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Density contrast between silicate melts and crystals in the deep mantle: An integrated view based on static-compression data

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ABSTRACT

Mineral-physics data of SiO_2, $MgSiO_3$, and MgO under static compression, together with the physical theories of melting and structural changes in liquid, suggest that the density of silicate melts does not exceed that of crystalline assemblages with the same chemical composition at the pressure range of the deep mantle. Because drastic structural changes accompanied by the increase in the coordination number of silicon are completed in the shallow mantle, SiO_2 component becomes stiff and the compressibility of magnesium silicate melts decreases with SiO_2 content in the deep mantle while it increases with SiO_2 content in the shallow mantle. If the ideal mixing of melts with respect to volume is valid in the deep mantle, as is the case for the shallow mantle, the density contrast is significant in a composition range close to $MgSiO_3$. Therefore, magmas in a wide composition range would be buoyant in the deep mantle. Chemical compositions of magmas which are neutrally buoyant in the deep mantle have been estimated with a simplified model in (Mg,Fe)O–SiO_2 system.

1. Introduction

The dynamics of the Earth and planetary interiors is controlled by the transportation of material and energy in a gravitational field. Therefore, the density contrast between silicate melts (magmas) and crystals (minerals and rocks) is essential to understanding the dynamic behavior of our planet. Studies on the density of silicate melts at the pressure range of the shallow mantle have been carried out by using various experimental techniques such as Archimedean density and sound-velocity measurements at zero pressure (Stolper et al., 1981; Lange and Carmichael, 1987; Rivers and Carmichael, 1987), sink–float density and melting-curve measurements under static compression (Ohtani, 1983; Agee and Walker, 1988; Agee, 1998; Ohtani and Maeda, 2001; Suzuki and Ohtani, 2003; Jing and Karato, 2008), and Hugoniot density measurements under shock compression (Rigden et al., 1984, 1989; Miller et al., 1991). These studies have clarified that the density of melts exceeds that of equilibrium crystals at the conditions of the deep upper mantle. On the other hand, studies to clarify the density contrast in the deep mantle are still limited.

Experimental techniques which can directly address the problem at the extreme conditions of the deep mantle have so far been limited to shock compression. Shock-compression experiments have suggested that the density of melts does not exceed that of crystals with the same chemical composition in SiO_2 but does exceed in $MgSiO_3$ and Mg_2SiO_4 at the conditions of the deep mantle (Lyzenga et al., 1983; Luo et al., 2004; Akins et al., 2004; Mosenfelder et al., 2007). However, in these experiments with solid starting materials, the data should be analyzed by interpreting the occurrence of phase transitions and melting and/or estimating the temperatures. Therefore, the suggestion of the density crossover may not be conclusive. In fact, more recent shock-compression experiments eliminate the density crossover in $MgSiO_3$ although they still suggest the density crossover in Mg_2SiO_4 (Mosenfelder et al., 2009). First-principles molecular-dynamics simulations have also addressed the problem and suggested that the density crossover occurs in SiO_2 but not in $MgSiO_3$ and Mg_2SiO_4 (Stixrude and Karki, 2005; Karki et al., 2007; Wan et al., 2007; de Koker et al., 2008; de Koker and Stixrude, 2009). The reliability of the simulations, however, may not yet be sufficiently verified when applied to the problems of silicate melts. As discussed above, the results of shock-compression experiments and first-principles molecular-dynamics simulations are not consistent with each other. In this Letter, we discuss the possibilities of the density crossover in the deep mantle based on various mineral-physics data obtained by static-compression experiments with the help of the physical theories of melting and structural changes in liquid.

2. Physical theories

Physical theories suggest that the density of materials normally decreases upon melting. The structure of simple liquids has often been

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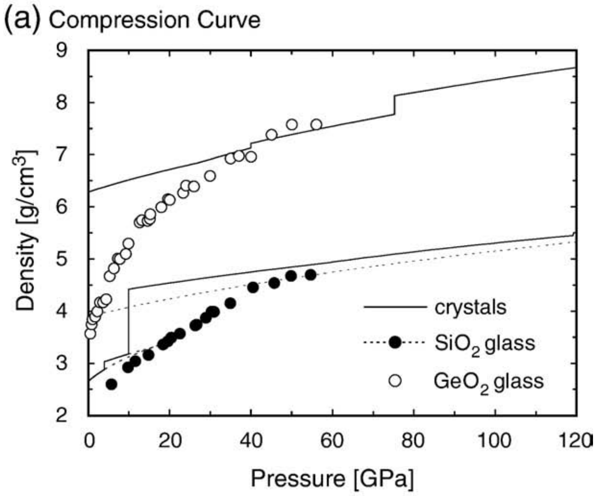
described by the hard-sphere model. It is known that both Monte-Carlo and molecular-dynamics simulations with hard-sphere potentials yield $\Delta V_{L-S}/V_S = \sim 0.10$ (Young, 1991; and references therein). Moreover, the Lindemann law, which is a criterion of melting in terms of the thermal vibration of atoms and the interatomic distance and is not limited to the application to simple liquids, yields $d\ln T_m/d\ln V_S = -2\gamma_S + 2/3$, and γ_S is normally larger than 1/3 (Anderson, 1995; and references therein). Therefore, the sign of dT_m/dP is positive and, since $dT_m/dP = \Delta V_{L-S}/\Delta S_{L-S}$, ΔV_{L-S} is also positive (ΔS_{L-S} is always positive). Here, P, V, T, and S are the pressure, volume, temperature, and entropy, respectively, and γ is the Grüneisen parameter. The subscripts m, L, and S denote the melting, liquid, and solid, respectively, and $\Delta X_{A-B} = X_A - X_B$.

