

New data on the forsterite–tephroite series

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Abstract

New data including electron microprobe analyses, unit cell parameters, and infrared spectra are reported for a suite of fourteen metamorphic samples which span the entire forsterite–tephroite series. Regression equations relating composition to unit cell parameters, and infrared band position were calculated. Perhaps the most useful determinative curve is the relationship:

$$\% \text{Mg}/\text{M}^{2+} = -31981.250 + 23707.779d_{130} - 4378.2695(d_{130})^2$$

Huggins' (1973) method of calculating the degree of cation order from infrared spectra was tested. The results suggest that IR spectroscopy may indeed be a rapid and reliable method for determining the mole fraction of Mg on the M(1) site when sensitivity numbers (S) are known better.

Zincian olivines ranging in composition from $(\text{Mg}_{1.33}\text{Mn}_{0.41}\text{Zn}_{0.25}\text{Fe}_{0.01})$ to $(\text{Mn}_{1.89}\text{Mg}_{0.05}\text{Zn}_{0.05}\text{Fe}_{0.01})$ occur in the metamorphosed Zn–Mn–Fe deposits at Franklin and Ogdensburg, Sussex Co., New Jersey. Individual crystals contain oriented lamellae of willemite that evince an exsolution origin from tephroite which originally contained ~20 mol.% Zn_2SiO_4 components. Unit cell parameters vary nonlinearly as a function of mean octahedral cation radius calculated from microprobe analyses and strongly imply the ordering of cations. Zinc is thought to have a moderate preference for the M(1) site.

Introduction

Olivines are commonly referred to the ternary system forsterite (Mg_2SiO_4)–fayalite (Fe_2SiO_4)–tephroite (Mn_2SiO_4), but compilations of analyses (e.g., Burns and Huggins, 1972; Mossman and Pawson, 1976; Simkin and Smith, 1970) demonstrate that natural olivines are essentially binary solid solutions rarely containing more than ten mole percent of the third component. The preponderance of lunar, meteoritic, and terrestrial olivines are members of the forsterite–fayalite series, whereas tephroites and manganian olivines are rather restricted in occurrence and consequently have not been studied as closely.

Tephroite was first described from Sterling Hill by von Breithaupt in 1823 and was subsequently found in moderate abundance in the zinc–iron–manganese ores at both Franklin and Sterling Hill, Sussex Co., New Jersey (Palache, 1935). Tephroite is also well-known in Sweden at Pajsberg (Igelstrom, 1865) and Långban (Sjogren, 1883). Highly magnesian varieties were named “picrotephroite” by Paijkull (1877), and a manganian forsterite from Långban was reported by Sundius (1963). Magnesian tephroite was also described from the Noda Tamagawa Mine, Iwate Prefecture, Japan (Lee, 1955). The literature on the forsterite–tephroite series is reviewed by Francis (1980) and a more general review of olivine crystal chemistry is given by Brown (1982).

The present study is based on a suite of essentially

binary Mg–Mn olivines completely spanning the forsterite–tephroite series from Långban, Sweden and a second suite of zincian tephroites from Franklin and Ogdensburg, New Jersey (Table 1). The former were used to establish the dependence of the unit cell and infrared band position on composition and test Huggins' (1973) method of calculating the degree of cation ordering from infrared spectra. The latter were used to investigate the crystal chemical role of zinc in olivines with a view to elucidating their petrogenesis.

Chemistry

Chemical compositions were determined on an automated ARL-EMX electron microprobe operating at 15 kV and 0.02 μA sample current. Intensity data were reduced on-line using the technique of Bence and Albee (1968) and the correction factors of Albee and Ray (1970). The following simple oxides and silicates were used as standards: Balsam Gap, North Carolina forsterite (Mg and Si); synthetic fayalite (Fe); synthetic tephroite (Mn) (Takei, 1976); Crestmore, California wollastonite (Ca) and synthetic zincite (Zn). In reconnaissance analyses Al, Cr, Ni, and Ti were sought but not observed above the 0.05 wt.% level. Cation proportions in the tables are normalized to two M^{2+} cations per formula unit, and compositions are expressed as the ratio $\text{Mg}:\text{M}^{2+}$. The minor amounts of iron and calcium are thus lumped with manganese, which is a crystal-chemically

Table 1. Sample numbers, locations and sources. For further description see Francis (1980, Tables 2.1 and 3.1).

Sample Number	Locality	Harvard University Catalogue Number
1	Synthetic (Takei & Kobayashi, 1974)	
2	Langban, Sweden	116477
3	"	116487
4	"	116483
5	"	116349
6	"	116493
7	"	116474
8	"	116481
9	"	116463
10	"	116492
11	"	116494
12	"	86142
13	"	106580
14	"	116498
15	Madagascar	108206
16	Synthetic (Takei, 1976)	
21	Ogdensburg, New Jersey	113721
22	"	85551
23	Franklin, New Jersey	85548B
24	"	105624E
25	"	105617
26	"	88064
27	Ogdensburg, New Jersey	85547
28	Franklin, New Jersey	81225

reasonable procedure, considering the relative sizes and masses of these cations.

The new analyses of Långban specimens (Table 2) document the natural existence of the entire forsterite-tephroite series as expected in light of experimental phase equilibria studies (Kallenburg, 1914; Glasser and Osborn, 1960). They are noteworthy for their purity: $(Mg + Mn)/M^{2+} > 0.98$. Calcium and iron are the only significant minor elements present. Low iron concentrations are a function of bulk composition of the rock at Långban because iron and manganese were geochemically segregated into separate ore bodies (Moore, 1970). The observed calcium concentrations (< 1.0 wt.%) are consistent with those observed by Simkin and Smith (1970) in their study of more than 200 igneous Mg-Fe olivines. The present work suggests that older analyses with $CaO > 1.0$ wt.% (e.g., Igelstrom, 1865; Pisani, 1887) require confirmation before being interpreted as genuine calcian varieties. Further, because Långban tephroites and forsterites coexist with abundant calcite, they may be regarded as saturated with respect to calcium at the prevailing conditions of metamorphism.

