Iron spin state in silicate glass at high pressure: Implications for melts in the Earth's lower mantle

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A B S T R A C T

We report a Mössbauer spectroscopic study of a Fe^{2+}-rich aluminous silicate glass and a Fe^{3+}-rich sodium silicate glass measured in a diamond anvil cell up to 84 GPa. The hyperfine parameters vary smoothly with pressure and are consistent with a gradual increase in coordination number with pressure. Fe^{2+} and Fe^{3+} remain in the high-spin state and show no evidence of spin crossover over the measured pressure range. A spin crossover may eventually occur at higher pressures; however the strong thermal broadening of the crossover region due to Boltzmann statistics would prevent any spin crossover from occurring sharply at P,T conditions down to the base of the lower mantle. Our results in combination with recent solid/melt partitioning data in a chondritic system imply that strong preferential partitioning of iron into the melt phase cannot give rise to negatively buoyant melts in the Earth's lower mantle.

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1. Introduction

The physical properties of melts in the Earth's mantle have a fundamental influence on the chemical and thermal evolution of the Earth. Especially the density contrast between solid and melt is a major factor affecting chemical stratification during an early magma ocean after the moon-forming impact (Tonks and Melosh, 1993; Agnor et al., 1999). At low pressure melt densities are usually smaller than the density of the corresponding solids, resulting in a buoyant melt ascending to the Earth's surface. However, experiments have shown that ultramafic melts become denser than the surrounding solids in the upper mantle, while in the transition zone this density relationship is reversed (Rigden et al., 1984; Agee and Walker, 1988; Miller et al., 1991). For the lower mantle, extrapolation of low pressure experiments suggests that density crossovers between solids and melts will also occur near the core mantle boundary (CMB) (Ohtani and Maeda, 2001). In support of this suggestion Williams and Garnero (1996) have proposed stable

partial melts at the CMB as a possible explanation of seismological data.

In principle there are two mechanisms for melts becoming denser than solids. The first mechanism is by faster densification of the melt network with pressure, e.g., coordination changes occurring in a melt at lower pressure than in the solid, while the second mechanism is by preferential partitioning of heavier elements into the melt. The first mechanism has been suggested to occur at the base of the Earth's lower mantle for $MgSiO_3$ melt (Murakami and Bass, 2011), whereas first-principle molecular dynamics calculations (Stixrude and Karki, 2005; De Koker et al., 2013) indicate that a density crossover only occurs in Fe-bearing systems near the CMB, suggesting a combination of both mechanisms. Recently Nomura et al. (2011) proposed the preferential partitioning mechanism to occur at lower pressures in the mid part of the lower mantle based on experiments in an olivine composition $(Mg_{0.89}Fe_{0.11})_2SiO_4$. They observed a sharp discontinuity in the pressure dependence of the Fe/Mg solid/melt partition coefficient at 76 GPa, resulting in a strong enrichment of Fe in the melt, which would produce a denser negatively buoyant melt. The sharp discontinuity was explained by an iron spin crossover seen in their X-ray emission spectroscopy (XES) data collected on $(Mg_{0.95}Fe_{0.05})SiO_3$ glass during room temperature compression.

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However, Andrault et al. (2012) reported a much lower degree of iron enrichment in silicate melt based on partitioning experiments at liquidus temperatures on a (Ca, Mg, Al, Si, Fe) oxide glass with chondritic composition, resulting in a melt that would be lighter than the surrounding mantle and hence would segregate upwards.

In order to reconcile the difference between the results of Nomura et al. (2011) and Andrault et al. (2012), it is important to understand the electronic behavior of iron in both glass and melt as a function of composition. Partitioning experiments can only provide an indirect indication of the iron spin state, while a more direct determination comes from a method such as Mössbauer spectroscopy, which is a sensitive probe for detecting structural and spin changes in Fe-bearing materials. Direct investigation of iron spin states in silicate melts at high pressures and high temperatures using Mössbauer spectroscopy is beyond current experimental capabilities; however, silicate glasses can be used as structural analogues for melts in the Earth's lower mantle.

In this paper we present a Mössbauer spectroscopic study of a Fe^{2+}-rich and a Fe^{3+}-rich silicate glass measured *in situ* in a diamond anvil cell at pressures up to 84 GPa. We investigate the effect of pressure on the hyperfine parameters of these silicate glasses and determine whether spin crossover occurs, and then apply our results to the behavior of silicate melts at lower mantle conditions.

2. Experimental details

The mainly Fe^{3+}-bearing $(Na_{0.98}Fe_{1.04})Si_{2.05}O_6$ (NaFe-silicate) and Fe^{2+}-bearing $(Mg_{0.823}Fe_{0.135})(Al_{0.057}Si_{0.982})O_3$ (MgFeAl-silicate) glasses were prepared from stoichiometric mixtures of dried, reagent grade oxides of Na_2CO_3, $MgCO_3$, Al_2O_3, SiO_2, and $^{57}Fe_2O_3$ (95.86% ^{57}Fe). The powdered mixtures were decarbonated at 750°C for 12 h in platinum crucibles. The starting material of NaFe-silicate glass was melted at 1100°C in an electric furnace in air for 2 h. The temperature was then brought to 1300°C for 2 h and finally to 1450°C for 30 min. The melts were quenched by rapid immersion of the bottom of the crucible in water, ground to a powder and re-melted with the same cycle. This grinding–melting process was repeated three times to ensure good chemical homogeneity. Transmission electron microscope images confirmed the absence of nanometer-sized heterogeneities in the MgFeAl-silicate glass and its composition was determined using an electron microprobe. The starting material of MgFeAl-silicate glass was melted at 1600°C in a Fe-saturated platinum crucible for 4 h and quenched by rapid immersion in a crucible of water. The ground glass was then reduced in a gas-mixing furnace in a H_2–CO_2 atmosphere at 700°C and $\log fO_2 = -21$ for 1 h. The composition of the resulting MgFeAl-silicate glass was determined using an electron microprobe and no inhomogeneity was observed within the resolution of the measurements.

