THE CRYSTAL CHEMISTRY OF STAUROLITE

by

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I. INTRODUCTION

For many years the chemical composition and crystal structure of staurolite have been subjects of debate. The structure determination by Naray-Szabo (1929) was based on space group *Ccmm*, whereas Hurst *et al.* (1956) determined from morphological and optical evidence that staurolite is monoclinic. Hanisch (1966) refined the structure of a zincian staurolite and reported it to be orthorhombic (*Ccmm*). Since then very weak 0*kl* (*l* odd) reflections have been observed by single crystal methods in a ferroan staurolite (Smith, 1968). This staurolite showed slight but significant deviation from orthorhombic symmetry in both positional parameters and site occupancies, indicating that its space group is *C*2/*m*. More recently, Dollase and Hollister (1969) suggested that the intensities of the 0*kl* (*l* odd) reflections indicate the degree of cation ordering in the pseudo-equivalent Al(3A) and Al(3B) sites (cf. Smith, 1968) and are therefore a measure of the deviation from orthorhombic symmetry.

Our understanding of the chemistry of staurolite has been complicated by three major factors: (1) the uncertainty in chemical analyses with respect to H_2O content, (2) the uncertainty regarding the valence state of Fe and (3) the existence of several partially-occupied cation sites in the structure (Smith, 1968). These factors have led to difficulty in specifying the chemical formula and have precluded unequivocal site assignments for the major cations. In a comprehensive study of staurolite chemistry, Juurinen (1956) postulated an over-simplified formula ($H_4Fe_4Al_{18}Si_8O_{48}$) deduced from six wet chemical analyses; Smith (1968) suggested a more generalized formula -- "(7 octahedral sites, principally Al)$_{\sim 18}$(1 tetrahedral site, principally Fe)$_{\leqslant 4}$(1 tetrahedral site, principally Si)$_8$O$_{48}$H$_{\sim 4}$" -- but he was unable to make absolute site assignments on the basis of x-ray data because some sites are only partly filled and the chemical substituents are numerous.

The present study was undertaken (1) to establish chemical and lattice parameter ranges for natural staurolites from many localities, (2) to amend the relationship between optical properties and composition, (3) to further elucidate the unit cell H^+ content, and (4) to investigate the problem of assigning atomic species to the octahedral "Al" and the tetrahedral "Fe" and "Si" sites. Ganguly (1972) has recently stated that ". . . no convincing evidence has yet been mustered to discount the idealized stoichiometry of staurolite [i.e., $Fe_4Al_{18}Si_8O_{46}(OH)_2$], at least as a limiting composition." In this paper we will present experimental evidence to contest this idealized formula; our results confirm the general formula suggested by Smith (1968).

II. EXPERIMENTAL PROCEDURES

Microprobe Analyses

The twenty specimens listed in Table 1 were analyzed with an ARL microprobe, using the EMPADR VII computer program (Rucklidge and Gasparrini, 1969) for data reduction. The elements Co, Zn, Cr, and V were found in nearly all specimens in statistically significant amounts; Ni, Cu and Ca were not detected at the 0.01 wt. % level.

Lattice Parameters

Unit cell parameters were obtained from x-ray powder patterns for the fifteen specimens for which sufficient material was available. The patterns were recorded on a Norelco diffractometer using monochomatized CuK_α radiation, a 0.2° receiving slit, a diffractometer speed of 0.25°2θ/min. and a chart speed of 1"/min. The internal standard chosen was CaF_2, twice annealed for one hour at 800°C (a = 5.4633Å). Peaks were indexed with reference to the calculated powder patterns of Borg and Smith (1969). The least-squares program of Evans *et al.* (1963) was then used to refine the lattice parameters. Unit weights were assigned to all reflections; alternative weighting schemes were tested with virtually no differences in the results.

Since staurolite is pseudo-orthorhombic ($C2/m$; $\beta = 90°$), many of the powder diffraction peaks correspond to planes whose Bragg diffraction indices could be either hkl or $\bar{h}kl$, or $h0l$ or $\bar{h}0l$. The powder pattern calculated using Smith's (1968) data (Borg and Smith, 1969) indicates approximately equal intensities for both peaks of such pairs; therefore,

TABLE I. CHEMICAL ANALYSES AND LATTICE PARAMETERS OF STAUROLITES

Specimen No.	1	2	3	4	5	6	7	8	9	10	11
Original No.[1]	VPI&SU	VPI&SU	VPI&SU	VPI&SU	M-1	H-NH-2	H-GS	H-NS-JF-14	H-4-66-DB	USNM-117189	USNM-78332
Locality	Pizzo Forno, Switzerland	Fannin Co., Ga.	unknown	unknown	Cherokee Co., Ga.	Littleton, N.H.	Gassetts, Vt.	Jordan Falls, Nova Scotia	Reynolds Bridge, Conn.	Stratford, N.C.	Taganay Mt., Urals, USSR

WEIGHT PERCENT OXIDES

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	27.81	27.78	28.14	27.61	27.49	27.97	28.66	27.78	27.83	27.93	27.52
TiO_2	0.57	0.53	0.63	0.55	0.53	0.55	0.57	0.43	0.68	0.53	0.48
Al_2O_3	53.18	52.79	52.71	52.11	51.94	53.31	52.47	54.28	54.10	52.12	53.40
Cr_2O_3	0.00	0.03	0.03	0.02	0.02	0.04	0.05	0.03	0.05	0.03	0.03
FeO	12.91	14.26	13.24	14.66	14.54	14.66	13.80	14.86	13.62	9.40	14.44
MnO	0.21	0.05	0.02	0.14	0.10	0.09	0.01	0.24	0.05	0.11	0.05
ZnO	0.27	0.25	0.12	0.30	0.34	0.25	0.56	0.13	0.71	6.86	0.06
CoO	0.01	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.02
MgO	2.21	1.72	2.72	2.15	2.52	1.74	2.27	1.50	1.57	1.98	1.72
V_2O_5	0.03	0.06	0.05	0.04	0.04	0.05	0.04	0.04	0.07	0.05	0.06
Total	97.21	97.50	97.67	97.60	97.54	98.48	98.75	99.31	98.70	99.03	97.78

ATOMS PER UNIT CELL, NORMALIZED TO 44(O)+4(OH)

	1	2	3	4	5	6	7	8	9	10	11
Si	7.752	7.766	7.809	7.740	7.713	7.746	7.911	7.661	7.674	7.791	7.670
Ti	0.119	0.111	0.131	0.116	0.112	0.115	0.118	0.089	0.141	0.111	0.101
Al	17.472	17.393	17.239	17.218	17.175	17.400	17.071	17.595	17.583	17.136	17.541
Cr	0.000	0.007	0.007	0.004	0.004	0.009	0.011	0.007	0.011	0.007	0.007
Fe	3.010	3.334	3.073	3.437	3.412	3.349	3.186	3.418	3.141	2.193	3.366
Mn	0.050	0.012	0.005	0.033	0.024	0.021	0.002	0.056	0.012	0.026	0.012
Zn	0.056	0.052	0.025	0.062	0.070	0.051	0.175	0.026	0.145	1.413	0.012
Co	0.002	0.004	0.002	0.004	0.004	0.004	0.002	0.004	0.004	0.002	0.004
Mg	0.918	0.717	1.125	0.898	1.054	0.718	0.934	0.615	0.645	0.823	0.715
V	0.006	0.011	0.009	0.007	0.007	0.009	0.007	0.007	0.013	0.009	0.011
H_2O (calc.)	1.92	1.91	1.92	1.90	1.90	1.91	1.91	1.91	1.91	1.89	1.91

