

Staurolite end-member molar volumes determined from unit-cell measurements of natural specimens

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ABSTRACT

Unit-cell parameters of 22 natural staurolite samples have been expressed as linear functions of chemical composition using multiple linear regression. Two models were used: Model A involves only those ions that substitute for each other on the T2 site and, to a lesser extent, other sites, including Fe^{2+} , Mg, Li, Zn, Mn, Ti, \square , and Fe^{3+} , and predicts unit-cell volume to 0.3 \AA^3 . Model B involves all major ions, Si, Al, Fe^{3+} , Fe^{2+} , Mg, Li, Zn, Mn, Ti, and H, and predicts unit-cell volume to 0.45 \AA^3 . Over the range of composition studied, the unit-cell volumes of analyzed staurolite are very well approximated by linear combinations of the various end-member volumes. These end-member unit-cell volumes may be converted to partial molar volumes.

Constants from Model A may be used to estimate unit-cell parameters and molar volumes of natural staurolite and chemical end-member staurolite, such as $\text{H}_3\text{Fe}_{4.35}\text{Al}_{17.90}\text{Si}_{7.65}\text{O}_{48}$. In order to determine unit-cell parameters and molar volumes of stoichiometric end-member staurolite, Model A may be used in combination with an exchange operator, $\text{Al}_{0.10}\text{Si}_{0.35}\text{H}_{-1.70}$, using constants from Model B. Molar volumes for iron staurolite are, for $\text{H}_2\text{Fe}_4\text{Al}_{18}\text{Si}_8\text{O}_{48}$, 44.61 ± 0.03 , for $\text{H}_4\text{Fe}_3\text{Al}_{18}\text{Si}_8\text{O}_{48}$, 44.39 ± 0.03 , and for $\text{H}_6\text{Fe}_2\text{Al}_{18}\text{Si}_8\text{O}_{48}$, $44.17 \pm 0.03 \text{ J/bar}$.

Constants from Model A may also be used to make reasonable estimates of staurolite compositions produced in synthesis studies. Such staurolite is nonstoichiometric, reasonably approximated by the average Al and Si of natural staurolite (17.90 and 7.65, respectively), and indicates decreasing H with increasing Fe^{2+} in solid solutions with Mg, Li, or Zn, where syntheses were performed at the same P - T conditions.

INTRODUCTION

Staurolite, a common mineral of medium-grade pelitic schists, poses many problems relative to its crystal chemistry, stability relations, and thermochemical data. Recent work by Hawthorne et al. (1993a, 1993b, 1993c) has involved determination of the site occupancies of a large number of representative staurolite compositions and has shown that the ideal stoichiometric Fe end-member formula is $\text{H}_2\text{Fe}_4\text{Al}_{18}\text{Si}_8\text{O}_{48}$. Dyar et al. (1991) have determined the Fe^{3+} content of a similarly large number of staurolite specimens and shown that about 14% of Fe is $^{61}\text{Fe}^{2+}$, and the remainder is ^{54}Fe . Holdaway et al. (1991) have discussed site occupancies, chemical end-member formulas, and an activity model for staurolite, based on the two studies cited above and on the earlier chemical data of Holdaway et al. (1986a, 1986b) and Dutrow et al. (1986). These studies have demonstrated the existence of

a major $\text{R}^{2+}\text{H}_{-2}$ substitution and laid the groundwork for the determination of end-member molar volumes from unit-cell measurements.

For naturally occurring staurolite, unit-cell measurements have been previously made by von Knorring et al. (1979), Smith (1968), Griffen and Ribbe (1973), Tagai and Joswig (1985), Bringham and Griffen (1986), Holdaway et al. (1986b), Stahl et al. (1988), Dutrow and Holdaway (1989), Alexander (1989), and Hawthorne et al. (1993a). For the last five studies, the formulas were well constrained except for Fe^{3+} content; however, Fe^{3+} is now known for four of the specimens of Hawthorne et al. (Dyar et al., 1991). The study by Holdaway et al. (1986b) was done with older, less precise X-ray diffraction equipment than what is now available. Thus there are both complete analytical and precise X-ray data for four of the staurolite samples of Hawthorne et al. (1993a), but for none of the

other studies. The situation is comparable for synthetic staurolite. Measurements have been made by Richardson (1967), Ganguly and Newton (1968), Schreyer and Seifert (1969), Griffen (1981), Phillips and Griffen (1986), Dutrow (1991), and Tattersall (1991) on Fe, Mg, Zn, and Co end-members and for Fe-Li, Fe-Mg, Fe-Zn, and Fe-Co solid solutions. To date it has not been possible to directly measure the composition and H content of synthetic staurolite, and so the unit-cell measurements can only be used if a formula is assumed. The extent of the substitution $R^{2+}\square_2\square_{-1}H_{-2}$ (Holdaway et al., 1986b; Hawthorne et al., 1993a) in synthetic staurolite could be estimated on the basis of careful chemical analysis (Holdaway et al., 1991), but such measurements are very difficult on synthetic minerals.

The only previous effort to regress staurolite compositions against unit-cell dimensions is that of Griffen and Ribbe (1973). The assumption of constant H and lack of knowledge of Fe^{3+} hampered that effort.

In this study, we attempt to rectify the problems discussed above with state-of-the-art unit-cell measurements on 23 analyzed natural staurolite samples. Using multiple linear regression, we explore the relations between unit-cell parameters and composition using two compositional models to describe the independent variables: (1) eight hypothetical (fictive) chemical staurolite end-members, and (2) total chemical content of each of ten cations. From these, we calculate the molar volumes of various end-members, including stoichiometric $H_2Fe_4Al_{18}Si_8O_{48}$, $H_4Fe_3Al_{18}Si_8O_{48}$, and $H_6Fe_2Al_{18}Si_8O_{48}$. These results will be important for (1) estimation of H content of synthetic staurolite for which precise unit-cell data are available, (2) retrieval of thermochemical data from experimental results on staurolite stability, and (3) estimation of metamorphic pressures and temperatures for natural staurolite-bearing assemblages from mineral chemistry, combined with thermochemical data for end-member reactions.

METHODS

Chemical analyses

The staurolite samples used for this study were the same 23 natural staurolite samples studied by Dyar et al. (1991). These were analyzed with the electron microprobe at Southern Methodist University using the same set of standards and the methods discussed by Holdaway et al. (1986b). All but two (82TP9A and HV-10) have been analyzed for H using the H_2 extraction line at SMU. Of these 21, 13 have also been analyzed for H with the ion microprobe (Holdaway et al., 1986a), and the remaining eight have been analyzed with the extraction line only (Dyar et al., 1991). For 82TP9A and HV-10, H content was estimated using methods described by Holdaway et al. (1991). Fe^{3+} content was determined for all 23. Of these, 13 had no resolvable Fe^{3+} doublet and were assumed to have a threshold value of 3% of Fe as Fe^{3+} (Dyar et al., 1991).

Because solid solution occurs on every site, the crystal

chemistry of staurolite is so complicated as to defy use of a comprehensive linear regression approach to determine the effect of chemical composition on unit-cell parameters (Hawthorne et al., 1993a; Holdaway et al., 1991). To simplify the problem, we have worked with two idealized approaches, a chemical end-member method and a chemical stoichiometry method. Each has advantages and disadvantages, and the best information can be obtained by examining the results of both methods.

