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Staurolite-lusakite series. II. Crystal structure and optical properties of a cobaltoan staurolite

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ABSTRACT

A cobaltoan staurolite from near the original lusakite locality has the composition $Fe_{2.05}Mg_{1.23}Co_{0.55}Ti_{0.13}Zn_{0.04}Mn_{0.04}Al_{17.94}Si_{7.46}O_{44}(OH)_4$. It is monoclinic, $C2/m$, with $a = 7.782$ Å, $b = 16.608$ Å, $c = 5.648$ Å, and $\beta = 90.04°$. The crystal structure has been refined to $R = 0.034$ for 1011 reflections with $I > 3\sigma(I)$, using graphite-monochromatized Mo$K\alpha$ radiation, and is only slightly different from the structure of two ferroan Fe-Mg staurolites, the only others previously refined in a monoclinic space group. Indices of refraction are $\alpha = 1.721$, $\beta = 1.730$, and $\gamma = 1.740$; the measured $2V_X$ is 84.8°. The optical orientation is $X = \mathbf{a}$, $Y = \mathbf{b}$, and $Z = \mathbf{c}$, with pleochroism X = blue to blue violet, Y = blue violet, and Z = violet. If Co^{2+} is assumed to have the same optical effect as Fe^{2+}, then a previously established relationship between composition and optic axial angle predicts a $2V_X$ of 85°.

Two models of Fe-Al ordering in staurolite have been proposed on the basis of both diffraction data and Mössbauer spectra. In one model, Fe and Al are both distributed between the **Fe** and **Al(3)** sites; in the other, Fe is essentially restricted to the **Fe** site, and the **Al(3)** sites are Fe free. Our X-ray diffraction data fit the disordered model best, with 84% of the total (Fe + Co) in the **Fe** site and 36% of the **Fe** sites occupied by Al.

The causes and mechanisms of ordering in staurolite are as yet obscure. This cobaltoan staurolite is about half as ordered as (i.e., "less strongly monoclinic" than) a refined ferroan staurolite (0.17 and 0.33, respectively, by our proposed ordering parameter), but about the same as the other ferroan staurolite (0.16). Differences in ordering may be a function of detailed compositional differences (including differences in hydroxyl content) or of geologic history. The detailed geometry of the electron-density anisotropy about the tetrahedral **Fe** site suggests the possibility of a metal-metal attractive interaction between the atoms at the face-sharing **Fe** and **U** sites. The polyhedral distortions are qualitatively similar in this cobaltoan staurolite and the ferroan specimens, but are generally smaller in the former. The distortions in the kyanite-like layer of staurolite are remarkably similar to those in kyanite itself.

INTRODUCTION

Staurolite, a complex mineral both crystallographically and chemically, crystallizes in the monoclinic space group $C2/m$. The initial determination of the staurolite structure by Naray-Szabo (1929) assumed orthorhombic symmetry and was later revised (Naray-Szabo and Sasvari, 1958) in space group $C2/m$, consistent with evidence for monoclinic symmetry (Hurst et al., 1956). Hanisch (1966) refined the structure of a Zn-rich staurolite, but refinement was carried out in space group *Ccmm* owing to the difficulty in measuring the intensities of the weak $0kl$ (l odd) reflections that violate that space group. Smith (1968) refined the crystal structure of a ferroan staurolite in space group $C2/m$ and found that it was more complex than that reported by Naray-Szabo and Sasvari (1958). It consists of alternating layers of approximately kyanite structure, and layers one atom thick (monolayers) that contain cation sites occupied principally by Fe, Al, and perhaps Mg. He identified two previously unreported octahedral cation sites in the monolayer, designated **U(1)**[1] and **U(2)**, which were weakly occupied. Tagai and Joswig (1985) have reported a neutron-diffraction structure refinement of a staurolite from the same region; their cation-occupancy scheme differs slightly from Smith's. The chemical variability of staurolite was discussed by Griffen and Ribbe (1973). Donnay and Donnay (1983) have recently reviewed progress on the chemical and structural investigation of this mineral. Synthetic varieties include Fe-Mg staurolites (Richardson, 1967; Hellman and Green, 1979), Mg staurolite (Schreyer and Seifert, 1969), Fe-Zn staurolites (Griffen, 1981), and Fe-Co staurolites (Phillips and Griffen, 1986).

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[1] To avoid confusion between chemical symbols and Smith's site names, the latter are printed in boldface type. Site occupancies referred to are based on Smith's (1968) structure refinement.

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Table 1. Microprobe analysis of cobaltoan staurolite

	Wt%	Cations per 48(O,OH)
SiO_2	27.06	7.46
TiO_2	0.37	0.13
Al_2O_3	55.20	17.94
FeO*	8.89	2.05
MgO	3.00	1.23
CoO	2.50	0.55
MnO	0.12	0.04
ZnO	0.15	0.04
Total	97.29	

* Total Fe as FeO.

