

Composition, order–disorder and lattice parameters of olivines: determinative methods for Mg–Mn and Mg–Ca silicate olivines

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Abstract

A method has been derived to estimate both the bulk composition and the distribution of Mg and Mn and of Mg and Ca atoms between the M1 and M2 octahedral sites in olivines of the forsterite–tephroite and forsterite–monticellite series, making use of the regression equations, $a = 0.932r_{M1} + 0.236r_{M2} + 3.918$, $b = 0.505r_{M1} + 3.211r_{M2} + 7.535$, determined by Lumpkin and Ribbe (1983). The strong dependence of a on r_{M1} , the radius of the M1 cation, and of b on r_{M2} is exploited on an a – b plot contoured for composition, $100 \text{ Mg}/[\text{Mg} + (\text{Mn or Ca})]$, and for the Mn (or Ca) content of the M2 site. Predictions of bulk composition from a – b are within $\pm 1.5\%$ Fo (on the average), and of site occupancies are usually better than ± 0.05 Mn or Ca. Natural olivines of the forsterite–tephroite series and zincian varieties from Franklin, New Jersey are found to be highly ordered with 90% or more of the total Mn in M2 for samples with less than one Mn atom per formula unit and with >0.94 Mn in M2 for those specimens with more than one Mn atom per formula unit. Synthetic Mg–Mn olivines are more highly disordered; synthetic Mg–Zn olivines are completely disordered. Single-phase Mg–Ca olivines synthesized by Warner and Luth (1973) are highly ordered: in Fo_{SS} $>80\%$ of the Ca present is in M2, in Mo_{SS} $>95\%$ of the Ca present is in M2.

The d -spacings for the 130 and 131 peaks in X-ray powder patterns of olivines are very sensitive to Mg–Mn and Mg–Ca order–disorder, but d_{112} was found to be insensitive (to within one part in 2500) to cation distribution in M1 and M2. Regression equations to estimate compositions are

$$100 \text{ Mg}/[\text{Mg} + \text{Mn} + \text{minor (Fe,Zn,Ca)}] = 2484.87 - 970.42d_{112},$$

and

$$100 \text{ Fo}/(\text{Fo} + \text{Mo}) = 1946.25 - 752.14d_{112};$$

precision is estimated at better than ± 1.5 mole% Fo.

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Introduction

Despite many crystal structure refinements of silicate olivines $[M1][M2]SiO_4$, showing a wide range of composition ($M^{2+} = Ni, Mg, Co, Zn, Fe, Mn, Ca$) and a variety of ordering schemes (see Brown, 1982, Table 5 and Lumpkin and Ribbe, 1983, Table 1), no method of estimating both the bulk composition and ordering of the M^{2+} octahedral cations from physical properties has yet been developed (but see Smyth and Taftø (1982) for a description of CHEXE—CHannelling Enhanced X-ray Emission spectroscopy—used to obtain, directly and quantitatively, Fe, Ni, Mn and Ca concentrations in M1 and M2 sites.) Determinative methods for composition in the Mg-Fe olivines are well known, beginning with earliest optical studies and including the recent work of Laskowski and Scotford (1980) relating refractive indices to Mg/(Mg+Fe). Bloss (1952) established the nonlinear relationship of density to Mg/(Mg+Fe), and Yoder and Sahama (1957), Fisher and Medaris (1969), Schwab and Kustner (1977), and others (see Shinno, 1980) have produced determinative curves based on the d_{130} spacing.

To determine compositions of Mg-Fe-Mn olivines, Mossman and Pawson (1976) used relationships between the refractive index β and d_{130} . But Shinno (1980) and Francis (1980) have recently demonstrated that d_{130} is strongly dependent on the degree of M cation ordering, severely limiting the utility of this parameter.

Equations or diagrams relating unit cell dimensions to composition have been produced for Mg-Fe olivines (Louisnathan and Smith, 1968; Fisher and Medaris, 1969; Schwab and Kustner, 1977), for Fe-Mn olivines (Shinno, 1980), for Mg-Mn olivines (Nishizawa and Matsui, 1972; Akimoto *et al.*, 1976; Shinno, 1980; Francis, 1980), for Mg-Mn-Zn olivines (Francis, 1980), and for Mg-Zn, Mg-Ni and Mg-Co olivines (Akimoto *et al.*, 1976). Fewer data exist for olivines containing substantial amounts of calcium, but see Warner and Luth (1973) for data on Mg-Ca olivines. Brown (1970, 1982) attributed the nonlinearity in plots of certain lattice parameters versus composition or versus mean radii of the octahedral cations to M-cation ordering.

In Part I of this work, Lumpkin and Ribbe (1983, see also 1982) quantified the relationships among unit cell parameters and the radii and formal charges of both octahedral (M) and tetrahedral (T) cations in a wide range of compounds that crystallize with the olivine structure ($M = Li, Na, Mg, Al, Ca, Sc, Cr, Mn, Fe, Co, Ni, Zn, Ga, Y, Cd, Sm, Gd$ and Lu ; $T = Be, B, Si, P$ and Ge), using multiple linear regression techniques. They successfully used cell volume to estimate the ordering schemes of a variety of synthetic compounds with the olivine structure. They also calculated individual sets of regression equations for the phosphate, beryllate and silicate olivines, correlating a, b, c and volume V to the mean radii of the M1 and M2 octahedral cations. These results unequivocally supported Brown's suggestion of

the importance of the effect of ordering in the M sites on lattice parameters, and in this paper we will exploit these relationships to devise a method of simultaneously determining the bulk composition and the ordering of octahedral cations in binary silicate olivines. We will emphasize the Mg-Mn olivines and others in the same series containing up to 0.25 Zn atoms, using the recent studies of Francis (1980) as our primary data base. Data for the Mg-Ca olivines are taken from Warner and Luth (1973) and others. Preliminary reports of this work were presented by Ribbe and Lumpkin (1982), Lumpkin *et al.* (1982) and in Figure 11 of Lumpkin and Ribbe (1983).

