Thermodynamic properties of stoichiometric staurolite $H_2Fe_4Al_{18}Si_8O_{48}$ and

$H_6Fe_2Al_{18}Si_8\ O_{48}$

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For deposit: Table 1

Data sheets for Table 1, Thermodynamic Properties of Stoichiometric Staurolites $H_2Fe_4Al_{18}Si_8O_{48}$ and $H_6Fe_2Al_{18}Si_8O_{48}$, by Holdaway, Mukhopadhyay, and Dutrow

Introduction

These data sheets represent an expanded version of our paper on thermodynamic properties of staurolite. In the main, they include the various algebraic calculations that were necessary for the paper. In order to follow the logic of the calculations, it is necessary to work closely with the paper, which is in approximately the same order. References are given in the report, except that references not cited in the report are given at the close of these data sheets [brackets].

Structural Analog

We choose the same structural analog for $\underline{C}_P$ as for $\underline{S}$. To adjust the formula of 355-1 (Zen, 1981; used by Hemingway and Robie, 1984 for $\underline{C}_P$ and $\underline{S}$) with formula $H_{3.317}Fe^{2+}_{3.239}Mg_{0.458}Mn_{0.028}Zn_{0.052}Li_{0.326}Co_{0.007}Al_{17.741}Fe^{3+}_{0.117}Cr_{0.013}V_{0.006}Si_{7.706}Ti_{0.084}O_{48}$ (Holdaway et al., 1986b), assuming that 3.5% of Fe is ferric (Dyar et al., 1991; Holdaway et al., 1991). We eliminate unwanted elements by subtracting appropriate amounts of $\underline{C}_P$ or $\underline{S}$ for MgO, MnO, ZnO, Li_2O, CoO, Fe_2O_3, Cr_2O_3, and V_2O_5. In order to adjust the H,Fe,Al,Si formula to each of the two end-member formulas above we do the following steps in order: (1) add or subtract pyrophyllite to give the correct H, (2) add or subtract fayalite to give the correct Fe^{2+}, (3) add or subtract kyanite to give the correct Al, (4) add or subtract alpha quartz to give the correct Si.

Calorimetric Entropy

Chemical Entropy (J/mol K)

Component	Contribution	Product	Reference[1]
Staurolite 355-1	+1 x 980.00 =	+980.00	HR84
MgO	-0.458 x 26.90 =	-12.32	HP90
MnO	-0.028 x 59.70 =	-1.67	HP90
ZnO	-0.052 x 43.64 =	-2.27	RHF78
Li_2O	-0.163 x 37.57 =	-6.12	RHF78
CoO	-0.007 x 52.97 =	-0.37	RHF78
Fe_2O_3	-0.059 x 87.40 =	-5.16	HP90
Cr_2O_3	-0.007 x 81.17 =	-0.57	RHF78

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[1] HR84 = Hemingway and Robie (1984), HP90 = Holland and Powell [1990], RHF78 = Robie et al. [78], HM93 = Holdaway and Mukhopadhyay (1993), HGMD93 = Holdaway et al. (1993).

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Cr_2O_3	-0.007 x 81.17 =	-0.57	RHF78
V_2O_3	-0.003 x 98.07 =	-0.29	RHF78
TiO_2	-0.084 x 50.30 =	-4.23	HP90
$H_{3.317}Fe_{3.239}Al_{17.741}Si_{7.706}$		+947.00	sum
$Al_2Si_4O_{10}(OH)_2$	-0.6585 x 266.30 =	-175.36	HP90
Fe_2SiO_4	+0.3805 x 151.00 =	+57.46	HP90
$Al_2SiO_5^{ky}$	+0.788 x 82.86 =	+65.29	HM93
SiO_2^{α}	+1.7595 x 41.50 =	+73.02	HP90
$H_2Fe_4Al_{18}Si_8O_{48}$		+967.41	sum
$Al_2Si_4O_{10}(OH)_2$	+1.3415 x 266.30 =	+357.24	HP90
Fe_2SiO_4	-0.6195 x 151.00 =	-93.54	HP90
$Al_2SiO_5^{ky}$	-1.212 x 82.86 =	-100.43	HMms
SiO_2^{α}	-3.2405 x 41.50 =	-134.48	HP90
$H_6Fe_2Al_{18}Si_8O_{48}$		+975.79	sum

Disorder Correction

Disorder correction is

$H_2Fe_4Al_{18}Si_8O_{48}$	+34.59
$H_6Fe_2Al_{18}Si_8O_{48}$	+57.65

Volume Correction

The formula for 355-1, recalculated without trace elements is $H_{3.319}Fe^{2+}_{3.241}Mg_{0.458}Mn_{0.028}Zn_{0.052}Li_{0.326}Al_{17.754}Fe^{3+}_{0.117}Si_{7.712}Ti_{0.084}O_{48}$. Molar volume using Holdaway et al. (1993) Model A = 44.576 J/b , Model B = 44.588 J/b. We choose 44.576 J/b because Model A is more precise, and assume this volume is valid for 355-1 <u>with</u> trace elements.