Natural zincian olivines are known only from the ore deposits at Franklin and Ogdensburg, New Jersey. They are predominantly tephroites and exhibit a considerable range in composition (Table 3). Tephroite occurs in the primary zinc ores as large (≤ 10 cm) gray, pink or reddish-brown crystals which crystallized with franklinite and zincite but not willemite in a gangue of white calcite. Hurlbut

Table 2. Electron microprobe analyses of forsterites and tephroites mostly from Långban, Sweden.

Sample	1	2	3	4	5	6	7	8
SiO ₂	34.79	41.17	40.58	40.57	38.58	38.39	37.21	37.14
MgO	65.21	53.75	50.61	50.98	39.90	40.41	34.67	34.43
MnO	--	3.90	7.96	7.98	20.44	20.86	27.91	28.59
FeO	--	0.11	0.16	0.21	0.02	0.05	0.11	0.09
CaO	--	0.04	0.05	0.05	0.04	0.11	0.14	0.10
	100.00†	98.97	99.36	99.79	98.98	99.82	100.04	100.35
M^{2+}/Si	2.000	2.029	2.030	2.045	1.992	2.034	2.031	2.039
Mg	2.000	1.918	1.832	1.832	1.548	1.543	1.368	1.356
Mn	--	0.079	0.164	0.163	0.451	0.453	0.626	0.640
Fe	--	0.002	0.003	0.004	0.000	0.001	0.002	0.002
Ca	--	0.001	0.001	0.001	0.001	0.003	0.004	0.003

Sample	9	10	11	12	13	14	15	16
SiO ₂	34.89	34.15	33.47	32.10	31.25	30.71	30.33	29.75
MgO	24.61	21.78	17.10	13.27	9.82	7.71	3.72	--
MnO	40.62	44.91	50.28	51.92	56.07	59.09	64.43	70.25
FeO	0.08	0.07	0.12	0.61	0.17	0.14	0.97	--
CaO	0.20	0.25	0.35	0.24	0.70	0.13	0.37	--
	100.40	101.16	101.76*	98.14	98.01	97.78	99.82	100.00†
M^{2+}/Si	2.046	2.074	2.058	2.010	2.017	2.012	2.022	2.000
Mg	1.028	0.917	0.740	0.613	0.465	0.372	0.181	--
Mn	0.964	1.074	1.237	1.363	1.507	1.620	1.780	2.000
Fe	0.002	0.002	0.003	0.016	0.005	0.004	0.026	--
Ca	0.006	0.008	0.011	0.008	0.024	0.005	0.013	--

†Ideal Composition

*Includes 0.44% ZnO

(1961) demonstrated that such tephroites typically contain exsolution lamellae of willemite. The new analyses show that these tephroites carry approximately 10 mole% Zn₂SiO₄ component, and conversely the exsolved willemite lamellae (Table 4) carry approximately 10 mole % "olivine" components. As at Långban, iron and calcium are minor elements in these tephroites. Because natural inter-

Table 3. Electron microprobe analyses of zincian tephroites from New Jersey.

Sample	1	2	3	4	5	6	7	8
SiO ₂	36.19	33.07	32.13	31.26	30.36	30.61	29.86	29.87
MnO	18.00	40.00	47.25	52.20	52.96	57.29	59.79	65.93
MgO	33.63	17.30	10.52	7.45	4.67	3.71	1.82	0.97
ZnO	12.78	9.41	9.52	7.90	6.79	6.62	5.13	1.81
FeO	0.45	1.48	1.18	1.05	3.75	1.00	0.93	0.10
CaO	0.08	0.23	0.50	0.93	0.36	1.30	1.06	0.47
	101.13	101.49	101.10	100.79	98.89	100.53	98.59	99.15
EM^{2+}/Si	2.080	2.059	2.000	2.016	1.988	1.998	1.976	1.982
Mn	0.405	0.995	1.246	1.403	1.486	1.587	1.715	1.886
Mg	1.332	0.757	0.488	0.352	0.231	0.181	0.092	0.049
Zn	0.251	0.204	0.219	0.185	0.166	0.160	0.128	0.045
Fe	0.010	0.036	0.031	0.028	0.104	0.027	0.026	0.005

Table 4. Electron microprobe analyses of willemite lamellae.

Sample	1	2	3	4	5	6	7	8
SiO ₂	28.23	27.90	27.85	27.90	27.46	27.77	27.11	27.74
MnO	2.14	3.06	4.81	4.67	4.19	5.13	5.11	2.87
MgO	2.72	1.81	1.83	1.45	0.23	0.90	0.14	0.00
ZnO	67.43	66.89	64.62	65.81	67.12	66.99	66.60	69.44
FeO	0.03	0.16	0.52	0.07	0.32	0.14	0.16	0.04
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
	100.55	99.82	99.63	99.90	99.32	100.93	99.15	100.09
$\Sigma M^{2+}/Si$	1.972	1.965	1.960	1.963	1.957	1.991	1.988	1.937
Mn	0.065	0.095	0.150	0.144	0.132	0.157	0.160	0.090
Mg	0.145	0.099	0.100	0.079	0.013	0.048	0.008	0.000
Zn	1.789	1.801	1.748	1.775	1.844	1.790	1.825	1.909
Fe	0.001	0.005	0.002	0.002	0.010	0.004	0.005	0.001
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000

mediate Fe-Mn olivines are well-known from the Bluebell Mine, British Columbia (Mossman and Pawson, 1976), Broken Hill, NSW (Mason, 1973), and central Sweden (Henriques, 1956), the low and relatively constant Fe contents (0.10 atoms per formula unit) presumably reflect low Fe contents of the bulk rock compositions, although partitioning of Fe²⁺ between franklinite (Zn, Mn²⁺, Fe²⁺) (Fe³⁺, Mn³⁺)₂O₄, and tephroite may occur. Calcium is strongly partitioned into the manganoan calcite gangue and there is no evidence of a natural solid solution between tephroite and glaucocroite (CaMnSiO₄), at the conditions of metamorphism prevailing in northwestern New Jersey. Similarly, there is very little calcium present in forsterite coexisting with monticellite (CaMgSiO₄) at Cascade Mountain in the Adirondack Mountains, a nearby Grenville-age metamorphic terrane (Tracy et al., 1978).

