

Methods for determination of composition and intracrystalline cation distribution in Fe–Mn and Fe–Ni silicate olivines

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Abstract

Multiple linear regression analysis has been used to determine the relationship between the unit cell parameters and the average radii, $rM1$ and $rM2$, of the octahedral cations in Fe–Mn and Ni–Fe binary olivines, using data from Annersten et al. (1982, 1984a,b) and other sources. The resulting regression equations are given below. The coefficients of correlation exceed 0.997 in all cases.

Fe–Mn binary olivines

$$\begin{aligned}a &= 3.527 + 1.341rM1 + 0.317rM2 \\b &= 8.586 - 1.856rM1 + 4.281rM2 \\c &= 3.468 + 2.204rM1 + 1.155rM2 \\V &= 32.43 + 150.1rM1 + 202.5rM2\end{aligned}$$

Ni–Fe binary olivines

$$\begin{aligned}a &= 4.007 + 1.053rM1 - 0.012rM2 \\b &= 7.331 + 1.375rM1 + 2.636rM2 \\c &= 4.521 + 0.984rM1 + 1.032rM2 \\V &= 90.72 + 156.3rM1 + 121.9rM2\end{aligned}$$

Because for both systems the a cell edge is mainly dependent on $rM1$ and b on $rM2$, these equations may be used to construct a vs. b diagrams which may be contoured for bulk composition, M2 site occupancy, and the distribution coefficient, K_D . Similar determinative diagrams may be drawn using calculated d -spacings of the 130 peak, which is sensitive to cation order in the M1 and M2 sites, and the 112 peak, which is composition dependent.

Tests of these diagrams using Shinno's (1980) d_{130} -spacings and cation site occupancy data for numerous synthetic Fe–Mn olivines, indicate that this model is reliable; agreement of predicted and observed Mn content of the M2 site is within 0.03 atoms on the average. Eleven natural olivines ($Fe_{45-85}Te_{50-8}Fo_{2-11}$), for which cell dimensions and in several cases site refinements were available, were critically evaluated using the equations and diagrams for the Fe–Mn binary, with mixed results.

Introduction

Using end-member and site-refined crystal structure data for silicate olivines as determined by many investigators and reviewed by Brown (1982), Lumpkin and Ribbe (1983) discovered that rather precise linear regression equations could be written for each unit cell parameter in terms of the effective radii of the divalent metal cations occupying the M1 and M2 octahedral sites, using the radii of Shannon (1976). The a cell edge was found to be approximately 4 times more dependent on $rM1$ (the mean radius of the cation(s) occupying M1) than on $rM2$, and the b cell edge approximately 6 times more dependent on $rM2$ than on $rM1$. Thus relative position on an a vs. b plot theoretically could be used to predict both M1 and M2 site occupancies and bulk composition, at least for those binary olivines whose end members have M-cation radii differing by 0.1 Å or more. (Rationalization in structural terms is given by Lumpkin and Ribbe, 1983, p. 165f.)

Later, Lumpkin et al. (1983) used the Lumpkin and Ribbe equations successfully with the forsterite-tephroite

(Fo–Te) series to predict occupancies to 0.03 Mn and bulk compositions to better than 3 mole% Te, on the average. However, in order to obtain results of that precision, the a and b values estimated by the general Lumpkin and Ribbe regression equations for the Mg_2SiO_4 and Mn_2SiO_4 end members had to be brought into exact register with observed values of a and b for Fo and Te, and “correction factors” likewise had to be applied to the predicted a and b values of all chemically intermediate phases in proportion to their Mg–Mn content. In practice, these factors were calculated for a pair of end-member olivines and for their ordered and reverse-ordered 1:1 compounds (e.g., $Mg^{M1}Mn^{M2}$ and $Mn^{M1}Mg^{M2}$), which were then used as reference points in a vs. b plots for individual binary systems (see Fig. 2 and Table 1 of Lumpkin et al.). At least for the Mg–Mn binary, these “corrected” a and b values provided an excellent base for predictions of Mn/(Mg + Mn) ratios for the M1 and M2 sites and could even be used for specimens containing minor amounts of Zn (Fig. 3 of Lumpkin et al., 1983).