Table 2. Optical properties of cobaltoan staurolite

Grain	$2V_X$ (°)	α	β	γ
1	81.0(6)	1.724	1.733	1.740
2	87.5(6)	1.717	1.728	1.738
3	88.3(8)	1.718	1.730	1.741
4	84.8(9)	1.722	1.730	1.738
5	82.4(6)	1.726	1.734	1.741
Mean	84.8	1.721	1.731	1.740

Note: Numbers in parentheses are esd's, expressed in units of last (here, also first) decimal. Estimated errors for indices of refraction are ±0.001.

Lusakite, described by Skerl and Bannister (1934), is the only known silicate mineral with an essential amount of Co (Cech et al., 1981). It is monoclinic, isostructural with staurolite, and has Co > Fe,Mg. The type (and only known) locality lies 130 km east of Lusaka, Zambia, though the exact location, described by Skerl and Bannister, is uncertain. Cech et al. (1981) obtained specimens from this general area, which are megascopically similar to those described by Skerl and Bannister (1934), but in which they found Fe > Co,Mg. They referred to these as cobaltoan staurolites and proposed reserving the name lusakite for the case Co > Fe,Mg. Professor Cech has graciously provided samples of cobaltoan staurolite for our investigation of the staurolite-lusakite series.

PROCEDURES AND RESULTS

Microprobe analysis

The analysis was carried out on the ARL microprobe at the University of Utah. Silicates were used as standards for all elements but Co and Zn, for which pure metals were used. Small variations in raw X-ray counts from grain to grain exceeded variations within grains and was most noticeable for Fe, Co, and Mg. About 10 analyses from each of 10 grains were averaged, and the raw data were reduced using standard ZAF corrections (Goldstein et al., 1981). Oxide weight percents were reduced to a chemical formula based upon an assumed 44O + 4(OH) per unit cell (following Griffen and Ribbe, 1973). Table 1 shows the results of our microprobe analysis. If the number of Co atoms in our formula is included with Fe + Mg + Zn, this cobaltoan staurolite plots very close to the trend representing the majority of natural staurolites in Figure 3 of Griffen et al. (1982).

Optical properties

In unpolarized white light, the cobaltoan staurolite has an intense cobalt-blue color. Measurements of optical properties were carried out in Na_D light on five single crystals (including the one used for structure refinement) mounted on a spindle stage (Bloss, 1981). Indices of refraction were measured by standard oil-immersion techniques, and optic axial angles were determined from extinction-curve data, using the computer program EXCALIBUR (Bloss, 1981). Results are displayed in Table 2. The variation in optical properties suggests slight chemical inhomogeneity from crystal to crystal, and we suspect that the mean optical properties (Table 2) correspond essentially to the mean microprobe analysis (Table 1). Optical orientation, determined by optically orienting the crystal used for structure refinement and taking precession photographs, is $X = \mathbf{a}$, $Y = \mathbf{b}$, and $Z = \mathbf{c}$, the same as for ferroan staurolites. Pleochroism is strong, X = blue to blue violet, Y = blue violet, and Z = violet.

Unlike reported ferroan staurolites, all six of these crystals are optically negative. This is evidently due not to the presence of Co, but to the paucity of transition-metal atoms (principally Fe and Co) in the unit cell. Figure 1 of Griffen and Ribbe (1973) predicts that ferroan staurolite should be optically negative for Fe concentrations less than 2.9 atoms per unit cell. Our average specimen has 2.05 Fe atoms and 0.55 Co atoms per unit cell (Table 1). If we assume that Fe and Co have similar effects on optical constants [Batsanov (1959) lists their ionic refractivities as 1.14 cm^3 and 1.11 cm^3, respectively], then this mineral has the "optical equivalent" of about 2.6 Fe atoms per unit cell. Extrapolation of Figure 1 of Griffen and Ribbe (1973) to 2.6 Fe atoms yields a predicted $2V_X$ of 85°, in good agreement with the average optic axial angle of 84.8° (Table 2). Cech et al. (1981) reported that specimens from this locality had a large positive optic axial angle. In view of the range of $2V_X$ shown in Table 2, we think that it is plausible that some crystals might yield a positive sign, but we did not observe any.

Crystal structure

Experimental method. The crystal selected for X-ray intensity data collection was crudely cylindrical, about 0.23 mm in diameter and 0.18 mm in length. Intensities were collected on a Nicolet P3 automated four-circle X-ray diffractometer. Lattice parameters, obtained by least-squares refinement of 15 reflections automatically centered at $+2\theta$ and -2θ, were found to be a = 7.782(2) Å, b = 16.608(3) Å, c = 5.648(2) Å, and β = 90.04(3)°, with a unit-cell volume of 738.4(2) Å^3.