X-ray crystallography

The isotypism of the tephroite with the olivine group was confirmed by O'Daniel and Tscheischwili (1944) using powder methods. The structure of a synthetic, end-member tephroite was refined by Fujino et al. (1981). In the olivine structure the non-equivalent, cation-containing M(1) and M(2) octahedra share edges to form zig-zag chains which are cross linked by isolated silicate tetrahedra. Refinements of the structures of samples 9 and 15 by Francis and Ribbe (1980) demonstrate a very high degree of cation ordering in natural specimens of the forsterite-tephroite series with the larger Mn cation concentrated in the larger M(2) site.

X-ray powder data for natural tephroites were reported by Ross and Kerr (1932), Lee (1955) and Welin (1968). The only natural magnesian tephroite previously studied is from the Noda Tamagawa Mine, Japan (Lee, 1955). Powder data for synthetic tephroite are given by Hurlbut (1961) and on JCPDF card # 19-788. Nishizawa and Matsui (1972) reported unit cell parameters for five synthetic members of the forsterite-tephroite series.

X-ray powder data for the present study were recorded on a Philips Norelco diffractometer using monochromatic

CuK α radiation ($\lambda = 1.5418\text{\AA}$) with quartz C-105 (Frondele and Hurlbut, 1955) and BaF₂ ($a = 6.198(2)\text{\AA}$) as internal standards. Unit cell dimensions were refined from corrected peak positions in the range 17–40°2 θ using the program LCLSQ of Burnham (1962). The space group and structure type of sample 2 were confirmed by the precession method. Unit cell parameters for zinc-free samples are recorded in Table 5 and plotted as functions of composition in Figure 1.

In a study of fifty chemically diverse olivines Brown (1970, 1982) reported linear correlations of b , c , and V with mean octahedral radius in series which were known or presumed to be ordered. The a parameters, however, are smaller than those predicted by a straight line connecting end member values. In both the present study of natural samples and the earlier study of synthetic samples by Nishizawa and Matsui (1972) a , b , c , and V were all observed to be nonlinear functions of composition (Figs. 1 and 2) and consequently of mean octahedral radius. The departures from linearity are greatest at the series midpoint but small considering the wide range of values considered by Brown. Clearly, this nonlinearity is a function of cation order. The unit cell parameters of sample 9 (Fo₆₁), which is known to be highly ordered (Francis and Ribbe, 1980), show greater departures from linearity than those of a disordered synthetic Fo₅₃ crystal "heat treated at 1000°C" (Ghose and Weidner, 1974; Ghose et al., 1976) or those of the synthetic Fo₅₀ of Nishizawa and Matsui (1972).

The unit cell parameters of the zincian samples from

Table 5. Unit cell parameters of both natural and synthetic zinc-free forsterite and tephroite samples.

Sample Number	Comp'n*	d 130 (Å)	a (Å)	b (Å)	c (Å)	V (Å ³)
1	1.000	2.763	4.753(1)**	10.191(3)	5.982(2)	289.8(1)
2	0.959	2.770	4.757(2)	10.219(5)	5.993(3)	291.3(2)
3	0.916	2.775	4.760(2)	10.244(6)	6.006(3)	292.8(2)
4	0.916	2.777	4.761(2)	10.254(6)	6.007(3)	293.3(2)
5	0.774	2.795	4.775(1)	10.344(3)	6.049(2)	298.8(1)
6	0.772	2.796	4.773(1)	10.351(3)	6.055(2)	299.1(1)
†	0.75	2.796	4.782(1)	10.339(1)	6.063(1)	299.8(1)
7	0.684	2.807	4.778(3)	10.398(6)	6.078(4)	302.0(2)
8	0.678	2.807	4.782(1)	10.406(2)	6.083(1)	302.7(1)
††	0.530	2.816	4.811(2)	10.421(3)	6.116(2)	306.6
9	0.514	2.824	4.799(2)	10.499(4)	6.127(2)	308.7(2)
†	0.50	2.822	4.818(1)	10.447(2)	6.130(1)	308.5(1)
10	0.458	2.834	4.810(2)	10.540(4)	6.149(3)	311.7(2)
11	0.370	2.841	4.827(2)	10.549(4)	6.170(2)	314.2(1)
12	0.307	2.844	4.830(1)	10.553(3)	6.180(2)	315.0(1)
†	0.25	2.846	4.855(2)	10.536(3)	6.204(5)	317.4(3)
13	0.233	2.850	4.850(2)	10.568(3)	6.203(2)	317.9(1)
14	0.186	2.854	4.860(3)	10.580(6)	6.225(4)	320.1(2)
15	0.090	2.858	4.880(1)	10.586(4)	6.234(3)	322.0(2)
16	0.0	2.866	4.906(2)	10.598(5)	6.255(3)	325.2(2)

*Composition expressed as Mg/ ΣM^{2+}

**Number in parentheses represents one estimated standard deviation and refers to the last decimal place.

†Synthetic specimens (Nishizawa and Matsui, 1972)

††Synthetic crystal (Ghose et al., 1976)

Table 6. Quadratic regression equations for composition as a function of lattice parameters. Equations are of the form $\text{Percent Mg}/\sum M^{2+} = K_0 + K_1X + K_2X^2$.

