

The hydrogen locations and chemical composition of staurolite

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Auszug

Mittels Neutronenbeugung am Staurolith wurden aus $hk0$ -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(3A) und Al(3B) 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(1A) and O(1B) 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-Fe²⁺ interactions, and based upon SMITH's positional parameters of Fe²⁺, 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(3A) and Al(3B) 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 H₈Fe₄Al₁₆Si₈O₄₈. 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 $\beta = 90^\circ$. 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 H₂Fe₄Al₁₈Si₈O₄₈ 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 $4\text{H}^+ \rightleftharpoons \text{Si}^{4+}$ 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:

$$a = 7.87_9 \text{ \AA}, b = 16.63_5 \text{ \AA}, c = 5.66_4 \text{ \AA}, \beta = 90^\circ.$$

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 H₂O 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 ₂ O ₃	53.51		17.68	54.53	53.94
FeO	} 13.89	12.42%**	2.91	11.81	12.22
Fe ₂ O 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 ₂ O	(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, Fe₂O₃ and H₂O are taken from the left column.

** Calculated, based upon the FeO + Fe₂O₃ value determined by microprobe analysis and the Fe₂O₃ 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 *hk0* 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 allotted 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 \AA^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

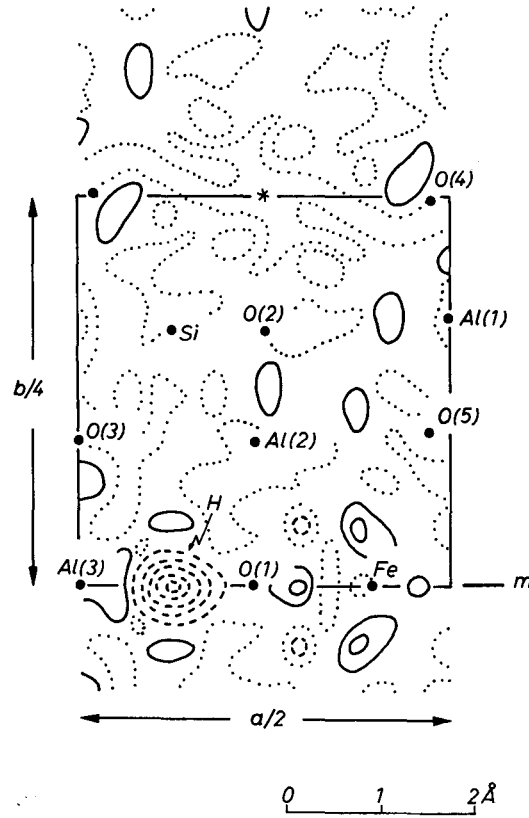


Fig. 1a

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(3A) and Al(3B) 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	-0.52		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

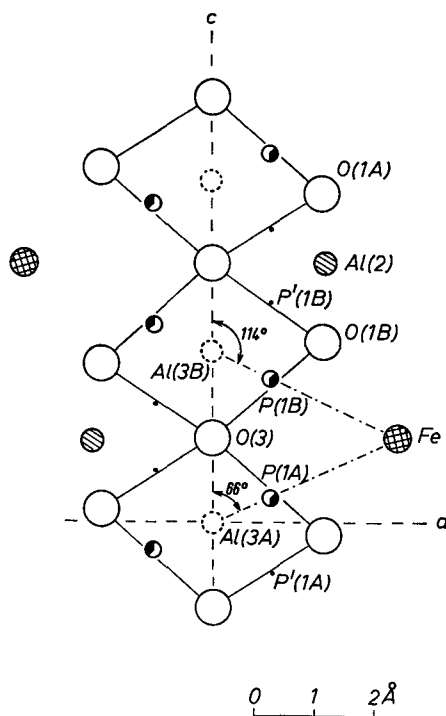


Fig. 1b

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(1A) and O(1B). The possible proton locations in space thus calculated are:

Notation of sites	x	y	z
P(1A)	0.1218	0	0.049
P(1B)	0.1218	0	0.454
P'(1A)	0.1218	0	-0.123
P'(1B)	0.1218	0	0.652

Among these, protons in the P'(1) sites are nearly colinear with O(1) and Fe atoms (Fig. 1b); 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(1A) and P(1B), seem to be the reasonable locations for protons.

