TEMPERATURE DEPENDENCE AND RECOIL-FREE FRACTION EFFECTS IN OLIVINES ACROSS THE MG-FE SOLID SOLUTION.

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Introduction: Olivine and pyroxene are the major ferromagnesian minerals in most meteorite types and in mafic igneous rocks that are dominant at the surface of the Earth. It is probable that they are the major mineralogical components at the surface of any planetary body that has undergone differentiation processes. *In situ* mineralogical studies of the rocks and soils on Mars suggest that olivine is a widespread mineral on that planet's surface (particularly at the Gusev site) and that it has been relatively unaffected by alteration [1]. Thus an understanding of the characteristics of Mössbauer spectra of olivine is of great importance in interpreting MER results.

However, variable temperature Mössbauer spectra of olivine, which are needed to quantify recoil-free fraction effects and to understand the temperature dependence of olivine spectra, are lacking in the literature. Thus, we present here a study of the temperature dependence and recoil-free fraction of a series of synthetic olivines.

Methods: Samples used in this study are the same as those used in [2]. Six samples of synthetic olivine were obtained from the Natural History Museum, London, UK and ten additional samples were synthesized in the Dept. of Earth Sciences, Bristol University, UK. These samples span the compositional spectrum from pure fayalite, Fe_2SiO_4 (Fa_{100}) to a near-forsterite composition, $Mg_{1.8}Fe_{0.2}SiO_4$ (Fo_{90}), in 10 mol% increments. Techniques used for syntheses are similar to those reported in [3].

Variable temperature Mössbauer spectra were acquired on each sample under low He gas pressure at 16 temperatures ranging from 12-295K. A source of 100-70 mCi ^{57}Co in Rh was used on a WEB Research Co. model W100 spectrometer equipped with a Janus closed-cycle He refrigerator. Run times ranged from 12-48 hours; results were calibrated against α-Fe foil. For each of the 10 samples, 16 spectra were collected, processed, and fit with quadrupole splitting distributions and hyperfine field distributions using the method of [4]; an average correlation between the isomer shift and quadrupole splitting of Fe^{2+} was assumed.

Recoil-free fraction calculations: The area of a Mössbauer doublet (pair of peaks) or a sextet is actually a function of peak width Γ, sample saturation *G(x)*, and the Mössbauer recoil-free fraction *f*. This relationship can be expressed mathematically in terms of doublets corresponding to Fe^{3+} and Fe^{2+} with areas equal to A^{3+} and A^{2+}, where N is the "true" amount of each species and C is the "correction factor," as in:

$$\frac{A^{3+}}{A^{2+}} = C\,\frac{N^{3+}}{N^{2+}}, \quad \text{where} \quad C = \frac{\Gamma_{3+}G(X_{3+})f_{3+}}{\Gamma_{2+}G(X_{2+})f_{2+}}.$$

Obviously, this expression can be rewritten to describe the relationship between Fe^{2+} in two different minerals, and/or it can be expanded to describe mixtures of >2 phases or sites. It is clear that knowledge of *f* for each valence state of Fe in each site in each mineral in a mixture is needed to accurately determine the amount of Fe present in each site and valence state.

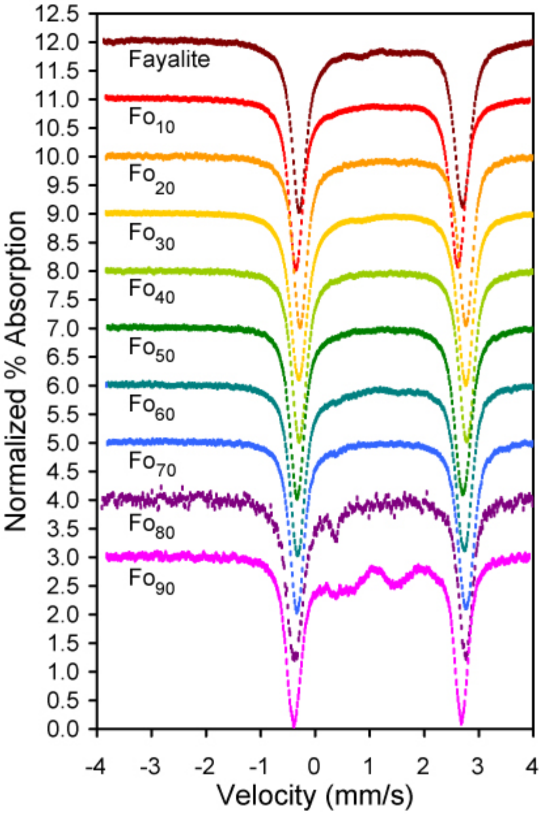

Fig. 1. 220K Mössbauer spectra of synthetic olvinies covering the range from pure fayalite to Fo_{90}; data were also collected at 15 other temperatures between 12-295K. Data are normalized to 3% absorption.

Of the parameters Γ, G(*X*), and *f*, the *f* is the most difficult to determine. The Mössbauer or recoilless fraction (*f*) is the fraction of nuclear events that take place without exciting the lattice; i.e., they produce no change in the quantum state of the lattice. This fraction of the recoil energy that cannot be transferred to exciting a lattice vibration can be quantified as $f = \exp[(-4\pi^2<X^2>)/\lambda^2]$, where $<X^2>$ is the mean square vibrational amplitude of the absorbing/transmitting nucleus in the solid, and λ is the wavelength of the γ photon. The value of $<X^2>$ (typically in the range of 10^{-4} Å^2) varies for different chemical compounds depending on the site geometry and valence state of the Fe atom. Therefore, *f* also varies for different valence states of iron in different types of sites.

