

## Effects of differential recoil-free fraction on ordering and site occupancies in Mössbauer spectroscopy of orthopyroxenes

M. DARBY DYAR,<sup>1,\*</sup> RACHEL L. KLIMA,<sup>2</sup> DONALD LINDSLEY,<sup>3</sup> AND CARLÉ M. PIETERS<sup>2</sup>

<sup>1,2</sup>Department of Earth and Environment, Mount Holyoke College, South Hadley, Massachusetts 01075 U.S.A.

<sup>2</sup>Department of Geological Sciences, Brown University, Providence Rhode Island 02912 U.S.A.

<sup>3</sup>Department of Geosciences, State University of New York, Stony Brook, New York 11794-2100, U.S.A.

### ABSTRACT

Room-temperature <sup>57</sup>Fe Mössbauer spectra of synthetic orthopyroxenes equilibrated between 900–1000 °C and spanning the compositional range from ferrosilite to nearly enstatite were acquired. Peak areas corresponding to Fe<sup>2+</sup> in the M1 and M2 sites of the structure were corrected for effects of thickness and differential recoil-free fractions (*f*) on the two sites using a constant value of *C* = 1.1, the correction parameter. The distribution coefficient, *K<sub>D</sub>*, for Fe and Mg in M1 and M2 was calculated for all samples, and results were compared to *K<sub>D</sub>* values from previous studies where *C* was assumed to be unity. Our results demonstrate that choice of *C* dramatically influences calculated *K<sub>D</sub>* values. Thus, the failure of previous studies to consider *C* corrections may well be responsible for differences between Mössbauer and XRD studies of site occupancies noted by previous workers. Further characterizations of *f* for pyroxenes of variable compositions are needed.

**Keywords:** Mössbauer, recoil-free fraction, orthopyroxene, enstatite, ferrosilite

### INTRODUCTION

In the Fe-Mg minerals of the (Ca-free) pyroxene group, M2M1(Si<sub>2</sub>O<sub>6</sub>), the two cations share two possible sites: the M1 site is regular octahedron, while the M2 site is a distorted 6-coordinated site. The two sites also have different sizes: the M-O distance is 2.078(1) to 2.135(1) for M1 and 2.151(1) to 2.223(1) Å for M2 across the solid solution from enstatite (En) to ferrosilite (Fs), making the M2 site consistently larger (Domeneghetti et al. 1995). The two major cations, Fe<sup>2+</sup> and Mg<sup>2+</sup>, are so similar in size (0.78 and 0.72 Å, respectively) that they might be predicted to occupy either site. However, Fe<sup>2+</sup> has a strong octahedral site preference energy (OSPE) due to the distortion on the M2 site (Burns 1993), causing Fe<sup>2+</sup> to favor the M2 site. Quantifying the extent of this preference is critical to thermodynamic treatments of orthopyroxene equilibria, which have been frustrated by uncertainties related to determination of M1 and M2 occupancies in, especially, low-Fe (enstatite) compositions (cf. Kroll 2003).

The data on site occupancies at various temperatures and pressures are important because they are used to define equilibrium coefficients (*K<sub>D</sub>* values) for Fe and Mg between the two sites as

$$K_D = \frac{X_{\text{Fe}}^{\text{M1}} X_{\text{Mg}}^{\text{M2}}}{X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}}}$$

Data on site occupancies come predominantly from Mössbauer spectroscopy (Evans et al. 1967; Besancon 1981; Anovitz et al. 1988, etc.) and occasionally from structure refinements of single crystals (Domeneghetti and Steffen 1992; Stimpfl et al. 1999; Kroll et al. 1997). A recent paper by Wang et al. (2005) adds two new low Fs compositions to the existing database on

the distribution of Fe and Mg in orthopyroxenes, but their results differ from previous Mössbauer and XRD data on low-Fs orthopyroxenes. The new data are interpreted to suggest that *K<sub>D</sub>* is roughly independent of *X<sub>Fs</sub>*, an assumption that simplifies thermodynamic treatments. However, many of the Mössbauer studies reviewed by Wang et al. (2005) assumed equal recoil-free fractions for the doublet corresponding to the M1 and M2 sites, and did not correct for thickness effects nor solve the full Hamiltonian lineshape. No study of a range of Fs-En compositions that addresses these issues and utilizes a high-resolution spectrometer capable of generating high-quality data on samples across the solid solution has yet been undertaken.