Component	Contribution	Product	Reference[1]
Staurolite 355-1	+1 x 44.576 =	+44.576	HGMD93
MgO	-0.458 x 1.125 =	-0.515	HP90
MnO	-0.028 x 1.322 =	-0.037	HP90
ZnO	-0.052 x 1.434 =	-0.075	RHF78
Li_2O	-0.163 x 1.476 =	-0.241	RHF78
CoO	-0.007 x 1.164 =	-0.008	RHF78
Fe_2O_3	-0.059 x 3.027 =	-0.179	HP90
Cr_2O_3	-0.007 x 2.909 =	-0.020	RHF78
V_2O_3	-0.003 x 2.985 =	-0.009	RHF78
TiO_2	-0.084 x 1.882 =	-0.158	HP90
$H_{3.317}Fe_{3.239}Al_{17.741}Si_{7.706}O_x$		43.334	sum

$Al_2Si_4O_{10}(OH)_2$	-0.6585 x 11.318 =	-7.453	HP90
Fe_2SiO_4	+0.3805 x 4.630 =	+1.762	HP90
$Al_2SiO_5^{ky}$	+0.788 x 4.408 =	+3.474	HM93
SiO_2^{α}	+1.7595 x 2.269 =	+3.992	HP90
$H_2Fe_4Al_{18}Si_8O_{48}$ calculated		45.109	sum
$H_2Fe_4Al_{18}Si_8O_{48}$ measured		44.610	HGMD93
$Al_2Si_4O_{10}(OH)_2$	+1.3415 x 11.318 =	+15.183	HP90
Fe_2SiO_4	-0.6195 x 4.630 =	-2.868	HP90
$Al_2SiO_5^{ky}$	-1.212 x 4.408 =	-5.342	HM93
SiO_2^{α}	-3.2405 x 2.269 =	-7.353	HP90
$H_6Fe_2Al_{18}Si_8O_{48}$ calculated		42.954	sum
$H_6Fe_2Al_{18}Si_8O_{48}$ measured		44.165	HGMD93

Assuming that the correction factor is 0.5 cal/cc, 20.92 J/(J/b)

$H_2Fe_4Al_{18}Si_8O_{48}$	-20.92 x 0.499 =	-10.44	product
$H_6Fe_2Al_{18}Si_8O_{48}$	+20.92 x 1.211 =	+25.33	product

Final Entropies

$H_2Fe_4Al_{18}Si_8O_{48}$ +967.41 + 34.59 -10.44 = 991.56 J/(mol K)

$H_6Fe_2Al_{18}Si_8O_{48}$ +975.79 + 57.65 + 25.33 = 1058.77 J/(mol K)

Entropy Error

Standard deviation in entropy is estimated as the rms combination of four terms, calorimetric error, plus 50% of chemical correction, plus 50% of volume correction, plus 50% of the disorder correction.

$$2H - (12^2 + 6.30^2 + 5.22^2 + 17.30^2)^{1/2} = 22.6$$

$$6H - (12^2 + 2.10^2 + 12.67^2 + 28.83^2)^{1/2} = 33.8$$

Volume

Molar volumes are those given by Holdaway et al. (1993):

$H_2Fe_4Al_{18}Si_8O_{48}$ 44.610 ± 0.030 J/b

$H_6Fe_2Al_{18}Si_8O_{48}$ 44.165 ± 0.030 J/b

Specific Heat[2]

For C_P, we use the same basic additivity rule, using the structural analogs used for entropy, except that there is no volume correction. Equation is $C_P = a + bT + cT^{-2} + dT^{-1/2} + eT^2$. Primes represent multiplied values.

Oxide	Multiplier	a (e)	b	c	d	a' (e')	b'	c'	d'
St. 355-1	+1	+2907.9	-0.0021866	-7376500	-26829	+2907.9	-0.0021866	-7376500	-26829
MgO	-0.458	+65.211	-0.0012699	-461850	-387.24	-29.867	+0.0005816	+211527	+177.35
MnO	-0.028	+59.749	+0.0036	-31362	-282.65	-1.673	-0.0001008	+878	+7.91
ZnO	-0.052	-13.664	+0.040569	-2188200	+1166.9	+0.711	-0.0021096	+113764	-60.68
e and e'		-0.000008703				+0.000000453			
Li$_2$O	-0.163	+117.48	+0.0053302	+151800	-1151.5	-19.149	-0.0008688	-24743	+187.69
CoO	-0.007	-30.468	+0.029459	-4165800	+1931.7	+0.213	-0.0002062	+29161	-13.52
Fe$_2$O$_3$	-0.059	+174.0	-0.003479	-1849500	-897.8	-10.266	+0.0002053	+109121	+52.97
Cr$_2$O$_3$	-0.007	+119.02	+0.0094964	-1441900	-3.4045	-0.833	-0.0000665	+10093	+0.02
V$_2$O$_3$	-0.003	+57.989	+0.0412	-3871800	+1351.0	-0.174	-0.0001236	+11615	-4.05
TiO$_2$	-0.084	+63.079	+0.011307	-986260	-5.616	-5.299	-0.0009498	+82846	+0.47
H$_{3.317}$Fe$_{3.239}$Al$_{17.741}$Si$_{7.706}$O$_x$						+2841.563	-0.0058250	-6832238	-26480.84
e'						+0.000000453			