X	K_0	K_1	K_2	Var.*
d_{130}	-3.1981×10^4	2.3708×10^4	-4.3783×10^3	99.8
a	7.3836×10^4	-2.9932×10^4	3.0335×10^3	99.5
b	-4.3117×10^4	8.5159×10^3	-4.1953×10^2	96.6
c	-6.8110×10^3	2.5983×10^3	-2.4125×10^2	99.8
V	-6.0555×10^2	7.0790	-1.6036×10^{-2}	99.8

*Var. is the percent variation explained by estimated model.

Franklin and Sterling Hill show the same nonlinear correlations with composition that the zinc-free samples from Långban show, strongly implying that the Franklin samples are ordered (Fig. 2). Cation ordering was, in fact, demonstrated by Brown (1970) who refined the structure of a Franklin tephroite closely similar in composition to sample 24 of this study. His reported site occupancies are $M(1): \text{Mn}_{0.432}\text{Mg}_{0.345}\text{Zn}_{0.18}\text{Fe}_{0.043}$ and $M(2): \text{Mn}_{0.868}\text{Fe}_{0.085}\text{Zn}_{0.045}$. An alternative interpretation favoring a fully ordered distribution with M(2) completely occupied by Mn is offered by Francis and Ribbe (1980). Regardless of which ordering scheme is preferred for Brown's refinement, zinc is observed to be more heavily concentrated on the M(1) site and manganese on the M(2) site.

Two X-ray determinative curves based on data from syn-

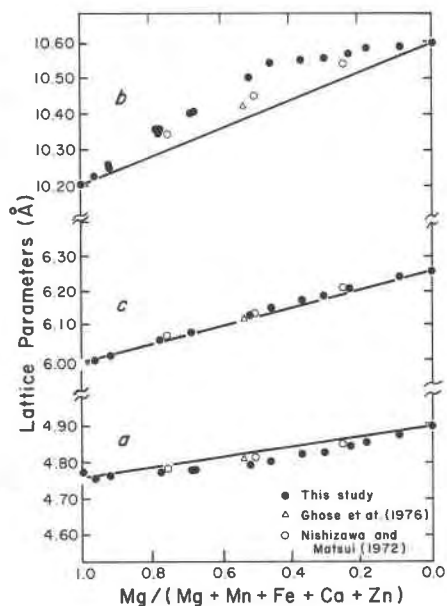


Fig. 1. Plot of unit cell parameters as a function of composition comparing natural samples from Långban, Sweden (dots) with synthetic samples (circles and triangle).

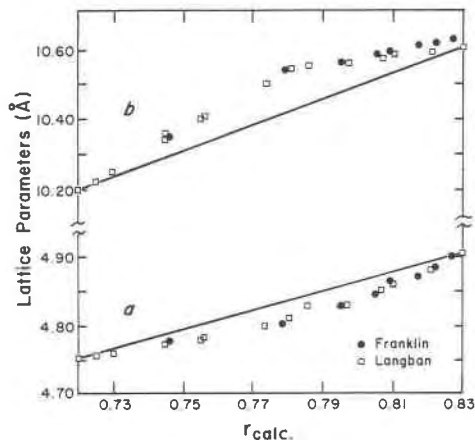


Fig. 2. Plot of unit cell parameters a and b as a function of calculated mean radius comparing Långban samples (squares) with zincian samples from New Jersey (dots).

thetic samples have been proposed for the forsterite-tephroite series. Glasser and Osborn (1960) reported that d_{222} values of their synthetic samples vary linearly with composition. Hurlbut (1961), following Yoder and Sahama (1957), plotted d_{130} values as a function of composition. Hurlbut's curve was used in the present study to initially identify compositionally-intermediate specimens for further study. Quadratic regression equations computed from the data on the zinc-free Långban samples are listed in Tables 7 and 8. Because unit cell parameters are sensitive to cation order, these equations may not be suitable for general use as a measure of composition. However, if applied to highly ordered samples, the equations and especially the d_{130} curve (Fig. 3) should be effective. It indicates, for example, that the unanalyzed Långban tephroite studied by Welin (1968) with $d_{130} = 2.86\text{\AA}$ is approximately $\text{Fe}_{10}\text{Te}_{90}$.

After the present study was completed, an investigation of the dependence of d_{130} on composition and cation ordering of Mg-Fe-Mn olivines was reported by Shinno (1980). His data represent 75 natural olivines including 4

Table 7. Quadratic regression equations for unit cell parameters as a function of composition. Equations are of the form $Y = K_0 + K_1X + K_2X^2$ where $X = \text{Percent Mg}/\sum M^{2+}$.

y	k_0	k_1	k_2	Var.*
d_{130}	2.865555	$-5.0986372 \times 10^{-4}$	$-5.1171683 \times 10^{-6}$	99.8
a	4.9038782	$-2.5457481 \times 10^{-3}$	1.0663628×10^{-5}	99.3
b	10.592903	1.9171704×10^{-4}	$-4.2792090 \times 10^{-5}$	99.3
c	6.2587929	$-2.2145719 \times 10^{-3}$	$-5.8085707 \times 10^{-6}$	99.7
Volume	325.199946	$-2.8044409 \times 10^{-1}$	$-7.6029124 \times 10^{-4}$	99.8

*Var. is the percent variation explained by the estimated model.

Table 8. Observed unit cell parameters for zincian tephroites (upper set) and calculated values for zinc-free samples with identical Mg/(Mg + Mn) ratios predicted from equations in Table 7 (lower set).

