High-pressure radiative conductivity of dense silicate glasses and implications for dark-magmas at the Earth's core-mantle boundary

The current structure of the Earth's interior is believed to have formed through dynamic differentiation from a global magma ocean in the early Earth. Elucidation of the heat transport properties of silicate melts in the deep Earth is fundamental to understanding the evolution and structure of Earth's interior. The possible presence of dense, gravitationally stable silicate melts at the bottom of the current mantle as remnants of the deep magma ocean has been proposed to explain the anomalously low seismic velocities above the core-mantle boundary (e.g., Ref. 1). If this is the case, heat fluxes through the core-mantle boundary (CMB) region would strongly depend on the thermal conductivity due to both lattice vibrations (k_{lat}) and radiation (k_{rad}) of such dense silicate melts and the constituent minerals of the lower mantle. However, the thermal properties of such silicate melts under the relevant high-pressure conditions are poorly understood, even though there have been several experimental studies on the thermal conductivity of lower mantle minerals such as magnesium-rich silicate perovskite [2] and ferropericlase [3]. Direct measurements of the thermal conductivity in silicate melts under ultrahigh-pressure conditions remain a great challenge and are currently beyond experimental capabilities. As an alternative, silicate glasses have been studied as analogs for quenched silicate melts to simulate their high-pressure behavior. We conducted visible and near-infrared optical absorption and synchrotron Mössbauer spectroscopic measurements of iron-enriched silicate glasses at high pressures up to 85 GPa using a diamond anvil cell high-pressure apparatus to clarify the potential influences of the pressure-induced electronic structure changes in dense silicate melts on the radiative part of the thermal conductivity [4].

Two types of silicate glasses were used as analogs for dense silicate melts at the CMB: $(Mg_{0.8}Fe_{0.2})SiO_3$ composition (E-glass) to extract the effect of iron and a multicomponent basaltic composition (M-glass) to simulate a more realistic compositional system at the CMB. In the optical absorption measurements, we observed significant increases in the absorption coefficients with increasing pressure (up to a factor of three for E-glass, and an order of magnitude for M-glass), particularly in the visible region above wavenumbers of ~10,000 cm^{-1}, and both samples apparently become optically darker with pressure, as shown in Fig. 1.

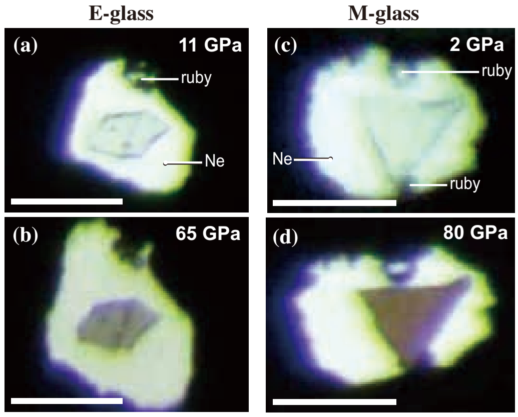

Fig. 1. Optical images of the glass samples under pressure in a diamond anvil cell. **(a)** E-glass at 11 GPa and 300 K, **(b)** E-glass at 65 GPa and 300 K, **(c)** M-glass at 2 GPa and 300 K, and **(d)** M-glass at 80 GPa and 300 K. Pressure medium is neon and the white scale bar is 100-μm long.

In situ high-pressure synchrotron Mössbauer spectroscopic measurements in the energy domain were performed on E-glass using beamline **BL11XU** [5]. As shown in Fig. 2(a), statistically sufficient Mössbauer spectra were obtained using a measurement time between 3 and 6 hours (Fig. 2(a)). Hyperfine structure parameters were determined by distribution analysis of the Mössbauer spectra (Fig. 2(b,c)). Above 20 GPa, a new quadrupole doublet (Sites 1 and 2) appears, which is derived from a low isomer shift (IS, ~0.67 mm/s relative to α-Fe) and moderate quadrupole splitting (QS, ~1.6 mm/s). If the nearest neighbor atoms around iron are oxygen, in principle, the IS should increase with an increase of the Fe-O coordination number. However, if the IS is derived from the new quadrupole doublet, it should show the opposite trend (Fig. 2(b)). Alternatively, this trend can be interpreted as a change in the electronic state in the absence of significant changes in the coordination number, which may be related to the formation of Fe^{2+} with a different electronic configuration from that expected at lower pressures. Given that the IS for Fe^{2+} with low spin states in common compounds is around –0.3 to 0.4 mm/s, our IS data, which has intermediate values between high and low spin, indicates the appearance of Fe^{2+} with an intermediate spin state, rather than a complete transition to low spin states.