Parameters for determining composition and cation ordering

Brown (1970) recognized significant negative departure from linearity in plots of a versus mean octahedral cation radius (r_M) for the Mg-, Fe- and Mn-Ca olivines, and Ganguli (1977) observed a positive deviation from linearity in a plot of b versus (r_M).

Figure 1 is a compilation of silicate olivine data, showing essentially straight-line trends for specimens in which the occupancies of the M1 and M2 sites are the same. Lines arbitrarily drawn between Mg_2SiO_4 (forsterite) and $MgCaSiO_4$ (fully ordered monticellite with all the Ca in M2), and between monticellite and α - Ca_2SiO_4 show how a, b and V vary for the ordered compounds (large cations in M2).

Akimoto *et al.* (1976, their Fig. 3 reproduced as Fig. 15 in Brown, 1982) also described significant nonlinearity in plots of cell parameters versus composition in synthetic binary olivines containing Mg with Mn, Co, Ni and Zn, and Francis (1980) found nonlinear trends for a, b, V , and d_{130} versus composition of ordered Mg-Mn olivines from Långban, Sweden and Madagascar (*cf.* Francis and Ribbe, 1980). Although Francis (*ms.*) fitted second-order equations to his data, each of his plots of a, b and d_{130} for naturally occurring specimens appear to be equally if not better fitted with two straight lines, one spanning the composition range Mg_2SiO_4 to $MgMnSiO_4$ and the other $MgMnSiO_4$ to Mn_2SiO_4 . Data for synthetic Mg-Mn specimens deviated toward the straight line presumed to represent disordered olivines (see discussion below).

As mentioned earlier, Lumpkin and Ribbe (1983) found that the lattice parameters of silicate olivines with divalent octahedral cations are highly correlated to the radii, r_{M1} and r_{M2} , of those cations. Their regression equations are given in Table 1. Notice that in the equation for a the regression coefficient of r_{M1} is ~ 4 times as large as that for r_{M2} , and in the equation for b the coefficient for r_{M2} is ~ 6 times as large as that for r_{M1} . Therefore it appears that a and b , when considered together, might be used to determine the degree of ordering of larger and smaller divalent cations between the M1 and M2 sites, at least in binary systems in which r_{M1} and r_{M2} differ by $\sim 0.1\text{\AA}$ or more. Of course, both a and b , as well as other lattice parameters, are also sensitive to bulk composition.

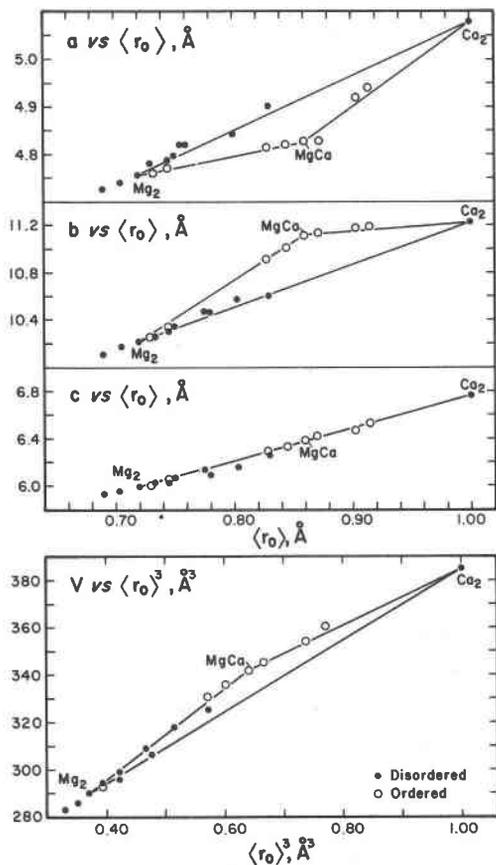


Fig. 1. Plots of a , b and c cell dimensions (in Ångstroms) versus the mean radius of the octahedral cations (r_o) (in Å) and of volume V versus $\langle r_o \rangle^3$ (in Å³) for a variety of binary silicate olivines. The specimens known to have chemically equivalent M1 and M2 site occupancies are shown as solid dots and generally fall along the lines joining Mg₂SiO₄ and Ca₂SiO₄. Those with fully ordered arrangements are plotted as open circles; lines drawn connecting Mg₂-MgCa and MgCa-Ca₂ represent the locus of ordered olivines containing Ca in M2. Data are from Table 1 of Lumpkin and Ribbe (1983).