Diamond anvil cells with diamond culet sizes of 250 μm and a rhenium gasket with a 120 μm diameter hole were employed. The fluorescence of ruby chips (Mao et al., 1986) was used to estimate pressure before and after each measurement, whereby the error in pressure was calculated from the difference of both values.

We ran three experimental series: (1) MgFeAl-silicate glass with neon as pressure transmitting medium measured on compression up to 83 GPa, (2) NaFe-silicate glass without pressure transmitting medium measured on compression and decompression up to 56 GPa, and (3) NaFe-silicate glass with neon as pressure transmitting medium measured on compression up to 84 GPa. For neon gas loading the method of Kurnosov et al. (2008) was employed.

Mössbauer spectra of MgFeAl-silicate glass from experimental series (1) were collected using the recently developed Synchrotron Mössbauer Source (SMS) (Potapkin et al., 2012) at the Nuclear Resonance beamline (ID18) (Rüffer and Chumakov, 1996) at the European Synchrotron Radiation Facility (Grenoble, France). SMS spectroscopy enables the collection of energy domain Mössbauer spectra of small samples with relatively low iron concentrations on a timescale of only minutes, compared to days of collection time using a conventional radioactive Mössbauer source. Mössbauer spectra of NaFe-silicate glass from experimental series (2) and (3) were recorded at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq ^{57}Co high specific activity source in a 12-μm-thick Rh matrix. The velocity scales for all series were calibrated relative to a 25-μm-thick natural α-Fe foil and center shift values are given relative to α-Fe. MgFeAl-silicate glass spectra were fitted using a full transmission integral with a normalized Lorentzian-squared source lineshape (Potapkin et al., 2012) to accommodate for the difference in Mössbauer source properties and beam intensity of SMS compared to conventional Mössbauer spectroscopy. The SMS linewidth was controlled before and after each sample measurement using $K_2Mg^{57}Fe(CN)_6$. NaFe-silicate glass spectra were fitted in the thin absorber approximation. All spectra were fitted using the extended Voigt based fitting method (xVBF) (Lagarec and Rancourt, 1997) as implemented in the MossA software package (Prescher et al., 2012).

3. Results

Fig. 1(a) shows selected Mössbauer spectra and Fig. 1(b) shows the variation in center shift (CS) and quadrupole splitting (QS) with pressure of MgFeAl-silicate glass in Ne. The asymmetry in the height and width of the two peaks can be explained by a correlation between the CS and the QS. This correlation can be successfully fitted using the xVBF method (Lagarec and Rancourt, 1997), which was especially developed for disordered systems such as glasses. In the xVBF approach Gaussian distributions of CS and QS are utilized, whereby a linear correlation is allowed between the two parameters. The spectra were fitted using a Fe^{2+} doublet with xVBF CS–QS coupling between -0.5 and -0.6; see Lagarec and Rancourt (1997) for further details. The plotted values of CS and QS are the means of the Gaussian distributions of the respective parameters. The CS decreases almost linearly up to 50 GPa and stays constant up to 83 GPa; whereas the QS increases up to 30 GPa and stays constant at higher pressures up to 83 GPa. No evidence was found for the presence of Fe^{3+} within the uncertainty of the data.

Fig. 2 shows selected spectra of the NaFe-silicate glass measurements. The spectra are composed of an intense Fe^{3+} doublet and a weak Fe^{2+} doublet. The widths of the doublets of the NaFe-silicate glass compressed without pressure medium are highly broadened compared to those compressed with Ne as pressure transmitting medium. This is likely an effect of higher pressure gradients and stress within the sample chamber due to the absence of a pressure transmitting medium. This broadening was accounted for by modeling the Fe^{3+}-site with two Gaussian QS components, whereas the NaFe-silicate glass in Ne was modeled with only one QS component. The correlation between CS and QS of Fe^{3+} is close to zero for both sites in both experiments. Fig. 3 shows the variation of hyperfine parameters with pressure. The CS and QS values of NaFe-silicate glass with no pressure medium were calculated as the weighted average of the two Gaussian QS distributions. The QS for both Fe^{2+} and Fe^{3+} increases up to 15 GPa, it is nearly constant between 15 and 60 GPa, and it increases moderately above 60 GPa. The CS of Fe^{2+} and Fe^{3+} increases up to 15 GPa and then remains constant within experimental uncertainty up to 84 GPa.

The area of the Fe^{3+} absorption increases relative to the Fe^{2+} absorption in the NaFe-silicate glass with increasing pressure (Fig. 4). Although there are differences in values between the samples measured with and without pressure transmitting medium,