Accordingly, the goal of this study is to determine carefully the site occupancy of Fe and Mg in synthetic orthopyroxenes across the solid solution from enstatite (MgSiO<sub>3</sub>) to ferrosilite (Fe<sup>2+</sup>SiO<sub>3</sub>), to evaluate the effect of composition on *K<sub>D</sub>*. Samples were synthesized at high temperatures (900–1000 °C) and quenched quickly to yield cation distributions that are representative of high-temperature equilibria. Accomplishing this goal will allow us to characterize the site occupancies in these particular samples for further study using visible and near-IR reflectance spectroscopy, results of which are presented in a companion paper (Klima et al., in review). Those results will enable relationships to be established between Fe site occupancies and the spectral features in the visible and near IR wavelengths.

### METHODS

#### Sample preparation

Samples for this study were synthesized by DHL and colleagues between 1972 and 2006, largely for use as starting materials for equilibria studies. Syntheses used procedures described in Turnock et al. (1973) with minor variations. All samples were prepared from reagent grade chemicals. Specific methods vary by composition, and were chosen to prevent nucleation of pyroxenoids and produce a single, homogeneous pyroxene. Hydrothermal syntheses were controlled to have *f<sub>O<sub>2</sub></sub>* below FMQ (fayalite-magnetite-quartz) by dissociation of oxalic acid. Samples made in

\* E-mail: mdyar@mtholyoke.edu

**TABLE 1.** Mössbauer parameters for synthetic Mg-Fe orthopyroxenes

$T$ (°C)	En	$t$	$^{[M1]}\text{Fe}^{2+}$				$^{[M2]}\text{Fe}^{2+}$				$\chi^2$	*[M1] pfu	*[M2] pfu
			IS	QS	$\Gamma$	Area	IS	QS	$\Gamma$	Area			
965–1005	97.5	0.53	1.17	2.55	0.26	13.9	1.14	2.12	0.26	86.1	1.6	0.007	0.043
950–990	90	0.51	1.16	2.45	0.26	15.9	1.14	2.09	0.26	84.1	1.4	0.030	0.170
970–980	80	0.51	1.17	2.47	0.27	17.5	1.15	2.10	0.27	82.5	1.9	0.066	0.334
950	80	0.64	1.17	2.50	0.27	16.4	1.15	2.11	0.27	83.6	1.7	0.062	0.338
960–1000	75	0.66	1.17	2.48	0.28	19.0	1.15	2.10	0.28	81.0	2.0	0.090	0.410
970–980	75	0.53	1.17	2.50	0.28	17.8	1.15	2.10	0.28	82.2	2.1	0.084	0.416
950	70	0.66	1.17	2.49	0.28	18.9	1.15	2.09	0.28	81.1	2.7	0.107	0.493
980	50	0.64	1.17	2.49	0.29	25.7	1.15	2.05	0.29	74.3	4.4	0.244	0.756
970–980	35	0.64	1.18	2.49	0.30	32.9	1.14	2.03	0.30	67.1	8.1	0.409	0.891
930–980	30	0.40	1.18	2.50	0.29	35.2	1.14	2.02	0.29	64.8	3.6	0.469	0.931
900	25	0.19	1.18	2.49	0.29	38.3	1.14	2.00	0.29	61.7	1.3	0.544	0.956
970–980	17	0.32	1.19	2.50	0.29	43.2	1.14	1.98	0.29	56.8	2.8	0.685	0.975
920	17	0.35	1.18	2.50	0.29	43.3	1.14	1.99	0.29	56.7	3.5	0.688	0.972
960–1000	8	0.32	1.19	2.51	0.29	47.9	1.14	1.97	0.29	52.1	4.7	0.846	0.994
940–980	0	0.48	1.18	2.51	0.27	51.6	1.13	1.92	0.27	48.4	7.6	1.000	1.000

Notes:  $t$  = thickness, calculated using the method of Long et al. (1983), expressed as mg Fe/cm<sup>2</sup>; IS = isomer shift in mm/s; QS = quadrupole splitting in mm/s;  $\Gamma$  = line width at half maximum in mm/s.