Data collection was done with graphite-monochromatized Mo$K\alpha$ radiation at 25°C, using a θ-2θ scan mode with a 2θ upper limit of 60°. The scan rate was automatically varied (1.5–29.3 deg/min) depending upon diffracted intensity. Variable scan width, dependent on diffraction angle, was used. Based on systematic absences, all reflections consistent with a C-centered lattice were collected, using three reflections to monitor instrumental and crystal stability at frequent intervals; intensities of these check reflections showed no significant variation. Background and Lorentz-polarization corrections were applied to the 1101 symmetrically unique reflections. Of these, 1011 had $I > 3\sigma(I)$ and were used in the structure refinement. No absorption correction was done because of the small size of the crystal and the moderate linear absorption coefficient ($\mu = 26$ cm^{-1}, based on the calculated density of 3.72 g/cm^3); rough calculations based on the data in Volume II of *International Tables for X-ray Crystallography* suggest that the variation in absorption factor would be on the order of 10%.

Table 4. Final atomic positional parameters and temperature factor coefficients (×10^4)

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.3909(1)	0.0	0.2495(2)	162(4)	57(3)	233(4)	0	2(3)	0
Si	0.1342(1)	0.1663(0)	0.2496(1)	24(3)	23(3)	41(3)	0(2)	2(2)	1(2)
Al(1A)	0.5	0.1747(1)	0.0	26(5)	29(5)	25(5)	0	1(3)	0
Al(1B)	0.5	0.1747(1)	0.5	24(5)	29(5)	21(5)	0	4(3)	0
Al(2)	0.2633(1)	0.4103(0)	0.2504(1)	38(3)	39(3)	71(4)	1(3)	1(2)	1(2)
Al(3A)	0.0	0.0	0.0	47(12)	43(12)	79(14)	0	24(9)	0
Al(3B)	0.0	0.0	0.5	33(14)	37(14)	82(17)	0	−26(10)	0
U(1)	0.5	0.0	0.0	135(41)					
U(2)	0.5	0.0	0.5	117(49)					
O(1A)	0.2345(3)	0.0	0.9642(5)	127(11)	63(11)	125(13)	0	31(9)	0
O(1B)	0.2351(3)	0.0	0.5356(3)	134(11)	65(11)	116(12)	0	−25(9)	0
O(2A)	0.2550(2)	0.1614(1)	0.0152(3)	59(7)	79(8)	81(8)	−2(6)	6(5)	−7(5)
O(2B)	0.2547(2)	0.1614(1)	0.4839(3)	56(7)	79(8)	76(8)	4(6)	2(5)	−7(5)
O(3)	0.0015(2)	0.0891(1)	0.2488(3)	56(6)	67(7)	150(8)	−1(6)	0(6)	6(6)
O(4)	0.0211(2)	0.2493(1)	0.2498(3)	71(7)	59(7)	75(8)	1(5)	1(6)	10(5)
O(5)	0.5271(2)	0.0993(1)	0.2499(3)	54(7)	64(7)	69(7)	2(6)	−1(5)	−3(5)

Note: esd's, given in parentheses, refer last digit. U_{ij} are coefficients in the expression $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

Structure refinement. Space group $C2/m$ (rather than $C2$ or Cm) was assumed by analogy with other staurolites. Neutral-atom scattering-factor coefficients in the expression $\Sigma a_i \exp(-b_i \sin^2\theta/\lambda^2) + c$ ($i = 1$ to 4) were obtained from Cromer and Mann (1968), and anomalous scattering factors from Cromer and Liberman (1970) were used. Smith's (1968) structure refinement of ferroan staurolite provided the initial atomic coordinates for least-squares refinement using SHELX-76 (Sheldrick, 1976). Initially, only Fe, Si, Al, and O scattering factors were employed. After the first three cycles of refinement in which only positional and isotropic thermal parameters were varied, anisotropic thermal parameters were introduced, and site-occupancy factors (for cations only) were also varied. Because of the small fractional occupancy of the **U(1)** and **U(2)** sites, their thermal parameters were left isotropic. In the last stages of refinement, weights proportional to $1/\sigma^2(F)$ were assigned, and scattering factors consistent with the microprobe analysis and postulated site occupancies were used. (See below under Discussion for assignment of cations to sites.) Table 3 contains a list of observed and calculated structure factors.[2] Final atomic positional and thermal parameters are listed in Table 4. Tables 5 and 6 contain interatomic distances and bond angles. Final conventional residuals for the 1011 reflections with $I > 3\sigma(I)$ were $R = 0.034$ and $R_w = 0.033$. Inclusion of all 1101 reflections resulted in an unweighted R of 0.035.