Here, we quantify *f* by using the temperature dependence of the center shift (δ), which can be written as $\delta(T) = \delta_I + \delta_{SOD}(T)$. To calculate *f*, Mössbauer spectra were acquired from 12-300K. Next, the Mössbauer temperature (an approximation of the Debye temperature, θ_D) and the center shift (δ) were calculated based on a fit of the Debye integral approximation to the experimental data. Finally, the recoil-free fraction for each site was calculated using the relation:

$$f = \exp[-6E_R/k\theta_D[1/4+T/\theta_D)^2\int(xdx)/(e^x-1)]],$$

where E_R is the recoil energy, related to the transition energy, E_γ by $E_R = E_\gamma^2/2Mc^2$.

Results: Mössbauer spectra of our olivines are shown in Fig. 1 at 220K (a temperature typical of the MER sites). It is apparent from this plot that some of the synthesized olivines contain small amounts of Fe^{3+}, as well as minor impurities; the extent to which they influenced the fundamental parameters is unknown. Isomer shifts for Fe^{2+} doublets are shown in Fig. 2. Finally, values for *f* were calculated at each temperature (Fig. 3) for use in future Mössbauer studies of olivine, such as those on the martian surface.

Discussion: Analogous studies of recoil-free fraction as a function of composition have been made for spinels [5] and clinopyroxenes [6]. Results of those studies, along with our own data, are plotted in Fig. 4 as mol% Fe (for olivine, cpx, and $MgFeCr_{2-x}O_4$) and mol% Zn (for $Mg_{1-y}Zn_yFe_{1.5}Cr_{0.5}O_4$). In our own olivine data, error bars on *f* values are roughly ±0.009-0.03 at this temperature, and we expect comparable errors on the other data. It is apparent that variations in *f* with composition do not follow a smooth trend for any of these phases. This reinforces the imperative to experimentally determine *f* values for all minerals of interest. when quantitative results for site occupancies or Fe^{3+}/Fe^{2+} ratios are required.

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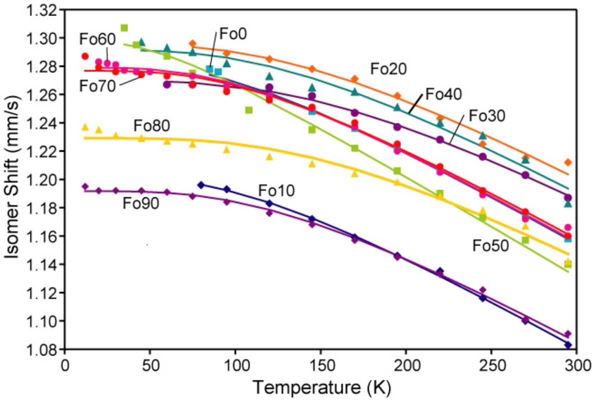

Fig 2. Experimental data (symbols) and modeled approximations (solid lines) for synthetic olivines.

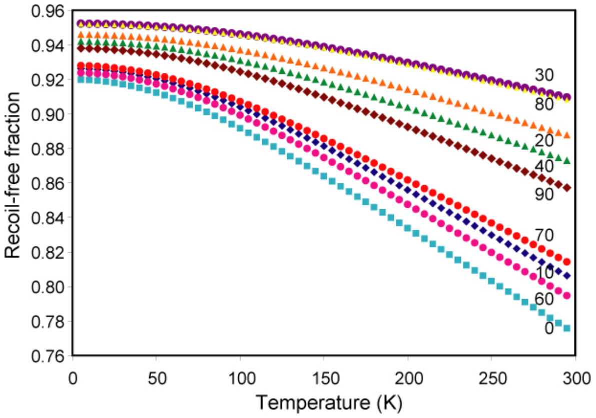

Fig. 3. Recoil-free fractions for Fe^{2+} as a function of temperature. Data for Fo_{50} are not included due to apparent problems with impurities in the run products.

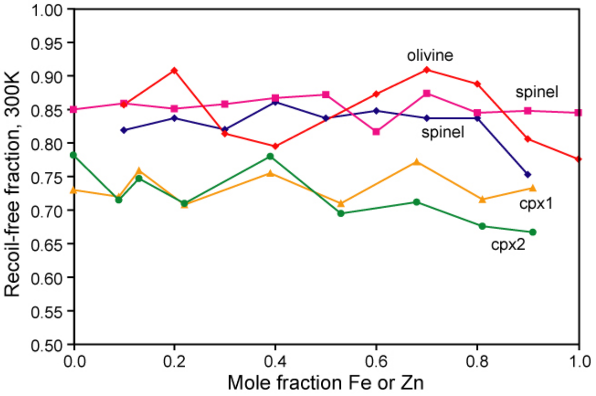

Fig. 4. Recoil-free fractions for Fe^{2+} and Fe^{3+} as a function of composition. Olivine and cpx are plotted as mol% Fe^{2+}, $MgFeCr_{2-x}O_4$ as mol% Fe^{3+}, and $Mg_{1-y}Zn_yFe_{1.5}Cr_{0.5}O_4$ as mol% Zn.

References: [1] Morris R.V. et al. (2004) *Science*, 305, 833-836. [2] Menzies, O.N. et al. (2001) *LPS XXXII*, abst.#1622. [3] Redfern S.A.T. et al. (2000) *PCM*, 27, 630-637. [4] Wivel C. and Mørup S. (1981) *J. Phys. E.: Sci. Instrum.* 14, 605–610. [5] deBakker P. (1994) Ph.D. Thesis, Univ. of Ghent. [6] Eeckhout S.G. et al. (2000) *Amer. Mineral.*, 85, 943-952.