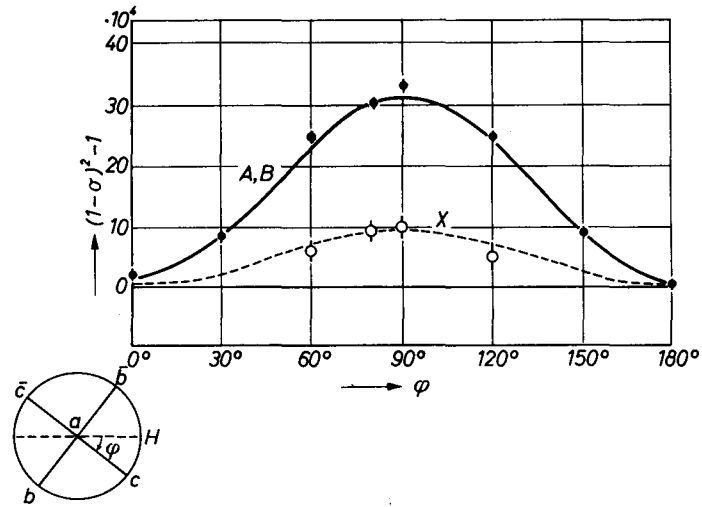


Fig. 2a

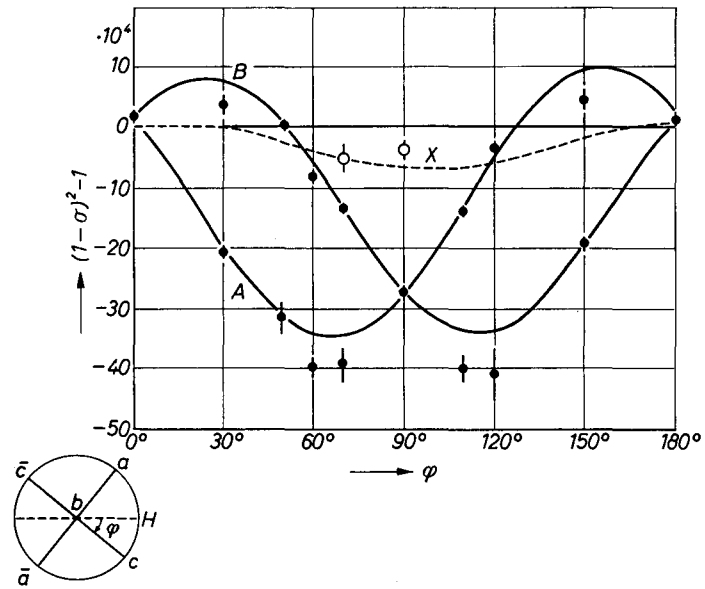


Fig. 2b

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) $[001] \perp H$

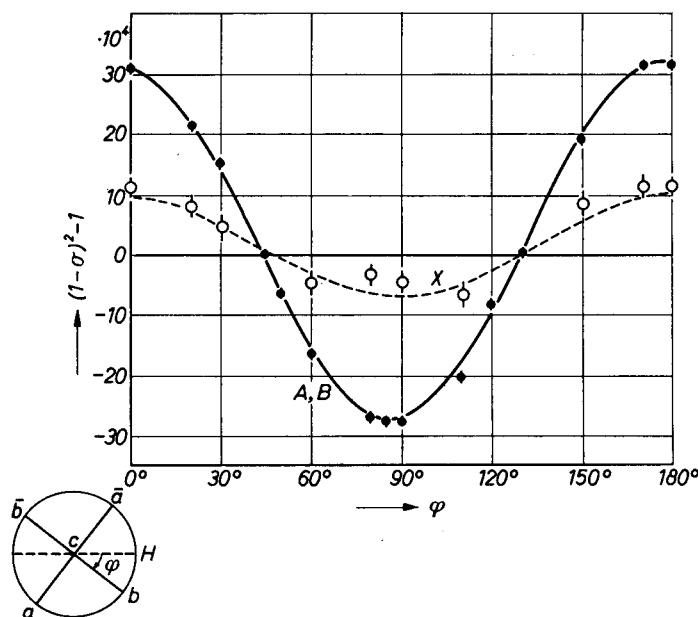


Fig. 2c

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 \pm 0.01	0.91	-0.05	0.40
	σ_2	-1.82 \pm 0.01	0.07	0.996	-0.05
	σ_3	-0.47 \pm 0.01	-0.40	0.07	0.91
B	σ_1	2.01 \pm 0.01	0.91	-0.04	-0.42
	σ_2	-1.82 \pm 0.01	0.06	0.998	0.02
	σ_3	-0.54 \pm 0.01	0.42	-0.04	0.91
X	σ_1	0.35 \pm 0.04	0.99	-0.04	0.11
	σ_2	-0.48 \pm 0.04	0.05	0.997	-0.06
	σ_3	-0.05 \pm 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 Fe²⁺ ions, the above result suggests that, for a given Fe²⁺ 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 Fe²⁺ 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 Fe²⁺ ion, provided that effect of anisotropy in the magnetization of Fe²⁺ is negligible. Although the knowledge of the magnetic anisotropy of Fe²⁺ 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-Fe²⁺ vectors. For a given set of crystallographic axes, the directions of σ_1 's are compared below with those of the P(1)-to-Fe²⁺ and P'(1)-to-Fe²⁺ vectors.

