náray-Szabó is essentially correct, the two additional aluminum atoms being distributed over the respective centers of a set of vacant oxygen octahedra of the original structure. In this investigation, they placed hydrogen atoms at the respective centers of another set of vacant octahedra. This is however not in accord with the currently recognized nature of O—H bonds.

More recently, Hanisch (1966) and Smith (1968) refined the structure of staurolite, utilizing modern techniques. Site-occupancy refinement carried out by Smith have made an especially significant contribution towards better understanding of the relationship between the chemical composition and the crystal structure of staurolite. In spite of Smith's thorough refinement, however, the locations of the hydrogen atoms were not detected. Since careful modern x-ray analysis can provide the locations of hydrogen atoms, though with less accuracy, even in silicates having heavy atoms (PREWITT, 1967; PAPIKE *et al.*, 1969; DOLLASE, 1968; TAKÉUCHI *et al.*, 1972), SMITH's result may suggest that hydrogen atoms in staurolite show a statistical distribution. SCHREYER and CHINNER (1966) have suggested a possible substitution scheme $4H^+ \rightleftharpoons Si^{4+}$ on the analogy of hydrogarnet (PABST, 1937). While, based upon considerations of local charge balance, HANISCH (1966) has suggested a set of distinct locations of hydrogen atoms. Thus the locations of hydrogen in staurolite are still left unsolved. Since it is thought that the presence of hydrogen is essential to the stability of staurolite, the problem of locating hydrogen is of the utmost importance.

In order to solve this problem, we have made an attempt to carry out a neutron-diffraction study of staurolite with the result reported in the present paper.

Experimental

Crystals of staurolite were selected from our collection of minerals. Large crystals suitable for our purpose were, unfortunately, of unknown locality. They are untwinned and have a typical habit characteristic of well developed {110} and small {010} faces. The lattice constants determined by x-ray are:

$$a = 7.87_9\ \text{Å},\quad b = 16.63_5\ \text{Å},\quad c = 5.66_4\ \text{Å},\quad \beta = 90°.$$

The space group is $C2/m$.

Microprobe analyses showed that the chemical composition of the specimens is spacially homogeneous, except that, in one crystal we found an inclusion of almandite. The result of the analyses is tabulated in the second column of Table 1. If we assume that the entire 2.02% not otherwise accounted for is due to the H_2O content, the number of hydrogen atoms in the unit cell is calculated to be 3.74 per 48 oxygen atoms. In order to find more accurate value for H_2O and to find the content of Fe^{3+}, a partial chemical analysis was carried out by H. HARAMURA, with the result as listed in the third column of Table 1. Based upon the results obtained by the microprobe analyses and the partial chemical analysis both combined, the number of atoms were calculated for 48 oxygen atoms per cell. This is listed in the fourth column of Table 1. The chemical composition thus derived is very similar to that of Pizzo Forno (Switzerland) specimen (Juurinen, 1956), except lower H_2O content in our specimen, and also to St. Gotthard (Switzerland) specimen which was used for the structure refinement by Smith (1968). The analyses of these specimens are listed in Table 1 for comparison with the present result.

Table 1. *Microprobe and chemical analyses*

	1			2	3
	Microprobe	Partial chemical	Number of atoms calculated for 48 oxygen atoms		
SiO_2	27.70%	*	7.77	26.97%	27.46%
TiO_2	0.65		0.14	0.72	0.58
Al_2O_3	53.51		17.68	54.53	53.94
FeO	13.89	12.42%**	2.91	11.81	12.22
Fe_2O_3		1.29	0.27	1.12	1.16
MnO	0.24		0.05	0.27	0.18
MgO	1.99		0.83	1.91	2.24
H_2O	(2.02)	1.61	3.00		2.37
Total	(100.00)	99.41			100.15

1. Present study.
2. St. Gotthard specimen (Smith, 1968).
3. Pizzo Forno specimen (Juurinen, 1956).

* Values other than those of FeO, Fe_2O_3 and H_2O are taken from the left column.

** Calculated, based upon the $FeO + Fe_2O_3$ value determined by microprobe analysis and the Fe_2O_3 value by partial chemical analysis.

A crystal having dimensions of 6 × 12 × 15 mm on the *a*, *b* and *c* axes respectively was then used for our neutron-diffraction study. Intensities of the *hk*0 zone were measured at Research Reactor Institute, Kyoto University, using a neutron diffractometer. The wavelength used was 1.01 Å. The measured intensities were reduced to structure factors in the usual way. Absorption corrections were neglected. As will be observed later, final agreement between observed and calculated structure factors suggests that possible effect of extinction is not significant. Presumably the crystal is imperfect enough to minimize this effect.

Analysis

Fourier projection

Structure factors were initially calculated using atomic parameters given by SMITH (1968). Since the chemical composition of our specimen is, as mentioned above, quite close to that of SMITH's specimen, atoms were alloted to respective site according to the mode of site-occupancy found by SMITH, except $U(1)$ and $U(2)$ sites. To these particular sites, SMITH located 0.08 (0.68 Fe + 0.32 Mn) and 0.038 (0.68 Fe + 0.32 Mn) respectively. The population of atoms locating in these sites is thus very low. Moreover, for neutron diffraction the scattering amplitude of manganese nuclei is negative in contrast to positive amplitude of iron nuclei. It follows that the effective contributions from these composite atoms to structure factors are further reduced. These sites were therefore not taken into account to our calculation. The coherent scattering amplitudes used are those by SHULL and WOLLAN (1951).