Oxide	Multiplier	a	b	c	d	a' (e')	b'	c'	d'
Py	-0.6585	+545.0	+0.02068	-8331200	-2283.0	-358.883	-0.0136178	+5486095	+1503.36
Fa	+0.3805	+59.9	+0.07062	-5743700	+2012.1	+22.792	+0.0268709	-2185478	+765.60
Ky	+0.788	+279.435	-0.007124	-2055600	-2289.36	+220.195	-0.0056137	-1619813	-1804.02
Q$^\alpha$	+1.7595	+97.9	-0.00335	-636200	-774.0	+172.255	-0.0058943	-1119394	-1361.85

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[2] Sources of C_P data include Hemingway and Robie (1984), Hemingway et al. (1991), Berman (1988), Robie et al. [1978], Holland and Powell [1990].

$H_2Fe_4Al_{18}Si_8O_{48}$
e'   +2897.922 -0.0040799 -6270828 -27377.75
+0.000000453

Oxide	Multiplier	a	b	c	d	a' (e')	b'	c'	d'
Py	+1.3415	+545.0	+0.02068	-8331200	-2283.0	+731.118	+0.0277422	-11176305	-3062.64
Fa	-0.6195	+59.9	+0.07062	-5743700	+2012.1	-37.108	-0.0437491	+3558222	-1246.50
Ky	-1.212	+279.435	-0.007124	-2055600	-2289.36	-338.675	+0.0086343	+2491387	+2774.70
Q^α	-3.2405	+97.9	-0.00335	-636200	-774.0	-317.245	+0.0108557	+2061606	+2508.15

$H_6Fe_2Al_{18}Si_8O_{48}$
e'   +2879.653 -0.0023419 -9897328 -25507.13
+0.000000453

Final Average Site Assignments (Hawthorne et al., 1993a, excluding 2 low-Fe; Holdaway et al., 1991; Henderson et al., 1993)[3]

		71-62R	EH6	3-3	6038	7189	6-3	WARD	MOT	MUS	PIO	DW-7	DER	MAR	Ave	Corrected
M1	Al	7.833	7.477	7.725	7.730	7.705	7.745	7.540	7.710	7.745	7.720	7.695	7.770	7.732	7.702(94)	7.701
	Mg	0.067	0.413	0.180	0.265	0.235	0.090	0.340	0.170	0.235	0.225	0.190	0.220	0.172	0.216(92)	0.216
	Fe	0.100	0.110	0.095	0.015	0.060	0.165	0.120	0.120	0.020	0.055	0.115	0.010	0.096	0.083(47)	0.083
M2	Al	7.840	7.724	7.820	7.820	7.755	7.780	7.680	7.850	7.880	7.785	7.710	7.860	7.754	7.789(62)	7.789
	Mg	0.020	0.123	0.050	0.070	0.100	0.020	0.090	0.050	0.070	0.055	0.050	0.100	0.048	0.065(31)	0.065
	Fe	0.140	0.153	0.130	0.110	0.145	0.200	0.230	0.100	0.050	0.160	0.240	0.040	0.198	0.146(69)	0.056
	Ti															0.090
M3	Al	1.690	1.823	1.965	1.885	1.870	1.915	1.680	1.770	1.810	1.900	1.905	1.890	1.834	1.841(86)	1.841
	Mg	0.030	0.200	0.090	0.130	0.075	0.040	0.170	0.080	0.115	0.100	0.095	0.110	0.086	0.102(46)	0.102

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[3]Averaged by first averaging the occupancies for each specimen, and then averaging the specimen values.

	Fe	0.067	0.027	0.035	0.005	0.025	0.025	0.000	0.000	0.000	0.000	0.000	0.000	0.040	0.017(21)	0.017
	❑	2.213	1.950	1.910	1.985	2.030	2.020	2.150	2.150	2.075	2.000	2.000	2.000	2.040	2.040(86)	2.040
M4	Fe	0.413	0.113	0.095	0.135	0.095	0.000	0.190	0.140	0.155	0.140	0.220	0.135	0.186	0.127(60)	0.110
	Zn															0.009
	Li															0.008
	❑	3.587	3.887	3.905	3.865	3.905	4.000	3.810	3.860	3.845	3.860	3.780	3.865	3.814	3.845(95)	3.845
T1	Si	7.673	7.703	7.655	7.460	7.690	7.780	7.660	7.420	7.540	7.480	7.645	7.525	7.618	7.604(108)	7.604
	Al	0.327	0.297	0.345	0.540	0.310	0.220	0.340	0.580	0.460	0.520	0.355	0.475	0.382	0.396(108)	0.396
T2	Fe*	2.360	2.703	3.165	2.350	2.030	2.360	2.330	3.180	3.040	2.985	2.645	3.400	2.670	2.709(416)	2.551
	Fe^{3+}															0.115
	Mn															0.060
	Zn	0.037	0.057	0.040	0.645	1.365	0.100	0.030	0.030	0.085	0.080	0.210	0.030	0.160	0.221(382)	0.212
	Mg	0.153	0.913	0.425	0.625	0.350	0.215	0.820	0.400	0.540	0.455	0.450	0.400	0.406	0.473(213)	0.473
	Li	0.400	0.017	0.125	0.010	0.060	1.085	0.030	0.090	0.055	0.120	0.135	0.100	0.132	0.181(289)	0.173
	Al	0.227	0.093	0.055	0.105	0.000	0.245	0.560	0.220	0.075	0.130	0.215	0.000	0.248	0.167(148)	0.167
	❑	0.823	0.230	0.190	0.265	0.195	0.000	0.380	0.280	0.310	0.280	0.440	0.270	0.372	0.310(188)	0.310