When similarly “corrected” a and b values were used

with synthetic Ni-Fe olivines, the method of Lumpkin et al. predicted somewhat less highly ordered distributions (i.e., more Ni²⁺ and less of the larger Fe²⁺ in M2) than the Mössbauer results of Annersten et al. (1982). This discrepancy persisted even after adjustments were made by Annersten et al. (1984a) for errors detected in the initial data set by Ribbe and Lumpkin (1984). However, when appropriately corrected values were used with the Fe-Mn system, a Lumpkin et al. *a* vs. *b* plot predicted much more highly ordered cation distributions, i.e., less Fe²⁺ but up to 0.15 more of the larger Mn²⁺ in M2 than the Mössbauer results indicated (Annersten et al., 1984b, their Fig. 5).

The conclusions of Annersten and coworkers led us to re-evaluate the generalized Lumpkin and Ribbe equations, which were based on 29 silicate olivine structures. Some of these were chemically complex, and untested assumptions had been made about the distribution of cations from their third and fourth components (see Brown, 1970, 1982). Our subsequent attempts to use 25 synthetic and natural (Ni,Mg,Co,Fe,Mn,Ca)-olivines, with what we considered to be more trustworthy site refinements, led to improved statistics, but our weighted regression analyses produced similar equations:

$$a = 3.849 + 0.941rM1 + 0.203rM2$$

$$R^2 = 0.993; F = 2391.$$

$$b = 7.601 + 0.429rM1 + 3.206rM2$$

$$R^2 = 0.995; F = 4726.$$

There was no substantial improvement in applying these rather than the Lumpkin and Ribbe equations to individual binary systems, so additional independent variables were introduced into the regression, including parameters to account for electronegativity and nonlinear terms for crystal field effects with Fe-, Co-, and Ni-containing olivines. As expected, correlation statistics improved. In spite of this, hope of finding generalized equations for *a* and *b* that would be applicable to *all* silicate olivines has been abandoned for the time being, in part because the M²⁺ cations in this data set range in size between rNi = 0.69 Å and rCa = 1.00 Å (Shannon, 1976), and in part because radii are not perfect bond-length predictors. This paper describes our efforts to investigate each binary separately.

By exploring systematic variation of the cell parameters as a function of M1 and M2 occupancy *within* a binary system, we simplify the problem considerably. We shall assume that changes are linear over the composition range under consideration, and that bonding effects such as electronegativity and crystal-field stabilization energy will also be linear and thus accounted for in the regression coefficients. The Fe-Mn binary was chosen initially to test this assumption because there is a relatively large data base with which to work. Such data must include a good chemical analysis, accurate cell parameters, and unambiguous site occupancies. Furthermore, there is a large amount of data that, although unusable in establishing the regression equations, could serve to test the validity of the model.

The Fe-Mn binary

Regression equations

Multiple linear regression techniques (SAS, 1982) were applied to data for the five Fe-Mn olivines synthesized by Annersten et al. (1984b), using a model of the type

$$X = b_0 + b_1rM1 + b_2rM2,$$

where *X* represents the cell parameter, *a*, *b*, *c*, or volume (*V*), and the *b*'s are the regression coefficients. The resulting equations were used to predict the cell parameters for pure fayalite (Fa) and tephroite (Te), and these fell within the range of observed values for synthetic Fa and Te. In a second regression analysis, average cell dimensions for these end members were added to the data base. As expected, the resulting equations estimate the Fa and Te cell dimensions more precisely than at first, but without increasing the residuals associated with the data points for the five synthetic phases by more than 0.002 Å (0.2 Å³ for *V*). See Table 1.

Determinative diagrams

The linear equations may be used to estimate unit cell dimensions for any imaginable combination of Fe and Mn in the M1 and M2 octahedral sites. Thus we may construct an *a* vs. *b* plot like Figure 1a which is contoured for bulk composition and for Mn/(Mn + Fe) in M2; M1 occupancy is obtained by difference. The line joining Fa and Te is the locus of *a* and *b* cell edges for completely disordered olivines. The line joining the point for disordered (Fe_{0.5}Mn_{0.5})₂SiO₄ to the point labelled "ordered FeMnSiO₄" is the locus of expected cell edge variation with increasing cation order in olivine of Fa₅₀Te₅₀ composition. It is a simple matter to contour an *a* vs. *b* plot for

Table 1. Compositions, octahedral cation distributions, and cell parameters of Fe-Mn silicate olivines used in the regression analyses. The regression coefficients, root mean square error (Root MSE), coefficient of correlation (R²), and F-value are given for each unit cell parameter. Data from Annersten et al. (1984a) except as noted. See Fig. 1a.