DISCUSSION

Cation site assignments

As Smith (1968) pointed out, the assignment of cations to sites in staurolite, based on X-ray diffraction data, neither is trivial nor does it admit of a unique solution. We have a total of 29.44 cations comprising seven elements to place into 36 sites of nine different kinds, some of which are necessarily only partially occupied. Even elimination of all of the solutions that are *not* crystallochemically reasonable leaves a number of solutions that are. Tetrahedrally coordinated Co is known to cause blue color, whereas octahedrally coordinated Co yields pink color (e.g., Young, 1960). The color of this mineral does not specifically rule out some of the Co being in octahedral sites, because the resulting pink hue would likely be masked by the stronger blue (Centre d'Information du Cobalt, 1960; Weyl and Marboe, 1962), but no rationale for dividing Co among the two kinds of sites was apparent to us, so we chose for simplicity to assign all of the Co to the tetrahedrally coordinated **Fe** site. We constrained the distribution of Fe between tetrahedral and octahedral sites to be consistent with the Mössbauer spectrum of synthetic $Fe_{80}Co_{20}$ staurolite (Phillips and Griffen, 1986). For most of the remainder of the cations, the site assignments suggested by Smith (1968) and Griffen and Ribbe (1973) were qualitatively followed initially, except that we assigned Mg to the **Al(3)** sites, rather than to **Al(1A)**, **Al(1B)**, or **Al(2)**, on the basis of the mean bond lengths that Smith reported for these octahedra. Observed occupancies were calculated by SHELX-76, using the scattering factors of "model" atoms having the same atomic number as the weighted average atom postulated for a particular site. To determine the calculated occupancy of that site, we essentially reversed the procedure and computed the number of equivalent "model" atoms in the site based on our postulated occupancy. We then iteratively adjusted the numbers of each type of atom in each site to obtain self-consistency between the observed and calculated occupancies. When that was accomplished, we calculated bond-valence sums (Table 7) by the method of Donnay and Allmann (1970) and further adjusted the site assignments to obtain satisfactory bond valences consistent with the "model atom" site-population parameters.

Table 8 gives the results. The discrepancies between observed and calculated occupancies are minor and may be partly due to differences between the average microprobe analysis of several grains and the composition of this particular crystal, as well as to random errors in both the microprobe analysis and the diffraction data. Another likely source of error arises from the use of scattering-factor coefficients for real atoms in SHELX-76, whereas the

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[2] To obtain a copy of Table 3, order Document AM-86-320 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

Table 5. Interatomic distances (Å)