Fictive chemical end-members (Model A)

Holdaway et al. (1986b, 1991) determined average compositions of staurolite chemical end-members, for example $H_3Fe_{4.35}Al_{17.90}Si_{7.65}O_{48}$ for 3H Fe staurolite, and showed that in common staurolite Al and Si vary only slightly from the values 17.90 and 7.65, respectively. If we allow the ionic substitution $R^{2+}\square_2\square_{-1}H_{-2}$ to go to its compositional extremes, we have the chemical end-members $Fe_{5.85}Al_{17.90}Si_{7.65}O_{48}$ (fictive Fe^{2+} end-member) and $H_{11.70}Al_{17.90}Si_{7.65}O_{48}$ (fictive vacancy end-member, so designated because all the R^{2+} sites are vacant). The other fictive R^{2+} end-members are analogous to the fictive Fe^{2+} end-member, but the Ti and Li end-members are possibly $Ti_{5.85}Al_{14.00}Si_{7.65}O_{48}$ and $Li_{5.85}Al_{19.85}Si_{7.65}O_{48}$, with the assumption of charge balance by Al (e.g., Dutrow et al., 1986; Holdaway et al., 1991). Obviously, none of these end-members is physically possible, but a fictive vacancy end-member and a fictive end-member with full site occupancy may be linearly combined to make physically realistic end-members. For example, the iron staurolite end-member containing 3 H atoms (above) is a combination of 25.6% fictive vacancy staurolite and 74.4% fictive iron staurolite. The use of these fictive staurolite end-members allows us to undertake multiple linear regression analysis on the staurolite chemical data. With, in pfu, a 48-O formula unit, $R^{2+} + Li + Ti + 0.5 H = 5.85$, there are seven fictive end-members, Fe^{2+} , Mg, Li, Zn, Mn, Ti, and a vacancy end-member. Among these, the Mn and Ti end-members always make up a trivial proportion of natural (and possibly synthetic) staurolite, whereas the other five can each be substantial in any given staurolite sample. This approach is analogous to the use of $Ca_2Si_2O_6$ or Al_4O_6 as fictive pyroxene end-members, except that none of the fictive staurolite end-members is physically realizable in any structure because six of them have no H and one has complete substitution of R^{2+} , Li, and Ti by H.

To these seven end-members, we add an additional component, fictive Fe^{3+} , which must be taken into account if we are to obtain maximum precision. Each of the seven end-members discussed above quantitatively reduces the content of the others as it increases in amount, but the same cannot be said for Fe^{3+} , which probably dilutes only Al in the T2 site (Holdaway et al., 1986b, 1991; we use the redefined site nomenclature of Hawthorne et al., 1993a; see Holdaway, 1991, for a structure diagram of staurolite). Fe^{3+} can be included with the others in terms of the major site of occupancy (T2), but

TABLE 1. Content of fictive chemical end-members (Model A)* and unit-cell constants for 23 analyzed staurolite samples**

Sample	Fe ²⁺	Mg	Li	Zn	Mn	Ti	□	Fe ³⁺	a Å	b Å	c Å	V Å ³
356-1	0.5710	0.1181	0.0212	0.0082	0.0021	0.0188	0.2606	0.0171	7.8676	16.6253	5.6621	740.61
EH-6	0.4511	0.2865	0.0019	0.0106	0.0044	0.0169	0.2285	0.0604	7.8800	16.6228	5.6599	741.37
B14040	0.5019	0.1583	0.0115	0.0101	0.0084	0.0217	0.2882	0.0150	7.8710	16.6216	5.6590	740.36
117189	0.3530	0.1385	0.0097	0.2250	0.0062	0.0191	0.2485	0.0143	7.8681	16.6082	5.6589	739.48
6-3	0.4066	0.0638	0.1703	0.0344	0.0171	0.0142	0.2937	0.0214	7.8731	16.5908	5.6547	738.62
3-3	0.5464	0.1349	0.0212	0.0063	0.0195	0.0195	0.2522	0.0163	7.8717	16.6286	5.6630	741.26
114-1	0.5610	0.0957	0.0713	0.0103	0.0029	0.0159	0.2429	0.0168	7.8702	16.6188	5.6620	740.55
53-2	0.5700	0.1039	0.0441	0.0085	0.0092	0.0179	0.2463	0.0170	7.8727	16.6261	5.6633	741.28
ER-70	0.5662	0.1162	0.0193	0.0096	0.0115	0.0191	0.2581	0.0349	7.8711	16.6313	5.6642	741.48
117183	0.5365	0.1540	0.0019	0.0080	0.0089	0.0222	0.2685	0.0160	7.8675	16.6096	5.6585	739.43
82TP9	0.2974	0.1764	0.0383	0.1391	0.0774	0.0162	0.2551	0.0252	7.8818	16.6097	5.6611	741.13
82TP9A	0.3699	0.1691	0.0403	0.0974	0.0554	0.0132	0.2547	0.0352	7.8799	16.6117	5.6589	740.75
203	0.5094	0.0889	0.0453	0.0080	0.0123	0.0142	0.3219	0.0152	7.8743	16.6144	5.6567	740.05
HV-4	0.5467	0.1315	0.0479	0.0084	0.0044	0.0198	0.2414	0.0337	7.8714	16.6281	5.6632	741.23
HV-10	0.5285	0.1321	0.0465	0.0402	0.0038	0.0209	0.2281	0.0158	7.8708	16.6215	5.6615	740.66
HV-112	0.5174	0.1588	0.0366	0.0063	0.0097	0.0198	0.2513	0.0499	7.8729	16.6280	5.6627	741.31
HV-116	0.5457	0.1463	0.0270	0.0074	0.0036	0.0217	0.2484	0.0398	7.8733	16.6322	5.6642	741.72
77-55C	0.4961	0.0125	0.1055	0.0010	0.0048	0.0123	0.3678	0.0362	7.8690	16.6073	5.6538	738.86
71-60E	0.4850	0.0557	0.0456	0.0031	0.0137	0.0152	0.3817	0.0145	7.8646	16.6177	5.6518	738.65
71-62R	0.4915	0.0485	0.0550	0.0084	0.0092	0.0152	0.3721	0.0147	7.8633	16.6170	5.6512	738.41
71-62U	0.4928	0.0768	0.0267	0.0063	0.0089	0.0144	0.3742	0.0147	7.8645	16.6155	5.6513	738.47
71-62T	0.5021	0.0795	0.0246	0.0044	0.0096	0.0154	0.3644	0.0150	7.8622	16.6178	5.6516	738.40
71-62B	0.5172	0.0598	0.0115	0.0043	0.0065	0.0144	0.3864	0.0154	7.8649	16.6201	5.6536	739.01

* Chemical data for Model B are tabulated by Dyar et al. (1991, their Table 3).

** Errors as follows: element ratios as average relative percent based on counting statistics (Holdaway et al., 1986b), Fe²⁺ = 1%, Mg = 1.4%, Li = 10%, Zn = 7%, Mn = 20%, Ti = 9%, □ = 2.8%, Fe³⁺ = 3% of Fe_{tot}; unit-cell data as average σ based on calculations, a = 0.0005 Å, b = 0.0009 Å, c = 0.0004 Å.

cannot dilute ions other than Al. In order to incorporate Fe³⁺ into the regression, this complication was dealt with as follows: the fictive components were determined by dividing the ionic content (48-O basis, Dyar et al., 1991) of each R²⁺, Ti, Li, or Fe³⁺ by 5.85 (the average sum of the seven fictive end-members), and subtracting the sum of R²⁺, Li, and Ti, occupied end-members from 1.00 to calculate the fictive vacancy end-member. This means that the end-members sum to 1.00 for Fe³⁺-absent staurolite, and (1.00 + Fe³⁺ component) for Fe³⁺-bearing staurolite. The range for the sum of all eight end-member values is 1.014–1.060 (Table 1). The approach allows for meaningful regression of all eight variables and can be expected to work well only if the Fe³⁺ end-member content is much less than one.