This first calculation gave a residual $R = 0.10$ for 69 observed reflections. A difference-Fourier synthesis, which was then calculated, shows a significant negative peak at $x = 0.121_8$, $y = 0$ (Fig. 1), obviously indicating the location of hydrogen atoms. Since the location in the projection is fourfold, we placed a proton weighted by $3.0 \times \frac{1}{4} = 0.75$ at the center of the negative peak and calculated structure factors, including proton contributions. The result turned out to reduce the value of R to 0.08, justifying the location of protons. The temperature factor of protons used for this calculation was 1.5 Å^2. An attempt was further made to refine the x parameter and the temperature factor of protons by full-matrix least-squares program ORFLS (BUSING *et al.*, 1962), but we failed to obtain a significant result.

Nevertheless, it is now clear that protons are in the form of OH at the O(1) positions according to the notation given by SMITH (1968), and that each O—H bond lies on a mirror plane parallel to (010). This result is consistent with the suggestion made by HANISCH (1966) from a view point of local charge balance. The observed and calculated structure factors are compared in Table 2.

The proton location in the projection, thus revealed, gives the O(1)—H distance as 0.87 Å. Since this value is somewhat smaller than the ordinary O—H bond length 1.00 Å, the z parameters of the protons must be different from those of the O(1) atoms. If we assume the

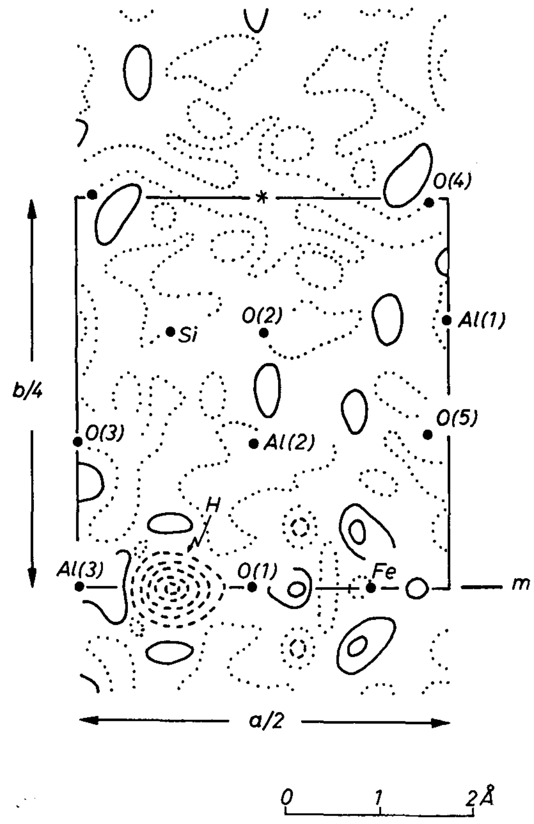

Fig. 1*a*

Fig. 1. (*a*) Difference-Fourier projection on the *c* axis, showing the negative peak of protons. Broken lines indicate negative contours, zero contours being dotted. Atomic sites determined by Smith (1968) are indicated. The mirror plane passing through the origin of the unit cell is indicated by *m*. (*b*) The *b* axis projection of a chain of octahedra formed by oxygen atoms about Al(3*A*) and Al(3*B*) sites. Proton sites and neighbouring atoms are indicated

Table 2. *Observed and calculated structure amplitudes in staurolite*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
4	0	0	25.35	26.18	8	4	0	5.87	- 5.13	8	8	0	0	- 0.52	1	13	0	3.39	3.26
6			3.09	- 1.51	1	5	0	2.98	- 3.24	1	9	0	3.47	- 3.44	3			3.96	3.73
8			26.55	25.60	3			1.08	- 1.50	3			3.92	3.39	5			6.05	7.26
10			4.40	- 2.88	5			0	0.44	5			9.31	10.39	0	14	0	5.32	- 5.40
3	1	0	1.07	- 1.09	7			3.50	- 3.30	7			5.41	- 5.19	2			10.99	-11.43
5			5.53	5.45	9			6.12	- 6.77	9			5.04	5.65	4			3.80	- 4.50
7			0	- 0.15	0	6	0	7.87	6.90	0	10	0	4.67	4.30	6			9.11	-10.05
9			2.94	2.97	2			18.99	-18.56	2			5.47	5.21	1	15	0	0	- 0.03
4	2	0	0	- 0.27	4			1.75	- 1.96	4			3.14	3.40	3			5.71	6.31
6			3.69	- 3.94	6			16.02	-14.35	6			2.80	2.30	5			7.41	9.25
8			1.50	- 1.18	8			8.13	8.47	1	11	0	2.39	- 2.66	0	16	0	6.29	- 6.69
3	3	0	7.32	6.43	1	7	0	4.00	- 3.84	3			2.30	- 2.28	2			4.74	5.28
5			11.91	11.95	3			1.64	- 1.74	5			4.08	4.82	4			5.15	- 6.10
7			4.86	- 4.70	5			0	0.49	7			2.10	- 2.10	1	17	0	5.95	- 6.05
9			4.18	3.85	7			1.07	- 1.60	0	12	0	33.14	31.97	3			3.90	- 4.95
0	4	0	4.40	- 4.45	0	8	0	6.11	5.49	2			1.50	- 1.74	0	18	0	10.01	9.41
2			2.02	1.95	2			2.65	2.53	4			20.25	20.03	2			10.63	-10.64
4			4.92	- 4.64	4			3.53	3.60	6			2.20	- 2.49	1	19	0	4.55	- 4.16
6			0	- 0.27	6			1.52	- 1.42	8			19.63	21.76	0	20	0	12.76	11.84