The a - b plot: its construction

To illustrate this determinative method we have chosen the forsterite-tephroite (Fo-Te) series, because (1) a substantial number of lattice parameter refinements are available for both natural (Francis, 1980; Francis and

Table 1. The regression equations relating unit cell parameters of silicate olivines to the radii of cations in the M1 and M2 octahedral sites. From Lumpkin and Ribbe (1983, Table 5): radii used were those of Shannon (1976).

a	= 0.932 r_{M1}	+ 0.236 r_{M2}	+ 3.918	($R^2 = 0.982$; esd = 0.010 Å)
b	= 0.505 r_{M1}	+ 3.211 r_{M2}	+ 7.535	($R^2 = 0.996$; esd = 0.025 Å)
c	= 1.231 r_{M1}	+ 1.484 r_{M2}	+ 4.010	($R^2 = 0.993$; esd = 0.019 Å)
V	= 149.4 r_{M1}^3	+ 187.6 r_{M2}^3	+ 46.8	($R^2 = 0.997$; esd = 1.64 Å ³)

Ribbe, 1980) and synthetic Mg-Mn olivines (Nishizawa and Matsui, 1972; Ghose *et al.*, 1975), (2) the compositions of Francis' natural specimens include less than 2 mole% [Fe+Ca+Zn], and (3) site refinements of crystal structures indicate significant disorder in synthetic samples (Ghose and Weidner, 1974; Ghose *et al.*, 1975), and nearly complete order in natural Mg-Mn olivines (Francis and Ribbe, 1980), providing the means of testing the method.

To construct the a - b plot shown in Figure 2, cell dimensions of four forsterites and four tephroites were averaged, giving the end-point values of $a = 4.753$ Å, $b = 10.193$ Å for Fo and $a = 4.904$ Å, $b = 10.598$ Å for Te (see also Table 2). The line joining these values represents the locus of a and b for the disordered Mg-Mn olivines, and distance along it is presumed proportional to the Mg/(Mg+Mn) ratio.

Given the broad range of data from which the equations in Table 1 were determined, it is not surprising that values for a and b for Fo and Te calculated from these equations do not agree exactly with the observed values. Small correction factors, Δa and Δb , have been introduced to compensate for these differences. They are applied in proportion to the bulk Mg-Mn content of all calculated reference points in this (or for that matter, any) binary system (see Table 2 footnote for a sample calculation). Having thus calculated corrected a and b dimensions based on ordered MgMnSiO₄, disordered (Mg_{0.5}Mn_{0.5})₂SiO₄ and antioderred MnMgSiO₄ (with Mn in M1, Mg in M2), these values are then plotted in Figure 2. The straight line joining these three points represents the locus of all possible a and b values for FO₅₀TE₅₀, and distance along it is proportional to x , the Mn content of the M2 site (and thus to $1-x$, the Mg content of M2). The parallelogram can be contoured with compositional determinative lines parallel to this diagonal, and labelled in

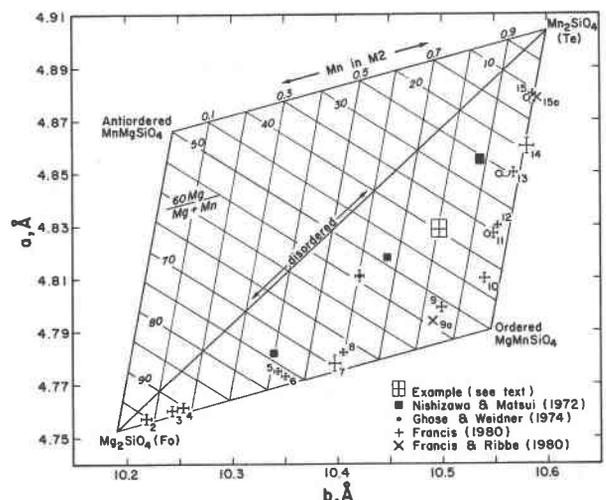


Fig. 2. An a - b plot for the Mg-Mn silicate olivines. See text for details of its construction and use and Tables 2 and 3 for data.

Table 2. Calculated and observed cell parameters of certain end-member silicate olivines and calculated and corrected cell parameters of intermediate compositions. Calculated values of a and b were derived from equations in Table 1 and the Shannon (1976) ionic radii. Observed values of end members are averages of values taken from the references listed in the right hand column (see footnote of Table).

Site contents		Calculated parameters		Correction factors*		Corrected or observed values		a^{calc} 112	Refs.
M1	M2	a	b	Δa	Δb	a'	b'		
Mg	Mg	4.759	10.210	-0.006	-0.017	4.753	10.193	2.456	1, 2, 3, 4
Mn	Mn	4.887	10.619	+0.017	-0.021	4.903	10.598	2.559	1, 5
Mg	Mn	4.785	10.564	+0.006	-0.019	4.791	10.545	2.507	
Mn	Mg	4.861	10.266	"	"	4.867	10.247	2.506	
Mg _{0.5}	Mg _{0.5}	4.823	10.415	"	"	4.829	10.396	2.506	
Mn _{0.5}	Mn _{0.5}								
Ca	Ca	5.086	11.251	-0.008	-0.026	5.078	11.225	2.729	6
Mg	Ca	4.825	11.110	-0.007	-0.022	4.915	11.088	2.586	
Ca	Mg	5.020	10.352	"	"	5.013	10.330	2.585	
Mg _{0.5}	Mg _{0.5}	4.922	10.731	"	"	4.915	10.709	2.586	
Ca _{0.5}	Ca _{0.5}								
(Zn	Zn)**	4.782	10.285	+0.008	+0.013	4.790	10.298		
Mg	Zn	4.764	10.274	+0.001	-0.002	4.765	10.272		
Zn	Mg	4.778	10.220	"	"	4.779	10.218		
Mn	Zn	4.866	10.330	+0.012	-0.003	4.878	10.327		
Zn	Mn	4.803	10.574	"	"	4.815	10.571		
Fe	Fe	4.829	10.433	-0.009	+0.041	4.820	10.474		3, 7, 8, 9

* Values of Δa and Δb are determined for end members by subtracting a and b (as calculated from the equations in Table 1) from the observed values. Correction to calculated a for, say, MgMnSiO₄ is $\Delta a = +0.0065$ exactly half way between Δa of -0.006 for Mg₂SiO₄ and $+0.017$ for Mn₂SiO₄.