Sample	Comp'n*	$d_{130}(\text{\AA})$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$v(\text{\AA}^3)$
21	0.76	2.797	4.777(2)	10.349(4)	6.050(2)	299.1(2)
		2.797	4.772	10.360	6.057	299.5
22	0.42	2.834	4.804(2)	10.532(3)	6.135(2)	310.4(1)
		2.835	4.815	10.525	6.155	312.0
23	0.27	2.844	4.828(2)	10.558(3)	6.172(2)	314.6(2)
		2.848	4.842	10.566	6.194	316.9
24	0.19	2.853	4.847(2)	10.584(3)	6.203(2)	318.2(1)
		2.854	4.859	10.580	6.245	319.4
25	0.12	2.858	4.862(3)	10.588(5)	6.211(3)	319.7(2)
		2.858	4.874	10.589	6.230	321.6
26	0.10	2.861	4.870(5)	10.609(5)	6.234(3)	322.1(3)
		2.860	4.980	10.591	6.237	322.4
27	0.05	2.868	4.882(2)	10.614(3)	6.235(2)	323.1(1)
		2.863	4.892	10.593	6.238	323.8
28	0.03	2.868	4.899(2)	10.621(3)	6.251(2)	325.3(2)
		2.864	4.898	10.593	6.253	324.5

*Composition = Percent Mg_2SiO_4 .

†Numbers in parentheses represent one estimated standard deviation and refer to last decimal place.

tephroites (82.8, 87.3, 93.0 and 94.9 mole% Te) and 44 synthetics including 6 at 20 mole % intervals along the Fo-Te join. He calculated regression equations of the form

$$d_{130}(\text{\AA}) = (A(1)\text{Te}) + (A(2)\text{Fa}) + (A(3)\text{Te}^2) \\ + (A(4)\text{Fa}^2) + A(5)$$

with different sets of coefficients for the natural and synthetic samples. Shinno observed that natural specimens have larger d_{130} values than synthetic specimens and that heating natural specimens decreases d_{130} values significantly. Mossbauer spectra of a synthetic ferroan tephroite showed the proportion of Mn on M(2) increased with an-

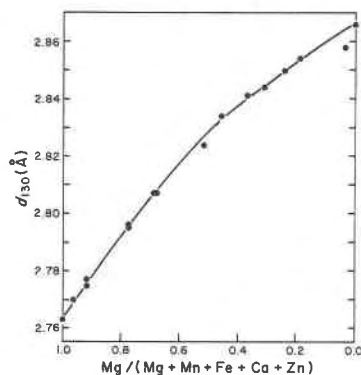


Fig. 3. Plot of $d_{130}(\text{\AA})$ as a function of composition for natural, zinc-free forsterites and tephroites.

nealing time. These observations are consistent with the present study.

Unit cell parameters of zincian tephroites are expected to be somewhat smaller than those of zinc-free tephroites with identical Mg/(Mg + Mn) ratios because the effective ionic radius of zinc ($r = 0.74\text{\AA}$) is less than the mean of the radii of magnesium ($r = 0.72\text{\AA}$) and manganese ($r = 0.83\text{\AA}$). Using the equations from Table 7, unit cell parameters were calculated for comparison with those observed for samples 21-28 (Table 8). In general the observed a and c values are smaller while b values are larger than the calculated values which leads to the interesting situation that the d_{130} curve (Fig. 3) predicts the Mg/(Mg + Mn) ratio for these zincian tephroites quite well.

Infrared spectroscopy

Systematic studies of olivines by infrared spectroscopy, which is sensitive to the bending, stretching, and twisting modes of molecules and atomic clusters in crystals, have established that olivines exhibit a characteristic configuration in their absorption spectra. Four bands attributed to the ν_1 , ν_3 , and ν_4 modes of the silicate anion occur between 1000 and 800 cm^{-1} , and a second group attributed to both the silicate and MO_6 groups occurs below 650 cm^{-1} (e.g., Jeanloz, 1980). The band positions are compositionally dependent. Duke and Stephens (1964) and Tarte (1963) observed linear correlations ($r > 0.99$) between frequency and composition for five synthetic members of the forsterite-tephroite series. Burns and Huggins (1972) reported nonlinear variations for some absorption bands on the basis of extrapolated data for the end-members and observed data for two Franklin tephroites. Non-linearity was attributed to cation ordering and a method of calculating octahedral site populations was subsequently devised by Huggins (1973). Because microprobe analyses of Franklin tephroites (Note that sample 17 of Burns and Huggins is the same as sample 22 of this study) reveal that they typically contain approximately ten mole percent Zn_2SiO_4 ; the possibility that the nonlinearity observed by Burns and Huggins is due to the unrecognized third component, rather than Mg-Mn ordering must be considered.

To address this question spectra with 2 cm^{-1} precision were recorded on a Nicolet fourier transform spectrometer over the frequency range $1000\text{--}400\text{ cm}^{-1}$ using powdered samples imbedded in 200 mg KBr pellets. The data obtained for the synthetic end-members and four natural intermediate compositions from Långban, Sweden are listed in Table 9 and illustrated in Figure 4. The figure demonstrates that care must be taken in correlating bands, especially bands 1 and 3, from specimen to specimen. Band positions for forsterite (and tephroite) agree closely with the results of previous investigations (Table 10) except those of Tarte (1963) whose values are consistently higher, presumably due to systematic errors. Quadratic regression equations relating band position with composition are listed in Tables 11 and 12. Nonlinearity may be confidently attributed to cation ordering because the present data are from natural samples known to be ordered, and the syn-

Table 9. Infrared band positions (cm⁻¹) for forsterites and tephroites.

Sample	Comp'n*	Bands (cm ⁻¹)										
		1A	1B	2	3A	3B	4	5	6	7	8	9
1	1.0	985	957	883	838	612	545	526	511	477		
6	0.772	979	949	878	831	604	540	520	502	463		
9	0.514	971	940	874	828	597	530	514	495	450		
11	0.370	964	933	869	860	822	589	527	509	489	441	
15	0.090		946	914	860	817	569	512	497	467		
16	0.0		943	909	860	817	564	510	486	461		

*Mg/ΣM²⁺

thetic samples of Duke and Stephens (1964) and Tarte (1963) show strictly linear correlations.