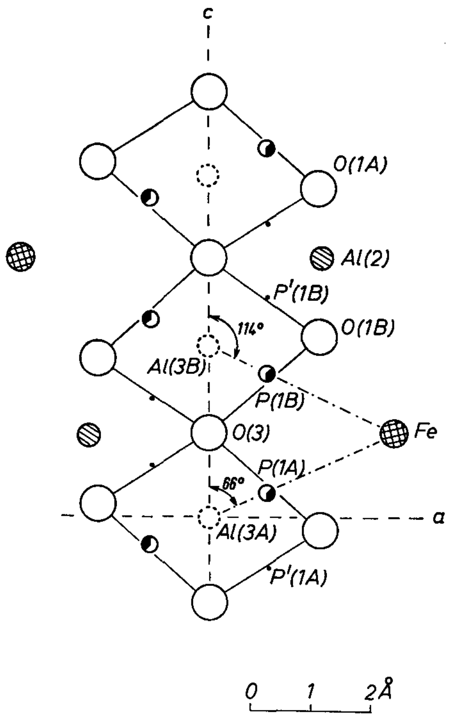

Fig. 1*b*

O—H bond length of 1.00 Å, the possible *z* parameters of the protons can be calculated based upon the above *x* and *y* parameters of the protons and Smith's positional parameters of O(1*A*) and O(1*B*). The possible proton locations in space thus calculated are:

Notation of sites	x	y	z
P(1*A*)	0.1218	0	0.049
P(1*B*)	0.1218	0	0.454
P′(1*A*)	0.1218	0	−0.123
P′(1*B*)	0.1218	0	0.652

Among these, protons in the P′(1) sites are nearly colinear with O(1) and Fe atoms (Fig. 1*b*); moreover they are very close to Al(2), the distance being only 1.8 Å. On the other hand, those in the P(1) sites are almost tetrahedrally coordinated to O(1) together with Al(2) and Fe. Therefore, the sites P(1), namely P(1*A*) and P(1*B*), seem to be the reasonable locations for protons.

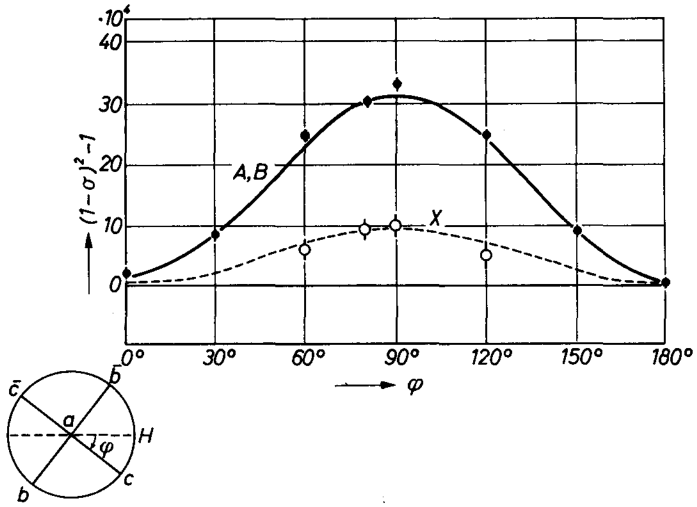

Fig. 2a

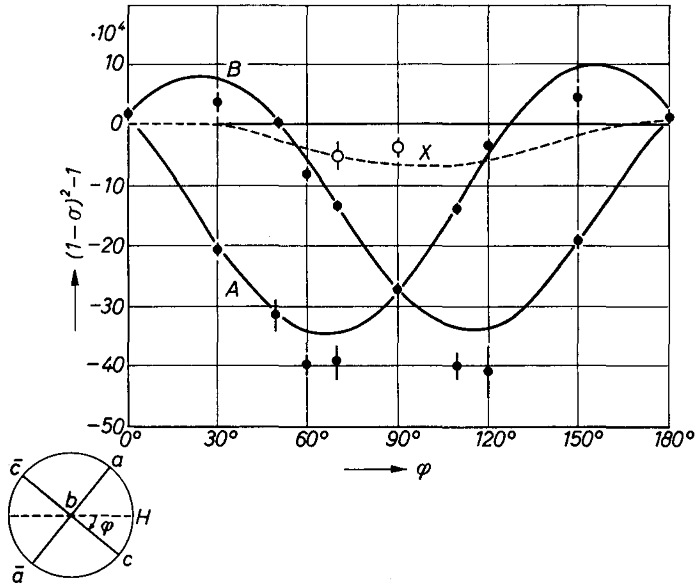

Fig. 2b

Fig. 2. Variations of the paramagnetic shifts of proton nuclear-magnetic resonance spectra as a function of the angular orientations of the specimen with respect to the magnetic field H. (a) [100] $\perp$ H, (b) [010] $\perp$ H, (c) [001] $\perp$ H

