Cation ordering in Ni–Fe olivines: corrections and discussion

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Several apparent errors and one major inconsistency have been discovered in our examination of the relationships among the unit cell dimensions, bulk compositions and octahedral site occupancies of the Ni–Fe olivines synthesized and studied by Annersten *et al.* (1982).

The first but probably least important of these discrepancies involves nonconformity among bulk compositions (X_{ol}^{Fe}), the M1 and M2 site occupancies (X_M^{Fe}) calculated from fitted, high-temperature Mössbauer spectra, and the areas themselves. The spectra were "corrected for different recoil-free fractions of iron in the M1 and M2 sites," and although it is not clear to the nonspecialist how (or why) these corrections were applied, they may account for some but not all of the discrepancies reported in Table 3 of Annersten *et al.* For their sample H14, reported values $X_{M1}^{Fe} = 0.87$ and $X_{M2}^{Fe} = 0.99$ add up to $X_{ol}^{Fe} = 0.93$ (not 0.91, as given), but if the areas of the deconvoluted Mössbauer spectra from Fe in M1 and M2 are assumed to be correct and are used unmodified to recalculate X_{M1}^{Fe} and X_{M2}^{Fe}, the new values are 0.83 and 0.99. A similar conflict arises with sample 15: $(X_{M1}^{Fe} + X_{M2}^{Fe})/2 = 0.865$, in slight disagreement with the given value of $X_{ol}^{Fe} = 0.88$. Recalculated from bulk composition and the areas, $X_{M1}^{Fe} = 0.79$ and $X_{M2}^{Fe} = 1.00$, not 0.77 and 0.96, as given. In sample 16 X_{ol}^{Fe} and X_M^{Fe} are consistent, but the areas yield somewhat different values for X_{M1}^{Fe} and X_{M2}^{Fe} than those reported (0.67 and 0.99 rather than 0.69 and 0.96). By contrast, the data for H11 are apparently free from inconsistencies.

There is an error of a different sort in the reported values of X_{ol}^{Fe} and X_{M2}^{Fe} for sample H12. If the bulk composition of 0.25 is correct, then the chemical formula is $Ni_{1.5}Fe_{0.5}SiO_4$. The Mössbauer spectrum of H12 (their Fig. 3) is interpreted to indicate that all the iron is in the M2 site, and thus $X_{M2}^{Fe} = 0.5$, not 0.25 as reported and plotted in their Figure 4. Revised ("new") X_{M1}^{Fe} and X_{M2}^{Fe} values are collected in Table 1, to-

gether with "new" K_D values calculated from them: $K_D = X_{M1}^{Fe}(1-X_{M2})^{Fe}/X_{M2}^{Fe}(1-X_{M1}^{Fe})$.

The last and most substantial problem with the data of Annersten *et al.* (1982) is summarized in Figure 1, which is a plot of the *a* versus *b* cell dimensions superimposed on a triangular net contoured for both bulk composition (parallel lines of equal X_{ol}^{Fe} in mol % Fe_2SiO_4 running roughly NW–SE) and the amount of Fe in the M2 site (lines roughly N–S). The utility and precision of the *a–b* plot has been demonstrated by Lumpkin and Ribbe (1983) and Lumpkin *et al.* (1983) for the Mg–Mn, Mg–Ca and Mg–Zn olivines and by the present authors (unpublished) for the Mg–Ni, Mg–Co, Fe–Mn, Fe–Ca and other binary silicate olivines. It is based on regression equations for the *a* and *b* cell edges (from Lumpkin and Ribbe, 1983),

$$a = 0.932\ r_{M1} + 0.236\ r_{M2} + 3.918 \text{ and}$$
$$b = 0.505\ r_{M1} + 3.211\ r_{M2} + 7.535,$$

which show that the *a* dimension is ~4 times more dependent on the effective ionic radius of the M1 site (r_{M1}) than on r_{M2}, and that the *b* dimension is ~6 times more dependent on r_{M2} than on r_{M1}.