These data provide an opportunity to test an empirical relation devised by Huggins (1973) which relates cation site distributions to infrared band positions. Huggins derived the expression:

$$S = \frac{2(x - ZI)}{(K_x - ZI)}$$

which equates a sensitivity number *S* to the mole fraction of Mg on M(1) (denoted by *ZI*), to the bulk composition (*x*), and to the band position relative to that of the endmembers (denoted by *K_x*). For sample 9, *ZI* is known to be 0.92 from the X-ray site refinement (Francis and Ribbe, 1980). From this, *S* values were computed for each band in the spectrum of sample 9. Assuming that *S* values are insensitive to variations in composition, these *S* values were

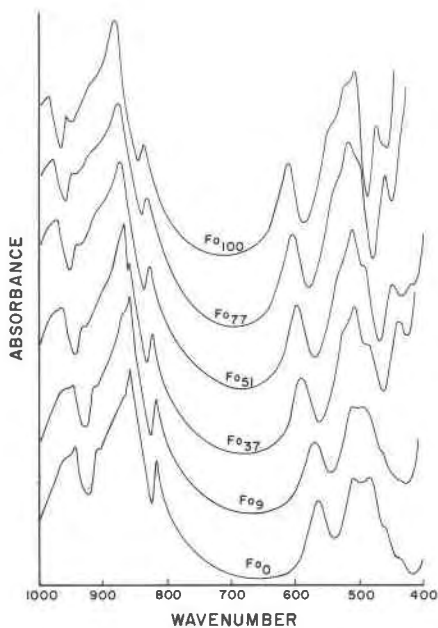


Fig. 4. Infrared spectra of zinc-free forsterites and tephroites.

Table 10. Comparison of published infrared band positions (cm⁻¹) of forsterite with the present observations.

Band	A	B	C	D	E	Mode
1	985.4	985	985	984	1001	ν ₃
2	957.3	957	957	954	963	ν ₃
3	886.9	883	884	885	892	ν ₃
4	839.3	838	839	837	842	ν ₁
5	611.0	612	609	608	615	ν ₄

A. Burns and Huggins (1972). Extrapolated values.

B. This study. Precision ±2 cm⁻¹.

C. Jeanloz (1980). Precision ±1 cm⁻¹.

D. Duke and Stephens (1964). Precision is ±1 cm⁻¹.

E. Tarte (1963).

used with each band in the spectra of samples 6, 11, and 15 to calculate *ZI* from a rearrangement of the foregoing equation:

$$ZI = \frac{(SK_x - 2x)}{(S - 2)}$$

Table 13 compares the several estimates of *ZI* with the ranges permitted by the compositions of Samples 6 and 11 and with the refined value for Sample 15.

For bands 2, 5, 7, and 8 with sensitivity numbers near or above 3.0 most of the estimates of *ZI* are reasonable but for bands 4 and 6 with sensitivity numbers near 2.0 the estimates are physical impossibilities. These results suggest that when sensitivity numbers are better known, infrared spectroscopy may indeed provide a rapid and reliable method for determining the degree of cation order in Mg-Mn olivines.

Petrogenesis of zincian tephroites

The tephroite-willemitte exsolution pairs from Franklin and Ogdensburg hold petrogenetic information. Micro-

Table 11. Quadratic regression equations for infrared band positions as a function of composition. Equations are of the form Band (cm⁻¹) = K₀ + K₁X + K₂X² where X = Mg/ΣM²⁺.

Band	k ₀	k ₁	k ₂	Var.*
1A	944.12988	0.62414145	-2.1677709 × 10 ⁻³	99.7
2	908.53955	0.73574626	-2.5570965 × 10 ⁻³	99.8
3A	858.58179	0.32453465	-8.2741049 × 10 ⁻⁴	98.5
4	816.30981	0.16320294	5.1488238 × 10 ⁻⁴	97.8
5	563.37622	0.79250497	-3.1359249 × 10 ⁻³	99.6
6	509.06519	0.50131553	-1.3990561 × 10 ⁻³	99.3
7	488.47803	0.64523691	-2.7953230 × 10 ⁻³	98.3
8	460.84985	0.83448994	-3.4535902 × 10 ⁻³	99.2
9	422.11157	0.50611848	4.0698517 × 10 ⁻⁴	99.8

*Var. is the percentage variation explained by the estimated model.

Table 12. Quadratic regression equations for compositions as a function of infrared band position. Equations are of the form $\text{Percent Mg}/\sum M^{2+} = K_0 + K_1X + K_2S^2$ where $X = \text{Band}$ (cm^{-1}).

Band	k_0	k_1	k_2	Var.*
1A	5.5299949×10^4	-116.38806	6.1266761×10^{-2}	100.0
2	1.8792637×10^4	-42.257736	2.3746464×10^{-2}	99.9
3A	6.7614875×10^4	-158.87309	9.3333483×10^{-2}	98.8
4	-3.2080574×10^4	73.168488	$-4.1487742 \times 10^{-2}$	97.8
5	8.9933281×10^3	-32.516769	2.9388372×10^{-2}	99.5
6	7.2606250×10^3	-30.111832	3.1137913×10^{-2}	99.4
7	1.2780094×10^4	-529.46365	5.4833077×10^{-2}	99.9
8	6.1024297×10^3	-269.69727	2.976928	99.4
9	-1.1639136×10^3	3.5951729	$-1.9806267 \times 10^{-3}$	99.8

*Var. is the percent variation explained by the estimated model.