** Hypothetical end member. The values of a and b (given) and $c = 6.019$ Å predicted from equations in Table 1 agree well with those determined by extrapolation ($a = 4.79$ Å, $b = 10.31$ Å, and $c = 6.02$ Å) by Akimoto et al. (1976, their Fig. 3 and Table 1). Our extrapolation (see Fig. 2) gives $b \sim 10.298$ Å.

References

1. Fujino et al. (1981) Acta Cryst. B37, 513.
2. Hazen (1976) Am. Mineral. 61, 1280.
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9. Hazen (1977) Am. Mineral. 62, 286.

terms of 100 Mg/(Mg+Mn) or mole% Fo. Lines parallel to the Mn₂SiO₄-MgMnSiO₄ and Mg₂SiO₄-MnMgSiO₄ sides represent loci of equal x , the Mn-content in M2. The sum, Σx , of the x values at the opposite ends of a compositional contour is equal to the total number of Mn atoms per formula unit.

An example will suffice to illustrate how to interpret data on the a - b plot. Suppose an unknown olivine in this binary system has dimensions $a = 4.828 \pm 0.003$ Å, $b = 10.497 \pm 0.007$ Å (open rectangle in Fig. 2). The NW-SE compositional contour on which this value lies indicates 40 mole% Mg (\equiv Fo₄₀Te₆₀) to be the bulk composition. The ends of this line have $x = 0.20$ and $x = 1.00$, thus $\Sigma x = 1.20$ Mn atoms. The chemical formula is Mg_{0.8}Mn_{1.2}SiO₄. The Mn content of the M2 site is $x = 0.80$, and the structural formula, in the order [M1][M2]SiO₄, is [Mg_{1- Σx + x} Mn _{Σx - x}][Mg_{1- x} Mn _{x}]SiO₄ or [Mg_{0.6}Mn_{0.4}][Mg_{0.2}Mn_{0.8}]SiO₄. Estimated errors in x are ± 0.03 Mn and in $\Sigma x \pm 0.02$ Mn or ± 2 mole% Mg, based on the given esd 's of a and b . Systematic error in estimating Mg-Mn content and distribution will result if the Ca content exceeds 0.1 atoms. See discussion below.

The a - b plot: its use

Included on Figure 2 are the a - b values of natural and synthetic Fo-Te specimens from Table 3. There is excellent agreement between the reported compositions, expressed as 100 Mg/(Mg+Mn), and those estimated from the contoured a - b plot: the mean deviation is ± 1.1 mole% Fo, only slightly greater than that expected on the basis of estimated errors in a and b .

There are clearly two populations of samples. Natural specimens are highly ordered, with the M2 site containing 90+ % of the total Mn for samples with less than one Mn atom per formula unit ($x < 1$), and ≥ 0.94 Mn for samples with $x > 1$ (see Table 3). The least-squares site refinements of two of these, 9a from Långban, Sweden (Fo_{51.3}Te_{48.7}) and 15a from Madagascar (Fo_{9.1}Te_{90.9}), have structural formulas [Mg_{0.92}Mn_{0.08}][Mg_{0.11}Mn_{0.89}]SiO₄ and [Mg_{0.17}Fe_{0.03}Mn_{0.80}][Ca_{0.01}Mn_{0.99}]SiO₄, respectively, which agree rather well with those predicted from the a - b plot: [Mg_{0.92}Mn_{0.08}][Mg_{0.17}Mn_{0.83}]SiO₄ (predicted composition: Fo₅₄Te₄₆) and [Mg_{0.22}Mn_{0.78}][Mg_{0.00}Mn_{1.00}]SiO₄ (Fo₁₁Te₈₉).

Only two of the natural specimens—15a (see above)

Table 3. Observed *a* and *b* and calculated d_{112} values, observed and estimated *M*-cation distributions of natural and synthetic specimens in the systems forsterite-tephroite and forsterite-monticellite.