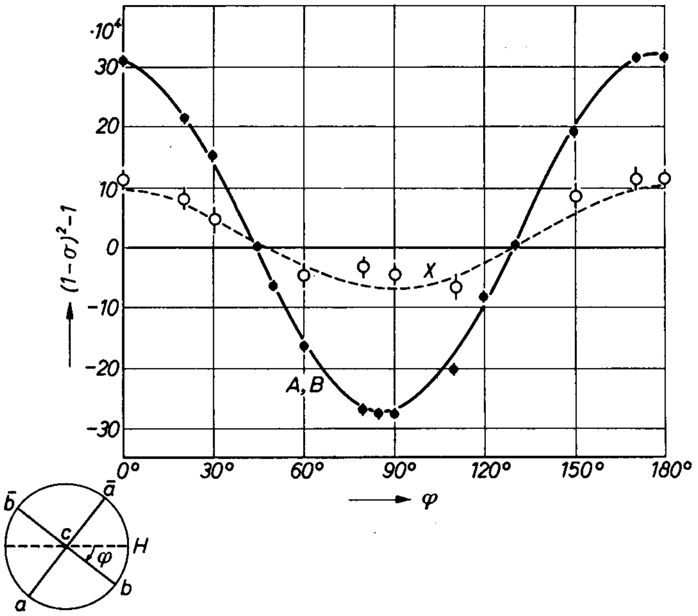

Fig. 2c

Nuclear-magnetic-resonance spectra

In order to confirm the above result, a study of nuclear-magnetic-resonance spectra of staurolite was carried out at the Chemistry Department of the University of Tokyo. Since the OH groups in the O(1) sites are coordinated to Fe^{2+}, it was expected that dipole-dipole interactions between protons and electron spins of the paramagnetic Fe^{2+} ions would yield the proton-to-Fe^{2+} vectors.

The single crystal of staurolite which was used for the neutron work was placed in a static magnetic field so that one of the crystallographic axes was perpendicular to the field, and the crystal was rotated around the axis. At various angular orientations, proton-resonance spectra were recorded. Such a procedure was repeated around each of the three principal crystallographic axes. The resonance frequencies of protons thus recorded indeed show significant shifts, indicating obvious effect of the magnetic dipole of Fe^{2+} spin averaged by a fast electron-spin relaxation. After due computations were made, variations of the magnitudes of the paramagnetic shifts were plotted, for each set of spectra, in a diagram as a function of Φ, the angle between the magnetic field and one of the two axes perpendicular

Table 3. *Parameters of paramagnetic-shift tensors of protons*

Shift tensor		Principal axes (10^2 ppm)	cos (σ_i, a)	cos (σ_i, b)	cos (σ_i, c)
A	σ_1	1.91 ± 0.01	0.91	-0.05	0.40
	σ_2	-1.82 ± 0.01	0.07	0.996	-0.05
	σ_3	-0.47 ± 0.01	-0.40	0.07	0.91
B	σ_1	2.01 ± 0.01	0.91	-0.04	-0.42
	σ_2	-1.82 ± 0.01	0.06	0.998	0.02
	σ_3	-0.54 ± 0.01	0.42	-0.04	0.91
X	σ_1	0.35 ± 0.04	0.99	-0.04	0.11
	σ_2	-0.48 ± 0.04	0.05	0.997	-0.06
	σ_3	-0.05 ± 0.01	-0.10	0.06	0.992

to the rotation axis (Fig. 2). In Fig. 2, it will be observed that there are two kinds of shifts *A* and *B* in the set of spectra around the *b* axis, while they are combined in those around the *a* and *c* axes respectively to give a composite set of shifts. Analyses show that the shifts *A* and *B* respectively yield the shift tensors **A** and **B** as given in Table 3, in which it will be observed that one of the principal axes σ_2 of each of the tensors is parallel to the *b* axis. This is consistent with the fact that each proton is in a mirror plane. Table 3 further shows that the two shift tensors are, within experimental error, mutually symmetrical about a plane parallel to (001). Since the shifts of proton nuclear-magnetic-resonance spectra have been caused by the magnetic dipole of nearest Fe^{2+} ions, the above result suggests that, for a given Fe^{2+} ion in a mirror plane parallel to (010), there is, in the mirror plane, a pair of nearest protons which are symmetrically locating about the plane passing through the Fe^{2+} ion and parallel to (001), Fig. 1*b*.

The two principal axes σ_1 and σ_3 of each of the shift tensors are in a mirror plane parallel to (010). Of the two axes, the axis σ_1 which has the largest value should be directed to the nearest Fe^{2+} ion, provided that effect of anisotropy in the magnetization of Fe^{2+} is negligible. Although the knowledge of the magnetic anisotropy of Fe^{2+} ions in staurolite is not available, we may disregard the anisotropy for such a particular case of staurolite in that Fe ions are tetrahedrally coordinated by oxygen atoms, and the oxygen tetrahedra, having point symmetry *m*, are of fairly regular shape. Thus it seems very probable that the axes σ_1's of the tensors **A** and **B** are closely parallel to the corresponding proton-to-Fe^{2+} vectors. For a given set of crystallographic axes, the directions of σ_1's are compared below with those of the P(1)-to-Fe^{2+} and P′(1)-to-Fe^{2+} vectors.

Vectors	Angles between vectors and the *c* axis	
$\sigma_1(A)$	66.4°	
$\sigma_1(B)$		114.2°
P(1*A*)—Fe	62.1°	
P(1*B*)—Fe		118.5°
P′(1*A*)—Fe	44°	
P′(1*B*)—Fe		136°

As observed in this table, the good agreements in the directions between $\sigma_1(A)$ and *P*(1*A*)—Fe, and $\sigma_1(B)$ and P(1*B*)—Fe, strongly support the view that the sites P(1) are, as we have discussed, the most probable locations for protons in staurolite.