\* M1 and M2 site occupancy corrected for thickness ( $t$ ) and differential recoil-free fractions using value of  $C = 1.10$ ; see text for explanation.

Fe capsules had  $f_0$  values below IW (iron-wüstite) but above IQF (iron-quartz-fayalite). The end result was that no Fe<sup>3+</sup> was observed in any of these samples.

All samples were cooled to room temperature from 900–1005 °C in 2–10 minutes. Disordering rates quantified for Fe-Mg in orthopyroxenes by Besancon (1981) and Anovitz et al. (1988) suggest that quench times used here were rapid enough to prohibit ordering below the equilibration temperatures. Compositions range from En<sub>97.5</sub>Fs<sub>2.5</sub> to Fs<sub>100</sub> in roughly 10 mol% increments (Table 1). Pyroxene compositions and the orthopyroxene space group (*Pbca*) were confirmed by X-ray diffraction.

### MÖSSBAUER SPECTROSCOPY

Approximately 20–30 mg of each sample were crushed to a fine powder with sugar under acetone before mounting in a sample holder confined by Kapton tape. Mössbauer spectra were acquired at 295K using a source of 100–60 mCi <sup>57</sup>Co in Rh on a WEB Research Co. model WT302 spectrometer (Mount Holyoke College). For each sample, the fraction of the baseline due to the Compton scattering of 122 keV gammas by electrons inside the detector was determined by measuring the count rate with and without a 14.4 keV stop filter (~2 mm of Al foil) in the gamma beam. Compton-corrected absorption was calculated for each individual spectrum using the formulation  $A/(1 - b)$ , where  $b$  is the Compton fraction and  $A$  is the uncorrected absorption. This correction does not change the results of the fits per se but does allow accurate determination of percent absorption in the spectra. It is necessary because the range of energy deposited in the detector by Compton events extends from 0 to 40 keV, overlapping both the 14 and 2 keV energies deposited by the 14 keV gammas.

Run times were 6–24 hours, and baseline counts ranged from ~2.2 to 14.0 million after the Compton correction. Results were calibrated against a 25  $\mu$ m  $\alpha$ -Fe foil.

Spectra were processed using the MEX\_FielDD program, an implementation of software described in Wivel and Mørup (1981). The program uses Lorentzian line shapes and solves full Hamiltonians for isomer shift and quadrupole splitting distributions in each of two valence states. Isomer shifts (IS) and quadrupole splittings (QS) of the doublets were allowed to vary, and widths of all four peaks were coupled to vary in unison. Errors on isomer shift and quadrupole splitting of well-resolved peaks are usually  $\pm 0.02$  mm/s. Errors on peak areas based on repeated fits using different constraints and fitting models are  $\pm 0.3\%$  absolute for these well-resolved spectra. This is the same error reported in an analogous study by Skogby et al. (1992) on natural Fe<sup>2+</sup> orthopyroxenes.

To determine the number of cations of  $^{[M1]}\text{Fe}^{2+}$  and  $^{[M2]}\text{Fe}^{2+}$  per formula unit, the final Mössbauer peak areas were corrected to account for thickness and differential recoil-free fractions ( $f$ ) of  $^{[M1]}\text{Fe}^{2+}$  and  $^{[M2]}\text{Fe}^{2+}$  using the formulation of Bancroft (1969), as follows:

$$\frac{^{[M1]}A_{\text{Fe}^{3+}}}{^{[M2]}A_{\text{Fe}^{2+}}} = C \frac{^{[M1]}N_{\text{Fe}^{3+}}}{^{[M2]}N_{\text{Fe}^{2+}}}$$

where,

$$C = \frac{\Gamma_{M1} f_{M1} G(X_{M1})}{\Gamma_{M2} f_{M2} G(X_{M2})}$$

$A$  is the doublet area of Fe<sup>2+</sup> or Fe<sup>3+</sup>,  $N$  is the “true” amount of each species present,  $\Gamma$  is the linewidth, and  $G(X)$  is the saturation correction factor (see also Dyar et al. 2006 for more information). The line width component is easily dealt with by constraining peak widths to vary in pairs, as described above. Thickness effects caused by saturation will cause underestimation of the amount of Fe ordering (Skogby et al. 1992), but methods to correct for them as described by Rancourt (1989) are difficult to implement on multiple samples. Accordingly, we use the empirical correction to zero thickness as developed by Skogby et al. (1992), where:

$$\left[ \frac{^{[M1]}\text{Fe}}{\text{Fe}(\text{total})} \right]_{\text{corrected}} = \left[ \frac{\left( \frac{^{[M1]}\text{Fe}}{\text{Fe}(\text{total})} \right)_{\text{measured}} - 0.004085t}{1 - 0.003031t} \right]$$