Forsterite-Tephroite										
Sample number	<i>a</i> (Å)	<i>b</i> (Å)	d_{112}^{calc} (Å)	100 Mg/(Mg + Mn)			Site occupancy from <i>a-b</i> ($\times 10^2$)			
				observed	from <i>a-b</i>	from d_{112}^{calc}	M1:Mg	Mn	M2:Mg	Mn
FSTS	4.753	10.190	2.456	100	100	100.5	100	00	120	00
T&K	4.753	10.191	2.457	100	100	101.5	100	00	100	00
F2	4.757	10.219	2.461	95.6	96.5	96.7	100	00	93	07
F3	4.760	10.244	2.465	91.6	92	92.8	98	02	86	14
F4	4.761	10.254	2.466	91.6	91	91.8	99	01	83	17
F5	4.775	10.344	2.481	77.4	76	77.3	94	06	58	42
F6	4.773	10.351	2.482	77.2	76	76.2	96	04	56	44
N&M	4.782	10.339	2.485	75.0	74.0	73.4	88	12	60	40
F7	4.778	10.398	2.490	68.4	69.5	68.5	97	03	42	58
F8	4.782	10.406	2.492	67.8	67	66.5	94	06	40	60
G&W	4.811	10.421	2.505	53.0	54.5	54.0	69	31	40	60
F9	4.799	10.499	2.507	51.4	51.5	52.0	88	12	15	85
FR9a	4.794	10.491	2.506	51.3	54	53.4	92	08	17	83
N&M	4.818	10.447	2.510	50.0	49	49.1	65	35	33	67
F10	4.810	10.540	2.516	45.8	43	43.3	81	19	05	95
F11	4.827	10.549	2.524	37.0	35.5	35.5	67	33	04	96
F12	4.830	10.553	2.527	30.7	33.5	32.6	63	37	04	96
N&M	4.855	10.536	2.537	25.0	26	22.9	40	60	12	88
F13	4.850	10.568	2.537	23.3	24	22.9	50	50	02	98
F14	4.860	10.580	2.544	18.6	19	16.1	39	61	00	100
F15	4.880	10.586	2.550	09.0	11	10.2	20	80	01	99
FR15a	4.879	10.589	2.549	09.1	11	10.8	22	78	00	100
FSTS	4.902	10.596	2.559	00.0	01	01.6	00	100	01	99
TAKEI	4.906	10.598	2.559	00.0	<00	01.6	00	100	01	99
M&R	4.091	10.598	2.559	00.0	01.5	01.6	03	97	00	100

Forsterite-Monticellite										
	<i>a</i> (Å)	<i>b</i> (Å)	d_{112}^{calc} (Å)	100 Fo/(Fo + Mo)			Mg		Ca	
				**	00.5	-1.2	Mg	Ca	Mg	Ca
S&H	4.822	11.100	2.586	**	00.5	-1.2	100	0	00	100
L&M	4.825	11.111	2.589	**	-01	-1.2	99	01	00	100
ONKEN	4.822	11.108	2.588	00.0	00	-0.3	100	00	00	100
WL1	4.821	11.091	2.585	01.0	01.5	2.0	100	00	01.5	98.5
WL2	4.820	11.053	2.580	05.5	05	5.7	99	01	06	94
WL3	4.820	11.510	2.579	06.5	05.5	6.5	99	01	06.5	93.5
WL4	4.818	11.007	2.573	11.0	09.5	11.0	98.5	01.5	11	89
WL5	4.815	10.960	2.565	16.4	14.5	17.0	98	02	16.5	83.5
WL6	4.814	10.913	2.560	21.8	19	20.8	98	02	21	79
WL7	4.769	10.318	2.476	82.0	83.5	83.9	97	03	86.5	13.5
WL8	4.766	10.293	2.471	86.3	87	87.7	97.5	02.5	89.5	10.5
*WL9,10	4.760	10.248	2.464	90.9	92.5	93.0	98	02	94.5	05.5
*WL11-13	4.758	10.207	2.461	95.5	96.5	95.2	99	01	97.5	02.5
*WL14-16	4.755	10.198	2.457	100.0	99.5	98.2	100	00	99.5	00.5

* Average values of cell parameters. See Warner and Luth (1973, Table 3).

** Actual compositions given as $Mg_{100.6}Fe_{0.016}Ca_{0.962}SiO_4$ for S&H and $Mg_{0.936}Fe_{0.071}Ca_{1.008}Si_{0.992}O_4$ for L&M (references below).

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- F2-15 Francis (1980) Ph.D. Dissertation (see References)
 FR9a,15a Francis & Ribbe (1980) *Am. Mineral.* 65, 1263
 FSTS Fujino et al. (1981) *Acta Cryst.* B37, 513
 G&W Ghose & Weidner (1974) *Geol. Soc. Am. Abstr.* 6, 751
 L&M Lager & Meagher (1978) *Am. Mineral.* 63, 365
 M&R Muller & Roy (1974) *Major Ternary Struc'l. Families*
 N&M Nishizawa & Matsui (1972) *Phys. Earth Plan. Int.* 6, 377
 ONKEN Onken (1965) *Tcherm. Min. Pet. Mitt.* 10, 34
 S&H Schwab & Kustner (1977) *N. Jhb. Min. Mn.*, 205
 TAKEI Takei (1976) *J. Crystal Growth* 34, 125
 T&K Takei & Kobayashi (1974) *J. Cryst. Growth* 23, 121
 WL1... Warner & Luth (1973) *Am. Mineral.* 58, 998

and 13—contain sufficient calcium to affect the value of *x*. The open circles in Figure 2 represent *a-b* points corrected to account for 0.013 and 0.024 Ca, assuming the Ca is in the M2 site. (See the discussion in the next section where Ca content is of major concern in the interpretation of the zincian tephroites from Franklin, New Jersey.)

The four synthetics are, in terms of the "order parameter" defined by Lumpkin and Ribbe (1983, Fig. 11), between 66 and 76% ordered. This simply means that the

a-b datum (and thus the value of *x* = Mn in M2) is located 66 to 76% of the distance along the composition contour from the antiordered side of the parallelogram toward the ordered side. Ghose and Weidner's (1974) sample is the only synthetic specimen whose structure has been determined, and the observed structural formula, $[Mg_{0.72}Mn_{0.28}][Mg_{0.34}Mn_{0.66}]SiO_4$, and bulk composition, $Fe_{53}Te_{47}$, agree reasonably well with calculated values: $[Mg_{0.69}Mn_{0.31}][Mg_{0.40}Mn_{0.60}]SiO_4$ and $Fe_{54.5}Te_{45.5}$.