Fe tetrahedron		
Fe–O(1A)	2.027(3)	
–O(1B)	2.029(3)	
–O(5)	1.967(2)	×2
Mean	1.998	
O(1A)–O(1B)	3.227(4)	
–O(5)	3.259(3)	×2
O(1B)–O(5)	3.258(3)	×2
O(5)–O(5)	3.298(3)	
Mean	3.260	
Si tetrahedron		
Si–O(2A)	1.633(2)	
–O(2B)	1.631(2)	
–O(3)	1.653(2)	
–O(4)	1.642(2)	
Mean	1.640	
O(2A)–O(2B)	2.647(2)	
–O(3)	2.677(2)	
–O(4)	2.699(2)	
O(2B)–O(3)	2.680(2)	
–O(4)	2.696(2)	
O(3)–O(4)	2.666(2)	
Mean	2.678	
Al(1A) octahedron		
Al(1A)–O(2A)	1.942(2)	×2
–O(4)	1.900(2)	×2
–O(5)	1.899(2)	×2
Mean	1.914	
O(2A)–O(4)	2.887(2)	×2
–O(4)	2.747(2)	×2
–O(5)	2.721(2)	×2
–O(5)	2.499(2)	×2
O(4)–O(4)	2.841(3)	
–O(5)	2.514(2)	×2
O(5)–O(5)	2.855(3)	
Mean	2.703	
Al(1B) octahedron		
Al(1B)–O(2B)	1.945(2)	×2
–O(4)	1.902(2)	×2
–O(5)	1.899(2)	×2
Mean	1.915	
O(2B)–O(4)	2.889(2)	×2
–O(4)	2.752(2)	×2
–O(5)	2.721(2)	×2
–O(5)	2.504(2)	×2
O(4)–O(4)	2.846(3)	
–O(5)	2.514(2)	×2
O(5)–O(5)	2.855(3)	
Mean	2.705	
Al(2) octahedron		
Al(2)–O(1A)	1.921(2)	
–O(1B)	1.918(2)	
–O(2A)	1.921(2)	
–O(2B)	1.921(2)	
–O(3)	1.875(2)	
–O(5)	1.867(2)	
Mean	1.904	
O(1A)–O(1B)	2.421(4)	
–O(2A)	2.701(2)	
–O(3)	2.663(3)	
–O(5)	2.776(3)	
O(1B)–O(2B)	2.700(2)	
–O(3)	2.672(3)	
–O(5)	2.774(3)	
O(2A)–O(2B)	3.001(2)	
–O(3)	2.783(2)	
–O(5)	2.499(2)	
O(2B)–O(3)	2.791(2)	
–O(5)	2.504(2)	
Mean	2.690	
Al(3A) octahedron		
Al(3A)–O(1A)	1.858(2)	×2
–O(3)	2.040(2)	×4
Mean	1.979	
O(1A)–O(3)	2.852(3)	×4
–O(3)	2.663(3)	×4
O(3)–O(3)	2.810(4)	×2
–O(3)	2.959(3)	×2
Mean	2.800	
Al(3B) octahedron		
Al(3B)–O(1B)	1.862(2)	×2
–O(3)	2.050(2)	×4
Mean	1.987	
O(1B)–O(3)	2.863(3)	×4
–O(3)	2.672(3)	×4
O(3)–O(3)	2.838(4)	×2
–O(3)	2.959(3)	×2
Mean	2.811	
U(1) octahedron		
U(1)–O(1A)	2.099(2)	×2
–O(5)	2.182(2)	×4
Mean	2.154	
O(1A)–O(5)	2.776(3)	×4
–O(5)	3.260(3)	×4
O(5)–O(5)	2.855(3)	×2
–O(5)	3.298(3)	×2
Mean	3.038	
U(2) octahedron		
U(2)–O(1B)	2.095(2)	×2
–O(5)	2.182(2)	×4
Mean	2.153	
O(1B)–O(5)	2.774(2)	×4
–O(5)	3.257(3)	×4
O(5)–O(5)	2.855(3)	×2
–O(5)	3.298(3)	×2
Mean	3.036	

Note: Numbers in parentheses are esd's and refer to last decimal place.

Table 6. Bond angles (°)

Fe tetrahedron			
O(1A)–**Fe**–O(1B)		105.4	
–	–O(5)	109.4	×2
O(1B)–	–O(5)	109.2	×2
O(5)–	–O(5)	114.0	
Si tetrahedron			
O(2A)–**Si**–O(2B)		108.4	
–	–O(3)	109.1	
–	–O(4)	111.0	
O(2B)–	–O(3)	109.4	
–	–O(4)	110.9	
O(3)–	–O(4)	108.0	
Al(1A) octahedron			
O(2A)–**Al(1A)**–O(4)		97.4	×2
–	–O(4)	91.3	×2
–	–O(5)	90.2	×2
–	–O(5)	81.2	×2
O(4)–	–O(4)	96.8	
–	–O(5)	82.9	×2
O(5)–	–O(5)	97.5	
Al(1B) octahedron			
O(2B)–**Al(1B)**–O(4)		97.3	×2
–	–O(4)	91.3	×2
–	–O(5)	90.1	×2
–	–O(5)	81.3	×2
O(4)–	–O(4)	96.9	
–	–O(5)	82.8	×2
O(5)–	–O(5)	97.5	
Al(2) octahedron			
O(1A)–**Al(2)**–O(1B)		78.2	
–	–O(2A)	89.3	
–	–O(3)	89.1	
–	–O(5)	94.3	
O(1B)–	–O(2B)	89.4	
–	–O(3)	89.6	
–	–O(5)	94.2	
O(2A)–	–O(2B)	102.7	
–	–O(3)	94.3	
–	–O(5)	82.6	
O(2B)–	–O(3)	94.7	
–	–O(5)	82.8	
Al(3A) octahedron			
O(1A)–**Al(3A)**–O(3)		86.0	×4
–	–O(3)	94.0	×4
O(3)–	–O(3)	87.1	×2
–	–O(3)	92.9	×2
Al(3B) octahedron			
O(1B)–**Al(3B)**–O(3)		86.1	×4
–	–O(3)	94.0	×4
O(3)–	–O(3)	87.6	×2
–	–O(3)	92.4	×2
U(1) octahedron			
O(1A)–**U(1)**–O(5)		80.9	×4
–	–O(5)	99.2	×4
O(5)–	–O(5)	81.7	×2
–	–O(5)	98.3	×2
U(2) octahedron			
O(1B)–**U(2)**–O(5)		80.8	×4
–	–O(5)	99.2	×4
O(5)–	–O(5)	81.8	×2
–	–O(5)	98.2	×2

Note: esd's of all bond angles are 0.1°.

weighted average atom often had a nonintegral "atomic number," corresponding to something intermediate between two real atomic species. Although we feel that these postulated occupancies have crystal-chemical merit, an equally self-consistent solution might have been derived by assuming reasonable alternative sites for some of the atoms. We consider, for example, that some Mg in the **Al(3)** sites could be exchanged with some Al in the **Al(1)** sites of our model, with acceptable results.