LATTICE PARAMETERS

	1	2	3	4	5	6	7	8	9	10	11
No. of peaks	73		53	53	46	50	47	43		72	47
a(Å)	7.870(1)		7.870(1)	7.875(1)	7.876(1)	7.870(2)	7.870(1)	7.873(1)		7.866(1)	7.869(1)
b(Å)	16.612(1)		16.623(2)	16.627(1)	16.630(1)	16.631(2)	16.623(1)	16.620(1)		16.606(1)	16.624(2)
c(Å)	5.657(1)	n.d.[3]	5.657(1)	5.658(1)	5.663(1)	5.660(1)	5.664(1)	5.664(1)	n.d.	5.657(1)	5.662(1)
β(°)	90.00(1)		90.00(1)	90.00(2)	90.00(1)	90.01(3)	90.00(2)	90.00(1)		90.00(1)	90.04(2)
Volume (Å^3)	739.58(8)		740.08(9)	740.84(10)	741.76(7)	740.86(17)	740.95(8)	741.04(11)		738.88(5)	740.69(12)

TABLE I, CONTINUED

Specimen No.	12	13	14	15	16	17	18	19	20	J-2	J-6
Original No.	USNM-12517	USNM-117183	USNM-119551	USNM-119034	USNM-36764	USNM-B14039	USNM-17935	USNM-106038	VPI&SU	J-2	J-6
Locality	St. Gotthard Switzerland	Fannin Co., Ga.	Mitchell Co., N.C.	Copperhill, Tenn.	Windham, Me.	Petersdorf, Czech.	Fannin Co., Ga.	Macon Co., Ga.	Galax, Va.	Pizzo Forno, Switzerland	Cherokee Co., Ga.

WEIGHT PERCENT OXIDES

	12	13	14	15	16	17	18	19	20	J-2	J-6
SiO_2	28.28	27.91	28.34	28.35	27.89	27.70	28.00	27.28	28.07	26.46	28.64
TiO_2	0.60	0.60	0.69	0.61	0.59	0.47	0.47	0.35	0.56	0.58	0.56
Al_2O_3	53.27	53.18	53.06	53.44	53.99	53.78	53.18	54.97	53.94	53.94	50.14
Cr_2O_3	0.01	0.07	0.03	0.01	0.07	0.02	0.02	0.00	0.01	n.d.[3]	n.d.
FeO	13.23	13.80	14.03	13.23	14.11	15.77	14.10	10.19	12.78	13.26[2]	7.94[2]
MnO	0.22	0.22	0.03	0.17	0.10	0.13	0.37	0.34	0.08	0.18	0.16
ZnO	0.23	0.23	0.11	0.24	0.16	0.01	0.22	3.30	0.13	n.d.	7.44
CoO	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	n.d.	n.d.
MgO	2.28	2.15	2.32	2.39	1.71	0.92	1.94	2.79	2.15	2.24	3.44
V_2O_5	0.04	0.06	0.06	0.05	0.06	0.05	0.04	0.02	0.04	n.d.	n.d.
Total	98.19	98.24	98.69	98.50	98.72	98.88	98.35	99.26	97.77	97.78	98.40

ATOMS PER UNIT CELL, NORMALIZED TO 44(O)+4(OH)

	12	13	14	15	16	17	18	19	20	J-2	J-6
Si	7.811	7.733	7.808	7.802	7.689	7.677	7.760	7.482	7.756	7.620	8.025
Ti	0.125	0.125	0.143	0.126	0.122	0.098	0.098	0.072	0.116	0.121	0.118
Al	17.341	17.365	17.229	17.334	17.542	17.566	17.370	17.770	17.565	17.641	16.559
Cr	0.007	0.015	0.007	0.002	0.015	0.004	0.004	0.000	0.002	n.d.	n.d.
Fe	3.056	3.197	3.233	3.045	3.253	3.655	3.268	2.337	2.953	3.077[2]	1.861[2]
Mn	0.051	0.052	0.007	0.040	0.023	0.031	0.087	0.079	0.019	0.054	0.038
Zn	0.047	0.047	0.022	0.049	0.033	0.002	0.045	0.668	0.027	n.d.	1.539
Co	0.002	0.002	0.002	0.002	0.002	0.004	0.004	0.002	0.002	n.d.	n.d.
Mg	0.939	0.888	0.953	0.980	0.703	0.380	0.801	1.141	0.885	0.926	1.437
V	0.007	0.011	0.011	0.009	0.011	0.009	0.007	0.004	0.007	n.d.	n.d.
H_2O (calc.)	1.92	1.91	1.92	1.92	1.92	1.90	1.91	1.91	1.93	1.92	1.89

LATTICE PARAMETERS

	12	13	14	15	16	17	18	19	20	J-2	J-6
No. of peaks		80	62		40	77		72	56	50	51
a(Å)		7.874(1)	7.873(1)		7.868(1)	7.865(1)		7.879(1)	7.871(1)	7.874(1)	7.876(1)
b(Å)		16.624(1)	16.627(1)		16.621(1)	16.633(1)		16.600(1)	16.619(1)	16.616(1)	16.626(1)
c(Å)	n.d.	5.660(1)	5.659(1)	n.d.	5.660(1)	5.662(1)	n.d.	5.656(1)	5.656(1)	5.658(1)	5.660(1)
β(°)		90.00(1)	90.00(1)		90.00(1)	90.00(1)		90.00(1)	90.00(2)	90.00(1)	90.00(1)
Volume (Å)^3		740.88(5)	740.80(8)		740.15(9)	740.72(7)		739.76(6)	739.85(11)	740.24(9)	740.96(7)

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[1] USNM = U.S. National Museum; H = Dr. D.A. Hewitt; M = Mr. Edward C. Martin; J = Juurinen (1956); VPI&SU = VPI&SU collections

[2] Includes Fe_2O_3 recalculated to FeO

[3] n.d. = not determined

Table 2. Comparison of Lattice Parameters for Different Indexing Methods

Specimen	No. of peaks	a(Å)	b(Å)	c(Å)	β(°)	Volume(Å^3)
#1 $hk\ell$	49	7.871(1)	16.612(1)	5.657(1)	90.02(2)	739.71(14)
both	73	7.870(1)	16.612(1)	5.657(1)	90.00(1)	739.58(8)
$\bar{h}k\ell$	49	7.871(1)	16.612(1)	5.657(1)	89.98(2)	739.71(14)
#11 $hk\ell$	36	7.870(1)	16.625(2)	5.663(1)	90.06(2)	740.91(17)
both	47	7.869(1)	16.624(2)	5.662(1)	90.04(2)	740.69(12)
$\bar{h}k\ell$	33	7.869(1)	16.622(2)	5.661(1)	90.08(3)	740.40(21)
#20 $hk\ell$	40	7.871(1)	16.621(1)	5.657(1)	90.09(3)	740.10(16)
both	58	7.871(1)	16.619(1)	5.656(1)	90.00(1)	739.85(11)
$\bar{h}k\ell$	40	7.871(1)	16.621(1)	5.657(1)	89.91(3)	740.10(16)

to avoid biasing the lattice parameter refinements, these peaks were indexed both ways. For comparison alternate refinements were also carried out (1) indexing all such peaks as *hkl* (referred to as "*hkl*" refinements below), and (2) indexing them as $\bar{h}kl$ ("$\bar{h}kl$" refinements). The values of standard errors for refinements using "double indexing" are admittedly too small, since *hkl* and $\bar{h}kl$ peaks of any given pair were both assigned exactly the same 2θ values.