A reviewer has raised a question regarding this approach, asking why Fe³⁺ cannot be treated in such a way that it becomes a true end-member, or as an exchange operator, Fe³⁺Al₁. According to our present knowledge of staurolite, Fe³⁺ adds to the otherwise approximately constant sum of the other seven end-members. We cannot include Al in the end-members or as Fe³⁺Al₁ because even though Al is nearly constant, it is a major constituent of M1–M3 and shows small variations in every cation site except M4, and such variation would randomize an Fe³⁺Al₁ operator. On a 48-O basis, the known pfu range of Fe³⁺ of natural staurolite is 0.084–0.292, with an error of 0.1 (Dyar et al., 1991). With this limited range and large error, the main value of incorporating Fe³⁺ into the regression is to extrapolate to Fe³⁺-free staurolite specimens whose end-members do sum to one. Similarly, the primary value of incorporating Ti and Mn into the

regression is to extrapolate to Ti- and Mn-free staurolite. At present, we believe it is inappropriate to devise an Fe³⁺-bearing end-member. However, our approach does allow calculation of molar volumes of Fe³⁺-bearing (or Ti- or Mn-bearing) natural staurolite.

For an example of the calculation, we use specimen 356-1. Dyar et al. (1991) gave (in pfu) Fe²⁺ = 3.340, Mg = 0.691, Li = 0.124, Zn = 0.048, Mn = 0.012, Ti = 0.110, Fe³⁺ = 0.100. Thus fictive Fe²⁺ = 3.340/5.85 = 0.5710, fictive Mg = 0.691/5.85 = 0.1181, etc., fictive vacancy = 1 - fictive (R²⁺ + Li + Ti) = 1 - 0.7394 = 0.2606, fictive Fe³⁺ = 0.100/5.85 = 0.0171, and the sum of fictive end-members is 1.0171 (Table 1). (Discrepancies in the fourth decimal place result from the fact that the data were kept on a spreadsheet, and they preserve additional precision).

We emphasize that these are strictly chemical end-members and relate only approximately to site occupancies. R²⁺, Li, and Ti act as a group of ions that primarily occupy the T2 site, but Mg and Fe²⁺ also occupy a small proportion of the M1–M3 sites, and Fe²⁺ and probably Zn and Li occupy a small proportion of the largely vacant M4 site (Hawthorne et al., 1993a; Holdaway et al., 1991). Therefore, one cannot be sure that the relations are strictly linear, nor can one expect large extrapolations to be meaningful. However, since the staurolite samples being studied are common varieties, the end-member molar volumes obtained from the linear (ideal) mixing assumption are good approximations to partial molar volumes for typical staurolite. It is also important to note that these ions substitute almost entirely for each other even in the M1–M4 sites. The exception is Fe³⁺, which is treat-

TABLE 2. Comparison of unit-cell values measured in the present study with those of Hawthorne et al. (1993a)

Sample	Source	<i>a</i> Å	<i>b</i> Å	<i>c</i> Å	β °	<i>V</i> Å ³
EH-6	This study	7.8800(4)*	16.6228(9)	5.6599(4)	90.00**	741.37(7)
EH-6	Hawthorne et al.	7.881(2)†	16.624(2)	5.661(1)	90.02(3)	741.6(1)
117189	This study	7.8681(5)	16.6082(9)	5.6589(4)	90.00	739.48(8)
117189	Hawthorne et al.	7.868(1)	16.609(2)	5.659(1)	90.22(18)	739.5(1)
6-3	This study	7.8731(4)	16.5908(8)	5.6547(3)	90.00	738.62(7)
6-3	Hawthorne et al.	7.871(0)	16.580(11)	5.653(3)	90.01(1)	737.7(9)
71-62R	This study	7.8633(5)	16.6170(10)	5.6512(5)	90.00	738.41(9)
71-62R	Hawthorne et al.	7.864(1)	16.611(3)	5.650(1)	90.15(7)	738.1(0)

* Estimated standard deviation resulting from unit-cell calculation.

** Assumed to be 90.00°, as is necessary for powder patterns (Griffen and Ribbe, 1973).

† Standard deviation of two to four analyses on different crystals; real variation.

ed separately, as discussed above. We do not include Al end-members in the regression, because the Al content of T2 is nearly constant, as is the total Al content of most staurolite (Holdaway et al., 1986b; Hawthorne et al., 1993a; Holdaway et al., 1991). Finally, the fictive vacancy end-member is not the same as the actual vacancy content of T2, but is related to it through a complicated expression (see Holdaway et al., 1991, for an approach to calculating T2 vacancy). Amounts of these fictive chemical end-members are given in Table 1.

Chemical stoichiometry (Model B)

Dyar et al. (1991) gave the chemical stoichiometry of the 23 staurolite analyses on the basis of 48 O atoms. On a strictly chemical basis, unit-cell parameters are regressed for ten cations Si, Al, Fe³⁺, Fe²⁺, Mg, Li, Zn, Mn, Ti, and H, to give partial cation oxide cell parameters for each. The sum of the cations ranges from 32.63 to 33.74 (pfu). Here we use the cation numbers as independent variables in the regression analysis and then use the coefficients from the regression equation for unit-cell constants to multiply by the cation numbers for any given staurolite sample. In so doing we obtain partial molar volumes, which also account for the volume of O in the unit cell. The molar volume of any given staurolite sample may be determined by summing the partial volume of each cation oxide multiplied by its numerical coefficient. This approach ignores chemical end-members but allows Si and Al to vary, in addition to the other ions. As with the end-member approach, significant extrapolation is unwise. However, this method does allow limited extrapolation to the stoichiometric end-members H₂Fe₄Al₁₈Si₈O₄₈, H₄Fe₃Al₁₈Si₈O₄₈, and H₆Fe₂Al₁₈Si₈O₄₈, in which pfu Si is increased from 7.65 to 8, R²⁺ + Li + Ti + 0.5 H is reduced from 5.85 to 5, and Al is increased from 17.90 to 18.

Unit-cell dimensions

The unit-cell dimensions of the 23 natural staurolite samples were measured using a Scintag PAD V powder X-ray diffractometer with a Peltier-cooled solid-state detector, which serves as a monochromator. Finely ground staurolite was mixed with synthetic fluorophlogopite (NBS-675) used as an internal standard, dried from a H₂O slurry on a zero-background quartz slide, and scanned

at 0.25° 2 θ per minute, with counts collected every 0.01°. The data were refined using the personal computer refinement programs provided by the manufacturer, which use the digital raw data output to perform a background correction, locate peaks, adjust the peaks to the internal standard, and retrieve unit-cell parameters. Because of the pseudoorthorhombic nature of staurolite, the β angle was assumed to be 90°, as is necessary for powder diffraction study of staurolite (Griffen and Ribbe, 1973). For this program, diffraction lines are not automatically rejected if they do not agree with lines determined from calculated unit-cell dimensions. The worst lines were individually rejected until all lines agreed with calculated powder pattern within 0.024° in 2 θ , and within 0.004 Å in *d*. A few lines were found to be generally inconsistent with calculated values, and these were completely rejected. Between 31 and 37 lines were accepted for each individual specimen. The values of *a*, *b*, *c*, and *V* are given in Table 1.