Sample	Mole % Fa	Fe in M1	Fe in M2	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
*	00	0.000	0.000	4.902	10.596	6.257
011	09	0.135	0.045	4.896	10.603	6.241
012	30	0.404	0.197	4.871	10.594	6.200
013	47	0.611	0.311	4.856	10.585	6.168
014	69	0.826	0.556	4.840	10.556	6.135
015	89	0.976	0.805	4.826	10.514	6.105
*	100	1.000	1.000	4.820	10.479	6.087

X	Regression coefficients (+)			Root MSE	R ²	F-value
	b(0)	b(1)	b(2)			
<i>a</i> (Å)	3.52712 (0.03341)	1.34112 (0.13385)	0.31679 (0.13986)	0.002	0.998	855
<i>b</i> (Å)	8.58558 (0.03598)	-1.85628 (0.14416)	4.28131 (0.15964)	0.002	0.999	1575
<i>c</i> (Å)	3.46835 (0.03703)	2.20437 (0.14836)	1.15529 (0.15503)	0.002	0.999	2802
<i>V</i> (Å ³)	32.4325 (3.92457)	150.134 (15.7252)	202.529 (16.4316)	0.227	0.999	2687

* Synthetic fayalite and tephroite from Fujino et al. 1981.
+ Regression coefficients for equation of the form:
 $X = b(0) + b(1)rM1 + b(2)rM2$, where *X* is one of the cell edges.
Numbers in parentheses are estimated standard errors in the regression coefficients.

K_D where

$$K_D = \frac{Fe^{M1}Mn^{M2}}{Mn^{M1}Fe^{M2}};$$

see Figure 1d. Or we may calculate d -spacings for specific intense peaks in an olivine powder pattern and, for example, contour the a vs. b plot for d_{130} (which is dependent only on a and b and thus is sensitive to Fe–Mn order/disorder) and for d_{112} (which is almost independent of Fe–Mn distribution between M1 and M2); see Figure 1b,c.

Discussion

To further illustrate the utility of the regression equations and the determinative diagrams derived from them,

we shall evaluate the data of Shinno (1980), Henriques (1957), Annersten et al. (1984b), and Brown (1970, 1982).

Shinno (1980) synthesized and heat-treated a suite of Fe–Mn olivines, reporting their compositions, d_{130} values, and—for some specimens—the Fe contents of the M1 and M2 sites, as determined by Mössbauer spectra. (Unfortunately, site occupancies were not reported for his untreated starting mixes.) Plotting available compositions and d_{130} spacings on an appropriately contoured a vs. b diagram (Fig. 1c), one can estimate a and b and then either calculate the Fe [= (1 – Mn)] contents of M1 and M2 or read them from another a vs. b plot, such as Figure 1a. In Table 2 we compare his site occupancies and compositions with those estimated by our technique. Agreement for five of the seven