Using Shannon's (1976) radii, these equations may be used to predict *a–b* for any bulk composition X_{ol}^{Fe} and any degree of Fe–Ni order in the M1 and M2 sites. By virtue of the wide composition range of the data set used to determine these equations and the only approximate values of radii used (there ought to be a set determined just for divalent cations in silicate olivines), the calculated values do not exactly replicate observed *a–b* values for the end-member olivines. Thus small correction factors are needed, as explained by Lumpkin *et al.* (1983), and these are applied to calculated values (open crosses in Fig. 1) in proportion to Fe/(Fe+Ni) content, yielding the corrected and observed values (indicated by solid dots). The apex of the triangle labelled "ordered NiFeSiO₄" represents the *a–b* values expected for $X_{M1}^{Fe} = (1-X_{M1}^{Ni}) = 0$, $X_{M2}^{Fe} = (1-X_{M2}^{Ni}) = 1.0$. The line joining Ni_2SiO_4 and Fe_2SiO_4 is the locus of expected *a–b* values for fully disordered binary members with $0 < X_{ol}^{Fe} < 1.0$, and the

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Table 1. The compositions, *a–b* cell dimensions and area ratios of Fe-Mössbauer spectra from the synthetic Fe–Ni silicate olivines of Annersten *et al.* (1982); data for Ni_2SiO_4 are from Brown (1980). New values for X_{M1}^{Fe}, X_{M2}^{Fe} and K_D were calculated from given compositions and area ratios (no errors stated). The columns labelled "Calc X_{ol}^{Fe}" and "Calc $X_{M1,M2}^{Fe}$" contain data obtained from Fig. 1; the K_D values (right column) were calculated from these data.

| Spec | X_{ol}^{Fe} | Area % | | New X^{Fe} | | New K_D | *Cell edge, Å | | Calc X_{ol}^{Fe} | Calc X^{Fe} | | K_D |
		M1	M2	M1	M2		a	b		M1	M2	
17	1.00	48.6	51.4	1.00	1.00	–	4.821(1)	10.478(2)	1.00	1.00	1.00	–
H14	0.91	45.4	54.6	0.83	0.99	0.05	4.807(1)	10.457(2)	0.905	0.84	0.97	0.16
15	0.88	43.2	56.8	0.76	1.00	0.00	4.797(1)	10.447(3)	0.835	0.71	0.96	0.10
16	0.83	40.4	59.6	0.67	0.99	0.02	4.788(1)	10.437(2)	0.77	0.60	0.94	0.10
H11	0.52	23.1	76.9	0.24	0.80	0.08	4.779(6)	10.335(5)	0.59	0.57	0.61	0.85
H12	0.25	∿0	∿100	0.00	0.50	0.00	4.738(1)	10.241(2)	0.24	0.09	0.39	0.15
B–Ni	0.00	–	–	0.00	0.00	–	4.727(1)	10.118(3)	0.00	0.00	0.00	–

*Estimated standard errors are given in parentheses.

line joining its midpoint to "ordered $NiFeSiO_4$" is the line of constant $X_{ol}^{Fe} = 0.50$.

The *a–b* cell dimensions of Annersten *et al.* (1982) are plotted in Figure 1 as *X*'s numbered according to mol % Fe_2SiO_4. These data are replotted as open circles representing the points where their specimens *ought* to plot (based on the new X_{M2}^{Fe} values in Table 1) *if* the linear model we have assumed is indeed correct for the system Fe_2SiO_4–Ni_2SiO_4. The discrepancies between their reported X_{ol}^{Fe} values and our interpretation of X_{ol}^{Fe} based strictly on *a–b* values are not great, amounting to an average 0.04 in X_{ol}^{Fe} (Table 1). And except for the $X_{ol}^{Fe} = $