The standard deviations resulting from the unit-cell refinements were less than 0.0008 Å for *a*, 0.0012 Å for *b*, and 0.0006 Å for *c*. We compared our results with the measurements of Hawthorne et al. (1993a) for the four staurolite samples analyzed in both studies (Table 2). The studies differ in that the measurements of Hawthorne et al. were performed on between two and four individual single crystals, and standard deviations of their results partly reflect real variation in composition between crystals of the same sample. For this reason, the agreement between the two studies is not satisfactory for sample 6-3 and is not very good for sample 71-62R. Sample 6-3 is highly heterogeneous (Holdaway et al., 1986b), and the same may be true for 71-62R, but to a lesser extent. In such cases, the powder results are more representative of the bulk sample than the single-crystal results. Both the chemical data of Holdaway et al. (1986b) and the Mössbauer data of Dyar et al. (1991) refer to the bulk sample. It is also clear that the assumption of 90° for the β angle has an insignificant effect on both the individual unit-cell dimensions and the volume.

Multiple linear regressions

Prior to conducting multiple linear regressions, scatter plots were constructed by plotting the chemical and unit-cell variables against each other. As expected, most of the

TABLE 3. Root mean square errors for six cases of multiple linear regression

Model	Case	Specimens used	a Å	b Å	c Å	V Å ³
A	1	All data	0.0021	0.0050	0.0011	0.42
A	2	HV-10, 82TP9A deleted	0.0022	0.0052	0.0009	0.41
A	3	117183 deleted	0.0022	0.0026	0.0010	0.29
B	4	All data	0.0038	0.0084	0.0027	0.52
B	5	HV-10, 82TP9A deleted	0.0029	0.0079	0.0017	0.46
B	6	117183 deleted	0.0039	0.0081	0.0028	0.45

scatter plots appear to be quite random, but a number of observations were made. (1) For Mg, Li, Mn, and Zn, there are one or two specimens each with unusually high abundances. These high values, although absolutely necessary for the best possible results, tend to have a disproportionate weight in the determination of coefficients for these elements. Fortunately, none of these elements dominates in most common staurolite samples. (2) There are moderately to highly negative correlations between vacancies and a ($r = -0.66$), c ($r = -0.91$), and V ($r = -0.84$), moderately positive correlations between Ti and b ($r = 0.53$), c ($r = 0.66$), and V ($r = 0.55$), a moderately negative correlation between Li and Mg ($r = -0.51$), a moderately positive correlation between Ti and Mg ($r = 0.49$), and a moderately positive correlation between Mn and Zn ($r = 0.50$).

The multiple linear regressions were carried out using PROC REG in SAS (SAS, 1985). Only the actual measurements were used in the analyses, the measurement errors being deemed small enough that they could effectively be ignored in the regression modeling. A linear regression model for a specific unit-cell characteristic, e.g., V , has the form

$$y = b_0 + b_1x_1 + \dots + b_kx_k + e \quad (1)$$

where y represents a V measurement on a single specimen, x_1 through x_k represent the individual calculated end-members for Model A ($k = 8$) or ionic measurements for Model B ($k = 10$) for the same specimen, b_0 through b_k are unknown regression coefficients, and e is an estimate of the error representing all sources of uncertainty (e.g., measurement errors, inexactness of the model) that prevent the relationship between V and ionic proportions from being exact.

For both Model A and Model B, the sum of the chemical constituents is very nearly constant, slightly greater than one for Model A and about 33 for Model B, and they are therefore well approximated by chemical mixture models. Because of this property, it is preferable to fit regression models that do not contain intercept terms, i.e., b_0 is set equal to zero (Sec. 2.2 of Cornell, 1981; Sec. 23.4 of Mason et al., 1989). This has the added value that the individual volume coefficients become partial unit-cell volumes (Model A) or partial ion oxide volumes (Model B) over the range of compositions that can be represented by linear mixtures of the various end-members or ions.

In all, six cases were examined. For both Model A and

Model B, regressions included (1) all 23 specimens, (2) 21 specimens, excluding HV-10 and 82TP9A, the two specimens for which H was estimated, and (3) 22 specimens, excluding 117183. Each unit-cell variable was regressed separately against the end-member amounts (Model A, Table 1) or ionic contents (Model B; Dyar et al., 1991). The root mean square errors (RMSE) for each of these six cases are given in Table 3 and are estimates of the model error standard deviations. These estimates give a measure of the typical deviation of the calculated unit-cell parameter from the measured value for a given composition.

RESULTS

Table 3 shows that, in general, Model A provides a more precise representation of variation of unit-cell parameters with composition than Model B, as indicated by the somewhat lower RMSE for Model A. However, for V , the differences are not large. It can be seen that deleting the samples for which H was estimated has no effect on the results for Model A and only a small effect for Model B. On the other hand, deleting 117183, which showed substantial discrepancies in b and V for case 1 in Table 3 (observed $b = 16.6096$ Å, predicted $b = 16.6241$ Å, observed $V = 739.4$ Å³, predicted $V = 740.5$ Å³) substantially improves the RMSE for b and V in Model A, while having little effect on Model B.

An individual specimen that has extreme values, or an unusual combination of values, in a regression model can severely distort a regression fit. Such a specimen may be unusual because of inaccurate data or because it does not fit the model. Numerous influence diagnostics are available for detecting such specimens (e.g., Ch. 2 of Belsley et al., 1980; Cook and Weisberg, 1982; Ch. 24 of Mason et al., 1989). A diagnostic that was especially effective in identifying influential specimens in this data set is RSTUDENT. RSTUDENT compares actual cell measurements with those predicted from the fitted models. Because individual RSTUDENT values have Student- t distributions, a cutoff value of ± 3 is used to identify cell dimensions that are not well fitted.

For the six cases shown in Table 3, RSTUDENT was determined for each specimen in each regression. Specimen 117183 has exceptionally large values (in magnitude) for RSTUDENT in two cases: -5.9 for b in case 1, -6.4 for b in case 2 (Model A). As noted above, Model A for case 1 predicts b to be 0.0145 Å higher than the measured value. Sample 117183 also has unusually low

TABLE 4. Linear regression coefficients, Model A, case 3, 117183 deleted

Variable	$a \text{ \AA}^*$	%Err.	$b \text{ \AA}$	%Err.	$c \text{ \AA}$	%Err.	$V \text{ \AA}^\dagger$	%Err.
Fe ²⁺	7.8836	0.14	16.6604	0.08	5.6909	0.09	746.89	0.20
Mg	7.9196	0.22	16.5338	0.13	5.6359	0.15	737.83	0.32
Li	7.9063	0.20	16.4147	0.11	5.6411	0.13	732.73	0.29
Zn	7.8719	0.17	16.5642	0.10	5.6733	0.11	739.25	0.25
Mn	8.0127	0.44	16.7494	0.25	5.7502	0.29	769.63	0.61
Ti	7.4208	3.79	17.3000	1.95	5.8595	2.28	772.13	4.87
□	7.8378	0.11	16.5505	0.06	5.5902	0.07	725.32	0.16
Fe ³⁺	0.0713	7.32	0.2377	26.34	0.0847	29.28	26.15	26.73
RMSE**	0.0022		0.0026		0.0010		0.29	
RSTUDENT values								
Sample	a		b		c		V	
356-1	-0.76		-0.71		0.44		-0.71	
EH-6	0.41		1.72		1.05		0.81	
B14040	1.18		-1.73		0.74		0.71	
117189	0.61		0.88		1.55		0.98	
6-3	-0.72		-1.16		0.28		-0.46	
3-3	-0.16		0.30		0.27		0.05	
114-1	-0.84		0.61		0.36		-0.21	
53-2	1.27		1.31		0.86		1.18	
ER-70	-0.20		-0.83		-0.03		-0.39	
82TP9	0.62		0.59		2.10		1.16	
82TP9A	-0.88		-0.89		-2.83		-1.51	
203	3.50		-0.51		1.19		2.54	
HV-4	-0.74		0.29		-0.72		-0.29	
HV-10	-0.25		-0.39		-2.19		-0.96	
HV-112	-0.31		0.57		0.26		-0.43	
HV-116	0.62		-0.15		-0.01		0.83	
77-55C	1.23		-1.06		0.66		0.71	
71-60E	-0.13		1.56		0.11		0.32	
71-62R	-0.27		2.86		-0.46		-0.26	
71-62U	-0.83		-0.87		-1.08		-0.96	
71-62T	1.80		-0.09		-1.49		-2.27	
71-62B	-0.26		-0.92		0.99		0.81	

* All parameters are given to the same number of decimal places as the original measurements.