Based upon the *x* coordinate of protons as determined by the neutron-diffraction study and SMITH's coordinates of Fe, the directions of the proton-to-Fe vectors as deduced from the study are now used to calculate the final *z* coordinates of the P(1) sites for protons. They are given below together with *x* and *y* coordinates.

Site	*x*	*y*	*z*
P(1*A*)	0.1218	0	0.072
P(1*B*)	0.1218	0	0.424

The populations of protons at the P(1*A*) and P(1*B*) sites are nearly identical. This is because the corresponding nuclear-magnetic-resonance lines that define the shift-tensors **A** and **B** are of similar intensities. Since both sites are fourfold in the space group of staurolite, the result implies that the three protons in the unit cell are statistically distributed over these two sets of fourfold site with nearly the same occupancy of $3/(4+4) = 0.375$.

In addition to the two kinds of major line shifts, as argued, it appears that in the proton resonance spectra the line shifts of another kind are overlapped. Although the lines that define the shifts are exceedingly broad, the magnitudes of the shifts are estimated to give a shift-tensor **X** as given in Table 3. The variations of the shifts with respect to the magnetic field applied are indicated in Fig. 2 by broken lines. However, the extreme broadness of the lines does not permit conclusive assignment of this kind of shifts.

Hydrogen atoms

Location

The proton locations thus revealed are in oxygen octahedra which are located in two sets of twofold site in the space group $C2/m$: $2a$, 000 and $2c$, $00\frac{1}{2}$. Since the c repeat of staurolite is only 5.66 Å, the octahedra are joined together by sharing edges to form chains parallel to the c axis (Fig. 1b). The protons in the component octahedra of the chains are, however, not at the centers of the octahedra as suggested by NÁRAY-SZABÓ and SASVÁRI (1958) but they are very close to octahedral faces. Deviation from the octahedral faces towards inside of the octahedra is about 0.1 Å.

Hydrogen-bonded system

The O—H bond lengths calculated from the above coordinates of protons and SMITH's coordinates of O(1) are: 1.0_7 Å for P(1A)—O(1A), and 1.0_8 Å for P(1B)—O(1B). The major source of errors in the O—H bond lengths would be the errors in the proton-to-Fe^{2+} directions observed by the nuclear-magnetic-resonance study. Since it is likely that the possible errors in the directions do not exceed ± 5°, the accuracy in the O—H bond lengths will be higher than ±0.10 Å. This estimation of errors is, however, correct only if the shifts of proton resonance spectra have not been seriously perturbed by anisotropic magnetization of Fe^{2+} ions. The P(1A)—O(1A) bond occurs nearly in the triangle defined by O(1A) and two O(3) atoms. Likewise, the P(1B)—O(3) bonds in the triangle defined by O(1B) and two O(3) atoms. The distances between protons and O(3) are 2.0_3 Å for P(1A)—O(3), and 2.0_3 Å for P(1B)—O(3), Fig. 3a. Each O(3) is surrounded by three cations and one proton. The coordination is roughly tetrahedral, Fig. 3b.

It is to be noted that the bond between Si and O(3) has a length of 1.651(2) Å, whereas the lengths of three other bonds are 1.634, 1.637 and 1.641 Å (SMITH, 1968). This significant lengthening of the Si—O(3) bond in contrast to others may be attributed to an influence of neighbouring hydrogen atoms, Fig. 4. Hence it appears that a weak hydrogen bond occurs between hydrogen and O(3). As will be observed in Fig. 3a, the hydrogen bond is bifurcated. The formation of such a weak hydrogen bond in staurolite is consistent with the infrared absorption spectra obtained by HANISCH (1966). He observed an absorption at 3450 cm^{-1} which can be assigned to the O—H stretching

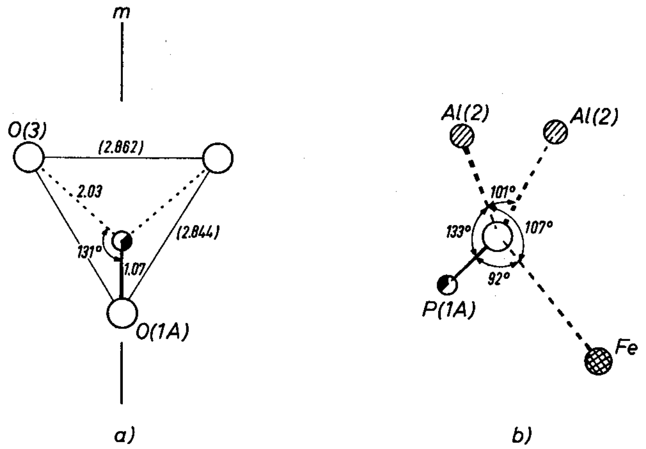

Fig. 3. *a)* The triangle formed by oxygen atoms about the hydrogen atom in the P(1*A*) site. *b)* The tetrahedral coordination about O(1*A*). Atomic distances and bond angles in parentheses are those found by Smith (1968)

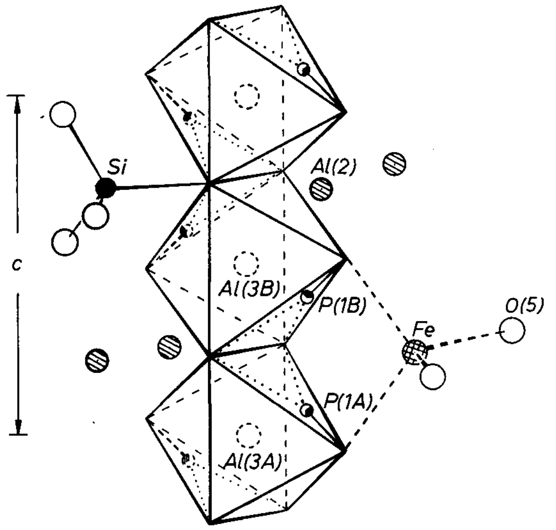

Fig. 4. The linkage of octahedra formed by oxygen atoms about Al(3*A*) and Al(3*B*) sites. One of the adjoining silicon-oxygen tetrahedra and some of the neighbouring cations are shown

mode. In the event that the O—H bonds are stronger, like those of the OH groups which do not form hydrogen bond, they tend to give the absorptions of the mode at larger wave numbers.