probe analyses of five such pairs, illustrated in Figure 5, define isothermal pairs of points and presumably an isotherm on the olivine-willemite solvus which represents the temperature at which exsolution ceased. The position of a second isotherm, representing the temperature of crystallization, can be defined by the bulk compositions of the exsolved tephroite-plus-willemite crystals. Specimen 25 was calculated to have originally contained 16 mol% Zn_2SiO_4 by point counting of an oriented thin section (Fig. 2 in Hurlbut, 1961) in traverses normal to the willemite lamellae. A second estimate of a bulk composition is provided by the most zinc-rich tephroite analysis reported by Palache (1935), $\text{Te}_{43}\text{Fo}_{35}\text{Wi}_{22}$, which the writer interprets to be an unseparated or very poorly separated tephroite-willemite sample. Both estimates are consistent with experimental studies. Saver and Hummell (1962), reported that the saturation limit for Zn_2SiO_4 in forsterite at one bar ranges from 16 mol% at 850°C to 24% at 1460°C and Syono et al. (1971) observed that the solubility increases with increasing pressure. These data indicate that the teph-

Table 13. Fraction of Mg on M(1) (i.e., Zl) calculated from infrared spectra according to the method of Huggins (1973) for samples 6, 11 and 15.

Band Number	S Value	Zl Estimates		
		6	11	15
2	2.96	0.97	0.64	0.13
4	2.05	-3.47	-5.04	-3.60
5	3.49	0.83	0.67	0.11
6	2.33	1.37	1.19	-0.14
7	3.68	0.94	0.82	0.50
8	3.38	0.89	0.84	0.16
		1.00-0.77*	0.74-0.37*	0.17**

*Range of values permitted by composition

**Refined value (Francis & Ribbe, 1980)

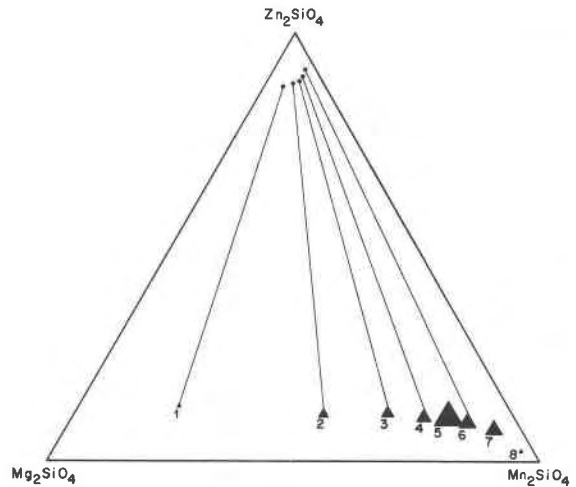


Fig. 5. Plot of compositions of zincian forsterite and tephroites (triangles) and coexisting willemite lamellae (dots). Triangle area proportional to nonternary components, principally Fe_2SiO_4 , of forsterite-tephroite samples.

roite from Franklin and Ogdensburg, N.J., which crystallized at sillimanite grade during Grenville-age metamorphism (Fron del and Baum, 1974), originally contained ~20 mol% Zn_2SiO_4 . Homogenization studies or calibration of the olivine-willemite solvus would further our understanding the thermal history of these deposits.

Two aspects of the phase relations may be rationalized in crystal chemical terms. Zinc commonly occurs in octahedral coordination in the rock-forming silicates at Franklin, substituting for Mn, Fe, and Mg whereas it is tetrahedrally coordinated in all of the silicates containing essential zinc. Willemite, the most abundant of these zinc silicates, crystallizes with the phenacite structure, an open trigonal framework in which each oxygen is shared between two Zn and one Si tetrahedra (for a review see Ganguli, 1975). Thus, the exsolution of willemite from zincian tephroite may be viewed as another manifestation of the well-known preference of zinc for tetrahedral coordination. The asymmetry of the miscibility gap, which is wider along the tephroite-willemite edge than along the forsterite-willemite edge, may be attributed to similarity in size of magnesium and zinc.

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References

Albee, A. L. and L. Ray (1970) Correction factors for electron microprobe microanalysis of silicates, oxides, carbonates, phos-