Ordering in staurolite

This staurolite and the one reported by Smith (1968) are crystallographically very similar. Based on the presumably reasonable assumption that the same kinds of atoms, if not the same number, occupy the two **Al(3)** sites, the most obvious difference between the two staurolites is the degree of difference in scattering power between the pseudoequivalent **Al(3A)** and **Al(3B)** sites. Dollase and Hollister (1969) suggested that the intensities of the $0kl$ (l odd) reflections—that is, those that violate orthorhombic symmetry—must reflect the difference between these two sites and are therefore an indication of the deviation from orthorhombic symmetry. Thus a completely disordered staurolite [i.e., one that possessed only one kind of **Al(3)** site] would be orthorhombic; with the onset of ordering, the more highly populated **Al(3)** site would become **Al(3A)**, and the mineral would be monoclinic. As stated by Smith (1968), the most monoclinic staurolite would have **Al(3B)** empty. Inasmuch as the total occupancy of these sites is not fixed, the difference in occupancy is not a useful expression of order. We suggest $\delta = [k_{\mathrm{Al(3A)}} - k_{\mathrm{Al\,(3B)}}]/k_{\mathrm{Al(3A)}}$ where k indicates fractional occupancies of the designated sites. If $\delta = 0$, then the staurolite is orthorhombic, and if $0 < \delta \leq 1$, it is monoclinic. Even

Table 7. Bond valences for cobaltoan staurolite

Site	O(1A)	O(1B)	O(2A)	O(2B)	O(3)	O(4)	O(5)	Σ*	Mean oxidation no.**
Fe	0.548	0.545					0.616(×2)	2.33	2.32
Si			0.989	0.993	0.950	0.971		3.90	3.90
Al(1A)		0.437(×2)				0.487(×2)	0.488(×2)	2.82	2.82
Al(1B)			0.434(×2)			0.486(×2)	0.490(×2)	2.82	2.82
Al(2)	0.476	0.480	0.476	0.476	0.543		0.555	3.01	3.00
Al(3A)	0.267(×2)				0.181(×4)			1.26	1.24
Al(3B)		0.213(×2)			0.147(×4)			1.01	1.00
U(1)	0.027(×2)						0.022(×4)	0.14	0.14
U(2)		0.023(×2)					0.018(×4)	0.12	0.12
Σ†	1.32	1.26	1.90	1.90	1.82	1.94	2.19		

* Sum of bond valences about each cation site.
** Weighted average oxidation number for cations in the site.
† Sum of bond valences about each oxygen.

though the exact value of δ is sensitive to small differences in occupancy factors that, at present, are themselves not known with certainty, it is true that δ can at least be used to characterize two staurolite crystals as similar or dissimilar in degree of order and should become more useful as understanding of staurolite crystal chemistry becomes more complete.

For example, we have for our cobaltoan specimen, δ = 0.17; for Smith's ferroan specimen, δ = 0.33; and for that of Tagai and Joswig (from the same general locale as Smith's), δ = 0.16. These differences may result from small differences in cation chemistry or some aspect of the geologic histories of the specimens. Differences in proton occupancies at the **P(1A)** and **P(1B)** sites (see Takéuchi et al., 1972; Tagai and Joswig, 1985) may also play a role in ordering at the **Al(3)** sites, if there are fewer than four hydroxyls per unit cell. Smith (1968) suggested that the "disorder" results from (001) microtwinning of fully ordered individuals, with the apparent occupancies of **Al(3A)** and **Al(3B)** being determined by the relative volumes of the two crystals in the twin. Fitzpatrick (1976) examined two staurolites by transmission-electron microscopy; one was pseudorthorhombic (weakly monoclinic) and the other definitely monoclinic, and she found no evidence for submicroscopic twinning in either. She did find, however, that the more strongly monoclinic specimen showed antiphase boundaries. At present the distinctions between causes and effects of staurolite ordering are obscure, and several more structure refinements, perhaps with transmission-electron microscopy on the same crystals, will be necessary before this problem can be properly addressed. Even the numerical values of the ordering parameter we have suggested must be treated with some caution, because the occupancies obtained for the **Al(3)** sites depend on the atomic species assumed to be there. [We could have used the occupancies of the **U** sites instead of the **Al(3)** sites in this discussion, but the former are so nearly empty that differences in their occupancies have less statistical validity.]