Zincian Fo-Te from Franklin, New Jersey. The a - b determinative diagram of Figure 2 is partially reproduced in Figure 3, but the zincian Fo-Te specimens (analyses and cell dimensions from Francis, 1980) plotted here contain up to 0.045 Ca (average 0.021), up to 0.104 Fe (average 0.033), and up to 0.251 Zn (average 0.17). The most notable feature is that specimens 4 through 8 plot off the Mg-Mn parallelogram altogether. This is due neither to the minor Fe nor the more significant Zn content, because the Shannon (1976) radii of Fe (0.78 Å) and Zn (0.74 Å) fall between the Mg (0.72 Å) and Mn (0.83 Å) radii. The corrected, calculated data points for (hypothetical) ordered ZnMnSiO₄ and end-member Zn₂SiO₄ are shown in Figure 3 (and inset), and indicate what the major effect of Zn content on Fo-Te specimens would be on the actual location of the composition contours.

It is in fact Ca that displaces the a - b points up to 0.025 Å higher values of b and 0.002 Å higher values of a . If one makes some assumptions about site occupancies in these samples, it is possible to adjust a and particularly b to correct for Ca content. The procedure is simple: first assume an ordered large cation distribution, *i.e.*, assign to M2 all the Ca and either all the Mn (plus Mg, as needed) or sufficient Mn to fill the site. The remaining cations (Mg, Fe, Zn and left-over Mn) are assigned to M1. Then calculate a' and b' using the equations of Table 1. These values presumably mimic the true distribution fairly well, since we know from structural studies that Ca is always in M2 (for Ca \leq 1.0 atoms), Mn likewise orders into M2 (see above) and Zn prefers M1 (see Francis and Ribbe's (1980) reinterpretation of Brown's (1970) refinement), even in synthetic Mg_{1.57}Zn_{0.43}SiO₄ (Ghose *et al.*, 1976). (The exact details of these assumptions about site assignments are not critical, because the Ca content, small though it be, controls the correction, and it is the differences in calculated a and b that are of interest.) The second step is to remove Ca from consideration by normalizing the formulas to 2.000 total cations, *i.e.*, multiplying all values by $[2/(1-\text{Ca content})]$. Then fill M2 with Mn (or Mn+Mg) and calculate a'' and b'' . The differences, $\delta a' = a' - a''$ and $\delta b = b' - b''$, represent corrections to be subtracted from the observed a and b values to account for Ca content. These are shown as open circles connected by lines to their respective data points. In all cases (except specimen #8), the corrected datum is in or on the edge of the parallelogram, indicating, as expected, highly ordered Mn distributions in these natural zincian tephroites.

Figure 3 will be useful only if both composition and cell dimensions are known. To predict δa and δb from total Ca content, use these equations: $\delta a = 0.04 \times (\text{Ca-content})$; $\delta b = 0.54 \times (\text{Ca-content})$. They were derived from data we calculated using the Franklin suite of Francis (1980), but they could be determined equally well from observed and corrected a and b values for Mn₂ and MnCa olivines in Table 2.

The only test of this diagram comes from the specimen that Brown (1970; 1982, p. 361-364) calls "zincian picro-

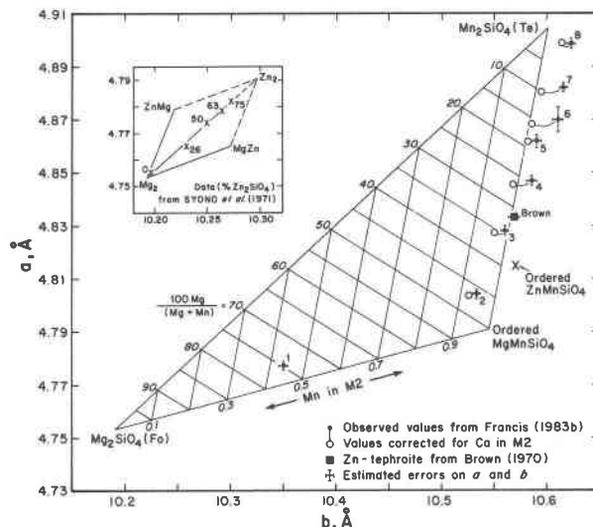


Fig. 3. A partial a - b diagram (*cf.* Fig. 2) for the Mg-Mn silicate olivines with data for zincian varieties plotted on it. The open circles represent a - b values corrected for Ca content in M2. See text for discussion. The inset (upper left) is an a - b plot for the Mg-Zn olivines synthesized at high temperatures and pressures (up to 90 kilobars) by Syono *et al.* (1971). The Zn²⁺SiO₄ point was determined by extrapolation (see footnote in Table 2 for details).

tephroite", and to which he assigned the [M1][M2] site occupancy $[\text{Mn}_{0.432}\text{Mg}_{0.345}\text{Zn}_{0.180}\text{Fe}_{0.043}][\text{Mn}_{0.868}\text{Fe}_{0.085}\text{Zn}_{0.045}]$. It is hard to defend this assignment, based on X-ray site refinement alone. Using mean M1-O and M2-O bond lengths and data from other crystal structures, Francis and Ribbe (1980) argued that 1.00 Mn is ordered into M2 in the specimen, with the remaining cations in M1. The a - b plot supports their analysis, predicting a fully ordered structure with 1.00 Mn in M2.