- phates, and sulfates. *Analytical Chemistry*, 42, 1408-1414.
- Bence, A. E. and A. L. Albee (1968) Empirical correction factors for the electron-microanalysis of silicates and oxides. *Journal of Geology*, 76, 382-403.
- Brown, G. E. (1970) *Crystal Chemistry of the Olivines*. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA.
- Brown, G. E. (1982) Olivines and silicate spinels. In P. H. Ribbe, Ed., *MSA Reviews in Mineralogy*, V. 5, Orthosilicates, p. 275-381. Mineralogical Society of America, Washington, D.C.
- Burnham, C. W. (1962) Lattice constant refinement. *Carnegie Institute of Washington Year Book*, 61, 132-135.
- Burns, R. G. and F. E. Huggins (1972) Cation determinative curves for Mg-Fe-Mn olivines from vibrational spectra. *American Mineralogist*, 57, 967-985.
- Duke, D. A. and Stephens, J. D. (1964) Infrared investigations of the olivine group minerals. *American Mineralogist*, 49, 1388-1406.
- Francis, C. A. (1980) *Magnesium-Manganese Solid Solution in the Olivine and Humite Groups*. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA.
- Francis, C. A. and Ribbe, P. H. (1980) The forsterite-tephroite series. I. Crystal structure refinements. *American Mineralogist*, 65, 1263-1269.
- Fron del, C. and Hurlbut, C. S., Jr. (1955) Determination of the atomic weight of silicon by physical measurements on quartz. *Journal of Chemical Physics*, 23, 1215-1219.
- Fron del, C. and J. L. Baum (1974) Structure and mineralogy of the Franklin Zinc-Iron-Manganese Deposit, New Jersey. *Economic Geology*, 69, 157-180.
- Fujino, K., Sasaki, S., Takeuchi, Y., and Sadanaga, R. (1981) X-ray determination of electron distributions in forsterite, fayalite, and tephroite. *Acta Crystallographica B37*, 513-518.
- Ganguli, D. (1975) Crystal chemistry of phenakite structures. *Neues Jahrbuch für Mineralogie Abhandlungen*, 123, 313-329.
- Ghose, S. and J. R. Weidner (1974) Site preference of transition metal ions in olivine. *Geological Society of America, Abstracts with Programs*, 6, 751.
- Ghose, S., Wan, C., Okamura, F. P., Ohashi, H., and Weidner, J. R. (1976) Site preference and crystal chemistry of transition metal ions in pyroxenes and olivines. *Acta Crystallographica*, A31 Supplement, S76.
- Glasser, F. P., and Osborn, E. F. (1960) The ternary system MgO-MnO-SiO. *Journal of the American Ceramic Society*, 43, 132-140.
- Henriques, C. A. (1956) Optical and physical properties of knebelite. *Arkiv For Mineralogi och Geologi*, 2, 255-269.
- Huggins, F. E. (1973) Cation ordering in olivines: Evidence from vibrational spectra. *Chemical Geology*, 11, 99-109.
- Hurlbut, C. S., Jr. (1961) Tephroite from Franklin, New Jersey. *American Mineralogist*, 46, 549-559.
- Igelstrom, L. J. (1865) *Oversigt af K.Vet.-Akad. Forhanlingar*, Stockholm, 22, 228.
- Jeanloz, R. (1980) Infrared spectra of olivine polymorphs: , -phase and spinel. *Physics and Chemistry of Minerals*, 5, 327-341.
- Kallenberg, S. (1914) Untersuchungen über die Binären Systeme: $Mn_2SiO_4-Ca_2SiO_4$, $Mn_2SiO_4-Mg_2SiO_4$ and $MnSiO_3-FeSiO_3$. *Zeitschrift für Anorganische und Allgemeine Chemie*, 48, 355-363.
- Lee, D. E. (1955) *Mineralogy of some Japanese manganese ores*. Stanford University Publication; University Series, Geological Sciences, 5, 1-64.
- Mason, B. (1973) Manganese silicate minerals from Broken Hill, New South Wales. *Journal of the Geological Society of Australia*, 20, 397-404.
- Moore, P. B. (1970) Mineralogy and chemistry of Langban-type deposits in Bergslagen, Sweden. *Mineralogical Record*, 1, 154-172.
- Mossman, D. J. and Pawson, D. J. (1976) X-ray and optical characterization of the forsterite-fayalite-tephroite series with comments on knebelite from Bluebell Mine, British Columbia. *Canadian Mineralogist*, 14, 479-486.
- Nishizawa, O. and Matsui, Y. (1972) An experimental study on partition of magnesium and manganese between olivine and orthopyroxene. *Physics of the Earth and Planetary Interiors*, 6, 377-384.
- O'Daniel, M. and Tscheischwili (1944) Strukturuntersuchungen an tephroite Mn_2SiO_4 , glaukochroit $(Mn,Ca)_2SiO_4$ and willemite Zn_2SiO_4 von Franklin Furnace. *Zeitschrift für Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie*, 105, 273.
- Pajikkull, S. R. (1877) Picrotephroite from Langban. *Geologiska Foereningen i Stockholm Foerhandlingar*, 3, 351.
- Palache, C. (1935) The minerals of Franklin and Sterling Hill, Sussex County, New Jersey. U.S. Geological Survey Professional Paper 180.
- Pisani (1877) *Comptes Rendus*, 84, 1511.
- Ross, C. S. and Kerr, P. F. (1932) The manganese minerals of a vein near Bald Knob, North Carolina. *American Mineralogist*, 17, 1-18.
- Saver, J. F., and F. A. Hummel (1962) Solid solubility and eutectic temperature in the system $Zn_2SiO_4-Mg_2SiO_4$. *Journal of the American Ceramic Society*, 45, 304.
- Shinno, I. (1980) Relations between (130) spacing, chemical composition, and cation site preference of olivine. *The Journal of the Japanese Association of Mineralogists, Petrologists, and Economic Geologists*, 75, 343-352.
- Simkin, T. and Smith, J. V. (1970) Minor-element distribution in olivine. *Journal of Geology*, 78, 304-325.
- Sjogren, A. (1883) On tefroit. *Geologiska Foereningen i Stockholm Foerhandlingar*, 6, 538-542.
- Sundius, N. (1963) Benstonite and tephroite from Langban. *Arkiv for Mineralogi und Geologi*, 3, 407-411.
- Syono, Y., S. Akimoto, and Y. Matsui (1971) High pressure transformations in zinc silicates. *Journal of Solid State Chemistry*, 3, 369-380.
- Takei, H. (1976) Czochralski growth of Mn_2SiO_4 (tephroite) single crystal and its properties. *Journal of Crystal Growth*, 34, 125-131.
- Takei, H. and T. Kobayashi (1974) Growth and properties of Mg_2SiO_4 single crystals. *Journal Crystal Growth*, 23, 121-124.
- Tarte, P. (1963) Etude infra-rouge des orthosilicates et des orthogermanates. II. Structures du type olivine et monticellite. *Spectrochimica Acta*, 19, 25-47.
- Tracy, R. J., H. W. Jaffe, and P. Robinson (1978) Monticellite marble at Cascade Mountain, Adirondack Mountains, New York. *American Mineralogist*, 63, 991-999.
- Welin, E. (1968) Notes on the mineralogy of Sweden. 6. X-ray powder data for minerals from Langban and the related mineral deposits of Central Sweden. *Arkiv for Mineralogi und Geologi*, 4, 499-541.
- Yoder, H. S. and Th. G. Sahama (1957) Olivine X-ray determinative curve. *American Mineralogist*, 42, 475-491.