The effect of data biasing is shown in Table 2 for selected specimens. For refinements in which "double indexing" was not used, and in which there were equal numbers of reflections accepted in the "*hkl*" and "$\bar{h}kl$" refinements, the values for β were symmetrically disposed about the value obtained using "double indexing." Of course, any deviation from equal numbers of accepted *hkl* and $\bar{h}kl$ peaks for a given sample causes a deviation from symmetrical disposition about the "doubly indexed" value. In all calculations involving lattice parameters, the values obtained by "double indexing" (i.e., those shown in Table 1) were used.

Juurinen (1956) determined lattice parameters by extrapolation methods for his chemically analyzed specimens #2 and #6 and included the observed 2θ values in his paper. These data have been subjected to least-squares refinement, and the results are presented in Table 1.

Physical Properties

Because of the numerous inclusions ubiquitously present in staurolite, only three specimens (#1, 13, 14) were judged satisfactory for density determinations. A Berman balance was used with toluene as the buoyant medium.

A low-iron, non-zincian specimen (#20) was chosen for measurement of optical properties because Juurinen's (1956) specimen of similar composition had refractive indices and optic axial angle inconsistent with those determined for four other more iron-rich staurolites. The values $\alpha = 1.737$, $\beta = 1.742$, $\gamma = 1.748$ were determined using conventional methods. A value of 88° for $2V_\gamma$ was found using extinction data (Bloss, Riess and Upshaw, in preparation). These data, together with those for Juurinen's five specimens, and one each from Chinner (1958), Snelling (1957), Leake (1958), and Hietanen (1969), are plotted in fig. 1. Juurinen's specimen #1 was omitted in the computation of the least-squares lines.

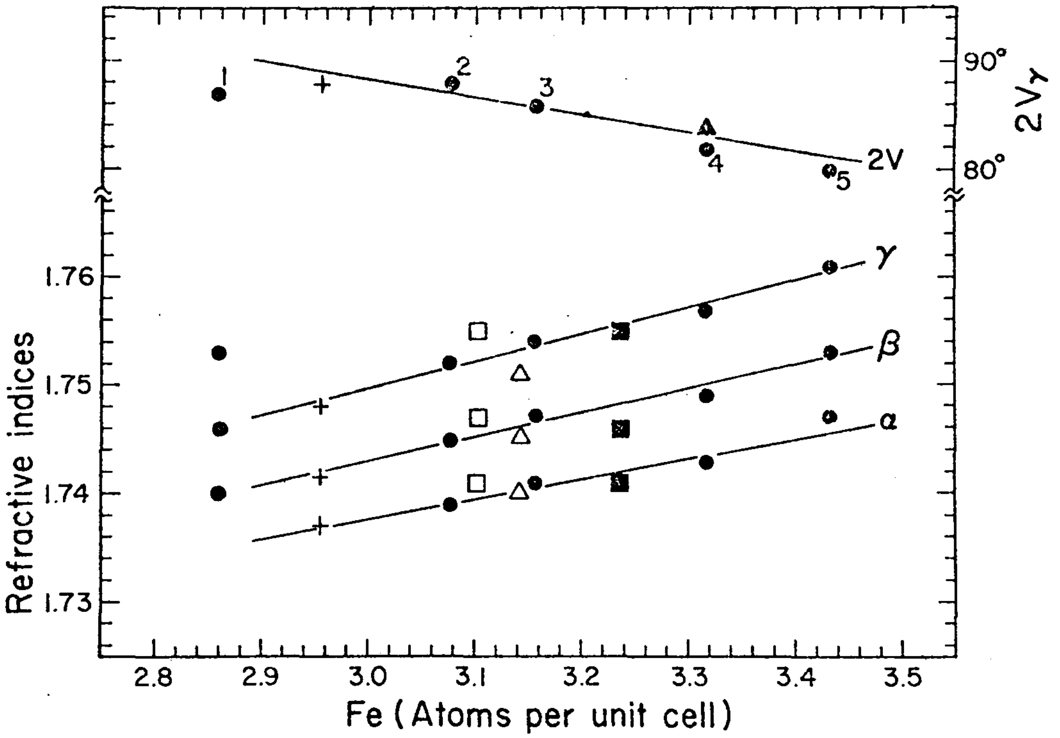

FIG. 1. Variations of optical properties with unit cell Fe content. Data are taken from Juurinen, 1956 (solid circles); Leake, 1958 (solid triangle); Chinner, 1958 (open squares); Snelling, 1957 (solid squares); Hietanen, 1969 (open triangles); and this study (crosses). Juurinen's specimen #1 was omitted in computing the regression lines.

III. DISCUSSION

General Chemistry and Unit Cell Contents

In confirmation of Juurinen's (1956) review of staurolite chemistry, the 20 specimens presented in Table 1 exhibit, especially among the major elements, remarkable chemical constancy for a mineral so chemically and structurally complex. This is also in general agreement with more recently published staurolite analyses (see Appendix II for a compendium of 43 analyses determined in the last 20 years), although several microprobe studies show higher aluminum and lower silicon contents than does the present one. The most pronounced differences occur in sector-zoned specimens (Hollister and Bence, 1967; Hollister, 1970). With but one exception, all Fe contents determined in the 43 referenced analyses fall within the extreme values found in this study.

It is assumed in this discussion that all iron in staurolite is divalent. Schreyer and Chinner (1966) suggested that Fe^{3+} reported in wet chemical analyses may have been oxidized during analysis. Bancroft *et al.* (1967) and Smith (1968) found no indication of Fe^{3+} in Mössbauer spectra, although they report that Fe^{2+} is located in two distinct coordination polyhedra. Smith's site refinement confirmed the presence of Fe in both tetrahedral and octahedral coordination.

The total variation observed in the concentrations of the minor elements Mg, Ti, Mn, Cr, Co, and V is also very small, although Zn ranges from nil to 5.51 wt. % in our specimens. Guidotti (1970) observed an increase in Zn content with decreasing modal staurolite, suggesting that, within limits as yet undefined, staurolite accommodates most of the Zn available in the rocks at the expense of other elements. Concentrations of Zn up to ∿6 wt. % (Juurinen, 1956; Hanisch, 1966) and Co as high as 6.7 wt. % (Skerl and Bannister, 1934) have been reported.