The present data obtained from silicate glasses with representative compositions for a dense silicate melt suggests the possible effect of pressure-induced changes in the electronic configurations, including the spin states of iron, on the thermal properties of the melt. The radiative component of the thermal conductivity, $k_{rad}(T)$, can be then calculated as:

$$k_{rad}(T) = \frac{4n^2}{3}\int_0^\infty \frac{1}{\alpha}\frac{\partial I(\nu,T)}{\partial T}\,d\nu \qquad (1)$$

where n is the refractive index, α is the measured absorption coefficient, $I(\nu,T)$ is the Planck function, and T is temperature. The radiative conductivity increases with temperature but decreases with pressure for both components, as shown in Fig. 3. The radiative thermal conductivity of materials with a constant absorbance was believed to be proportional to the third power of temperature (i.e., T^3). However, the temperature dependence of the radiative thermal conductivity estimated in the present study is significantly lower than that expected for the T^3 relationship. The radiative conductivities for both components increase only by a factor of 8 - 9 from 2000 K to 7000 K, which is about five times lower than expected for a T^3 dependence.

The significantly smaller contribution to heat transfer by radiative conductivity of a silicate melt strongly affects the heat flow at the CMB. The results presented here indicate that the estimated radiative thermal conductivity of a basaltic melt, calculated from the results of M-glass, under the lowermost mantle conditions (at ~130 GPa and ~3000 K), is ~0.19 $m^{-1}K^{-1}$. However, dense silicate melts with basaltic compositions are about 5 to 25 times less radiatively conductive than the silicate perovskite phase with representative iron contents in the lower mantle under conditions at the base of the mantle. This remarkable contrast at high pressures indicates the formation of deep magmas with higher heat absorption than that of the surrounding solid mantle phases. Such dense and dark magmas at the CMB may act as traps for heat from the underlying outer core. Seismological mapping at the CMB by detailed waveform modeling studies shows that the ultralow velocity zones (ULVZs) exist as laterally distributed thin layers over a wide region. The distribution of ULVZs correlates strongly with flux-weighted hot spot locations, which have been interpreted as a large-scale lower mantle thermal upwelling that is referred to as a "superplume." The presence of a heterogeneous distribution of such dense magmas with lower radiative thermal conductivity would result in a lateral heterogeneity of heat fluxes through the CMB, which may constrain the locations of stable hot mantle plumes rooted in CMB.

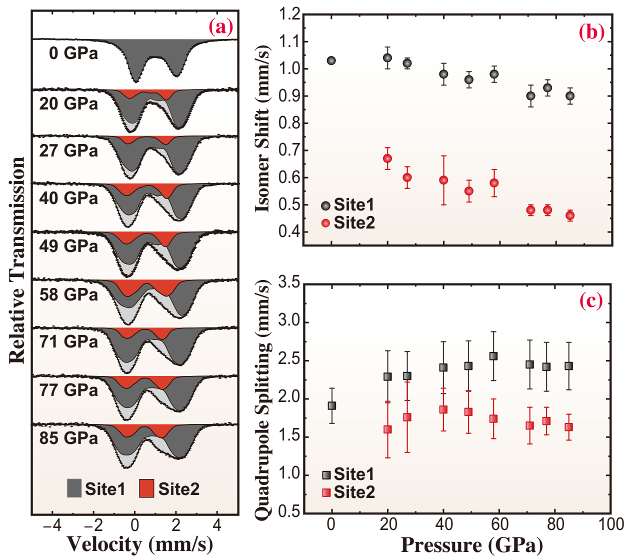

Fig. 2. Mössbauer transmission spectra determined for E-glass between **(a)** 0 and 85 GPa and **(b, c)** hyperfine structure parameters. **(b)** Isomer shift and **(c)** quadrupole splitting. Error bars are ±1σ from the mean value.

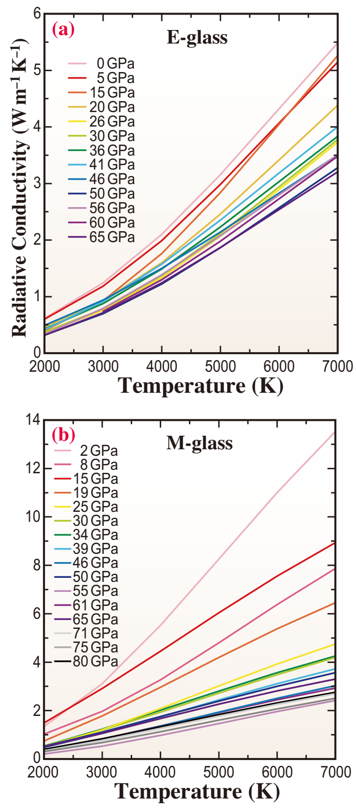

Fig. 3. Estimated radiative thermal conductivity of **(a)** E-glass and **(b)** M-glass as functions of temperature up to 7000 K.

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