Earlier estimates of cation ordering in two Franklin olivines equivalent to samples 2 and 4 (Fig. 3) were made by Huggins (1973) using an infra-red spectroscopic technique. For sample 4 (his #16), our estimate of 0.99 Mn on M2 is somewhat higher than Huggins' value of 0.91. The discrepancy for sample 2 (his #17) is considerably greater, with our prediction of 0.92 Mn on M2 far exceeding Huggins' estimate of 0.67. Readers are referred to the work of Francis (1980) for discussion concerning the general utility of the IR method.

The usefulness of Figure 3 for determining Mg/(Mg+Mn) ratios is obviously limited due to the chemical complexity of the zincian samples, but the corrected a - b points (open circles) give values of Σx (= total Mn) fairly close, although consistently higher than the observed values because of the Zn (plus minor Fe) for Mg substitution. The usefulness of Figure 3 is mainly in the prediction of order-disorder.

Significance of ordering in Mg-Mn olivines. The ability to determine ordering in synthetic and natural Mg-Mn(Zn) olivines makes it possible to analyze the depen-

dence of cation distribution on a sample's thermal history (cf. Francis and Ribbe, 1980; Shinno, 1980). Nishizawa and Matsui (1972) synthesized their samples by heating mixtures of Mg_2SiO_4 and Mn_2SiO_4 at 1300°C for 12 hours under controlled fO_2 , with $H_2/CO_2 = 1/3$. The olivine described by Ghose and Weidner (1974) and Ghose *et al.* (1976) was "heat treated at 1000°C" for an unspecified duration. As previously discussed, these synthetic Mg-Mn olivines are only partially ordered. It would appear likely that under certain conditions even more disordered arrangements could be quenched.

The highly ordered natural Mg-Mn olivines have equilibrated at lower temperatures on a geologic time scale. Moore (1970) gave an estimate of at least 650°C for the Mn orebodies and skarns at Långban based on the presence of manganosite and periclase. His estimate correlates well with the occurrence of andalusite and sillimanite in the metavolcanic rocks (leptites) associated with the skarns (Moore, 1970, Table 1). Zincian Mg-Mn olivines from the Franklin orebodies probably formed at similar temperatures. Frondel and Klein (1965) estimated a minimum temperature of 650–700°C in regard to hetaerolite exsolution from franklinite, in general agreement with the sillimanite grade of gneissic country rocks (Frondel and Baum, 1974).

The Mg-Ca olivines. Figure 4 is a partial *a-b* diagram constructed using forsterite (Fo) end-point data from Table 2, and *a* and *b* values for monticellite (Mo) from Onken (1965). The Fo and Mo solid solutions plotted there were synthesized hydrothermally by Warner and Luth (1973, see p. 1007 for techniques). The estimated compositions, 100 Fo/(Fo+Mo), of Warner and Luth's specimens have an average deviation of only 1.5 from their reported values, and they all appear to be very highly, though not completely ordered, with >80% of the Ca present in Fo_{55} in M2 and >95% of the Ca present in Mo_{55} in M2 (see Table 3).

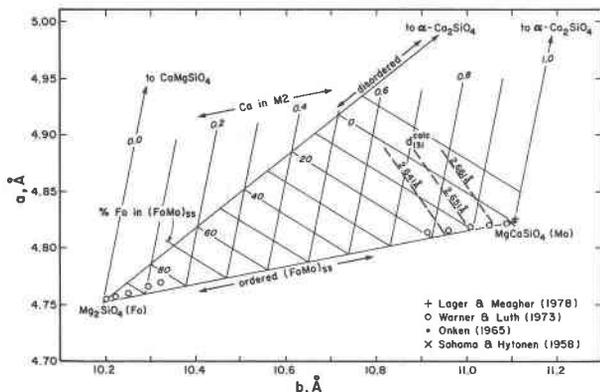


Fig. 4. A partial *a-b* plot for the Mg-Ca olivines constructed with data in Tables 2 and 3. The three parallel lines near the Mo corner of the diagram are lines of constant d_{131} -spacings, calculated from values of *a*, *b* and *c* expected in that range of composition and order-disorder.

It is of interest to note that Warner and Luth (1973) used the $2\theta_{131}$ values from $CuK\alpha$ powder patterns of the single-phase samples (those plotted in Fig. 4) to derive equations for predicting the compositions of the coexisting Fo_{55} and Mo_{55} phases in their experiments designed to delineate the solvi in the Fo-Mo system at high pressures and temperatures. They were troubled by their results (their Figs. 2a,b, p. 1002) which showed a widening solvus above 1200°C at 10 kilobars. However, this may well be an artifact of their using an Mg-Ca order-dependent parameter to estimate composition! In fact, d_{131} (and therefore $2\theta_{131}$) is the same for all compositions between $Fo_{12}Mo_{88}$ and Fo_2Mo_{98} if $Fo_{12}Mo_{88}$ is assumed to be ordered ($[Mg_{1.00}[Mg_{0.12}Ca_{0.88}]SiO_4]$) and Fo_2Mo_{98} ~25% disordered ($[Mg_{0.74}Ca_{0.26}][Mg_{0.28}Ca_{0.72}]SiO_4]$). Lines representing equal values of calculated d_{131} -spacings are plotted in Figure 4 to illustrate this point. The argument that higher pressures increase cation order while decreasing molar volume is invalid for these Mg-Ca olivines: the equation for *V* in Table 1 predicts smaller volumes for the more disordered polymorphs (cf. Fig. 1).