In order to ascertain the H^+ content of the staurolite unit cell, two assumptions were made: (1) the formula unit is electrostatically neutral, and (2) the microprobe analyses, density and lattice parameter measurements are free from significant systematic errors.[1] Based on these assumptions, the analyses can be "normalized" to unit cell masses. Densities determined on three nearly inclusion-free specimens (#1, ρ = 3.737 g/cc; #13, ρ = 3.746 g/cc; #14, ρ = 3.738 g/cc) were multiplied by their respective unit cell volumes, and the unit cell masses were then apportioned to the various cations on the basis of the analyses. Since there are 48 oxygens per unit cell (Naray-Szabo and Sasvari, 1958; Smith, 1968), the deviation of the cation formal charge total from +96 e.s.u. should equal the number of H^+ ions. These deviations were, respectively, 4.6, 3.6 and 3.3, averaging 3.8 H^+ per unit cell. This is sufficiently close to 4.0 to imply that there are indeed four H^+ or, equivalently, 4 $(OH)^-$ ions in the unit cell. In fact, the few inclusions in specimen #1 are mostly ferromagnesian minerals of lower density than staurolite, thereby leading to a low cation charge total and a high calculated H^+ content. The inclusions in specimens #13 and #14 appeared

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[1] This assumption may not be entirely justified, especially since the average total oxides is 98.5 wt. %, as opposed to 98.1 wt. % expected if there are indeed $4(OH)^-$ (= $2H_2O$) per unit cell.

to be mostly garnets whose densities are probably higher than that of staurolite, producing calculated H^+ contents somewhat lower than 4.0.

If indeed there are 4 H^+ in the ideal staurolite unit cell (the equivalent of 1.9 wt. % H_2O for natural staurolites), the H^+ contents calculated by the method described above will be greater than 4.0 when the unnormalized anhydrous oxide totals are less than 98.1 wt. % and vice versa. Thus a plot of total oxides *versus* calculated H^+ content should pass through 4.0 H^+ at 98.1 wt. %. In fact, the curve for specimens #1, 13 and 14 intersects at 97.9 wt % total oxides. Although slightly low, the proximity of 97.9 wt. % to the ideal value gives further credence to the proposition of $4(OH)^-$ per unit cell. The foregoing is supported by Juurinen's (1956) conclusion, based on empirical unit cell contents derived from six wet chemical analyses, that 4 H^+ is a more reasonable choice than the 2 theretofore postulated (and since suggested by Hollister (1970) and Ganguly (1972)). His H^+ determinations range from 3.24 to 4.49, averaging 3.89. In a study of staurolite stability, Ganguly and Newton (1966) earlier proposed a formula with 3.6 H^+ based on dehydration curves.

Assuming on the basis of the foregoing arguments that the staurolite unit cell contains ∿4 H^+, the chemical analyses then can be normalized to $44(O)^{2-} + 4(OH)^-$ by a process which amounts to normalization of total metal cation charges to +92 e.s.u. (Appendix I). The results are shown in Table 1. The formula of "normal" ferroan staurolite can be expressed in terms of the cation ranges found in this study as

$$Fe_{2.95-3.44}Al_{17.07-17.60}Mg_{0.38-1.13}Ti_{0.09-0.14}Zn_{0-0.17}Mn_{0-0.09}Cr_{0-0.02}$$
$$V_{\leqslant .01}Co_{\leqslant .004}Si_{7.64-7.91}O_{44}(OH)_4.$$

This corresponds well with the preliminary "average" formula calculated from the unit cell mass apportionment for specimens #1, 13 and 14 reported by Griffen and Ribbe (1972). No implication is intended that these cation ranges specify the limits of staurolite composition; for instance, there is no reason to suppose that the upper limits of Zn and Co concentration have been observed. Nevertheless, these ranges probably represent near-limits for *natural* ferroan staurolites. Staurolites with Fe and Mg concentrations outside these ranges have been synthesized by Ganguly and Newton (1966), Richardson (1967) and Schreyer and Seifert (1969).

Occupancy of Coordination Polyhedra

One of the principle hindrances to understanding staurolite crystal chemistry is the uncertainty in specifying the atomic species occupying the three (or four) coordination polyhedra (see Smith, 1968). It has been well-established that there is a tetrahedral site occupied principally by Si, another principally by Fe, and five octahedral sites occupied mainly by Al. With respect to the secondary elements occupying these sites, however, the opinions (some admittedly speculative) have been many and varied, and these are summarized in Table 3. In addition, Smith (1968) has found evidence for two almost vacant (4 to 8% occupied) octahedral sites, called "U" sites, which presumably contain transition metals.

In order to clarify the substitutions that may take place in the primary Si^{IV}, Fe^{IV} and Al^{VI} sites, a principle component analysis was undertaken. This method has been used by mineralogists and petrologists

Table 3

SUMMARY OF PREVIOUS CATION SITE ASSIGNMENTS IN STAUROLITE

Author(s)	Si^{IV}	Al^{VI}	Fe^{IV}	No. of H^+ ions
Juurinen (1956)	Si	Al, Fe^{3+}, Ti	Fe^{2+}, Mg, Mn, Zn	4
Naray-Szabo and Sasvari (1958)	Si	Al	Fe^{2+}	2
* Richardson (1966, 1967)	Si	Al	Fe, Mg	3.83
Schreyer and Chinner (1966)	Si	Al, Ti	Fe^{2+}, Mg, Mn	4
Hounslow and Moore (1967)	--	--	Fe, Mg, Mn	--
Hollister and Bence (1967)	Si, Al	Al, Ti, Fe^{3+}	Fe^{2+}, Mg, Mn, Zn	--
Bancroft _et al_. (1967)	Si	Al, Fe^{2+}	Fe^{2+}, Mg	--
** Smith (1968)	Si, Al	Al, Fe^{2+}, Mg, Mn	Fe^{2+}, Al, Ti	∿4
* Schreyer and Seifert (1969)	Si	Al	Mg	--
Hollister (1969, 1970)	Si, Al	Al, Ti, Mg	Fe^{2+}, Mg, Zn, Mn	2
Guidotti (1969)	Si	Al, Ti(?), Mn	Fe^{2+}, Mg, Zn	--

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* Synthetic specimens

** Based on least-squares site refinement; U sites included with Al^{VI}

for the differentiation of mineral or rock populations distinguishable on the bases of their bulk chemistries (e.g., Le Maitre, 1968; Saxena, 1969a; Saxena and Walter, 1972). The method also has been used to determine the relationships of cation substituents in biotite (Webb and Briggs, 1967), garnets and clinopyroxenes (Saxena, 1969b), calcic amphiboles (Saxena and Ekstrom, 1970) and lunar pyroxenes (Saxena and Walter, 1972). The most concise explanations in mineralogical literature of the technique of principle component analysis are found in Le Maitre (1968) and Saxena (1969c). Mathematical details are given in statistics textbooks (e.g., Rao, 1965).