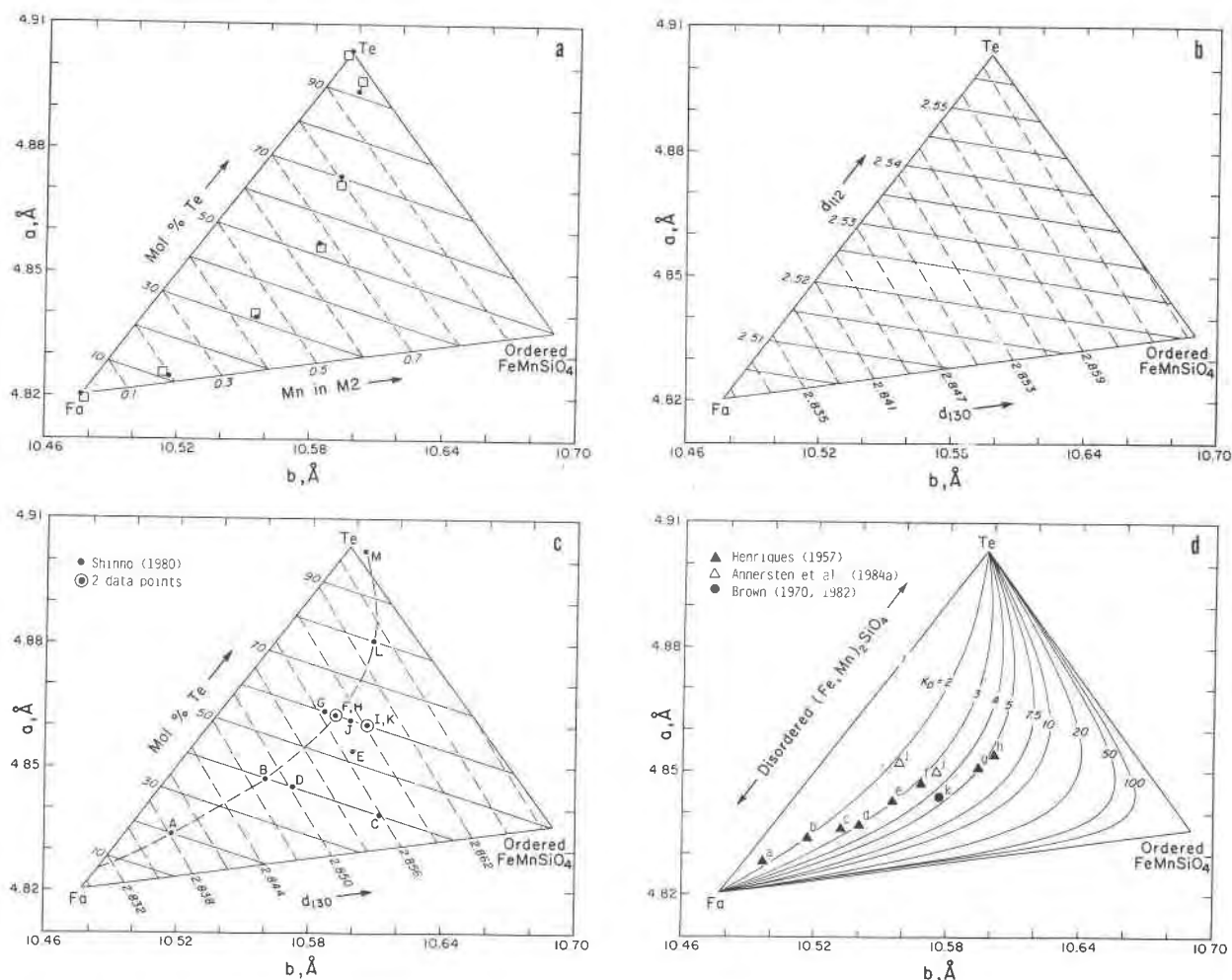


Fig. 1. Triangular plots of a vs. b cell dimensions for Fe–Mn silicate olivines as calculated from the equations in Table 1. (a) Diagram contoured for bulk composition (mole% Te = solid lines) and for Mn in the M2 octahedral site ($Mn/(Mn + Fe)$ = dashed lines). Data of Annersten et al. (1984b) are plotted with end-member values from Fujino et al. (1981) as dots; values calculated from the regression equations are shown as open squares. (b) Diagram contoured for d_{112} -spacing (solid lines) and d_{130} -spacing (dashed lines). The former is dependent mainly on bulk composition, being nearly independent of Fe–Mn order/disorder; the latter is heavily dependent on the Mn content of the M2 site as shown by Shinno (1980). (c) The data of Shinno (1980), on an a vs. b plot using d_{130} and bulk composition, on a diagram contoured for the same. Dashed line connects untreated starting materials; see text and Table 2 for details. (d) An a vs. b diagram contoured for the distribution coefficient, K_D . Data for natural knebelites, containing up to 11 mole% forsterite are shown (key in Table 3).

Table 2. Annealing conditions, d_{130} -spacing, and observed and predicted Mn distributions in Fe-Mn silicate olivines from Shinno (1980). See Fig. 1c.