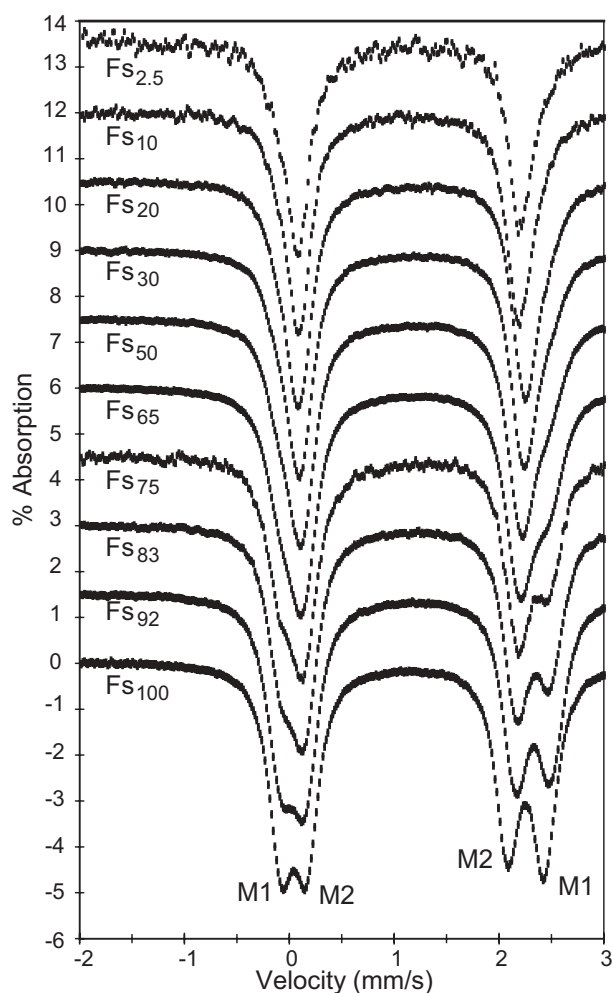
and  $t$  is the thickness calculated using the methods of Long et al. (1983).  $^{[M2]}\text{Fe}^{2+}$  is then calculated by difference.

Values for the recoil-free fraction ( $f$ ) are specific to mineral groups (and perhaps, species) and must be experimentally determined. For this study, we initially chose to use a value of  $C = 1.10$ , which was chosen to yield 1:1 site occupancy of Fe in the M1 and M2 sites in the ferrosilite end-member as is constrained by stoichiometry. This choice was vindicated by the nearly identical result observed in Mössbauer study of synthetic ferrosilite equilibrated at 950 °C and 20 kbar by Dowty and Lindsley (1973), even with different lineshapes and no thickness correction. This choice of  $C$  value has important implications that will be discussed further below.

### RESULTS

Mössbauer spectra of all samples are shown in Figure 1, along with fitted spectra for three samples (Fig. 2). Spectra were fit by two doublets; the outer doublet is assigned to  $^{[M1]}\text{Fe}^{2+}$ , while the inner doublet corresponds to  $^{[M2]}\text{Fe}^{2+}$ . Mössbauer parameters are given in Table 1, with the final  $^{[M1]}\text{Fe}^{2+}$  and  $^{[M2]}\text{Fe}^{2+}$  given in formula units (per six O atoms) in the right hand columns. These data have been corrected for Compton scattering, differential recoil-free fraction effects, and thickness effects.