Staurolite Thermodynamic Mole Fraction (Activity) Models

For activity models, dilution of Fe^{2+} in T2 is modelled on the basis of $(4 - {}^{T2}\square - {}^{M3}\square) = n$ ions. The activity model for 2H staurolite is

$$X_{2HFe\text{-}St}^{St} = \left(\frac{7.70}{8}\right)^8 \cdot \left(\frac{7.79}{8}\right)^8 \cdot {}^{M3}X_{Al}^2 \cdot {}^{T1}X_{Si}^8 \cdot {}^{M4}X_\square^2 \cdot {}^{T2}X_{Fe^{2+}}^n$$

$$= 0.5954 \; {}^{M3}X_{Al}^2 \cdot {}^{T1}X_{Si}^8 \cdot {}^{M4}X_\square^2 \cdot {}^{T2}X_{Fe^{2+}}^n$$

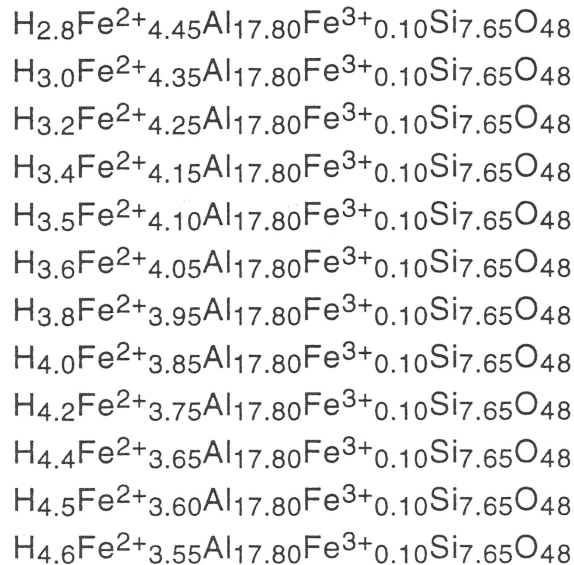where ${}^{T2}X_{Fe^{2+}} = {}^{T2}Fe^{2+}/n$. The activity model for 6H staurolite is

$$X_{6HFe\text{-}St}^{St} = \left(\frac{7.70}{8}\right)^8 \cdot \left(\frac{7.79}{8}\right)^8 \cdot {}^{M3}X_{Al}^2 \cdot {}^{T1}X_{Si}^8 \cdot {}^{M4}X_{Fe^{2+}}^2$$

$$= 0.5954 \; {}^{M3}X_{Al}^2 \cdot {}^{T1}X_{Si}^8 \cdot {}^{M4}X_{Fe^{2+}}^2 \, .$$

Activities of $H_2Fe_4Al_{18}Si_8O_{48}$ and $H_6Fe_2Al_{18}Si_8O_{48}$ in Experimental FASH Staurolites

We assume that the best compositional representation of experimental Fe staurolites in quartz-bearing systems is equivalent to average natural Fe^{3+}-free staurolites plus 0.10 Fe^{3+} replacing Al, to represent reducing conditions near the QFM buffer. Total Al remains constant (Holdaway et al. 1986a; Dyar et al. 1991). Thus we have a psuedobinary chemical solid solution series given by the following representative members:

$$H_{2.8}Fe^{2+}_{4.45}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{3.0}Fe^{2+}_{4.35}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{3.2}Fe^{2+}_{4.25}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{3.4}Fe^{2+}_{4.15}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{3.5}Fe^{2+}_{4.10}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{3.6}Fe^{2+}_{4.05}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{3.8}Fe^{2+}_{3.95}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{4.0}Fe^{2+}_{3.85}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{4.2}Fe^{2+}_{3.75}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{4.4}Fe^{2+}_{3.65}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{4.5}Fe^{2+}_{3.60}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$
$$H_{4.6}Fe^{2+}_{3.55}Al_{17.80}Fe^{3+}_{0.10}Si_{7.65}O_{48}$$