Vectors	Angles between vectors and the <i>c</i> axis	
$\sigma_1(A)$	66.4°	114.2°
$\sigma_1(B)$		
P(1 <i>A</i>)—Fe	62.1°	118.5°
P(1 <i>B</i>)—Fe		
P'(1 <i>A</i>)—Fe	44°	136°
P'(1 <i>B</i>)—Fe		

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	<i>x</i>	<i>y</i>	<i>z</i>
P(1 <i>A</i>)	0.1218	0	0.072
P(1 <i>B</i>)	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 \AA , the octahedra are joined together by sharing edges to form chains parallel to the c axis (Fig. 1*b*). 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 \AA .

Hydrogen-bonded system

The O—H bond lengths calculated from the above coordinates of protons and SMITH's coordinates of O(1) are: 1.07 \AA for P(1*A*)—O(1*A*), and 1.08 \AA for P(1*B*)—O(1*B*). The major source of errors in the O—H bond lengths would be the errors in the proton-to-Fe²⁺ directions observed by the nuclear-magnetic-resonance study. Since it is likely that the possible errors in the directions do not exceed $\pm 5^\circ$, the accuracy in the O—H bond lengths will be higher than $\pm 0.10 \text{ \AA}$. This estimation of errors is, however, correct only if the shifts of proton resonance spectra have not been seriously perturbed by anisotropic magnetization of Fe²⁺ ions. The P(1*A*)—O(1*A*) bond occurs nearly in the triangle defined by O(1*A*) and two O(3) atoms. Likewise, the P(1*B*)—O(3) bonds in the triangle defined by O(1*B*) and two O(3) atoms. The distances between protons and O(3) are 2.03 \AA for P(1*A*)—O(3), and 2.03 \AA for P(1*B*)—O(3), Fig. 3*a*. Each O(3) is surrounded by three cations and one proton. The coordination is roughly tetrahedral, Fig. 3*b*.

It is to be noted that the bond between Si and O(3) has a length of $1.651(2) \text{ \AA}$, whereas the lengths of three other bonds are 1.634 , 1.637 and 1.641 \AA (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. 3*a*, 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

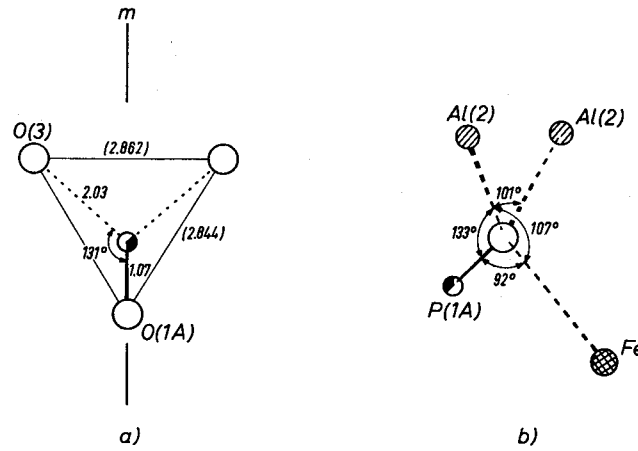


Fig.3. *a)* The triangle formed by oxygen atoms about the hydrogen atom in the P(1*A*) site. *b)* The tetrahedral coordination about O(1*A*). Atomic distances and bond angles in parentheses are those found by SMITH (1968)

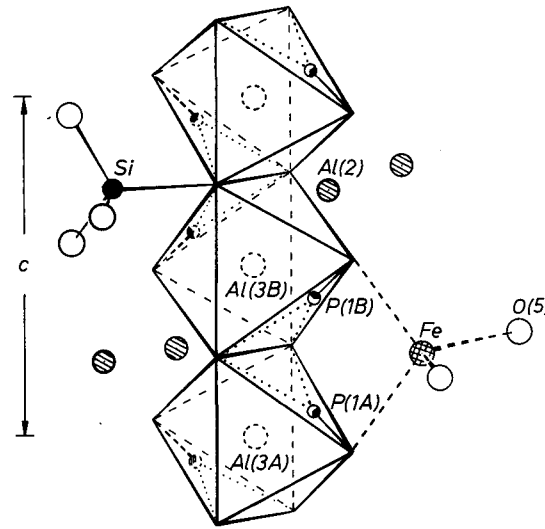


Fig.4. The linkage of octahedra formed by oxygen atoms about Al(3*A*) and Al(3*B*) sites. One of the adjoining silicon-oxygen tetrahedra and some of the neighbouring cations are shown

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.