Because the area of the paired peaks in each doublet is proportional to the abundance of Fe in that site, it is immediately clear that as required at the highest Fe contents (Fs<sub>100</sub>), Fe<sup>2+</sup> is evenly distributed between M1 and M2. This result was the reason for and a consequence of our choice of  $C = 1.1$ . As Mg is added to the pyroxene, Fe ordering into M2 is immediately apparent, with the M1 doublet rapidly decreasing in intensity relative to M2 as Mg is added, presumably first to the M1 sites. The spectra of the highest Mg samples are dominated by the M2 doublet, though



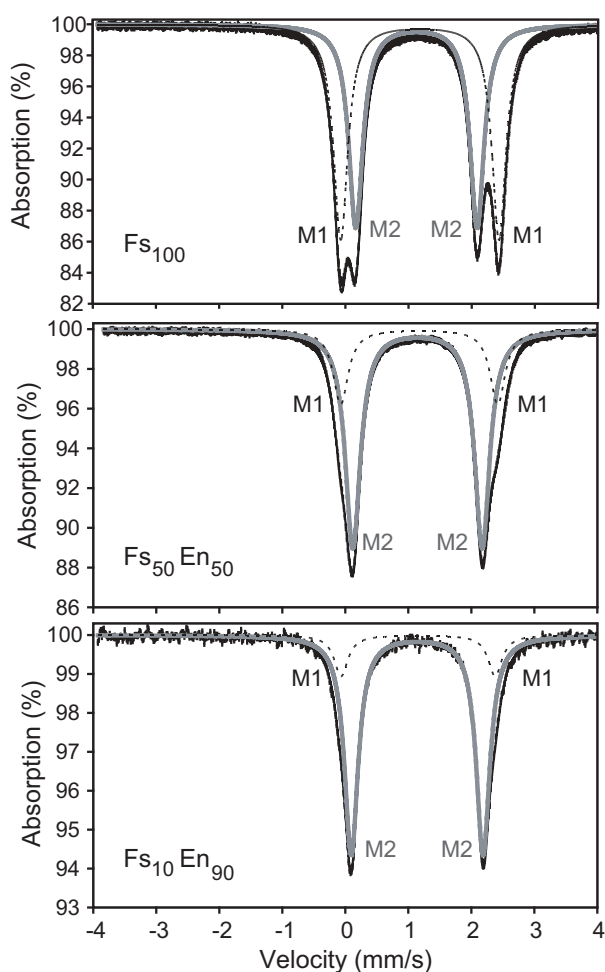
**FIGURE 1.** Mössbauer spectra of representative synthetic orthopyroxenes over the solid solution from near-enstatite to ferrosilite. Data points are plotted as error bars representing standard error. Spectra were normalized to 5% absorption effect for clarity.

there is a small shoulder representing  $\text{Fe}^{2+}$  in M1. As is known from previous work, these data indicate that  $\text{Fe}^{2+}$  shows a strong preference for the M2 site, presumably due to the strong OSPE for  $\text{Fe}^{2+}$  in the more distorted site.

### DISCUSSION

To test the assertion that  $K_D$  is independent of Fs/En, our new results are shown along with available data from the literature (on samples equilibrated at 900–1000 °C) in the top panel of Figure 3. The dashed horizontal lines in the figure represent the equation developed by Wang et al. (2005) to relate  $K_D$  to temperature ( $T$ ), namely  $\ln K_D = 0.391(\pm 0.131) - 2205(\pm 141)/T$ . It is clear from the plot that the observed  $K_D$  values are not constant, particularly in samples with high Fe contents. Nor do they consistently lie near the constant  $\ln K_D$  lines.

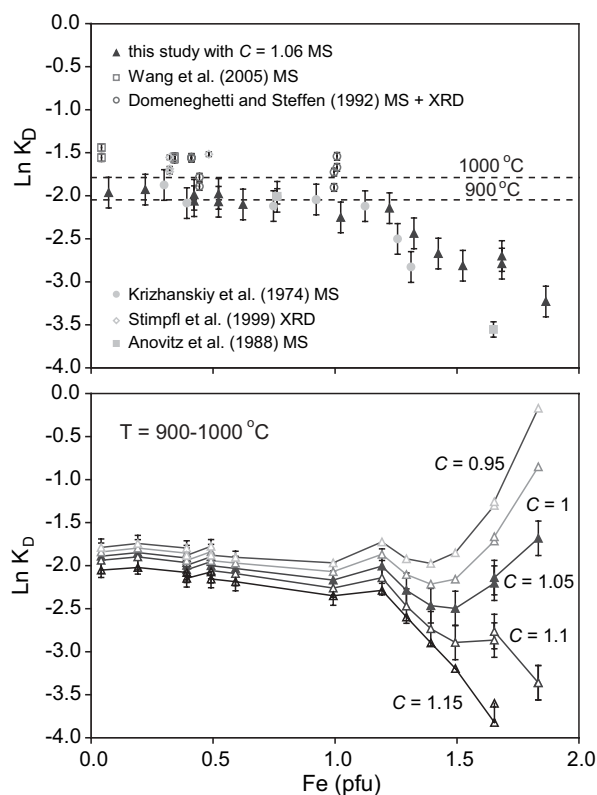
However, as noted earlier, none of these studies with the exception of the current work utilized a correction for differential recoil-free fractions between  $\text{Fe}^{2+}$  in the two different sites. In