0.52 specimen, the iron content of the M2 site, X_{M2}^{Fe}, is predicted to within an average 0.06 of the new X_{M2}^{Fe} values, as in earlier studies (Lumpkin *et al.*, 1983). The cell dimensions of this specimen (H11) indicate a high degree of disorder ($X_{M1}^{Fe} = 0.57$, $X_{M1}^{Fe} = 0.61$, $K_D = 0.85$), but the Mössbauer data indicate otherwise ($K_D = 0.08$!). Unfortunately, we have no solution to this problem, but simply call it to account. Oddly enough, the open circle representing expected *a–b* values based on the Mössbauer results of Annersten *et al.* falls very close to the $K_D = 0.10$ contour near which all their other data plot, suggesting that the error may be in the cell dimensions.
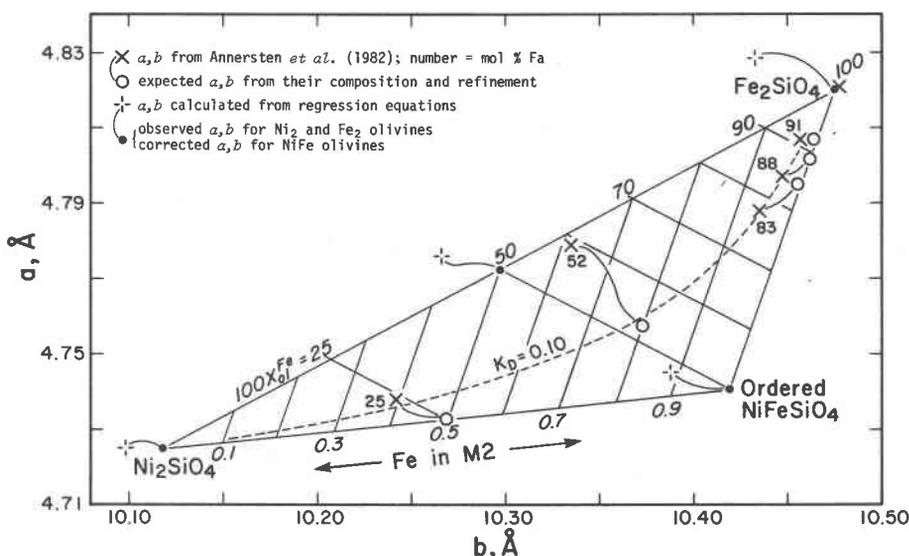
Fig. 1. An *a–b* plot for Fe–Ni olivines. Values for the end-members, Ni_2SiO_4 and Fe_2SiO_4, respectively, are averages of 4 and 5 sets of cell dimensions taken from the literature. Other data are from Table 1; details of construction and interpretation are in the text. The dashed curve is a line of constant $K_D = 0.10$.

Their interpretation of the Mössbauer spectrum of specimen H12 ($X_{ol}^{Fe} = 0.25$) seems unassailable, but it, too, is at variance with our estimate of $X_{M2}^{Fe} = 0.39$.

In conclusion it is only one specimen ($X_{ol}^{Fe} = 0.52$) that for unknown reasons is seriously inconsistent with the remainder of the data set. Except for some comments about the ideality of the solid solution of Fe^{2+} and Ni^{2+} in olivine (Annersten *et al.*, p. 1215), which are questionable, the general content of the work of Annersten *et al.* (1982) is very useful in promoting our understanding of the ordering of Ni and Fe in olivines (*cf.* Nord *et al.*, 1982). Some adjustments might be forthcoming in the reference coordinates for the contoured *a–b* plot if the variation of *a* and *b* were found to be nonlinear with X_{ol}^{Fe} for the completely disordered solid solution series, but these are expected to be minor. Clearly it would be advantageous to examine cation ordering in these and other olivines using the recently developed method called CHEXE (*CH*annelling *E*nhanced *X*-ray *E*mission spectroscopy), which has been successfully used by Smyth and Taftø (1982) to determine quantitatively Fe, Ni, Mn and Ca concentrations in the M1 and M2 sites of a San Carlos, Arizona forsterite.

Acknowledgment

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