The variables used for the principle component analysis of staurolite are atoms per formula unit, normalized to $44(O)^{2-} + 4(OH)^{-}$. Trace elements (V, Cr, and Co) were ignored because they account for so little of the total variation in the data. Since the twenty specimens studied were neither spatially, chronologically, nor petrogenetically related, it was decided to apply a principle component analysis first to Guidotti's (1970) data for eleven staurolites from a localized metamorphic terrain. (See Appendix II, for normalized formulas.) In order to simplify the principle component analysis one variable was removed by assuming that all of the Si is in the Si^{IV} site, with sufficient Al added to fill the site; the latter amount was then subtracted from the total number of Al atoms.[2] Since principle component analysis can be used to characterize cation substitutions, but not to distinguish amongst structural sites in which they occur, the five Al and two U octahedral sites were collectively designated Al^{VI}. The other site at which substitutions occur is the tetrahedral Fe^{IV} site. Henceforth any references made to the site of a specific substitution are based solely on our understanding of crystal chemical principles combined with fragmentary experimental evidence of Mössbauer and site refinement studies.

Table 4 contains the results of principle component analysis applied to Guidotti's data, using only the major elements Al, Fe, Mg and Zn as variables. The correlation coefficient matrix shows strong simple linear correlations among all of the variables. The first and second

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[2] Using site-refinement methods, Smith (1968) determined that the Si^{IV} site in a staurolite from St. Gotthard, Switzerland is essentially fully-occupied, and he logically chose Al to balance the Si "deficiency". His choice was consistent with the observed mean T-O bond length at the Si^{IV} site, which is ∿0.02Å longer than that expected for a mean Si-O bond to oxygen with a mean coordination number of 2.9 (Brown and Gibbs, 1969). For our twenty specimens there is, on the average, (0.967Si + 0.033Al) in the Si^{IV} site, producing a net positive charge of 3.97. Since the Si^{IV} atom is bonded to three formally charge-balanced oxygens ($\zeta O(2A) = \zeta O(2B) = \zeta O(4) = 2.0$; nomenclature of Smith), and one slightly underbonded oxygen ($\zeta O(3) \approx 1.85$), the net negative charge is in good agreement with the calculated positive charge.

latent vectors account for 97% of the total variance, with the first representing the overwhelmingly dominant trend. The direction cosines of the first latent vector are all nearly the same, indicating that the vector makes nearly the same "angle" with the Al-, Fe-, Mg-, and Zn-axes in 4-dimensional space. Opposite signs show that an antipathetic relationship exists between (Fe + Mg) and (Zn + Al), with the relative degrees of involvement for the four elements nearly identical. Because Al and Fe are the principle elements occupying the sites in question, and because of the correlation coefficients shown in Table 4, this is qualitatively interpreted as Al $\rightleftarrows$ (Fe + Mg) in the Al^{VI} site, and Fe $\rightleftarrows$ (Zn + Al) in the Fe^{IV} site. The second principle component shows an antipathetic relationship between (Al + Mg) and (Zn + Fe), but the respective direction cosines indicate that this latent vector is directed nearly normal to the Fe-axis, indicating near invariance of Fe. The major discernible substitutional relation is (Al + Mg) $\rightleftarrows$ Zn, and it is not unreasonable to assume that this substitution occurs in both Al^{VI} and Fe^{IV} sites. When Ti and Mn are included as variables, the same relations as above are noted with the addition of (Zn + Al) $\rightleftarrows$ Ti, possibly in both sites. The substitutional relationships involving Mn are not clear; Mn is presumed to be in octahedral coordination because of its large size. The bottom of Table 4 contains a summary of the qualitative site occupancies as determined from Guidotti's data.

The twenty analyses of the present study were next subjected to principle component analysis, starting with only Al, Fe, Mg, and Zn as variables. While the relationships are not as clearly-defined for this

Table 4

Principle Component Analysis for Guidotti's (1969) Data

Correlation coefficient matrix:

	Mg	Al	Fe	Zn
Mg	1.0000	-0.7222	0.8530	-0.9474
Al	-0.7222	1.0000	-0.8950	0.7164
Fe	0.8530	-0.8950	1.0000	-0.9145
Zn	-0.9474	0.7164	-0.9145	1.0000

Latent roots:

3.529	0.368	0.090	0.014

Percent total variance:

88	9	3	0

Latent vectors:

	PC-1	PC-2	PC-3	PC-4
Mg	0.5002	0.4600	0.6491	0.3420
Al	-0.4707	0.7493	-0.3374	0.3211
Fe	0.5192	-0.1912	-0.5797	0.5981
Zn	-0.5086	-0.4364	0.3588	0.6498

Interpreted substitutions:

	Al^{VI}	Fe^{IV}
PC-1	$Al \rightleftharpoons (Fe+Mg)$	$Fe \rightleftharpoons (Zn+Al)$
PC-2	$(Al+Mg) \rightleftharpoons Zn$	$Zn \rightleftharpoons (Al+Mg)$

Summary of Site Assignments

Si^{IV}	Al^{VI}	Fe^{IV}
Guidotti:		
Si,Al(constrained)	Al,Fe,Mg,Zn,Mn,Ti	Fe,Zn,Al,Mg,Ti
Present study:		
Si,Al(constrained)	Al,Mg,Fe,Zn,Ti,Mn	Fe,Zn,Mg,Al

random sampling of geologically unrelated staurolites as they are for Guidotti's specimens, the same general relations were discernible:

Latent vector	Al^{VI} sites	Fe^{IV} site	Variance
PC-1	Al $\rightleftarrows$ Mg (Mg $\rightleftarrows$ Fe?)	Fe $\rightleftarrows$ Zn (+ Mg?)	54%
PC-2	Al $\rightleftarrows$ Mg + Fe Mg $\rightleftarrows$ Zn	Zn $\rightleftarrows$ Mg	28%

With the addition of Ti and Mn as variables, the following substitutions were recognized:

PC-1	Ti $\rightleftarrows$ Mn Al $\rightleftarrows$ Mg (Mg $\rightleftarrows$ Fe?)	Fe $\rightleftarrows$ Zn (+ Mg?)	37%
PC-2	Al $\rightleftarrows$ Ti (Mn $\rightleftarrows$ Mg?)		30%
PC-3	Al $\rightleftarrows$ Fe Mg $\rightleftarrows$ Zn	Zn $\rightleftarrows$ Mg Fe $\rightleftarrows$ Al	15%

A summary of the qualitative site assignments implied by these relationships is also included in Table 4. The interpretation that Fe is in both sites is consistent with Smith's (1968) estimation, based on Mössbauer spectra, that ∿75% of the Fe is in tetrahedral and ∿25% in octahedral coordination.

It must be emphasized that the method of principle components is a statistical technique, and as such it cannot be used to "prove" any substitutional relationships. The assignments of sites in Table 4 were derived by the integration of known crystal chemical principles with the statistical method and some speculative choices of sites for certain of the substitutions. More direct experimental methods, such as the synthesis and structure analysis of Zn-staurolite planned by the author are needed to further elucidate staurolite crystal chemistry. Mössbauer and x-ray structural studies of synthetic Fe- and Fe/Mg-staurolite would also be helpful in determining the proportions of iron in octahedral and tetrahedral coordination. In short the major implication of principle component analysis is that the site occupancies are very complex, with nearly all cations present being both octahedrally and tetrahedrally coordinated (cf. Smith, 1968). The generally accepted view that Mg is the primary substituent for Fe in the Fe^{IV} site is not supported by the statistical analysis. It appears that Al and Zn (in that order) are the more important substituents in the Fe^{IV} site.