**FIGURE 2.** Fits to three of the synthetic pyroxenes:  $\text{Fs}_{100}$ ,  $\text{Fs}_{50}\text{En}_{50}$ , and  $\text{Fs}_{10}\text{En}_{90}$ . The outer M1 doublet is shown as a dashed line, while the inner M2 doublet is shown as a solid gray line.

fact, with the exception of De Grave and Van Alboom (1991), nearly all the other Mössbauer studies of orthopyroxene after 1970 make the simplifying assumption that values of  $C$  are always unity. Although this practice may simplify calculation of their results, it may be introducing significant bias into their  $K_D$  calculations.

Moreover, even in this study, we are utilizing the same value for  $C$  across the range of compositions. To assess the appropriateness of this assumption, data on  $f$  values for M1 and M2 in orthopyroxenes across the solid solution are badly needed. Unfortunately, there are only two published values for these parameters. De Grave and Van Alboom (1991) (Table 2) measured  $f$  values for two natural enstatites and found 293 K  $f_{\text{M1}}/f_{\text{M2}} = 0.99$  and 1.14 for  $\text{Fe}_{0.05}\text{Mg}_{1.95}\text{Al}_{0.05}\text{Si}_{1.96}\text{O}_6$  and  $\text{Fe}_{0.27}\text{Mg}_{1.65}\text{Al}_{0.03}\text{Si}_{2.02}\text{O}_6$ , respectively. To our knowledge, these are the only existing published values for  $f$  in orthopyroxenes. However, work by Eeckhout et al. (2003) and Eeckhout and DeGrave (2003) does provide an analogous data set for *clinopyroxenes*,



**FIGURE 3. (top)** Results of site occupancy studies of orthopyroxenes equilibrated at 900–1000 °C, including those from this study. The dashed horizontal lines represent the equation formulated by Wang et al. (2005) to relate  $\ln K_D$  to Fs content at these temperatures. The line does not adequately represent the Fe partitioning in samples with higher Fe contents. **(bottom)**  $K_D$  values from the current study using M1 and M2 occupancies calculated from a range of  $C$  values based on different, arbitrarily selected ratios of recoil-free fraction for the two sites. No choice of value for  $C$  will result in a horizontal line of equal  $K_D$  values.

and interestingly, their value of  $C_{293K} = 1.10$  for  $\text{FeSiO}_3$  is exactly the same as ours (Table 2).

Fortuitously, there are two other Mössbauer studies that included variable temperature data suitable for calculation of  $f$  values. Using the same method (and software) of De Grave and Van Alboom (1991), we modeled those data sets to calculate three additional values of  $C$  based on data from Regnard et al. (1987) and Lin et al. (1993). Of course, these two studies were not designed to provide input to  $f$  calculations, and thus the number of data points (11 for the former and 7 or 6 in the latter) and temperature range covered are not optimal. All these data are summarized in Table 2, and the results are inconclusive for orthopyroxene. To complicate matters further,  $f$  is known to be composition dependent (e.g., see Eeckhout et al. 2000 values in Table 2), so some of the observed variation in  $C$  is probably caused by changes in composition. Our assumption of uniform  $C$  value across the series (as used in this study) is almost surely invalid; moreover, the Debye approximation used to determine  $f$  values may not be robust. Clearly, this problem should be a topic

