EFFECT OF PRESSURE ON Fe^{3+}/Fe^{T} IN SILICATE LIQUIDS, ACCURATE DETERMINATION OF Fe^{3+}/Fe^{T} IN SILICATE GLASSES BY MÖSSBAUER SPECTROSCOPY, AND APPLICATIONS TO MAGMA OCEANS.

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Introduction: The oxygen fugacity (f_{O2}) prevailing in a magma ocean influences the geochemal behavior of volatile elements and in particular determines the compostion and mass of any overlying atmosphere as well as partitioning of volatiles between early terrestrial planetary interiors and exospheres . In a vigorously convecting, well-mixed magma ocean (MO) in contact with metallic Fe at depth, the $Fe^{3+}/\sum Fe$ ratio will be imposed by magma-metal equilibration. The f_{O2} imposed elsewhere in the MO depends on the effect of temperature and pressure on the activities of Fe^{3+} and Fe^{2+} in an isochemical liquid.

Previous studies have established the influence of temperature, composition and oxygen fugacity in silicate melt [1-5], but there constraints on the effect of pressure are limited to ≤3 GPa [4,6]. These studies establish that, at fixed f_{O2} relative to metal-oxide buffers, pressure decreases Fe^{3+}/Fe^{T}, meaning that an isochemical magma will become more oxidized with increasing pressure [5-7].

We have conducted high pressure experiments to further investigate the relationship between pressure and Fe^{3+}/Fe^{T} in f_{O2}-buffered silicate liquids. Quenched glasses were analyzed by Mössbauer spectroscopy. Mössbauer spectroscopy is a commonly-applied method for such determinations, but there is significant controversy about the accuracy of such measurements, owing to likely differences in the recoilless fraction (f) of Fe^{2+} and Fe^{3+}[8-10]. Consequently, we also undertook low temperature Mössbauer studies to determine independently the recoilless fraction of Fe^{3+} and Fe^{2+}.

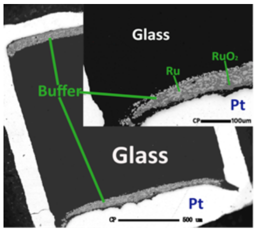

Fig 1: Backscatter image of one sample, quenched from 5 GPa, 1600 °C, 4 hours, showing relation between glass and f_{O2} buffer.

Experiments: The starting material is an andesitic composition [6], prepared from reagent grade oxides and silicates. For high pressure experiments 30 wt% of the total amount of Fe_2O_3 was added as $^{57}Fe_2O_3$. Samples were loaded into 2mm diameter Pt capsules and the f_{O2} within the capsule was controlled by the addition mixture of 10 wt.% Ru+10 wt.% RuO_2 loaded as layers in both the bottom and top (Fig. 1). For experiments performed at 1 atm, isotopically normal Fe was employed. .

Experiments up to 3 GPa were performed in a 0.1/2", end-loaded piston cylinder apparatus. Experiments above 3 GPa were performed in a 1000-ton multianvil device. Experiments were conducted above the liquidus at 1400-1750 °C and held at temperature for 4 h below 1600 °C and 12 min at 1750 °C. 1 atmosphere experiments were conducted in a vertical quench furnace with Ar-O_2 mixtures employed to control f_{O2}.

Homogeneity of the quenched glasses was verified by EMPA. Most glasses were ground into powder and analyzed for the $Fe^{3+}/\sum Fe$ ratio using Mössbauer spectrometer at the Institute for Rock Magnetism, UMN. Mössbauer spectra were collected at room temperature (295 K) for all samples, and for two samples, VF3 (1 atm) and the M544 (3.5 GPa), data were also collected from 27 K to 295 K in ~10-40 K intervals.

Results: Of the Mössbauer spectra collected at room temperature, 25 (including VF3 and M544), consist of two broadened quadrupole doublets corresponding to ferric and ferrous iron, and 11 also include broadened magnetic sextet corresponding to Fe^{3+}, as also observed previously [5,6]. The Mössbauer spectra were fitted using the xVBF method and the RECOIL software package. Fe^{2+} and Fe^{3+} paramagnetic absorption were fitting with quadrupole doublets with 2D Gaussian distributions of the center shift (CS) and quadrupole splitting (QS). We fitted Fe^{2+} paramagnetic absorption with variable parameters: CS, Gaussian standard deviation of the CS distribution (σ_{CS}), QS, Gaussian standard deviation of the QS distribution (σ_{QS}), and correlation between the CS and QS distributions (ρ) and Fe^{3+} paramagnetic absorption with variable parameters: CS, QS, σ_{CS} and σ_{QS}. Fe^{3+} paramagnetic absorption fitting do not use ρ parameters as it should be essentially zero for low Fe content (<10 wt%) [7]. Fe^{3+} magnetic absorption was fitting with CS, QS, σ_{QS}, magnetic field of the component (H) and the Gaussian standard deviation of H distribution (σ_H). The fraction of Fe^{2+} and Fe^{3+} was estimated from the area of the subspectral components.