Cell Dimensions

In their study of staurolite twinning, Hurst *et al.* (1956) gave ranges in cell dimensions as follows: a = 7.83-7.95Å; b = 16.50-16.82Å; and c = 5.62-5.71Å. The ranges found among our specimens were considerably smaller: a = 7.865-7.879Å; b = 16.600-16.633Å; and c = 5.656-5.664Å. Since the dimensions cited by Hurst *et al.* include both values obtained from measurements by relatively crude methods (apparently from precession photographs) and values from the early literature (1927-1934), it is felt that the larger ranges are inaccurate.

Figure 2 shows the relationships between the number of Fe^{2+} atoms per formula unit and the cell dimensions. Data from Juurinen (1956), Richardson (1967), Smith (1968) and Schreyer and Seifert (1969) are included for comparison, but the least-squares regression lines were calculated using only our 15 specimens. There is no systematic variation in the a cell edge with Fe content; the values for the synthetic

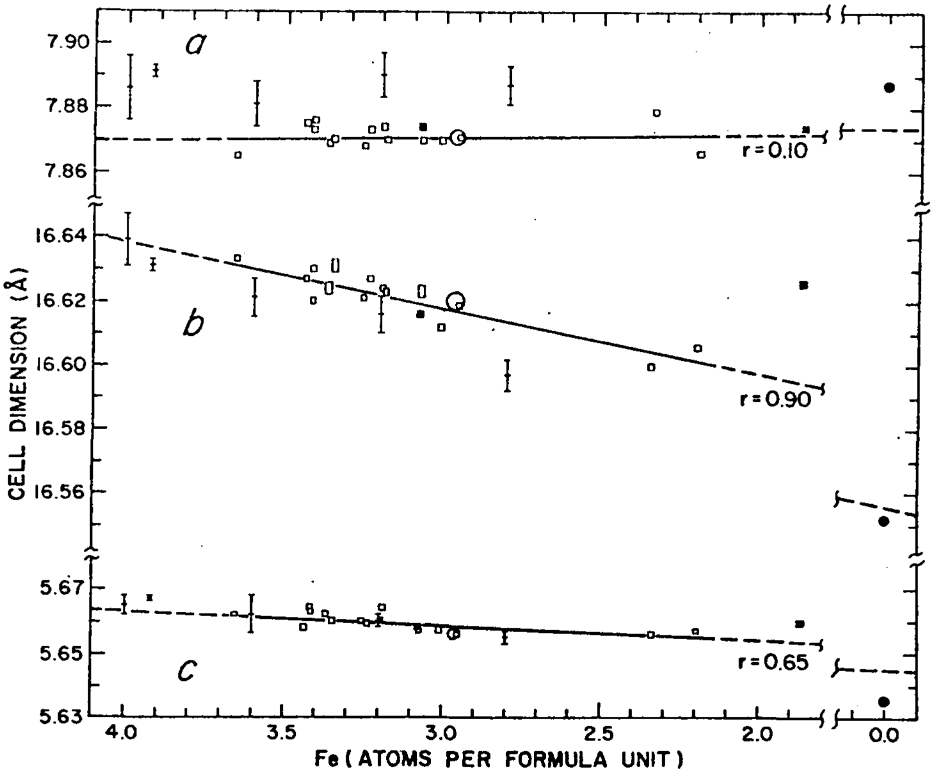

FIG. 2. Variations of cell edges with unit cell Fe content. Data from Richardson, 1967 (vertical bars) and Schreyer and Seifert, 1969 (triangles) are for synthetic staurolites. Other data are from Juurinen, 1956, recalculated from 2θ values by least-squares methods (circles); Smith, 1968 (ellipses); and this study (rectangles). All symbols are 2 e.s.d.'s in height. Regression lines were calculated using only data from this study.

materials are consistently and inexplicably larger than those for the natural minerals. The linear dependence of *b* on Fe is obvious. Schreyer and Seifert (1969), on the basis of a plot containing Richardson's (1967) data and theirs, have suggested that this curve is non-linear over the entire Fe-range; however, their *b* value for Mg-staurolite falls remarkably close to the extension of the regression line for the present data. The dependence of *c* on Fe is also statistically significant; for the test of the null hypothesis that the slope is zero, $|t| = 3.1$ with 13 degrees of freedom, indicating rejection down to a significance level of ~ 0.005. All three of these trends are consistent with the site assignments postulated above and with Smith's (1968) observed site occupancies.

The portrayal of the structure as alternating layers of kyanite and $AlFe_2O_3(OH)$ (Naray-Szabo and Sasvari, 1958; Bragg and Claringbull, 1965, p. 198; Deer *et al.*, 1962, p. 152) is not strictly correct. Because of partial occupancy of the Al(3A) and Al(3B) sites ($\sim$42% and $\sim$28%, respectively) and the assumption that half of the O(1) atoms are hydroxyls, the approximate "formula" for the monolayer nearly coincident with the (020) planes is $Al^{VI}_{0.7}Fe^{IV}_2O_2(OH)_2$ (cf. Heitanen, 1969).

Parallel to the *a* cell edge, which is independent of Fe content, the $Al_{0.7}Fe_2O_2(OH)_2$ layer consists of partially-filled Al-octahedra alternating with two Fe-tetrahedra (see fig. 3 and compare fig. 138 of Bragg and Claringbull, 1965). With an increase in Fe, the largest major cation in staurolite, the Fe-tetrahedra become larger on the average; however, *a* does not increase because the Al(3) octahedra, two-thirds