** Root mean square error.

† Volume was regressed separately; therefore values do not agree with the product abc .

Si + Al, 25.3. Because of its anomalous nature, we delete specimen 117183 from the data set for both models.

In the regression fits with specimen 117183 deleted (Tables 4, 5), only specimens 203 and HV-10 have RSTUDENT values somewhat greater than three in magnitude. The large RSTUDENT values for these specimens occur in one model each. Because of the lack of consistency across both models and because the RSTUDENT values are not significantly above three, we choose to retain specimens 203 and HV-10 in the data set. Thus, we accept cases 3 and 6 (Table 3) as appropriate models. Figures 1 and 2 display calculated vs. measured values of the various cell dimensions and show graphically that Model A is more precise than Model B, especially for the individual cell dimensions a , b , and c .

Tables 4 and 5 list linear regression coefficients and standard errors given in percent ($100 \times$ standard error/coefficient) in order to facilitate comparison among compositional values and between models. With one exception (Fe³⁺), the standard errors for Model B are larger than those for Model A by factors of between 7 and 90. This is explained by two features of the fits. First, the additional variables Si and Al in Model B make up a large part of the staurolite composition but involve very limited compositional variation. The large errors that occur in Si and Al lead to large errors in all the other ions. The

larger errors in turn lessen the predictive ability of the individual ions, as indicated by the larger estimate of the model error standard deviation (RMSE) for Model B than for Model A.

Second, the functional relationships among the ion measurements in Model B are stronger than those in Model A because of the inclusion of the more precise measurement of H in place of vacancy content, which is determined by its difference from 5.85 in Model A and the precise measurement of Si and Al, which are ignored in Model A. This stronger functional relationship implies less independent variation of the compositional measurements in each specimen and a consequent rise in the uncertainty of the corresponding coefficient estimates. This is the well-known phenomenon of variance inflation due to the presence of colinearities among the ion measurements (e.g., Sec. 3.2 of Belsley et al., 1980; Sec. 27.4 of Mason et al., 1989).

These errors in the compositional measurements tend to compensate for each other, at least in the range of compositions studied, so that the RMSE values for Model B are only about twice those for Model A. Even though standard errors in ionic values for Model B are substantially larger than those for Model A, Model B remains a useful predictor of unit-cell parameters, especially V .

Another observation of interest involves V . The per-

TABLE 5. Linear regression coefficients, Model B, case 6, 117183 deleted

Variable	a Å*	%Err.	b Å	%Err.	c Å	%Err.	V Å ³ †	%Err.
Si	0.3196	4.13	0.7206	3.77	0.2386	3.98	29.42	5.20
Al	0.2512	2.47	0.5103	2.51	0.1748	2.52	23.33	3.09
Fe ³⁺	0.2326	6.84	0.5019	6.52	0.1714	6.65	24.86	7.40
Fe ²⁺	0.1609	5.78	0.3532	5.44	0.1283	5.22	17.77	6.08
Mg	0.1765	4.08	0.3401	4.38	0.1227	4.24	17.14	4.90
Li	0.0916	8.41	0.1442	10.89	0.0636	8.65	8.62	10.32
Zn	0.1612	5.09	0.3329	5.05	0.1250	4.72	16.70	5.69
Mn	0.1643	10.83	0.3533	10.36	0.1310	9.69	19.83	10.44
Ti	0.2750	41.24	0.6145	37.90	0.2326	34.82	40.90	32.10
H	0.0761	4.60	0.1605	4.55	0.0537	4.66	7.02	5.84
RMSE**	0.0039		0.0081		0.0028		0.45	
RSTUDENT values								
Sample	a		b		c		V	
356-1	1.19		-0.91		-0.06		-0.04	
EH-6	1.50		1.95		1.65		1.56	
B14040	0.82		0.16		0.84		0.53	
117189	2.61		2.63		2.95		2.44	
6-3	0.22		-0.09		0.28		0.21	
3-3	0.29		0.44		0.35		0.32	
114-1	-0.03		0.28		0.37		0.23	
53-2	1.19		2.08		1.44		1.09	
ER-70	1.10		0.86		1.00		0.67	
82TP9	0.23		0.13		0.72		0.64	
82TP9A	-0.88		-0.86		-1.48		-1.27	
203	1.12		-0.20		0.45		1.17	
HV-4	-0.42		-0.02		-0.23		-0.13	
HV-10	-3.15		-2.44		-4.13		-3.33	
HV-112	-0.90		-0.43		-0.54		-0.87	
HV-116	0.22		-0.37		-0.23		0.46	
77-55C	0.03		-0.47		0.06		-0.10	
71-60E	1.10		1.27		0.89		1.20	
71-62R	0.75		1.47		0.55		0.56	
71-62U	-1.09		-0.94		-1.03		-1.11	
71-62T	-1.03		-0.18		-0.58		-1.45	
71-62B	-1.06		-1.33		-0.77		-0.42	

* All parameters are given to the same number of decimal places as the original measurements.

** Root mean square error.

† Volume was regressed separately; therefore values do not agree with the product abc .

cent error in V for a single specimen is given by the square root of the sum of the squares of the percent errors of a , b , and c . This relationship holds approximately for percent standard errors in the regression for Model A for all ions except Fe³⁺. For Model B, the standard error of V is substantially smaller than that predicted from the individual unit-cell dimension standard errors (Tables 4, 5). This suggests that regression using Model B predicts V better than it predicts the individual dimensions. This is borne out by the RMSE values, which are about 1.5 times higher in Model B than in Model A for V , but between 1.8 and 3.1 times higher for a , b , and c . The effects of solid solution end-members (Model A) on individual cell dimensions are seen additively on the unit-cell volume, whereas such relationships are less quantitative with a model (B) based purely on complex stoichiometry.

One variable, Fe³⁺, appears to be a better predictor of cell dimensions and volume with Model B than with Model A, as seen by the substantially smaller standard error for Fe³⁺ in Model B than in Model A (Tables 4, 5). This may be because Fe³⁺ is chemically substituting for Al rather than R²⁺ (Holdaway et al., 1991), and Al variation is not accounted for in Model A.

The regression program provides partial regression residual plots for each ionic variable against each unit-cell variable. The linearity of such plots is an indication of whether the linear mixing model (Eq. 1) satisfactorily predicts the unit-cell variables. None of these plots shows any clear sign of curvature, suggesting that within the composition range studied the compositional variables have a linear effect on unit-cell variables, e.g., no second or higher order power terms are necessary in Equation 1. Thus within the range studied, the volume of mixing is ideal or nearly so. However, it is important to note that large extrapolations outside the range of analyzed specimens, especially in Mg, may not be as linear. Hawthorne et al. (1993a) have shown that in Mg-rich staurolite, Mg occurs in more sites than in normal staurolite, and this could cause nonlinearity in the relation between Mg content and unit-cell parameters. Regardless of whether nonlinearity exists outside of the range studied, molar volumes calculated from these end-member unit-cell volumes (Tables 4, 5) should be very good approximations to partial molar volumes for staurolite in the range of compositions studied.