We use the activity model on p. 7 discussed in the text. For the synthetic system, activities of both 6H and 2H staurolite include a factor which covers M1, M2, and T1, equal to $(7.7/8)^8 \cdot (7.79/8)^8 \cdot (7.65/8)^8 = 0.4163$. The remaining factors relate to M3, M4, and T2. As seen below, the T2 expression for 2H staurolite is nearly constant at 0.83. The complete expressions are

$$0.4163 \cdot {}^{M3}X_{Al}^2 \cdot {}^{M4}X_{\square}^2 \cdot {}^{T2}X_{Fe^{2+}}^n \quad \text{for 2H,}$$

$$0.4163 \cdot {}^{M3}X_{Al}^2 \cdot {}^{M4}X_{Fe^{2+}}^2 \quad \text{for 6H.}$$

Based on the following ion amounts (p. 7),

H	T2$\square$	M3$\square$	M4Fe^{2+}	M4$\square$	M3Al	T2Al,Fe^{3+}	T2Fe^{2+}
2.8	0	0	0	2	1.8800	0.1800	3.8200
3.0	0.1368	0.0316	0.0684	1.9316	1.8484	0.2116	3.6516
3.2	0.2718	0.0641	0.1359	1.8641	1.8159	0.2441	3.4841
3.4	0.4050	0.0975	0.2025	1.7975	1.7825	0.2775	3.3175
3.5	0.4712	0.1144	0.2356	1.7644	1.7656	0.2944	3.2344
3.6	0.5368	0.1316	0.2684	1.7316	1.7484	0.3116	3.1516
3.8	0.6666	0.1667	0.3333	1.6667	1.7133	0.3467	2.9867
4.0	0.7948	0.2026	0.3974	1.6026	1.6774	0.3826	2.8226
4.2	0.9212	0.2394	0.4606	1.5394	1.6406	0.4194	2.6594
4.4	1.0456	0.2772	0.5228	1.4772	1.6028	0.4572	2.4972
4.5	1.1072	0.2964	0.5536	1.4464	1.5836	0.4764	2.4164
4.6	1.1678	0.3161	0.5837	1.4163	1.5639	0.4961	2.3361

Calculated activities are as follows:

H	${}^{M3}X_{Al}^2$	${}^{T2}X_{Fe^{2+}}^n$	${}^{M4}X_{\square}^2$	${}^{M4}X_{Fe^{2+}}^2$	$X_{2HFe\text{-}St}^{St}$	$X_{6HFe\text{-}St}^{St}$
2.8	0.8836	0.8318	1	0	0.3060	0
3.0	0.8541	0.8316	0.9328	0.00117	0.2758	0.000416
3.2	0.8244	0.8315	0.8687	0.00462	0.2479	0.00159
3.4	0.7943	0.8313	0.8078	0.0103	0.2221	0.00341
3.5	0.7793	0.8312	0.7783	0.0139	0.2099	0.00451
3.6	0.7642	0.8311	0.7496	0.0180	0.1982	0.00573
3.8	0.7338	0.8308	0.6945	0.0278	0.1763	0.00849

4.0	0.7034	0.8306	0.6421	0.0395	0.1562	0.0116
4.2	0.6729	0.8303	0.5924	0.0530	0.1378	0.0148
4.4	0.6422	0.8300	0.5455	0.0683	0.1210	0.0183
4.5	0.6269	0.8298	0.5230	0.0766	0.1133	0.0200
4.6	0.6114	0.8296	0.5015	0.0852	0.1059	0.0217

Staurolite-Quartz Reversals, Extended 2% in P and 15 °C in T away from Equilibrium

Staurolite + Quartz = Sillimanite + Almandine
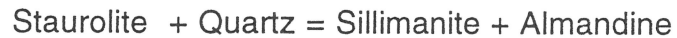
Pressure bar	Temperature °C	Stability	Reference[4]
3315	629	Staurolite	DH89
3185	673	Breakdown	DH89
5100	659	Staurolite	DH89
4900	718	Breakdown	DH89
9180	685	Staurolite	DU
8820	730	Breakdown	DU
14280	705	Staurolite	DU
13720	765	Breakdown	DU
5100	660	Staurolite	R68
4900	715	Breakdown	R68
10200	660	Staurolite	R68
9800	725	Breakdown	R68
7350	715	Breakdown	R68
1960	690	Breakdown	R68

Staurolite + Quartz = Kyanite + Almandine
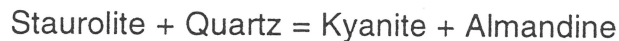
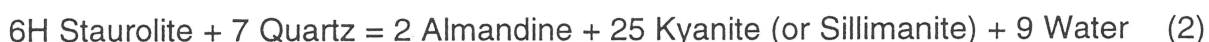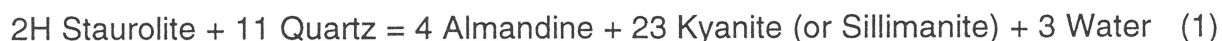| Pressure bar	Temperature °C	Stability	Reference[5]
14700	575	Staurolite	RJ79
15300	635	Breakdown	RJ79
9800	625	Staurolite	RJ79
10200	675	Breakdown	RJ79

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[4] DH89 = Dutrow and Holdaway (1989), DU = Dutrow, this report, R68 = Richardson (1968).