Structural details

Smith (1968) has discussed the geometrical effects of edge-sharing in staurolite, and this need not be reiterated here. Comparison of our Tables 5 and 6 with Smith's Tables 3 and 4, and with Table 4 of Tagai and Joswig, confirms that most structural details of the three minerals are qualitatively the same and that they do not differ quantitatively very much, either.

One difference worthy of mention does not appear in any of these tables. The **Fe–U(1)** and **Fe–U(2)** distances are 1.651 and 1.655 Å, respectively, for our cobaltoan staurolite; 1.638 and 1.656 Å, respectively, for Smith's ferroan staurolite; and 1.649 and 1.643 Å, respectively, for the ferroan specimen of Tagai and Joswig. The **Fe** and

Table 8. Site occupancies in cobaltoan staurolite

Cation site	Postulated occupancy	Model atom	Observed occupancy*	Calculated occupancy*	Fractional occupancy**
Fe	1.63Fe, 1.44Al, 0.55Co, 0.13Ti, 0.04Zn	Sc	0.95(1)	0.95	0.95
Si	7.46Si, 0.44Al	Si	0.98(1)	0.98	0.99
Al(1A)	3.55Al, 0.32Mg	Al	0.96(1)	0.96	0.97
Al(1B)	3.55Al, 0.31Mg	Al	0.96(1)	0.96	0.97
Al(2)	8.00Al	Al	1.00(1)	1.00	1.00
Al(3A)	0.30Mg, 0.56Al, 0.10Fe	Si	0.48(1)	0.48	0.48
Al(3B)	0.30Mg, 0.40Al, 0.10Fe	Si	0.41(1)	0.41	0.40
U(1)	0.12Fe, 0.02Mn	Fe	0.07(1)	0.07	0.07
U(2)	0.10Fe, 0.02Mn	Fe	0.06(1)	0.06	0.06

* Based on scattering power of the model ("average") atom. See Discussion in text.
** Number of atoms (of any species) divided by number of sites.

U sites share faces, and, as Smith points out, it would seem unfavorable that they be simultaneously occupied. Indeed, given the occupancies cited, it is possible to envision an ordering scheme that would avoid simultaneous occupancy of the **Fe** site and at least one of the two **U** sites for any of the specimens. It seems problematic, then, that the **Fe** site is closer to the more highly occupied **U(1)** site than to the less populous **U(2)** site both in Smith's specimen and, to a lesser extent, in ours. Our final difference Fourier map showed three small peaks about the **Fe** site, as did Smith's, but our A and B peaks (see Smith's Fig. 1) are nearly twice as far from the **Fe** site as his, and are one-third of the way along a straight line between the **Fe** site and each **U** site. Our C peak is at the same distance from **Fe** as Smith's C peak, but it is the highest of our three. The electron-density difference drops to zero between our peaks A and B; if the atom in the **Fe** tetrahedron occupied A, B, and C temporally (suggested as a possibility by Smith), we might expect to see some positive difference along the A-B axis resulting from the oscillation between these positions, unless only A-C and B-C oscillations occur. On the other hand, if it occupied the three positions spatially (also suggested by Smith), we would expect peak B to be smaller than peak A, because it is closer to the more highly populated of the two **U** sites. Just the opposite is observed in both staurolites; our peaks A and B lie nearly in the shared faces, with the larger one, like Smith's, closer to **U(1)** than the smaller is to **U(2)**. Tagai and Joswig (1985) refined the proton positions and occupancies, and found **P(1B)** to be more fully occupied than **P(1A)**; it would seem that proton-**Fe** repulsion should thus have shortened the **Fe–U(1)** distance more than the **Fe–U(2)** distance, but, in their specimen, **Fe–U(1)** is the longer distance.

Additional insight is found in the **Fe–U** face-sharing geometry. The means of the three O–**Fe**–O angles involving oxygens in the shared faces are (ours, Smith's, and Tagai and Joswig's, respectively) 110.2°, 110.4°, and 110.4°, and the means of the three O–**U**–O angles involving the same oxygen atoms are 98.9°, 99.1°, and 98.9°. All are wider than their respective polyhedral average values of 109.5° and 90°, owing to flattening of the **U** octahedra along the **Fe–Fe** vector. [Fig. 1 of Tagai and Joswig (1985) provides a helpful view of this portion of the structure.] Even though many of the steric details in the monolayer, including flattening of the **U** octahedra, are undoubtedly imposed by interaction with the more fully occupied sites of the kyanite-like layer, neither the **Fe–U** face-sharing geometry nor the electron-density distribution are suggestive of cation-cation repulsion, but of an attractive metal-metal interaction. There are thus at least three possible interpretations of the anisotropic electron density about the **Fe** site, and which is the correct one remains uncertain.