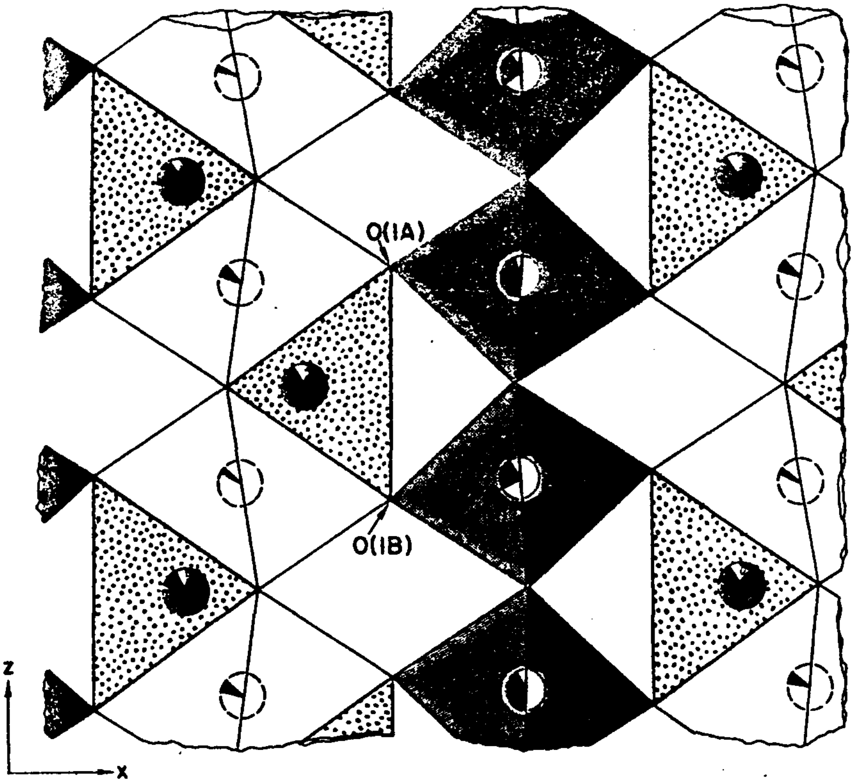

FIG. 3. The $Al^{VI}_{0.7}Fe^{IV}_{2}O_{2}(OH)_{2}$ layer viewed along *b*. Stippled tetrahedra (viewed parallel to one edge) enclose Fe^{IV} sites, and shaded octahedra enclose Al^{VI} sites. U^{VI} sites are indicated by dashed circles. Approximate percent occupancies are represented by filled portions of circles [Al(3A) > Al(3B)]. Only those oxygens lying in the plane of the cation sites are actually included in the monolayer, although polyhedra are completed for clarity.

of which are unoccupied, are easily distorted, being constrained by kyanite layers. If the Fe $\rightleftarrows$ Al substitution were to occur in the Al-octahedra of the kyanite layer, that layer would presumably expand and *a* would increase. Since such is not the case, it is proposed that this substitution occurs primarily in the $Al^{VI}_{0.7}Fe^{IV}_{2}O_{2}(OH)_{2}$ layer. This substantiates Hollister's (1970) assumption (based on microprobe analyses of kyanites by Chinner *et al.* (1969) and Albee and Chodos (1969)) that the kyanite layer in staurolite is nearly pure Al_2SiO_5.[3]

The alternating kyanite and Fe^{IV}-Al^{VI} layers are perpendicular to *b*, the cell edge along which the greatest percent variation is observed. An increase in Fe increases the thickness of the Fe^{IV}-Al^{VI} layer at both the Fe-tetrahedra and the partially filled Al-octahedra. Parallel to *b* the Fe-tetrahedra share corners with filled Al-octahedra of the kyanite layer, while the partially-filled octahedra of the Fe^{IV}-Al^{VI} layer share corners with filled Si-tetrahedra. Thus an increase in the thickness of this layer causes an increase in *b* (figure 2). The orientation of this layer of partially-filled sites normal to *b* also may explain the distinct (010) cleavage of staurolite.

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[3] If substitution occurs in the kyanite layer, it will likely be divalent cations for Al in the Al(2) octahedral site, because the ligancy of this site consists of three charge balanced oxygens ($\zeta O(2A) = \zeta O(2B) = \zeta O(5) = 2.0$), one slightly underbonded oxygen ($\zeta O(3) \simeq 1.85$) and the two O(1) atoms which are presumed to be half oxygen, half hydroxyl ($\zeta O(1) \simeq 1.2$) (cf. Smith, 1968).

In the kyanite layer the key structural units along *c* are chains of edge-sharing Al-octahedra cross-linked by Si-tetrahedra. In the Fe^{IV}-Al^{VI} layer, they are slightly kinked chains of partially filled Al-octahedra with corner-sharing Fe-tetrahedra alternating on either side of the chain (see figure 3). Since parallel kyanite layers are linked by these Fe-Al polyhedral chains, any increase in the size of the latter causes expansion of the former in the direction of *c*. The amount of expansion is restricted by the geometrical integrity of the nearly pure kyanite layer, thus the increase in *c* is slight.

IV. CONCLUSIONS

Microprobe analyses and lattice parameter refinements, together with density measurements for selected specimens, have provided data to substantiate the proposition that the staurolite unit cell contains $\sim 4\ H^+$ ions and to establish the relationships between Fe content and unit cell parameters. The positive correlations between the *b* and *c* cell edges and Fe content, as well as the lack of variation in *a* with composition, are explicable on the basis of the crystal structure and the locations of partially filled sites. The (010) cleavage may also be explained in terms of the structure, which consists of layers of kyanite alternating with $Al^{VI}_{0.7}Fe^{IV}_2O_2(OH)_2$ monolayers parallel to (010).

Principle component analysis has been used to determine substitutional relationships among the cations, which have been assigned to sites with the help of Mössbauer spectra (Bancroft *et al.*, 1967) an x-ray refinement (Smith, 1968) and general crystal chemical principles. The important substitutions are:

	Al^{VI} sites	Fe^{IV} sites	Si^{IV} site
Primary	Al $\rightleftarrows$ (Fe+Mg+Ti)	Fe $\rightleftarrows$ (Zn+Al)	Si $\rightleftarrows$ Al
Secondary	Mg $\rightleftarrows$ Zn	Zn $\rightleftarrows$ Mg	
	Ti $\rightleftarrows$ Mn	Al $\rightleftarrows$ Ti	

While it has been commonly assumed that Mg is the primary substituent for Fe in the Fe^{IV} site, this is not substantiated by principle component analysis of data from natural staurolites, although some Mg probably does occupy that site.

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APPENDIX I

NORMALIZATION OF CHEMICAL ANALYSES

Two methods were used in this study to obtain staurolite formulas from chemical analyses. One method involved normalization of analyses to unit cell masses and the other normalization to 92 e.s.u. (*i.e.*, to 44(O) + 4(OH)).

A. Normalization to unit cell masses. The unit cell mass of a specimen is obtained by multiplying its unit cell volume by the density. The mass is then apportioned among the various cations on the basis of the analysis; for example, if a given specimen contained 13.24% Si, then 13.24% of the unit cell mass was apportioned to Si. Thus the mass of each cation in the unit cell was calculated. In order to determine the number of atoms of each species, then, it was only necessary to divide the total mass of each element present by the mass of a single atom of that element (*i.e.*, the atomic weight divided by Avogadro's number).

B. Normalization to 44(O) + 4(OH). An equivalent weight of an oxide is its formula weight divided by the sum of the cation valences in the oxide. In normalizing an analysis to 44(O) + 4(OH), it is first necessary to divide each oxide weight percent in the analysis by its equivalent weight, thereby obtaining the number of equivalents present. Dividing 92 (the charge required to balance the oxygens and hydroxyls) by the total number of equivalents present in the unit cell (that is, by the summation of the number of equivalents of all oxides) gives a scale factor which is used to convert numbers of equivalents to numbers of atoms. This final step is accomplished by multiplying the number of equivalents of each oxide by the scale factor and dividing by the valence of the cation. Thus for Si and Al,

$$\text{number of equivalents of } SiO_2 = \text{wt.\% } SiO_2/(60.086/4),$$

$$\text{number of equivalents of } Al_2O_3 = \text{wt.\% } Al_2O_3/(101.96/6),$$

and

$$\text{No. of Si atoms} = (\text{no. equivalents of } SiO_2)(\text{scale factor}/4),$$

$$\text{No. of Al atoms} = (\text{no. equivalents of } Al_2O_3)(\text{scale factor}/3).$$

A more direct method, when working with microprobe analyses which normally provide cation weight percents, is to use these and substitute atomic weights for oxide weights.