**TABLE 2.** 293 K Recoil-free fractions for Fe in pyroxene

Composition	Phase	$f_{M1}$	$f_{M2}$	$C(M1/M2)$	Source
$\text{Fe}_{0.05}\text{Mg}_{1.95}\text{Al}_{0.05}\text{Si}_{1.96}\text{O}_6$	opx	0.710	0.717	0.99	1
$\text{Fe}_{0.18}\text{Mg}_{1.82}\text{Si}_2\text{O}_6$	cpx	0.730	0.782	0.93	5
$\text{Fe}_{0.27}\text{Mg}_{1.65}\text{Al}_{0.03}\text{Si}_{2.02}\text{O}_6$	opx	0.773	0.675	1.14	1
$\text{Fe}_{0.38}\text{Mg}_{1.62}\text{Si}_2\text{O}_6$	cpx	0.720	0.715	1.01	5
$\text{Fe}_{0.64}\text{Mg}_{1.36}\text{Si}_2\text{O}_6$	cpx	0.759	0.747	1.02	5
$\text{Fe}_{0.94}\text{Mg}_{1.06}\text{Si}_2\text{O}_6$	cpx	0.708	0.710	1.00	5
$\text{Fe}_{1.02}\text{Mg}_{0.98}\text{Si}_2\text{O}_6$	opx	0.735	0.641	1.11	2
$\text{Fe}_{1.22}\text{Mg}_{0.78}\text{Si}_2\text{O}_6$	cpx	0.755	0.780	0.97	5
$\text{Fe}_{1.56}\text{Mg}_{0.44}\text{Si}_2\text{O}_6$	cpx	0.710	0.695	1.02	5
$\text{Fe}_{1.60}\text{Mg}_{0.40}\text{Si}_2\text{O}_6$	opx	0.854	0.681	1.25	2
$\text{Fe}_{1.74}\text{Mg}_{0.26}\text{Si}_2\text{O}_6$	cpx	0.772	0.712	1.08	5
$\text{Fe}_{1.74}\text{Mg}_{0.26}\text{Si}_{2.02}\text{O}_6$	opx	0.859	0.804	1.07	3
$\text{Fe}_{1.82}\text{Mg}_{0.18}\text{Si}_2\text{O}_6$	cpx	0.716	0.676	1.06	5
$\text{Fe}_2\text{Si}_2\text{O}_6$	opx	–	–	1.10	4
$\text{Fe}_2\text{Si}_2\text{O}_6$	cpx	0.733	0.667	1.10	5

Notes: 1 = results taken directly from De Grave and Van Alboom (1991); 2 = calculated using variable temperature Mössbauer data from Lin et al. (1993); 3 = calculated using variable temperature Mössbauer data from Regnard et al. (1987); 4 = this study, calculated to make  $^{57}\text{Fe}^{2+}$  exactly equal  $^{57}\text{Fe}^{2+}$  using  $f = 1.10$  for the end-member; 5 = Eeckhout et al. (2000) and Eeckhout and DeGrave (2003).

for further study. However, lack of available data on  $f$  values is not a justification for ignoring the effects of differential recoil-free fraction: use of correction factors is desirable and, at least for the Fs end-members, necessary.

How might thermodynamic results ( $K_D$  values) be affected by modest changes in  $f$ ? To test this factor, data from the current study are plotted in Figure 2 (bottom) with values of  $K_D$  calculated with  $C = 0.95, 1.00, 1.05, 1.10,$  and  $1.15$ . The effect of increasing  $C$  is to push the rest of the data set to even higher values of  $M2/M1$ , resulting in lower values of  $K_D$ . Iron-rich compositions are particularly vulnerable to changes in  $K_D$  with different  $f$  values. Although Wang et al. (2005) asserted that  $K_D$  is roughly independent of Fe contents across this series, no single value of  $C$  can be used to make our data support this conclusion. Only if  $C$  values are variable across the series—and if that variation is a highly non-systematic—would this be the case. Instead, it seems that the “Achilles heel” of  $K_D$  calculations on the basis of Mössbauer data is the lack of knowledge of differential recoil-free fraction effects.

Improved knowledge of  $f$  values for pyroxene compositions across the Fs-En solid solution should lead to more accurate determinations of cation site occupancies. This may in turn help reconcile known discrepancies between Mössbauer and single crystal structure refinements [as noted by, e.g., Skogby et al. (1992) and Domeneghetti and Steffen (1992)], and lead to a better understanding of Fe-Mg distribution coefficients and the equilibria they represent.

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