In general, the polyhedra of the ferroan staurolites are more distorted than those of the cobaltoan staurolite. The octahedral angle variances (Robinson et al., 1971) for the **Al** and **U** sites fall into three widely separated groups (Table 9). Corresponding polyhedra in Hanisch's (1966) *Ccmm* refinement show similar distortions. As expected, the more different the occupancies of pseudoequivalent sites, the more different are their angle variances. Angle variances of the Al-containing octahedra in kyanite (Burnham, 1963) average 47.7, which corresponds closely to the values for corresponding sites [the **Al(1A)**, **Al(1B)**, and **Al(2)** octahedra] in the kyanite-like layer of staurolite.

Table 9. Tetrahedral and octahedral angle variances

Site	This study	Smith	Tagai and Joswig	Hanisch
Fe	7.45	11.40	11.45	12.48
Si	1.57	1.44	1.17	2.07
Al(1A)	42.83	45.50	45.74	47.89
Al(1B)	42.63	45.31	45.59	—*
Al(2)	44.15	46.25	45.14	46.79
Al(3A)	14.69	16.56	12.49	14.96
Al(3B)	13.44	12.25	13.61	—*
U(1)	85.94	90.42	86.92	—**
U(2)	86.01	85.78	88.07	—**

* Refined in space group *Ccmm*; **A** and **B** sites are symmetrically identical.
** Sites not detected.

CONCLUSIONS

Griffen and Ribbe (1973) commented on the remarkable chemical consistency, at least in terms of major-element composition, of staurolites from widely separated geographic localities. In light of the considerable complexity of the staurolite crystal structure, a similar observation could be made about the crystallography of staurolite; based on the four structures refined thus far, the similarities are more striking than the differences. Not only do absolute magnitudes of interatomic distances, bond angles, and polyhedral distortions vary but slightly from one structure to another, but the variations are, qualitatively, nearly identical.

Our cation site assignments are much more like those of Smith (1968) than they are like those of Tagai and Joswig (1985). The major difference is in the choice of sites for Fe. Tagai and Joswig placed all of the Fe, except for 6% needed in the **U** sites, in tetrahedral coordination, with 86% in the **Fe** site and 8% in the **Si** site; Smith placed about 80% in the **Fe** site and the remainder in the **Al(3)** and **U** sites in nearly a 3:1 ratio; we place 75% of the Fe in the **Fe** site, and divide the remainder roughly evenly among the **Al(3)** and **U** sites. Because they are so similar, there is nothing to recommend our cation assignment over Smith's or vice versa. We consider our cation assignment (or Smith's) to have the following advantages over that of Tagai and Joswig (T-J below):

1. We attempted to distribute our cations according to a T-J–like scheme, and found that the Al and Mg atoms left over after making assignments to all of the sites except **Al(3A)** and **Al(3B)** provided far too much electron density to agree with that observed. On the other hand, we found it possible to distribute cations in the T-J staurolite according to our model (with differences as required by dif-

ferences in chemistry between the two staurolite crystals) and obtain fairly reasonable agreement with the refined T-J neutron-scattering lengths.

2. T-J argued that the total occupancy of the **Fe** and **U** sites should be 4.00 atoms. For their preferred model, it is 4.20 atoms (although they miscalculated it as 4.06), whereas their alternate model yields 4.40 atoms. Although we did not intentionally adjust our occupancies to yield 4 atoms in these sites, our total is 4.05.

3. Our **Si** site, using their ordering model, would contain 0.03 atoms of Fe and be 94% filled. We see no reason for Fe to prefer the small **Si** tetrahedron or for that site not to be very close to fully occupied inasmuch as it occurs in the kyanite-like layer.

The order parameter δ is considerably different for our staurolite than for Smith's. Because of our reservations about the T-J site assignments, however, we consider it fortuitous that δ for their staurolite crystal agrees with that for ours.

Despite Griffen and Ribbe's (1973) observation on the chemical consistency of this mineral, some recent analyses of staurolites from nonpelitic rocks have revealed that staurolites of unusual compositions can crystallize in rocks of appropriate bulk chemistry (see, for example, Gibson, 1978; von Knorring et al., 1979; Ward, 1984). Although crystal-structure refinements of "normal" ferroan staurolites may provide some new insights into the crystal chemistry of this complex mineral, we expect that structure refinements of staurolites of unusual compositions, along with Mössbauer spectroscopy and electron microscopy where possible, have the highest potential of yielding answers to questions regarding cation site assignments, ordering, and the anisotropic electron-density distribution around the **Fe** site.

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