Other binary silicate olivines. The Mg-Co, Mg-Ni, Mg-Fe, Fe-Mn and Fe-Ca olivines have also been studied successfully using *a-b* plots. However, some practical difficulties arising from the similarities of the radii of Ni, Mg, Co, and Fe are under investigation. The data of Annersten *et al.* (1982) for ordered synthetic Ni-Fe olivines provide further confirmation of this method, with the exception of their aberrant datum at Fa_{52} . The synthetic Mg-Zn olivines of Syono *et al.* (1971) appear to be completely disordered (see inset to Fig. 3).

The *d*-spacings of diffraction peaks as determinative methods

The regression equations (Table 1) together with the study of the dependence of *a* and *b* on order-disorder of cations in olivine (above) lead to the following re-evaluation of *d*-spacings of peaks on powder diffraction patterns as compositional indicators.

In the orthorhombic crystal system,

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

This, together with our regression equations, requires that most of the peaks in an olivine powder diffraction pattern will have *d*-spacings that depend on order/disorder as well as on bulk composition. In the Fe-Mn (Shinno, 1980) and Mg-Mn olivines (Shinno, 1980; Francis, 1980; see Fig. 2) this fact was recognized for d^{130} , which, of course, depends solely on *a* and *b*. Warner and Luth (1973) used d_{131} to determine compositions in the Mg₂-MgCa silicate olivines. Like d_{130} , this parameter is extremely sensitive to Mg-Ca order-disorder, as noted above.

In a search for a diffraction peak in the powder pattern which is relatively insensitive to the distribution of large

and small cations on M1 and M2, it was discovered that d_{112} does not vary more than one part in 2500 from a singular value, regardless of whether Mg is assigned to M1 and Mn to M2 (the *ordered* arrangement) or $Mg_{0.5}Mn_{0.5}$ to both sites (the *disordered* arrangement) or Mn to M1 and Mg to M2 (the *antioderred* arrangement). The d_{112} spacings were determined using a , b and c values calculated from the equations in Table 1 and corrected as discussed above (values for a and b are in Table 2).

It is fascinating to note the same insensitivity of d_{112} calculated for hypothetical ordered, disordered and antioderred $FeCaSiO_4$ and $MgCaSiO_4$ (see Table 2), and to presume it holds for any pair of elements that form silicate olivines. This leads to the proposal that d_{112} replace d_{130} (which works for Mg-Fe olivines only because they are all nearly disordered) and d_{131} (which did *not* work for Warner and Luth (1973)) as the "composition parameter" for all binary olivines.

For the forsterite-tephroite series, the 112 diffraction peak is fortunately very intense, and if d_{112} is carefully measured with an internal standard (or calculated from a , b and c) it should give reasonable estimates of composition according to the following equation derived from data referenced in Figure 5:

$$100 \text{ Mg}/\Sigma M = 2484.87 - 970.42 d_{112}^{\text{calc}} \quad (R^2 = 0.998)$$

The compositional parameter we have used is the number of Mg atoms in the formula divided by the total number of cations in octahedral coordination. In natural specimens small amounts of Fe, Zn, Ca and Ni will affect d_{112} , contributing to an estimated error of ± 1.4 mole% Mg, less than half of which should be attributable to measuring d_{112} or calculating it from cell dimensions.

To test this equation the cell parameters of two Mg-Mn olivines refined by Francis and Ribbe (1980) were used to calculate d_{112} and then the Mg/ ΣM ratios. Observed and calculated compositions, respectively, are Mg/ $\Sigma M = 51.3$ and 53.4 and 9.1 and 10.8. The agreement between observed and calculated compositions is generally better than this—see Table 3.

The 112 peak in powder patterns of members of the forsterite-monticellite (Fo-Mo) series is also very intense, and thus d_{112} may be used to predict composition to about the same precision ($\pm 1.3\%$ Fo) as for the Fo-Te series. The regression equation, based on data in Table 3, is

$$100 \text{ Fo}/(\text{Fo}+\text{Mo}) = 1946.25 - 752.14 d_{112}^{\text{calc}} \quad (R^2 = 0.9993).$$

Cation ordering may have a dramatic effect on the intensities of diffraction peaks, and a study is underway to determine whether ratios of certain peak intensities might be of practical value in determining the distribution of cations of sufficiently different x-ray scattering powers between M1 and M2. In the meantime the a and b cell dimensions, determined by powder or single-crystal diffractometry, have proven to be highly sensitive indicators

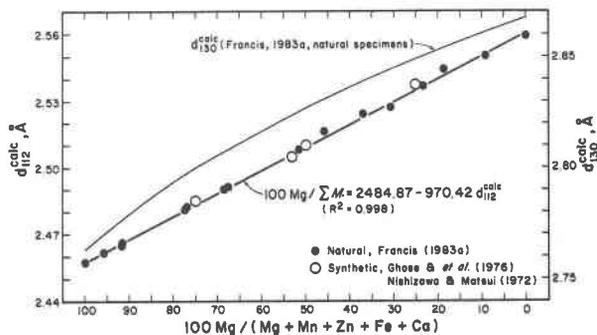


Fig. 5. A plot of d_{112} -spacings calculated for natural and synthetic Fo-Te specimens (Table 3 and Fig. 2) versus $100 \text{ Mg}/(\text{Mg}+\text{Mn}+\text{Fe}+\text{Zn}+\text{Ca})$, where $(\text{Fe}+\text{Zn}+\text{Ca})$ is less than 2% of total M cations. The light, curved line is the d_{130} curve calculated for highly ordered natural specimens by Francis (1980).

of both composition *and* order/disorder and should be used in preference to d_{112} .

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