APPENDIX II

PREVIOUS STAUROLITE ANALYSES IN ATOMS PER FORMULA UNIT, NORMALIZED TO 44(O) +4(OH)

Specimen[1]	Si	Ti	Al	Fe	Mg	Mn	Zn	wt.% H_2O calculated
S & B	7.691	0.106	16.884	1.861	1.078	0.019	-	1.89
J-1	7.583	0.229	17.442	2.860	1.305	0.047	-	1.93
J-2	7.620	0.121	17.641	3.077	0.926	0.054	-	1.92
J-3	7.538	0.117	17.677	3.157	0.966	0.054	-	1.92
J-4	7.797	0.112	17.230	3.318	1.006	0.012	-	1.91
J-5	7.517	0.115	17.550	3.434	0.878	0.099	-	1.90
J-6	8.025	0.118	16.559	1.861	1.437	0.038	1.539	1.89
Snelling	7.837	0.179	17.230	3.236	0.878	0.009	-	1.92
Leake	7.699	0.154	17.286	3.316	1.023	0.024	-	1.91
Chinner	7.985	0.168	17.138	3.104	0.861	0.021	-	1.93
S & C	7.551	0.118	17.789	3.190	0.739	0.049	-	1.92
L-215-E	7.615	0.115	17.530	3.295	0.841	0.035	0.074	1.91
L-215-N	7.752	0.115	17.502	3.151	0.776	0.019	0.068	1.92
L-216	7.746	0.113	17.413	3.298	0.775	0.012	0.076	1.91
H & M 2A	8.243	0.104	17.026	3.276	0.487	0.002	-	1.92
H & M 7B	7.539	0.122	17.707	2.676	1.253	0.186	-	1.93
H & M 7C	7.896	0.105	17.373	2.749	1.084	0.105	-	1.94
H & M 8	7.480	0.126	17.729	3.185	0.939	0.070	-	1.91
H & M 9B	7.643	0.141	17.664	3.094	0.811	0.030	-	1.92
H & B 1	* 7.180	0.067	18.231	3.254	0.820	0.045	0.041	1.92

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[1] Specimen identification symbols: S & B = Skerl and Bannister (1934; their analysis shows 1.92 Ni); J = Juurinen (1956); Snelling (1957); Leake (1958); Chinner (1958); S & C = Schreyer and Chinner (1966); L = Lebedev *et al.* (1967); H & M = Hounslow and Moore (1967); H & B = Hollister and Bence (1967)

* Microprobe analyses

Appendix II, continued

Specimen[1]	Si	Ti	Al	Fe	Mg	Mn	Zn	wt.% H_2O calculated
H & B 2	* 7.659	0.133	17.484	3.238	0.871	0.040	0.041	1.91
H & B 3	* 7.627	0.096	17.591	3.210	0.880	0.038	0.041	1.91
Smith	* 7.642	0.121	17.691	2.965	0.929	0.042	-	1.93
Hiet 143	7.781	0.123	17.430	3.198	0.684	0.009	0.154	1.91
Hiet 2096	8.094	0.129	17.005	3.142	0.822	0.020	0.051	1.92
H (001)	* 7.060	0.068	18.449	3.144	0.825	0.049	0.051	1.91
H (010)	* 7.571	0.149	17.600	3.137	0.930	0.042	0.051	1.92
H (110)	* 7.577	0.087	17.708	3.102	0.917	0.042	0.051	1.92
G O-C-3	* 7.426	0.117	17.943	3.330	0.523	0.049	0.099	1.91
G O-C-38	* 7.541	0.127	17.938	3.137	0.510	0.063	0.049	1.92
G O-C-41	* 7.616	0.125	17.648	3.423	0.520	0.042	0.061	1.91
G O-C-44	* 7.580	0.133	17.676	3.443	0.510	0.033	0.073	1.91
G O-J-66	* 7.574	0.120	17.745	3.394	0.514	0.042	0.043	1.91
G O-K-57	* 7.281	0.124	18.074	3.503	0.484	0.026	0.064	1.90
G O-J-73	* 7.559	0.130	17.909	3.061	0.488	0.075	0.134	1.92
G O-J-60	* 7.471	0.131	17.987	2.968	0.491	0.066	0.292	1.91
G O-K-46	* 7.675	0.108	17.483	2.726	0.371	0.030	0.541	1.91
G O-J-63	* 7.679	0.121	17.800	2.749	0.367	0.026	0.559	1.91
G O-J-55	* 7.623	0.108	17.948	2.778	0.377	0.028	0.435	1.92
Fox W-1	* 7.587	0.144	18.032	2.810	0.478	0.060	0.142	1.93
Fox W-2	* 7.637	0.076	18.086	2.804	0.479	0.060	0.099	1.93
Fox W-3	* 7.687	0.072	18.064	2.361	0.461	0.032	0.533	1.93
Fox W-4	* 7.695	0.087	17.970	2.699	0.480	0.072	0.230	1.93

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[1] Specimen identification symbols: H & B = Hollister and Bence (1967); Smith (1968); Hiet = Hietanen (1969); H(*hkl*) = Hollister (1970); G = Guidotti (1970); Fox (1971)

* Microprobe analyses

THE CRYSTAL CHEMISTRY OF STAUROLITE

by

Dana T. Griffen

(ABSTRACT)

Microprobe analyses of 20 staurolites from many localities indicate that the range of composition of natural ferroan specimens is $Fe_{2.95-3.44}Al_{17.07-17.60}Mg_{0.38-1.13}Ti_{0.09-0.14}Zn_{0-0.17}Mn_{0-0.09}Cr_{0-0.02}V_{\leqslant .01}Co_{\leqslant .004}Si_{7.64-7.91}O_{44}(OH)_{\sim 4}$. Our observations, together with chemical analyses and other experimental evidence from the literature, are sufficient to conclude that the staurolite unit cell contains ~ 4 H^+ in agreement with the structural formula of Smith (1968): (7 octahedral sites, principally $Al)_{\sim 18}$(1 tetrahedral site, principally $Fe)_{\leqslant 4}$(1 tetrahedral site, principally $Si)_8O_{48}H_{\sim 4}$. Assuming that Si and a small amount of Al fill the Si^{IV} site, we have used the method of principle component analysis to deduce that the primary substitution in the Al^{VI} sites is Al $\rightleftarrows$ (Fe+Mg+Ti) and that in the Fe^{IV} site is Fe $\rightleftarrows$ (Zn+Al). Secondary substituents in the Al^{VI} sites are Mn and Zn, and it is likely that small amounts of Mg and Ti are present in the Fe^{IV} site. The generally accepted view that Mg is the primary substituent for Fe in the Fe^{IV} site is not supported.

Lattice parameters determined by powder methods on 15 analyzed staurolites show the following ranges: $a = 7.865 - 7.879$Å; $b = 16.600 - 16.633$Å; $c = 5.656 - 5.664$Å; $\beta = 90.0°$. There are positive correlations of b and c with Fe content, while a is nearly independent of composition.

These relationships are explained on the basis of the crystal structure and site occupancies. Natural specimens have uniformly shorter *a* cell edges (by ∿0.015Å) than synthetic Fe-Mg staurolites.

Improved curves showing the relationship of 2V and refractive indices to Fe-content have been established.