For Mössbauer spectra, the ratio of the subspectral components owing to Fe^{3+} and Fe^{2+}, $A_T^{Fe^{3+}}/A_T^{Fe^{2+}}$, is related to the actual ratio of Fe^{3+} and Fe^{2+} present in the sample, $N^{Fe^{3+}}/N^{Fe^{2+}}$ by a constant, C_T: $A_T^{Fe^{3+}}/A_T^{Fe^{2+}} = C_T \times N^{Fe^{3+}}/N^{Fe^{2+}}$, where $C_T = f_T^{Fe^{3+}}/f_T^{Fe^{2+}}$. We investigated the influence of recoilless fraction on

Fe^{3+}/Fe^{T} by two methods. First, we measured the changes in intensities of the individual Fe^{3+} and Fe^{2+} doublets as a function of temperature, and fit the results to a Debye model [11] according to:

$$f_T = \exp\left\{-\frac{3E_R}{2k_B\theta_D}\times\left[1+4\left(\frac{T}{\theta_D}\right)^2\int_0^{\theta_D/T}\frac{x\,dx}{e^x-1}\right]\right\}. \qquad (1)$$

For glass M544, these resulted in Debye temperatures, θ_D of 373 K and 289 K for Fe^{3+} and Fe^{2+}, respectively, and for VF3, θ_D=383 K (Fe^{3+}) and 268 K (Fe^{2+}). Second, we extracted Debye temperatures from the temperature dependence to the center shift [11]

$$\delta(T)=\delta_0-\frac{9k_BT}{2Mc}\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3dx}{e^x-1}. \qquad (2)$$

In this case, for M544, θ_D of Fe^{3+} is 499 K and Fe^{2+} is 311 K and for VF3, θ_D of Fe^{3+} is 492 K and Fe^{2+} is 264 K. These Debye temperatures allow calculation of f_T via Eqn. 1.

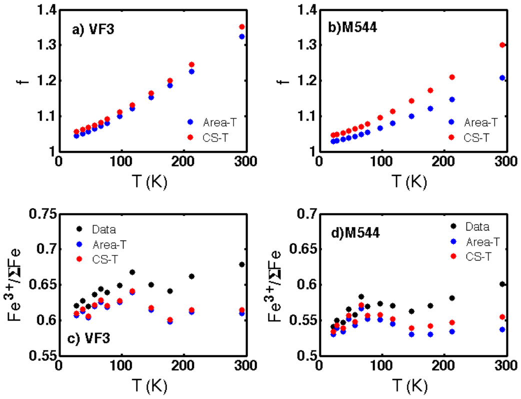

Fig. 2 a) and **b)** are the C_T obtained from equation (1) (blue dots) and (2) (red dots) for VF3 and M544 seperately. **c)** and **d)** are the $Fe^{3+}/\sum Fe$ ratios obtained from the Mössbauer spectra (black dots) and the corrected $Fe^{3+}/\sum Fe$ ratios by C_T obtained from equation (1) (blue dots) and equation (2) (red dots)

Differences between Debye temperatures from the methods are likely owing to anharmonicity in silicate glasses [8], but the resulting temperature-dependent values of C_T and N^{Fe3+}/N^{Fe2+} for VF3, the glass quenched at atmospheric pressure, are essentially identical (Fig 2a,c). For the high pressure glass, the resulting room temperature value differs by 0.1 (Fig. 2b), but this causes only a small difference in calculated N^{Fe3+}/N^{Fe2+} (Fig. 2d). In both cases, corrected values of N^{Fe3+}/N^{Fe2+} determined at 295K agree closely with corrected or uncorrected values determined at very low temperature (Fig. 2c,d), suggesting that the corrections are accurate and that appropriate values of C_T for these glasses at 295K are 1.3±0.05. Thus, at least for the andesite composition examined, room temperature Mössbauer measurements must be corrected for recoilless fraction effects.

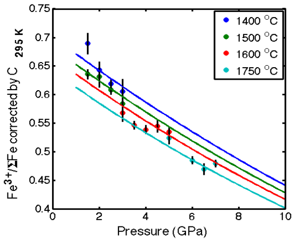

Fig. 3 $Fe^{3+}/\sum Fe$ ratios obtained from Mossbauer spectra and corrected by $C_{295\ K}$= 1.25. Curves indicate a simple thermodynamic model assuming ideal mixing of Fe^{2+} and Fe^{3}.

$Fe^{3+}/\sum Fe$ ratios in glasses quenched from high pressure experiments buffered by Ru/RuO_2 when corrected with $C_{295\ K}$=1.25, decrease with increasing pressure and with increasing temperature (Fig. 3). The effect of temperature is approximately similar to that expected from low pressure determinations [6], but the effect of pressure is more modest, particularly above 4.5 GPa. A simple thermodynamic model was applied to describe the trend, as shown in Fig 3.

Discussion and Application: Experimental data up to 7 GPa indicates that self-compression of Fe^{2+} and Fe^{3+} in a MO leads to more reducing conditions at low pressure. Consequently, atmospheres overlying MO for small planetary bodies such as the Moon or Mercury will be highly reducing, consisting chiefly of H_2 and CO. The same may also be true for Mars. The trend may reverse at higher pressure, as is the case for solid peridotite [12,13], and so for Earth, Venus, and possibly Mars, more oxidized atmospheres above MO are possible. Diamond anvil experiments are underway to examine this hypothesis.

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