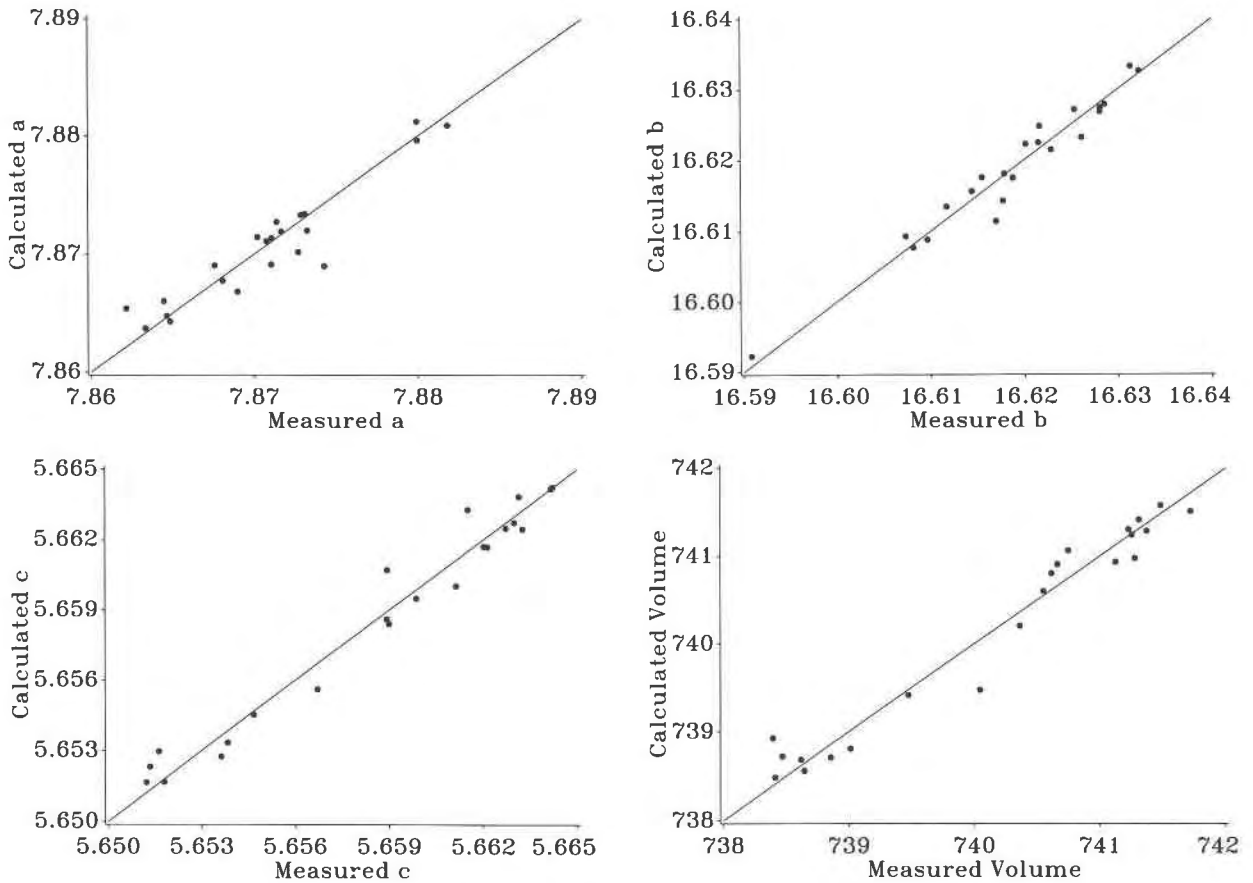


Fig. 1. Plots of actual vs. calculated values of a , b , c , and V for the 22 specimens used in multiple linear analysis with Model A.

CRYSTAL CHEMICAL CONSIDERATIONS

In discussing relationships between unit-cell variables and the various ionic radii, we rely mainly on the regression results for Model A (Table 4, Fig. 1), because it is more precise than Model B and because solid solution end-members directly affect all unit-cell variables partly on the basis of the radii of the ions. Most of the ions substituting for each other in Model A are on the T2 site of staurolite (see Holdaway et al., 1991 for a structure diagram). Cation-O distances for the ions in tetrahedral coordination (excluding Fe^{3+} and Al) are: Ti = 1.80 Å (Shannon, 1976); Mg = 1.95 Å (Shannon, 1976); Zn = 1.95 Å (Griffen, 1981); Li = 1.96 Å (Wenger and Armbruster, 1991); Fe^{2+} = 2.01 Å (Shannon, 1976); Mn = 2.04 Å (Shannon, 1976).

Because the fictive end-members (excluding Fe^{3+}) sum to one and have different variances in the data sets, the estimated regression coefficients are not directly comparable. In order to compare the relative influences of the solid-solution ions on the cell dimensions, the following adjusted coefficients are calculated (Section 5.7 of Cornell, 1981):

$$b_j^{\text{adj}} = R_j \left(b_j - \sum_{k \neq j} b_k / 6 \right) \quad (2)$$

where b_j is the j th estimated regression coefficient and R_j is the range (largest–smallest) of the 22 measurements (excluding 117183) on the j th ion. The adjusted coefficients for Model A are given in Table 6. These adjusted coefficients should only be used to compare the relative effects of the solid-solution ions on the cell dimensions; predictive equations for the cell dimensions should use the unadjusted coefficients in Tables 4 and 5.

Adjusted coefficients close to zero indicate that solid-solution ions have little influence on the average value of a cell parameter. Large adjusted coefficients indicate that ions have substantial influence on a cell parameter relative to other ions, positive coefficients increase the parameter, and negative coefficients reduce it. Because each cell parameter is fitted separately, coefficients should be interpreted separately for each parameter. The sequence of relative end-member size for each of the unit-cell parameters is given below on the basis of Table 6: a Ti < □ < Zn < Li < Fe^{2+} < Mn < Mg; b Li < Mg < Zn <