The O—H · · · O′ hydrogen-bonded systems terminating in oxygen atoms of silicate radicals have been reported in several silicates. The interatomic distances of some of these bonded systems are compared in Table 4 with those of the staurolite structure. Since most of them are based upon x-ray analysis, the O—H bond lengths have not been determined with required accuracy to discuss their variations. However, an obvious correlation is observed in this table between the O · · · O′ distance of a bonded system and the angle Ψ subtended by the proton and the oxygen O′ at the oxygen O. As has been reported by HAMILTON (1962), the angle becomes smaller with decreasing the O · · · O′ distance. On the other hand, from his investigation of borate structures, ZACHARIASEN (1963) has shown a correlation between the O · · · O′ lengths and strengths of hydrogen-oxygen bonds. Based upon his result, the bond strengths of O—H and H · · · O′ bonds are derived from the O · · · O′ distance of each bonded system in Table 4, and they are respectively compared, in the table, with strengths which are derived, as shown below, simply based upon valencies and coordination numbers of atoms involved in a bonded system.

Let v_i and p_i respectively be the valence and coordination number of a cation of the kind i in a structure. Then in general the strength of a cation-to-oxygen bond is given by a form v_i/p_i as would be true for regular coordinations, provided that second-nearest-neighbour interactions are neglected. If we assign such a strength to each of the bonds between cations (and silicon) and the oxygen O of an O—H · · · O′ bonded-system, and their sum is subtracted from two, the valency of oxygen, the resulting value may be assigned to the O—H bond. This is expressed by

$$\Delta = 2 - \sum_i v_i/p_i$$

where Δ represent the strength of O—H bond. In that event, the strength Δ' between H and O′ is obviously given by

$$\Delta' = 1 - \Delta .$$

As will be observed in Table 4, for each O—H bond, ZACHARIASEN's strength, which is expected to be closer to actual strength, is larger than Δ, and for each H · · · O′ bond it is smaller than Δ', suggesting that the actual value of $\sum_i v_i/p_i$ is smaller for the oxygen atom O, and larger for the oxygen atom O′. This means that, in a bonded system,

Table 4. *Hydrogen-bonded systems* (O—H · · · O′) *terminating in the oxygen atoms of silicate radicals*
The hydrogen-bonded system of diaspore is given for reference. In the fourth column, bond strengths Δ and Δ' (upper) are respectively compared with ZACHARIASEN's value (lower)

	Neighbours and bond lengths		$\Sigma v_i/p_i$ at the oxygen atom O	Bond strength		O · · · O′ distance	Ψ
	around O	around O′		O—H	H · · · O′		
Staurolite	2×Al[6] 1.920 Å	Si[4] 1.651 Å	1.50	0.50	0.25**	2.863 Å	
	Fe[4] 2.046	Al[6] 1.872		0.80	0.10		
		2×Al(Fe)[6] 2.060*					
Axinite[1]	Al[6] 1.950	Si[4] 1.635	1.33	0.67	0.33	2.780	20°
$Ca_2Al_2FeBO(Si_2O_7)_2OH$	1.882	Al[6] 1.945		0.79	0.21		
	Ca[6] 2.568	Ca[6] 2.329					
Diaspore[2]	2×Al[6] 1.980	2×Al[6] 1.851	1.50	0.50	0.50	2.650	12°
AlOOH	Al[6] 1.975	Al[6] 1.858		0.72	0.28		
Pectolite[3]	Si[4] 1.626	Si[4] 1.605	1.50	0.50	0.50	2.482	8°
$Ca_2NaHSi_3O_9$	Na[6] 2.471	Na[6] 2.498		0.59	0.41		
	Ca[6] 2.343	Ca[6] 2.321					
Afwillite[4] $Ca_3(Si_3OH)_2 \cdot 2H_2O$	Si[4] 1.65	Si[4] 1.61	1.62	0.38	0.62	2.56	?
	Ca[7] 2.69	Ca[7] 2.37		0.66	0.34		
	Ca[6] 2.44	H_2O 2.71					
	Si[4] 1.71	Si[4] 1.61	1.33	0.67	0.33	2.49	?
	Ca[6] 2.45	Ca[7] 2.35		0.60	0.40		
		H_2O 2.73					

* Weighted by 0.35. ** Bifurcated.

[1] TAKÉUCHI *et al.* (1972). [2] BUSING and LEVY (1958). [3] PREWITT (1967). [4] MEGAW (1952).

the strengths of cation—O or Si—O bonds tend to be smaller than those of cation—O′ of the same kind or Si—O′ bonds. In conformity with this, we observe in this table that at least one of the cation—O lengths or Si—O lengths in a bonded system is longer than the lengths of cation—O′ bonds of the same kind or Si—O′ lengths. This trend is evident especially if the difference between Zachariasen's O—H (or H ⋯ O′) bond strength and Δ (or Δ') is larger.