[5] RJ79 = Rao and Johannes (1979), G72 = Ganguly (1972)

5880	665	Staurolite	RJ79
6120	715	Breakdown	RJ79
15190	585	Staurolite	G72
15810	665	Breakdown	G72
14280	665	Breakdown	G72
10388	635	Staurolite	G72
10200	705	Breakdown	G72
6860	685	Staurolite	G72

Staurolite Decomposition Reactions in FASH

The following equilibria constitute all the reactions involving staurolite, garnet, Al silicates, and excess quartz in the simple FASH system:

2H Staurolite + 11 Quartz = 4 Almandine + 23 Kyanite (or Sillimanite) + 3 Water   (1)

6H Staurolite + 7 Quartz = 2 Almandine + 25 Kyanite (or Sillimanite) + 9 Water   (2)

6H Staurolite + Quartz = 2H Staurolite + 9 Kyanite (or Sillimanite) + 5 Water   (3)

6H Staurolite + 18 Almandine = 25 2H Staurolite + 38 Quartz + 44 Water   (4)

Maine M3 Staurolite and Garnet

All staurolite that coexists with garnet and quartz must obey Reaction 4: The specimens listed below formed at about 3.1 kbar, 540 °C, $\underline{a}(H_2O) = 0.86$ and contain staurolite, garnet, and quartz. Each have been analyzed for H, and some for Fe^{3+}/Fe^{2+}. The other Fe^{3+}/Fe^{2+} relations are determined by analogy with Dyar et al. (1991) and Holdaway et al. (1991) with 3.5% of Fe in staurolite assumed to be Fe^{3+}. Note that analyses of staurolite have been recalculated without trace Co, Cr, V, and F. The tabulated garnet compositions (below) are peak $\underline{T}$ garnet.

Maine Staurolite Compositions

Specimen	3-3	86	114-1	164	53-2
Si	7.631	7.655	7.624	7.663	7.501
Al	17.886	17.862	17.890	17.863	17.984
Ti	0.114	0.106	0.093	0.104	0.105
Fe^{2+}	3.200	3.294	3.285	3.165	3.337
Fe^{3+}	0.095	0.119	0.098	0.115	0.100
Mg	0.790	0.648	0.561	0.683	0.609

Mn	0.114	0.038	0.017	0.048	0.054
Zn	0.037	0.058	0.060	0.048	0.050
Li	0.124	0.226	0.417	0.204	0.258
CATSUM	29.991	30.006	30.045	29.893	29.998
H	2.673	2.713	2.903	2.907	2.965

The average value of CATSUM is 29.988 $\pm$ 0.058. Much of this standard deviation is due to random analytical error, since all the staurolites come from the same metamorphic conditions and from garnet-biotite-bearing rocks. Hawthorne et al. (1993a) have determined the cation occupancies of sample 3-3. Except for a Li-rich specimen, 3-3 has the lowest occupancy of M4 and the highest value of CATSUM of all the staurolites he has studied. In these low-H staurolites, there is significant potential for error in estimation of the occupancy of M4 from chemical analyses, whereas the crystal structure determinations give that value with more accuracy since it is mostly Fe^{2+}. The occupancy of M4 is a significant factor in determining the activity of 6H staurolite. In order to bring the occupancy of M4 in 3-3 into reasonable agreement with the crystal structure determination and lower the values of CATSUM below 30 we recalculated the staurolite stiochiometries on the basis of 0.3 additional H, equivalent to an upward correction of 3σ analytical error in H. This apparent analytical discrepancy in H may have resulted from quartz inclusions in the Maine staurolites, some of the most inclusion-filled staurolites analyzed by Holdaway et al. (1986a). The fact that $Si + Al + Fe^{3+} + 2/3Ti - 1/3Li$ for the recalculated staurolites averages within 0.1% of the best average value of 25.55 (Holdaway et al., 1991) supports this conclusion. The activity of 6H staurolite at this locality is expected to be low and uncertain.

Maine Staurolite Compositions Based on Addition of 0.3 H

Specimen	3-3	86	114-1	164	53-2
Si	7.606	7.630	7.599	7.638	7.477
Al	17.828	17.804	17.832	17.805	17.926
Ti	0.114	0.106	0.093	0.104	0.105
Fe^{2+}	3.190	3.283	3.274	3.155	3.323
Fe^{3+}	0.095	0.119	0.098	0.115	0.100
Mg	0.787	0.646	0.558	0.683	0.607
Mn	0.114	0.038	0.017	0.048	0.054
Zn	0.037	0.058	0.060	0.048	0.050

Li	0.124	0.225	0.415	0.204	0.257
CATSUM	29.895	29.909	29.946	29.800	29.899
H	2.973	3.013	3.203	3.207	3.265
$Si + Al + Fe^{3+} +$ .67Ti - .33Li	25.564	25.549	25.433	25.559	25.487

Maine Staurolite Cation Assignments

Using the procedure given in the text, the cations assignments are as follows:

Site	Ion	3-3	86	114-1	164	53-2
M1	Al	7.700	7.700	7.700	7.700	7.700
	Mg	0.203	0.182	0.165	0.190	0.175
	Fe^{2+}	0.097	0.118	0.135	0.110	0.125
M2	Al	7.790	7.790	7.790	7.790	7.790
	Mg	0.046	0.042	0.041	0.046	0.040
	Fe^{2+}	0.050	0.062	0.076	0.060	0.065
	Ti	0.114	0.106	0.093	0.104	0.105
M3	Al	1.847	1.851	1.863	1.816	1.848
	Mg	0.099	0.093	0.089	0.096	0.091
	Fe^{2+}	0.021	0.027	0.031	0.024	0.029
	❏	0.033	0.029	0.017	0.064	0.032
M4	Fe^{2+}	0.067	0.057	0.032	0.125	0.063
	Zn	0.001	0.001	0.001	0.002	0.001
	Li	0.003	0.004	0.004	0.009	0.005
	❏	1.928	1.938	1.963	1.864	1.931
T1	Si	7.606	7.630	7.599	7.638	7.477
	Al	0.394	0.370	0.401	0.362	0.523
T2	Fe^{2+}	2.955	3.019	3.000	2.836	3.041
	Mg	0.439	0.329	0.263	0.351	0.301
	Zn	0.036	0.057	0.059	0.046	0.049
	Li	0.121	0.221	0.411	0.195	0.252
	Mn	0.114	0.038	0.017	0.048	0.054
	Al	0.097	0.093	0.078	0.137	0.065
	Fe^{3+}	0.095	0.119	0.098	0.115	0.100
	❏	0.144	0.124	0.074	0.272	0.138

Maine Staurolite Activities

The important staurolite site contents are repeated below:

Spec.	T2 $\square$	M3 $\square$	M4 $\square$	M4Fe^{2+}	M3Al	T2Fe^{2+}	T1Si
3-3	0.144	0.033	1.928	0.067	1.847	2.955	7.606
86	0.124	0.029	1.938	0.057	1.851	3.019	7.630
114-1	0.074	0.017	1.963	0.032	1.863	3.000	7.599
164	0.272	0.064	1.864	0.125	1.816	2.836	7.638
53-2	0.138	0.032	1.931	0.063	1.848	3.041	7.477

Calculated activities are as follows. Note that the error in activity of 6H Fe staurolite is estimated as $\pm$ 50% due to the necessary method of refining stoichiometry.

Spec.	$^{M3}X^2_{Al}$	$^{T2}X^n_{Fe^{2+}}$	$^{M4}X^2_{\square}$	$^{M4}X^2_{Fe^{2+}}$	$^{T1}X^8_{Si}$	$X^{St}_{2HFe-St}$	$X^{St}_{6HFe-St}$
3-3	0.8529	0.3736	0.9293	0.00112	0.6676	0.1177	0.00038
86	0.8566	0.3936	0.9390	0.00081	0.6847	0.1291	0.00028
114-1	0.8677	0.3554	0.9633	0.00026	0.6627	0.1172	0.00009
164	0.8245	0.3912	0.8686	0.00391	0.6904	0.1152	0.00133
53-2	0.8538	0.4133	0.9322	0.00099	0.5822	0.1140	0.00029
Ave.						0.1186(60)	0.00047(49)

Maine Garnet Compositions

Specimen	3-3	86[*]	114-1	164[*]	53-2
Alm	0.690	0.820	0.812	0.752	0.766
Prp	0.106	0.090	0.093	0.103	0.107
Sps	0.166	0.062	0.035	0.111	0.093
Grs	0.038	(0.028)	0.060	(0.034)	0.034

[*]Stoichiometry estimated from analyses of FeO, MgO, and MnO (Guidotti, 1974)

Garnet Mole Fractions of Fe$_3$Al$_2$Si$_3$O$_{12}$

Specimen	3-3	86	114-1	164	53-2
X_{Fe}^3	0.3285	0.5514	0.5354	0.4253	0.4495
Ave.					0.4580(903)

Black Mountain, New Hampshire Staurolite with Kyanite

All staurolite that coexists with kyanite and quartz must obey Reaction (3): The specimens listed below formed at about 5.5 kbar, 495 °C, contain staurolite, kyanite, and quartz, and each have been analyzed for H, and for Fe^{3+}/Fe^{2+}. A correction procedure is not needed because there is substantially more occupancy of M4 (Hawthorne et al. 1993a, sample 71-62R). Analytical error for these staurolites would not greatly affect the vacancy content, as it does for the low-H staurolites.

Black Mountain Staurolite Compositions

Specimen	71-62U	71-62T	71-62B
Si	7.607	7.594	7.592
Al	17.900	17.775	18.030
Ti	0.084	0.090	0.084
Fe^{2+}	2.883	2.937	3.025
Fe^{3+}	0.086	0.088	0.091
Mg	0.449	0.465	0.350
Mn	0.052	0.056	0.038
Zn	0.037	0.026	0.025
Li	0.156	0.144	0.067
CATSUM	29.254	29.175	29.302
H	4.283	4.562	3.993

Black Mountain Staurolite Cation Assignments

Using the procedure given above, the cations assignments are as follows:

Site	Ion	71-62U	71-62T	71-62B
M1	Al	7.700	7.700	7.700
	Mg	0.156	0.160	0.126
	Fe^{2+}	0.144	0.140	0.174
M2	Al	7.790	7.790	7.790
	Mg	0.041	0.041	0.031
	Fe^{2+}	0.085	0.079	0.095
	Ti	0.084	0.090	0.084
M3	Al	1.623	1.593	1.642
	Mg	0.086	0.087	0.075