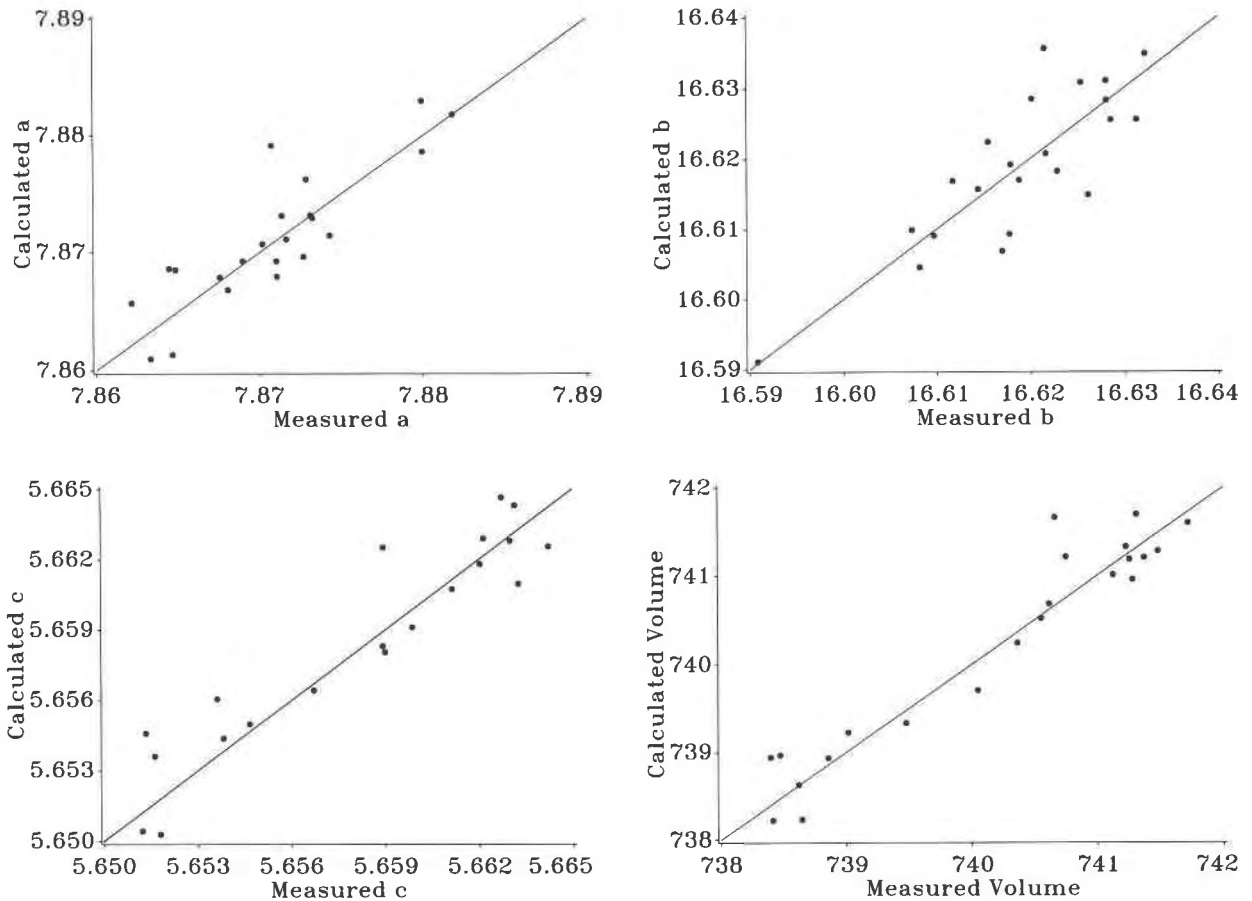


Fig. 2. Plots of actual vs. calculated values of a , b , c , and V for the 22 specimens used in multiple linear analysis with Model B. Note that the scatter is larger than for Model A (Fig. 1), especially for a , b , and c .

$\square < \text{Fe}^{2+} < \text{Mn} < \text{Ti}$; $c \square < \text{Mg} < \text{Li} < \text{Zn} < \text{Fe}^{2+} < \text{Ti} < \text{Mn}$; $V \square < \text{Mg} < \text{Li} < \text{Zn} < \text{Fe}^{2+} < \text{Ti} < \text{Mn}$. These values are similar, but not identical, to sequences based directly on the relative sizes of the coefficients of Table 4.

Based on these and previously published data, a number of observations may be made: (1) if we assume approximately constant H content for staurolite of a given solid-solution series, published synthetic results are roughly consistent with the above observations: for iron magnesium staurolite, a is approximately constant and b , c , and V decrease with increasing Mg (Richardson, 1967); for iron zinc staurolite, all cell parameters decrease with

increasing Zn; and for iron lithium staurolite, a is approximately constant and b , c , and V decrease with increasing Li. Griffen and Ribbe (1973) show a slight increase in a of natural staurolite with a decrease in Fe and an increase in other constituents, principally Mg. As will be seen later, small differences in H content are necessary along solid-solution series to bring synthetic staurolite unit-cell parameters into strict agreement with the present results. Such differences in H content may explain the fact that our results suggest that Mg substitution for Fe should actually increase a . (2) The R^{2+} end-members fall in the expected sequence in order of increasing ionic radius, except for Mg in the adjusted a dimension. (3) The small size of vacancies in T2, smaller than when occupied by any ion, suggested by Holdaway et al. (1986b), is corroborated by the present results. However, since the effect is actually that of the end-member and not the ion alone, the effect of increased H content is to increase the b dimension relative to that of smaller ions such as Mg and Zn. (4) The low-valence ion, Li, and the high-valence ion, Ti, exhibit opposite behavior. For a , a Ti end-member produces a small value, and a Li end-member produces a larger value, consistent with ionic radii. However, for

TABLE 6. Adjusted regression coefficients for Model A

Variable	a (Å)	b (Å)	c (Å)	V (Å ³)
Fe ²⁺	0.0148	-0.0069	-0.0002	0.2042
Mg	0.0263	-0.0473	-0.0178	-2.6924
Li	0.0135	-0.0525	-0.0099	-2.6578
Zn	0.0090	-0.0308	-0.0048	-1.8304
Mn	0.0167	0.0059	0.0052	2.0535
Ti	-0.0046	0.0068	0.0018	0.2838
□	0.0001	-0.0243	-0.0187	-3.8663

b, *c*, and *V*, a Ti end-member produces large values and a Li end-member produces small values. This behavior may be related to the positions of H atoms adjacent to the Ti- or Li-occupied T2 site, and to the different occupancies of these P sites, with high-charge or low-charge cations affecting adjacent P occupancy. The net result is a decrease in *b* and *c* with Li and an increase in *b* and *c* with Ti. The antipathetic behavior of Li and Ti end-members, presumably related to their charge, provides additional evidence that Ti and Li occupy similar sites, as suggested by Holdaway et al. (1991). The very limited compositional range of Ti in staurolite may be more a function of its charge than its size, given the fact that the site is large enough for it.

The results for Fe³⁺ (Table 4) provide limited evidence that Fe³⁺ replaces Al. (Holdaway et al., 1991, suggested the ions occur in the T2 site). The fact that the regression constants for Fe³⁺ are all positive indicates that the addition of Fe³⁺ to staurolite increases its cell dimensions. This must be the case, because in Model A no other ion in the model decreases as Fe³⁺ increases. In order to produce a positive coefficient in this case, Fe³⁺ should replace a smaller ion like Si or Al; Hawthorne et al. (1993a) have shown that Fe³⁺ cannot replace Si.

A brief explanation of the regression coefficients resulting from Model B (Table 5) is appropriate. Because variances on oxides are generally similar, coefficients may be compared directly without calculating adjusted coefficients. Using *V* as an example, partial cation oxide unit-cell volumes are as follows: HO_{0.5} 7.02, LiO_{0.5} 8.62, ZnO 16.70, MgO 17.14, FeO 17.77, MnO 19.83, AlO_{1.5} 23.33, FeO_{1.5} 24.86, SiO₂ 29.42, TiO₂ 40.90 Å³. Within each isoionic group the cation oxides follow an approximate ionic radius sequence, except for Ti, whose behavior is noted above. Thus the volume of cation oxides per O atom ranges from 14 to 20 Å³.

MOLAR VOLUMES OF Fe END-MEMBERS

For any given staurolite formula, unit-cell properties may be calculated by simply summing the products of end-member or cation contents and their coefficients given in Table 4 or 5. For Model A, the content of eight end-members, as described above, must be used. For Model B, the amounts of each of ten cations, including H, are simply those of the 48-O formula. Table 7 gives calculated unit-cell volumes (*V*) of Fe²⁺ end-member staurolite using both methods. The two models agree within 0.3 to 0.4 Å³. Model A (Table 4) can only be used for staurolite with about 17.90 Al and 7.65 Si, whereas the less accurate Model B may be used for any staurolite formula.

