# Self-Consistency for Each of XRD and Mossbauer Measurements of Fe-Mg Order-Disorder in Orthopyroxene



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# SELF-CONSISTENCY FOR EACH OF XRD AND MOSSBAUER MEASUREMENTS OF FE-MG ORDER-DISORDER IN ORTHOPYROXENE.

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Fe-Mg order-disorder reaction in orthopyroxene (opx) has often been used to determine cooling rates of rocks and meteorites. The reaction is homogeneous and can be written as:

$$Fe^{M2}Mg^{M1}Si_2O_6(opx) \Leftrightarrow Mg^{M2}Fe^{M1}Si_2O_6(opx), \quad (1)$$

where M1 and M2 are the two sites for $Fe^{2+}$ and $Mg^{2+}$ cations. The exchange coefficient $K_D$ for the above reaction is defined as:

$$K_D = \frac{(Fe/Mg)_{M1}}{(Fe/Mg)_{M2}}, \quad (2)$$

where the Fe/Mg ratio is the molar ratio (or atomic ratio). Earlier work (before 1988) on this reaction was mostly based on Mossbauer spectroscopic determination of Fe-Mg distribution between the two sites, but the uncertainty was relatively large. Recent advances are based on Fe-Mg distribution determined from X-ray diffraction study of single crystals (XRD). There are some systematic differences in $K_D$ determined from Mossbauer and XRD methods. Furthermore, Fe-Mg distribution in low-Fe opx ($X_{Fs}$ < 0.1) have not been reliably determined. Using our high-sensitivity Mossbauer spectrometer, we are carrying out a systematic study to improve the geospeedometer so that it can be applied to opx in meteorites (with either high or low FeO content) reliably. The purposes of this report are to investigate (i) whether each of the Mossbauer and XRD methods are self consistent and (ii) the apparent equilibrium temperature in Johnstown meteorite.

We used a newly constructed, wide-angle Mossbauer spectrometer at the University of Michigan. The instrument was originally designed to study natural abundance of iron in proteins. The instrument and the data collection procedure have been described elsewhere [1] and will only be summarized here. The new Mossbauer spectrometer has the best sensitivity of its kind in the world. The most innovative feature of the spectrometer is the eighty degree, conical acceptance geometry of its gamma-ray detector, which consists of 77 argon gas proportional counters. Compared to a conventional Mossbauer spectrometer (i.e., single counter), the new instrument has following advancements: (i) high count rate and high sensitivity (approximately 10 times more sensitive than a conventional spectrometer); (ii) high reproducibility of velocity (to an accuracy of ± 0.005 mm/s over periods of several weeks); and (iii) regulating the temperatures of the source and the sample (to an accuracy of ± 1 °C in the range of 125 to 300 K). These features allow study of natural samples that are low in Fe (such as $X_{Fs}$ of 1%), impossible for a conventional Mossbauer spectrometer. They also allow the use of an exceedingly small amount of sample. Hence we can now experimentally investigate the equilibrium and kinetics of reaction (1) from very low to relatively high $X_{Fs}$, and examine the dependence of $K_D$ and reaction rate on $X_{Fs}$ and temperature. Such experimental data will be critical to the accurate application of this geospeedometer to mantle or meteoritic opx crystals that often contain low $X_{Fs}$. Furthermore, the Mossbauer instrument significantly improves the determination of low $X_{Fe}$ in M1 site for slowly cooled opx, hence improving the accuracy of the calculation of slow cooling rates. Therefore, the new Mossbauer spectrometer has the potential to significantly advance the investigation of reaction (1) and its application to infer cooling rates of meteorites.

We have carried out experiments to investigate the dependence of $K_D$ on composition in the range of $X_{Fs}$ = 0.01 to $X_{Fs}$ = 0.16, a range with too low $X_{Fs}$ to be accessed by previous methods. Combined with previous Mossbauer data at $X_{Fs}$ = 0.4 from this lab using an older instrument [2], we found that $K_D$ is independent of composition and can be expressed as [3]:

$$\ln K_{D,Mossbauer} = 0.38(\pm 0.07) - 2184(\pm 82)/T, \quad \text{for } 0 < X_{Fs} \leq 0.4, \quad (3)$$

where T is temperature in K and uncertainties are at 2σ level hereafter unless otherwise specified. The above equation can be compared to recent results of Stimpfl et al. [4] using the XRD method:

$$\ln K_{D,XRD} = 0.55(\pm 0.10) - 2557(\pm 98)/T, \quad \text{for } 0.19 < X_{Fs} \leq 0.75; \quad (3a)$$

$$\ln K_{D,XRD} = 0.60(\pm 0.19) - 2854(\pm 172)/T, \quad \text{for } 0.11 < X_{Fs} \leq 0.17. \quad (3b)$$

The $K_D$ expression based on Mossbauer determination is significantly different from that based on XRD determination, meaning that the systematic difference remains and at least one of the methods has a systematic error. Without concluding which method is superior and gives the accurate site occupancy, it is interesting to determine whether each method is internally consistent. As long as such internal consistency is maintained, we can apply each method to cooling rate studies. Hence we determined Fe-Mg site occupancy in opx in Johnstown meteorite using Mossbauer spectroscopy. Another reason for selecting Johnstown meteorite is that there is still large uncertainty in estimating its cooling rate [5].

Johnstown meteorite was crushed to ~0.1 mm size grains. Clean opx crystals were hand-picked. They are then finely crushed and mixed with about 420 mg boric acid powder and pressed into a disc with a diameter of 16.2 mm and a thickness of 1.65 mm. Two measurements give $K_D$ values of 0.0493±0.0024 and 0.0491±0.0040. As expected, these values are significantly different from those determined by XRD (0.023 by [6]; 0.019 to 0.030 by [7]; 0.0326 by [5]. Nevertheless, the apparent equilibrium temperature recorded by Johnstown opx calculated from the Mossbauer data is 371±10°C and 370±16°C, similar to those based on XRD measurement and XRD calibration (379 ± 8°C by [6], and 311±29 to 375±17°C by [7]; 371°C by [5] using the calibration of [4]; it is not clear whether the uncertainties reported by these authors are at 1σ or 2σ level). Hence there is internal consistency for each method. Although each method can be applied to cooling rate studies, the superior ability of the new high-sensitivity Mossbauer spectrometer in analyzing Fe-Mg distribution in opx to very low FeO concentration (down to $X_{Fs} \leq 0.01$) and in determining very low Fe content in M1 site has great potential to investigate cooling rates of meteorites and terrestrial samples. We are conducting further equilibrium and kinetic experiments to calibrate the geospeedometer so that cooling rates of Johnstown meteorite and other meteorites can be accurately calculated.

**References:**


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