The chemical composition

Chemical analyses of staurolite show that the number of hydrogen atoms in the unit cell varies from around two to around four. Based upon the knowledge of hydrogen locations, this variety of hydrogen content in staurolite can now be interpreted from structural viewpoint.

The unit cell contains four octahedra which can accommodate protons, and each of the octahedra may contain two protons nearly in a pair of octahedral faces. It follows that in the unit cell eight locations are available for protons. On the other hand, at the centers of the four octahedra, octahedral cations like Al and Fe are statistically located as shown by Smith (1968). Since however each octahedron obviously can not accommodate both protons and octahedral cations simultaneously, the following relation holds between the number m of protons and the number n of the cations in the set of octahedra:

$$m \leq 8 - 2n .$$

This means that if two cations are distributed over the octahedral sites, the number of protons should not exceed four. Or, if three protons are present, the maximum number of aluminum atoms in the octahedra can not exceed 2.5. Thus, if we put

$$m = 8 - 2n, \tag{1}$$

this relation defines the upper limit for m with respect to a given number n, or vice versa.

Although we assumed in the above consideration a statistical distribution of protons with entirely equal weight, it is conceivable that for a given location of a proton there are some preferences of locating neighbouring protons. As the matter of fact, according to Smith (1968), the octahedral sites Al($3A$) and Al($3B$) are respectively occupied by 0.83 Al(Fe) and 0.56 Al(Fe). If this is correct, it is likely that the probabilities of locating protons at the P($1A$) and P($1B$)

sites could be different. Such a possible difference is, however, not essential within the scope of present paper.

We shall next consider the numbers m and n from different view point. Let R be the cations distributing over the sites Al($3A$) and Al($3B$). Then the chemical composition of staurolite may be given by the following simplified form:

$$[H_mR_n]^{q+}\,[Fe_4Al_{16}Si_8O_{48}]^{q-},$$

in which q represents the charge determined by the total elements in the right brackets. The number m of hydrogen and the number n of R may vary so as to satisfy the value of q. For this particular formula, q has the value of 8. Therefore, if R is entirely aluminum atoms, the relation between m and n is given by

$$m + 3n = 8 \qquad \text{or} \qquad m = 8 - 3n. \tag{2}$$

If R is not entirely aluminum atoms but contains divalent atoms like Fe^{2+} to some extent, the line defined by (2) is shifted, in an m vs n diagram, towards the line as defined by (1).

It should be noted however, the chemical analyses of staurolite have revealed that aluminum atoms are, without exception, replaced by divalent Mg atoms by considerable amount, and Si^{4+} by Al^{3+} to some extent. It follows that for the actual chemical composition of staurolite, the value of q is always larger than 8. Consequently, the relation (2) defines the lower limit of m with respect to a given n, or vice versa. This is expressed by

$$m \geq 8 - 3n. \tag{3}$$

Since it has so far been known that the hydrogen content in the unit cell of staurolite is larger than around 2.0 and smaller than 5.0, we may put

$$2.0 \leq m \leq 5.0. \tag{4}$$

The relations (1), (2) and (4) now define in an m vs n diagram an area as shown in Fig. 5, giving a restriction to the variation of hydrogen content with respect to a cation content in the sets of octahedra under consideration.

In order to see the validity of the above hypothesis for staurolite in general, we must find the way to estimate the number n of cation R for a given composition of staurolite. This can be done based upon the mode of site occupancy in staurolite which has been elucidated

Table 5. *Site contents of staurolite*

Site	Contents found by Smith					Number of equivalent positions per cell		Assumed contents
				Total				
Fe	2.35 Fe	1.17 Al	0.15 Ti	3.67		4		3.7
Si	7.42 Si	0.51 Al		7.93		8		8.0
Al(1*A*)	3.71 Al	0.19 Mg		3.90	15.67	4	16	15.7
Al(1*B*)	3.71 Al	0.20 Mg		3.91		4		
Al(2)	7.47 Al	0.39 Mg		7.86		8		
U(1)	0.11 Fe	0.05 Mn		0.16	0.24	2		0.2
U(2)	0.06 Fe	0.02 Mn		0.08		2		
Al(3*A*)	0.55 Al	0.28 Fe		0.83		2		
Al(3*B*)	0.37 Al	0.19 Fe		0.56		2		

by Smith (1968). The number of atoms locating at each site is listed in Table 5. If we exclude the cation sites Al(3*A*) and Al(3*B*), and proton sites, twenty-eight sites are available to locate cations in the unit cell of staurolite. However, it is observed in Table 5 that the occupancy in the Fe site is considerably deficient by about eight per cent. Those of the Al(1*A*), Al(1*B*) and Al(2) sites are also slightly deficient by about two per cent. In addition to these twenty-eight sites, very small amount of Fe and Mn are, according to Smith, locating at octahedral sites U(1) and U(2) which share faces with the Fe tetrahedra. As will be discussed later, it is very likely that such a distribution of vacancies over cation sites is not only particular to Smith's specimen but is a general feature characteristic of staurolite. Then if the number of atoms at each site found by Smith is rounded off to the corresponding number as shown in the last column of Table 5, we obtain, instead of twenty-eight, a total of $3.7 + 8.0 + 15.7 + 0.2 = 27.6$ atoms.