Sample	Annealing Conditions			Comments*	Mn content			Symbol Fig. 1c
	d_{130} (Å)	Temp (°C)	Time (hrs)		obs	pred	M2	
					M1	M2		
Te20	2.8381	1120	48					A
Te40	2.8485	1120	48					B
40S-1	2.8558	1150+25	24	1,3,6	25	55	68	C
40S-2	2.8502	950	48	3	23	48	56	D
Te52.3	2.8569	1150,1000	48,24	2	35	70	72	E
Te60	2.8573	1120	48					F
60-1	2.8566	1150	24	3				G
60-4	2.8573	950	82	3	48	72	73	H
Te60H	2.8591	1120,700	432					I
60H-1	2.8582	700	144	4	46	74	76	J
60H-5	2.8591	700	432	5	41	79	78	K
Te80	2.8638	1120	48					L
Te100	2.8674	1100	21					M

* 1. Slowly cooled. 2. CO₂/H₂ ratio at 1 atm = 1.0. 3. CO₂/H₂ ratio at 1 atm = 2.3. 4. P = 980 kg/cm². 5. P = 700 kg/cm². 6. Crystallized from melt.

data is remarkably good (± 0.02 Mn), but specimens Te40S-1 and -2 are substantially more discrepant.

Henriques (1957) studied a suite of natural "knebelites" (Fe,Mn-rich olivines) from skarns in central Sweden. He determined bulk compositions by wet chemical methods and reported forsterite components ranging between 2.6 and 29.5 mole percent. He attributed the Ca content to contamination and inclusions, but since Ca does not exceed 0.03 atoms per formula unit, it is quite reasonable to believe that at least a portion of it may be structurally combined. He determined cell dimensions for nine specimens, and then in one of the earliest multiple regression studies of minerals that we are aware of, Henriques derived equations for this suite of the type

$$P = b_1Fa + b_2Te + b_3Fo,$$

where P is the optic axial angle $2V$, a refractive index α , β , or γ , or a unit cell dimension a , b , or c .

We have plotted the a and b cell dimensions for all but the most Mg-rich of Henriques' specimens in Figure 1d. Neither our determinative diagrams nor our equations for the Fa-Te binary can be used in the strictest sense with these Ca-containing ternary olivines, but if one makes certain assumptions with regard to the distribution of Mg and Ca, the Fe (and Mn) contents of M1 and M2 can be calculated because the equations for a and b have unique solutions for $rM1$ and $rM2$. On the basis of structural studies by Brown (1970, 1982), we assumed that Ca is ordered into M2, but the presence or absence of Ca at such low concentrations is of little consequence in our calculations. We tested two assumptions for Mg distribution. A disordered Mg distribution seemed more reasonable than one in which Mg was fully ordered into M1; i.e., the calculated values of Mn ordered into M2 were higher and thus nearer to those expected for relatively slowly cooled natural specimens. The results (Table 3) are tentative, at best, especially

for low Mn compositions, some of which would appear to be reverse-ordered, i.e., with Mn ordered into M1.

Application of this method to the determination of site occupancies in the unheated natural specimen, #6A, of Annersten et al. (1984b) estimates 0.48 Fe in M2, assuming disordered Mg. This is greater by 0.20 Fe than that determined by Mössbauer spectroscopy (see Table 3). Their specimen #6B (heated for 168 hours at 1000°C) was found by Mössbauer to be more disordered than #6A with 0.35 Fe in M2. Our equations indicate 0.47 Fe, assuming Mg to be disordered. If Mg were assumed to be ordered into M1, our overestimates of Fe in M2 would increase. This is because simultaneous solution of the equations for a and b allow unique determination of $rM1$ and $rM2$, and by decreasing the proportion of Mg in M2, the Fe content of that site must be increased relative to Mn if the mean radius for the site is to remain constant.

For a natural knebelite, Brown (1970, 1982; sample Kn in Table 3) assumed Mg to be completely ordered into M1 and obtained 0.37 Fe and 0.63 Mn in M2 by site refinement. Given that these transition metals have nearly identical scattering factors, it is uncertain to what degree these results should be trusted. However, application of our equations for a and b yielded the same Fe,Mn content for M2, on the assumption that Mg is ordered into M1. If Mg is disordered, an estimate of 0.30 Fe, 0.675 Mn, 0.025 Mg is obtained for the occupancy of M2. Inconsistencies and uncertainties associated with applying our regression equations to any but pure Fe-Mn binary compounds indicate that further investigation is necessary to carefully correlate Mössbauer and site refinement data with cell dimensions to determine whether this method, or an extension of it, will have applicability for ternary compounds.