	Fe^{2+}	0.034	0.033	0.045
	□	0.257	0.287	0.238
M4	Fe^{2+}	0.456	0.506	0.445
	Zn	0.006	0.005	0.004
	Li	0.027	0.027	0.011
	□	1.511	1.462	1.540
T1	Si	7.607	7.594	7.592
	Al	0.393	0.406	0.408
T2	Fe^{2+}	2.164	2.179	2.266
	Mg	0.166	0.177	0.118
	Zn	0.031	0.021	0.021
	Li	0.129	0.117	0.056
	Mn	0.052	0.056	0.038
	Al	0.394	0.286	0.490
	Fe^{3+}	0.086	0.088	0.091
	□	0.978	1.076	0.920

The important staurolite site contents are repeated below:

Spec.	T2□	M3□	M4□	M4Fe^{2+}	M3Al	T2Fe^{2+}	T1Si
71-62U	0.978	0.257	1.511	0.456	1.623	2.164	7.607
71-62T	1.076	0.287	1.462	0.506	1.593	2.179	7.594
71-62B	0.920	0.238	1.540	0.445	1.642	2.226	7.592

Calculated activities are as follows.

Spec.	$^{M3}X^2_{Al}$	$^{T2}X^n_{Fe^{2+}}$	$^{M4}X^2_{□}$	$^{M4}X^2_{Fe^{2+}}$	$^{T1}X^8_{Si}$	$X^{St}_{2HFe-St}$	$X^{St}_{6HFe-St}$
71-62U	0.6585	0.1828	0.5708	0.0520	0.6683	0.0273	0.0136
71-62T	0.6344	0.2013	0.5344	0.0640	0.6592	0.0268	0.0159
71-62B	0.6740	0.1935	0.5929	0.0495	0.6579	0.0303	0.0131
Ave.						0.0281(19)	0.0142(15)

Correction for Possible Non-ideality in T2

All ions in the occupied portion of the T2 site are assumed to participate in non-ideal substitution except Al coupled with M3 vacancy. The model is pseudobinary, between Fe^{2+} as one end-member and all other ions in T2 as the other end-member (excluding T2 vacancies and the ^{T2}Al coupled to M3 vacancies). For a +9 kJ/site Margules parameter (Mukhopadhyay et al., 1990), the activity coefficient γ_1 is given by

$$\underline{R}\underline{T} \ln \gamma_1 = 9000n \left(\frac{n - ^{T2}Fe^{2+}}{n}\right)^2$$

For the naturally occurring specimens in the two localities, assuming average values of n, $^{T2}Fe^{2+}$, and $\underline{T}$, activity coefficients are as given below.

Locality	n	n - ^{T2}Fe	$\dfrac{n - ^{T2}Fe^{2+}}{n}$	$\underline{T}$	γ_1
Maine	3.8146	0.8444	0.2214	813	1.2827
Black Mtn.	2.7480	0.5583	0.2032	768	1.1734

Activity coefficient γ_1 is multiplied by the mole fraction of 2H staurolite and not that of 6H staurolite, and applies only to natural staurolites which have other R^{2+} and Li ions in the T2 site.

Possible Corrections for Non-ideality in the M4 Vacancy-Occupancy Substitution

In order to possibly improve the overall fit of the experimental and natural data with estimated values of hydrogen content, $\underline{H}$, and $\underline{S}$, we assume deviation from ideality. Negative deviation is possible because Hawthorne et al. (1993c) have shown that staurolite short-range charge balance is optimum at the stiochiometric compositions near 4H, whereas stoichiometric compositions at 2H and 6H have only long-range charge balance. We select a symmetrical model because we do not have enough information to model it any more precisely. For γ_2, coefficient for 2H end-member, and γ_3, coefficient for 6H end-member, we use the equations

$$\underline{R}\underline{T} \ln \gamma_2 = 2\underline{W}_G (1 - ^{M4}X_\square)^2$$

$$\underline{R}\underline{T} \ln \gamma_3 = 2\underline{W}_G \, ^{M4}X_\square^2.$$

For the various compositions, the values for γ_2 and γ_3 are given in the table below.

W_G	H	$1 - {}^{M4}X_\square$	${}^{M4}X_\square$	$\underline{T} \ln \gamma_2$	$\underline{T} \ln \gamma_3$
-4000	3.0	0.0342	0.9658	-1.126	-897.584
-4000	ME	0.0345	0.9655	-1.145	-897.027
-4000	3.2	0.0680	0.9321	-4.450	-836.038
-4000	3.4	0.1013	0.8988	-9.875	-777.369
-4000	3.5	0.1178	0.8822	-13.353	-748.919
-4000	3.6	0.1342	0.8658	-17.330	-721.333
-4000	3.8	0.1666	0.8333	-26.709	-668.196
-4000	4.0	0.1987	0.8013	-37.992	-617.862
-4000	4.2	0.2303	0.7697	-51.037	-570.091
-4000	B.M.	0.2345	0.7655	-52.916	-563.886
-4000	4.4	0.2614	0.7386	-65.752	-524.941
-4000	4.5	0.2768	0.7232	-73.728	-503.289

For positive deviations from ideality reverse the sign of $\underline{T} \ln \gamma$. For Wg = 8000 J/site, double $\underline{T} \ln \gamma$, etc.

References not Given in Report

Holland, T.J.B. and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O-Na_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H-O_2. Journal of Metamorphic Geology, 8, 89-124.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452, 456 p.