The first group of formulas in Table 7 shows that Model B may be used to calculate the effect of changing Al from 17.9 to 18 and Si from 7.65 to 8 to produce a stoichiometric end-member formula (e.g., H₂Fe₄Al₁₈Si₈O₄₈) from a chemical end-member formula (e.g., H_{3.7}Fe₄Al_{17.90}Si_{7.65}O₄₈), and this effect may be applied to a Model A calculation (numbers given in parentheses) for a more

TABLE 7. Unit-cell volumes of iron staurolite samples in Å³*

Formula	<i>V</i> , Model A	<i>V</i> , Model B
Determination of stoichiometric end-members		
H _{3.7} Fe ₄ Al _{17.90} Si _{7.65} O ₄₈	740.07	739.72
H ₂ Fe ₄ Al ₁₈ Si ₈ O ₄₈	(740.77)**	740.42
H _{5.7} Fe ₃ Al _{17.90} Si _{7.65} O ₄₈	736.38	735.99
H ₄ Fe ₃ Al ₁₈ Si ₈ O ₄₈	(737.08)	736.69
H _{7.7} Fe ₂ Al _{17.90} Si _{7.65} O ₄₈	732.69	732.26
H ₆ Fe ₂ Al ₁₈ Si ₈ O	(733.39)	732.96
Chemical end-members		
H ₃ Fe _{4.35} Al _{17.90} Si _{7.65} O ₄₈	741.36	741.03
H _{3.5} Fe _{4.10} Al _{17.90} Si _{7.65} O ₄₈	740.44	740.10
H ₄ Fe _{3.85} Al _{17.90} Si _{7.65} O ₄₈	739.52	739.16

* Model A is considered best. Errors are estimated at 0.5 Å³ for Model A.

** Values in parentheses have been calculated by analogy with Model B (see text).

precise value than if the procedures were done entirely with Model B. This is equivalent to an exchange operator of Al_{0.10}Si_{0.35}H_{-1.70}, which adds 0.70 Å³ to the molar volume of staurolite with the desired Fe calculated from data of Table 4. If the initial chemical staurolite formula is given at the desired H value instead of the desired Fe, the exchange operator becomes Al_{0.10}Si_{0.35}Fe_{-0.85}, it subtracts 2.47 Å³, and the final result is the same within 0.04 Å³. The best values for unit-cell and molar volumes (multiplying by Avogadro's number and converting units) for stoichiometric Fe end-members (Table 7) are H₂Fe₄-Al₁₈Si₈O₄₈ 740.77 Å³ or 44.61 ± 0.03 J/bar; H₄Fe₃-Al₁₈Si₈O₄₈ 737.08 Å³ or 44.39 ± 0.03 J/bar; H₆Fe₂-Al₁₈Si₈O₄₈ 733.39 Å³ or 44.17 ± 0.03 J/bar.

The second group of formulas in Table 7 shows calculated unit-cell volumes for other chemical end-member staurolite samples. These formulas should represent the compositional range expected in experimental studies on iron staurolite stability, with the assumption that Al and Si contents of synthesized staurolite are close to average natural compositions rather than stoichiometric values.

Molar volumes of other end-members (e.g., Zn, Li, Mg) may be calculated using the same procedures. However, care must be taken to use the calculated results properly. In most cases, the calculated values will be reasonable partial molar volumes for the composition range of common staurolite. The volumes shown in Table 7 represent a combination of the two most abundant constituents of common staurolite. Therefore, one may expect larger errors in molar volumes calculated for other end-members.

ESTIMATION OF H CONTENT OF SYNTHETIC STAUROLITE

Lonker (1983), Holdaway et al. (1986a), and Dyar et al. (1991) have demonstrated that H content of natural staurolite is variable and ranges from at least 2.7 to 4.6 H pfu. Holdaway et al. (1991) provided a method to estimate H content of natural staurolite from careful chemical analysis. It has become clear that we really do not know the compositions of staurolite grown from synthesis and hydrothermal stability experiments. If we don't know the compositions, it is not possible to retrieve ther-

TABLE 8. Formulas of synthetic staurolite samples calculated from unit-cell constants using Model A

Starting ratio R ²⁺ :Al:Si	Conditions (kbar, °C)	V Å ³	Formula*	Reference
4:18:8**	20, 715	743.4	H _{1.9} Fe _{4.9} Al _{17.9} Si _{7.65} O ₄₈	Richardson, 1967
4:18:8**	20, 715	740.2	H _{2.5} Fe _{3.22} Mg _{1.36} Al _{17.9} Si _{7.65} O ₄₈	Richardson, 1967
4:18:7.5	30, 750	742.2	H _{2.5} Fe _{4.6} Al _{17.9} Si _{7.65} O ₄₈	Griffen, 1981
4:18:7.5	30, 750	733.9	H _{4.5} Zn _{3.6} Al _{17.9} Si _{7.65} O ₄₈	Griffen, 1981
4:18:7.5	30, 720	741.2	H _{3.1} Fe _{4.3} Al _{17.9} Si _{7.65} O ₄₈	Dutrow, 1991
4:18.5:7.5†	30, 720	736.5	H _{3.7} Fe _{2.5} Li _{1.5} Al _{18.4} Si _{7.65} O ₄₈	Dutrow, 1991

* Fe³⁺ was assumed to be negligible.
** Minor quartz present with staurolite synthesis product.
† Minor corundum present with staurolite synthesis product.

modynamic data from such experiments, unless assumptions are made. The present results provide a way to estimate H contents of such staurolite specimens provided their unit-cell volumes are known. The advantage of working with synthesized staurolite samples is that there are constraints on their compositions and they are always simple systems. Disadvantages are that they are often grown at conditions outside the *P-T* range of most natural systems, and they may not always represent equilibrium compositions.

Table 8 gives formulas calculated from linear interpolation between unit-cell *V* of chemical end-members, like those at the bottom of Table 7, for two-component staurolite (e.g., Fe-H, Zn-H) and successive approximation for three-component staurolite (e.g., Fe-Mg-H, Fe-Li-H) synthesized by several authors. The calculations were done using Model A and assuming that Al = 17.90 and Si = 7.65, the average values for staurolite. If Al and Si were assumed to be stoichiometric, it would reduce H by 0.7 to 1.8 atoms and have little effect on R²⁺, leaving some H values well below two. The estimated error in H is about 1 atom pfu. Unit-cell volume is more sensitive to compositional change than any of the individual unit-cell dimensions. We found that the next most sensitive variable, *b*, gave much less consistent results.

Table 8 illustrates the following points: (1) The range of *V* measured for pure iron staurolite might be explained by variable H content as a result of differing synthesis conditions and varying degrees of attainment of equilibrium. (2) Synthesized staurolite probably has nonstoichiometric compositions as does natural staurolite. The compositions of synthesized staurolite may be approximated by assuming that the relatively constant contents of Al and Si are similar to those of average natural staurolite. (3) In synthesis studies done at the same *P* and *T*, Fe-rich compositions have less H (less vacancy in T2) than solid solutions or end-members with the smaller ions, Mg, Zn, and Li. Since these ions represent all the major solid solutions, it is safe to conclude that for staurolite in general, those samples with higher Fe content will tend to have less H than staurolite with larger amounts of the other components, if the conditions of formation and coexisting phases are the same. (4) Unit-cell volume measurements are useful in estimating the compositions of

synthesized staurolite, if reasonable assumptions regarding Al and Si content are made.

In some instances, unit-cell volume measurements may be useful for putting constraints on the chemistry of natural staurolite. In such staurolite, unit-cell volume may be used to confirm H or Li content estimated using methods of Holdaway et al. (1991).

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