Although in this treatment the assignment of the small number of atoms to the U(1) and U(2) sites appears to be inconclusive, it is based upon the following consideration. If the tetrahedral site Fe and either one of the octahedral sites U(1) and U(2) are occupied simultaneously, the tetrahedron and octahedron share faces. Since presence of face sharing would seem to be unlikely, for the occupancy of 3.7 in the Fe site, the U(1) and U(2) sites both together can accommodate only up to 0.3 atoms. According to Smith's result, 0.24 atoms are locating in the U sites. We therefore assumed, for our purpose, 0.2 atoms in the sites. Thus, if the 27,6 atoms are subtracted from total number of atoms (excluding hydrogen atoms) derived from a chemical analysis, the result would give the number n for cations locating in the Al($3A$) and Al($3B$) sites. This is expressed by

$$n \approx N - 27.6 \tag{5}$$

in which N represents a total number of tetrahedral and octahedral cations in the unit cell.

Based upon chemical analyses of staurolite from various localities, we calculated the value of n for each staurolite and made a plot in an m-vs-n diagram (Fig. 5). As will be seen in this diagram, all dots, each of which is defined by a pair of the m and n values for a composition, fall in the area defined previously. This agreement will strongly support the validity of the relation (1) that was derived based upon proton locations, and also will justify the assumption that the distribution of vacancies over the Fe, Al($1A$), Al($1B$) and Al(2) sites is a feature characteristic of staurolite. If vacancies were not present at the Fe and the Al sites but twenty-eight cation sites were fully occupied, the relation corresponding to (5) would be given by $n = N - 28$. In that event, several dots in the diagram are considerably shifted beyond the line $m = 8 - 3n$ to the left. This contradicts the relation (3).

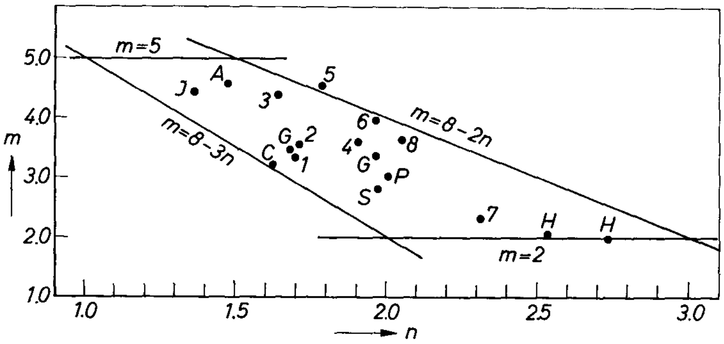

Fig. 5. Relation between the number of hydrogen atoms and that of cations in the Al(3) sites. 1–8: The numbering corresponds to that of the eight chemical analyses listed by **Deer** *et al.* (1962), *A*: **Uruno** and **Kanisawa** (1965), *C*: **Chinner** (1965), *G*: **Green** (1963), *H*: **Hollister** (1970), *J*: **Juurinen** (1956). *P*: Present work, *S*: **Schreyer** and **Chinner** (1966)

In the diagram, only one dot labelled by 5 is locating slightly over the limiting line as defined by the relation (1). Though this deviation is within the error in the approximation made to derive the relation (5), it should be noted that purity of the specimen is uncertain because it contains K_2O, Na_2O, P_2O_5 and S.

Remarks on the distribution of Fe^{2+} ions

The fact that the Fe site is occupied by only 77 per cent of Fe^{2+}, and that the site is deficient by about eight per cent, would suggest the complexity of charge balance in the staurolite structure. Since two of the oxygen atoms around the Fe site are those to which protons may come to attach, the complexity in the atomic occupancy in the site is obviously related to the location of protons. On the other hand, the deficiency of Fe^{2+} in the Fe site is eventually one of the governing factors to legitimate relation (5). In order to confirm this salient chemical feature of staurolite, Mössbauer measurements were made on our own specimen.

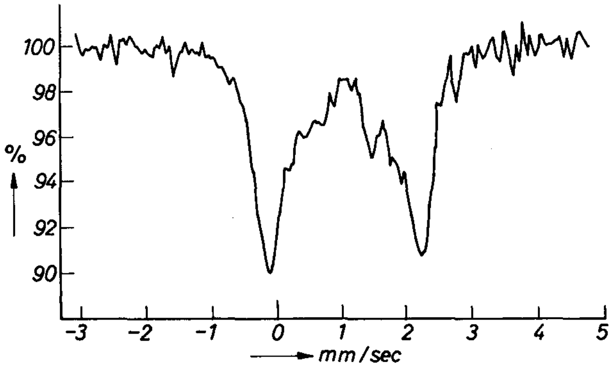

Fig. 6. The Mössbauer spectrum of Fe^{57} atoms in staurolite. The spectrum was taken with the Co^{57} in Cu source

A gamma-ray resonance spectrum as given in Fig. 6 shows a pattern which is similar to that obtained by Smith (1968). The parameters for the principal pair of peaks are: isomer shift, 0.98 mm/sec and quadrupole splitting, 2.41 mm/sec. The corresponding values reported by Smith are respectively 0.74 mm/sec and 2.33 mm/sec. The pair of principal absorptions, which is assigned to Fe^{2+} ion in the Fe site, is associated with ill-defined shoulders of smaller separation. Although we did not carry out further detailed analysis of this pattern, it obviously indicates that about 20% of Fe^{2+} are in the locations other than the Fe site. Similar results have also been reported by Bancroft *et al.* (1967). It is therefore very likely that the deficiency of Fe^{2+} in the Fe site is a general feature characteristic of the staurolite structure.

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