The Ni-Fe Binary

Using the model discussed above, multiple regression analysis was performed on Mössbauer and cell parameter data from 4 of the 5 synthetic Ni-Fe silicate olivines reported by Annersten et al. (1982, revised 1984a) plus average cell dimensions for the two end members, Fe- and Ni-olivine. The regression equations (see Table 4) estimate the cell parameters of these six compounds to within 0.003Å and the volume to within 0.14Å³.

One specimen (H12 of Annersten et al., 1982) was omitted from the analysis. When plotted on an a vs. b diagram contoured for composition and Fe content of M2 (Fig. 2), a bulk composition of Fa₂₉ and an M2 content of 0.44 Fe are estimated for that specimen. These values agree reasonably well with the totally ordered cation distribution reported by Annersten et al. (1982, 1984a), i.e., Fa₂₅ with 0.50 Fe atoms in M2; but the discrepancies are significantly greater than those for the other synthetics, and we chose to omit Fa₂₅ from our regression data base. If Annersten's observed composition and cation distribution are plotted on Figure 2 and the cell parameters read from the plot, the b cell edge is almost perfectly predicted; however, the a cell edge is >0.01Å higher than reported. Whether there is an

Table 3. Compositions, cell parameters, observed and estimated (in parentheses) octahedral cation distributions for natural knebelites. See Fig. 1d.

Sample	Atoms per formula unit				Cell parameters (\AA)			M1			M2				Ref [*]	Symbol Fig. Id
	Fe	Mn	Mg	Ca	a	b	c	Fe	Mn	Mg	Fe	Mn	Mg	Ca		
Bk1	1.708	0.165	0.117	0.010	4.828	10.498	6.100					0.13			1	a
Bk2	1.642	0.288	0.058	0.012	4.834	10.518	6.111	(0.788)	(0.154)	(0.059)	(0.920)	(0.012)	(0.059)	(0.010)	1	b
SK	1.248	0.555	0.194	0.002	4.836	10.533	6.121	(0.792)	(0.179)	(0.029)	(0.851)	(0.108)	(0.029)	(0.012)	1	c
VS	1.161	0.612	0.226	0.001	4.837	10.541	6.122	(0.630)	(0.273)	(0.097)	(0.618)	(0.282)	(0.097)	(0.002)	1	d
H1	1.131	0.696	0.144	0.028	4.843	10.556	6.133	(0.589)	(0.298)	(0.113)	(0.573)	(0.314)	(0.113)	(0.001)	1	e
TM	1.080	0.803	0.108	0.009	4.847	10.569	6.141	(0.735)	(0.193)	(0.072)	(0.396)	(0.503)	(0.072)	(0.028)	1	f
DM1	1.057	0.888	0.051	0.003	4.851	10.595	6.154	(0.611)	(0.334)	(0.054)	(0.468)	(0.468)	(0.054)	(0.009)	1	g
DM2	0.902	1.018	0.074	0.006	4.854	10.602	6.162	(0.646)	(0.328)	(0.026)	(0.411)	(0.560)	(0.026)	(0.003)	1	h
6A	1.069	0.859	0.069	0.004	4.852	10.576	6.142	(0.588)	(0.375)	(0.037)	(0.314)	(0.643)	(0.037)	(0.006)	2	i
6B	1.069	0.859	0.069	0.004	4.850	10.559	6.149	0.789 (0.594) 0.732 (0.604)	0.371 (0.371)	0.034 (0.034)	0.276 (0.475) 0.348 (0.465)	0.487 (0.487)	0.034 (0.034)	0.004 (0.004)	2	j
Kn	1.028	0.928	0.044	--	4.844	10.577	6.146	0.661 (0.724)	0.294 (0.251)	0.045 (0.025)	0.367 (0.300)	0.633 (0.675)	0.000 (0.025)	-- --	3	k

* 1. Henriques (1957); 2. Annersten et al (1984a); 3. Brown (1970, 1982).

error in the determination of the a cell edge, the cation distribution, or in our assumption that the cell parameters change linearly with composition and ordering, remains open to speculation. The lack of other data on this binary

system prevents a rigorous testing of these regression equations and the assumptions on which they are based.

Conclusions

When applied to data for well-characterized specimens in binary olivine systems, multiple linear regression analy-

Table 4. Compositions, octahedral cation distributions, and cell parameters of Ni-Fe silicate olivines which, except for H12, were used in the regression analyses. The regression coefficients, root mean square error, coefficients of correlation, and F-value are given for each cell parameter. Data from Annersten et al. (1982) except as noted. See Fig. 2.

Sample	Mole % Fa	Fe in M1	Fe in M2	a (\AA)	b (\AA)	c (\AA)	Regression coefficients (+)			Root MSE	R ²	F-value
							b(0)	b(1)	b(2)			
*	00	0.000	0.000	4.725	10.119	5.912						
H12	25	0.000	0.500	4.738	10.241	5.976						
H11	52	0.251	0.789	4.749	10.335	6.004						
16	83	0.692	0.968	4.788	10.437	6.066						
15	88	0.784	0.976	4.797	10.447	6.075						
H14	91	0.851	0.969	4.807	10.457	6.078						
**	100	1.000	1.000	4.819	10.476	6.088						

X	Regression coefficients (+)			Root MSE	R ²	F-value
	b(0)	b(1)	b(2)			
a (\AA)	4.00698 (0.01883)	1.05253 (0.04828)	-0.01168 (0.04767)	0.002	0.998	920
b (\AA)	7.35079 (0.03462)	1.37504 (0.08875)	2.63649 (0.08763)	0.003	0.999	3849
c (\AA)	4.52055 (0.04365)	0.98362 (0.11190)	1.03234 (0.11049)	0.003	0.998	605
v (\AA^3)	90.7194 (2.78125)	158.297 (7.13024)	121.861 (7.04016)	0.279	0.999	2832

* Cell parameters for synthetic Ni-olivine taken as average of 4 values reported by Akimoto et al. (1965), Akimoto et al. (1976), Brown (1970, 1982), and Lager and Meagher (1978).

** Synthetic fayalite taken as average of 7 values reported by Annersten et al. (1981), Akimoto et al. (1965), Akimoto et al. (1976), Schwab and Kustner (1977), Smyth (1975), Fujino et al. (1981), and Hazen (1977).

+ Regression coefficients for equation of the form $X = b(0) + b(1)*rM1 + b(2)*rM2$, where X is one of the cell edges. Numbers in parentheses are estimated standard errors in the regression coefficients.

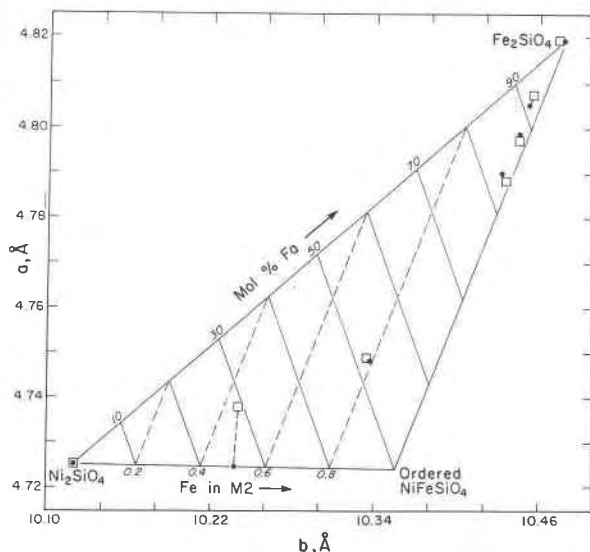


Fig. 2. An a vs. b plot for Ni-Fe silicate olivines contoured for bulk composition (mole% Fa = solid lines) and for Fe in the M2 octahedral site ($\text{Fe}/(\text{Fe} + \text{Ni})$ = dashed lines). Except for the Fa₂₅ datum, observed cell dimensions and Fe distributions from Annersten et al. (1982) and average end-member values were used in the regression analysis, yielding the equations used to generate the plot (see Table 4). Observed a , b values shown as dots, calculated values as open squares.

sis yields precise equations relating cell parameters to mean cation radii for the M1 and M2 octahedral sites. These equations may then be used to construct determinative diagrams that allow extraction of bulk composition and octahedral cation ordering parameters from as few as two *d*-spacings. The application of equations for binary systems to ternary and quaternary olivines apparently must be restricted to very small concentrations of the third and fourth components. The application of this technique to other olivine systems awaits only sufficiently precise data on which to perform the analysis. A re-evaluation of the Mg–Mn olivines and studies of the Mg-, Fe-, and Mn–Ca olivines are in progress.

Acknowledgments

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