The density crossover likely relates to the pressure-induced structural changes in liquid. At a given pressure and temperature, materials behave so as to minimize the Gibbs free energy $G = U + PV - TS$. Since the PV term is dominant at high pressures, structural changes in liquid take place at pressures close to the corresponding transition pressures in solid. At high temperatures, structural changes in liquid take place over a finite pressure interval because of the contribution of the $-TS$ term (i.e. the coexistence of low- and high-pressure local structures effectively reduces the Gibbs free energy). Using the two-species model (Rapoport, 1967), the molar fraction of the high-pressure local structure x can be formulated as $kT\ln[x/(1-x)] + (1-2x)w = \Delta\mu_{LII-LI}$ $(= \Delta U_{LII-LI} + P\Delta V_{LII-LI} - T\Delta S_{LII-LI})$, where k is the Boltzmann constant and w is the frustration between neighboring low- and high-pressure local structures ($w > 0$ for real liquids and $w = 0$ for ideal liquids). Subscripts I and II denote the low- and the high-pressure structure (or phase), respectively. In the neighborhood of the pressure for which $\Delta\mu_{LII-LI} = 0$ (i.e. $x = 0.5$), x increases significantly with increasing pressure. In the case of $w/kT \gg 1$ (i.e. at low temperatures), $x = 0$ or 1 and phase transitions take place in liquid. In most cases, however, critical temperatures are lower than melting temperatures and phase transitions in liquid cannot be observed. If ideal liquids are considered for simplicity, the condition for a negative dT_m/dP can be expressed as $\Delta V_{LI-SI} < -x\Delta V_{LII-LI}$ $(\approx -x\Delta V_{SII-SI})$. This is satisfied, i.e. the density crossover occurs, when structural changes accompanied by a large volume decrease take place at lower pressures in liquid than in solid.

Numerous studies have clarified that structural changes in silicate melts are complicated and are rather different from transitions in crystals (Wolf and McMillan, 1995; de Koker and Stixrude, 2009). This seems to be against the view on the density crossover discussed above. From a broader perspective, however, the above discussion may be even applicable to silicates. In the next section, the validity is examined first with static-compression data at low pressures. Then, the behavior of silicate melts and the possibility of the density crossover are discussed at the pressure range of the deep mantle. Effects of the difference in chemical compositions between melts and crystals are taken into account after the next section.


(a) Compression Curve

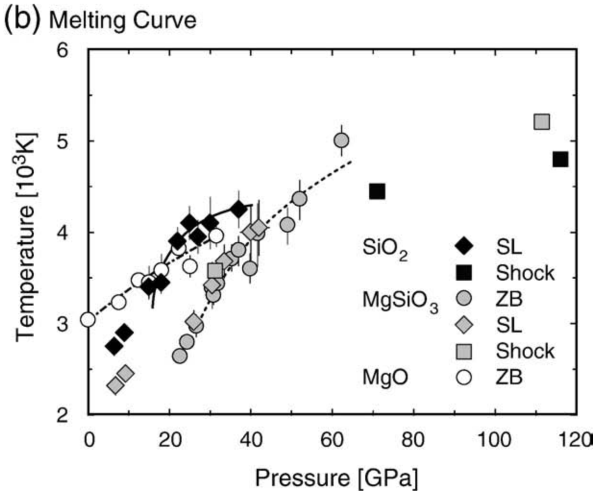

(b) Melting Curve

Fig. 1. (a) Pressure dependence of the densities of glassy and crystalline phases of SiO_2 and GeO_2 at 300 K (Haines et al., 2000; Andrault et al., 2003; Murakami et al., 2003; Ono et al., 2003; Prakapenka et al., 2003; Hong et al., 2007; Sato and Funamori, 2008; and references therein). The dotted line represents the equation of state for the sixfold-coordinated amorphous phase of SiO_2. The extrapolation of the equation of state may be possible up to at least 100 GPa (Sato and Funamori, 2008). (b) Melting curves of SiO_2, SL (Shen and Lazor, 1995); $MgSiO_3$, ZB (Zerr and Boehler, 1993) and SL (Shen and Lazor, 1995); and MgO, ZB (Zerr and Boehler, 1994). Lines are guides for the eyes. Melting temperatures based on shock-compression experiments are also shown for comparison (Lyzenga et al., 1983; Luo et al., 2004; Akins et al., 2004).

3. Discussion based on static-compression data

The pressure dependence of the densities of glassy and crystalline phases of SiO_2 and GeO_2 is shown in Fig. 1a. Glasses can be considered to be analogs that reflect the structure and density of melts (Wolf and McMillan, 1995; Schilling et al., 2001). In SiO_2, the density of glass exceeds that of metastable crystals, quartz and coesite, at ~20 GPa. This density crossover may be related to the transition from coesite (fourfold-coordinated) to stishovite (sixfold-coordinated), accompanied by a large volume decrease of ~40%. The density of SiO_2 glass increases greatly up to 40–45 GPa, and then relatively slightly above 40–45 GPa. The density crossover may not occur at least up to 100 GPa based on the equation of state determined for the sixfold-coordinated amorphous phase (Sato and Funamori, 2008). Although glasses show anelastic behavior (structural relaxation with time, inconsistent isothermal and adiabatic moduli, etc.) during structural transformations, each amorphous phase shows elastic behavior similar to crystalline phases (Zha et al., 1994; Wolf and McMillan, 1995; Tsiok et al., 1998; El'kin et al., 2002; Sato and Funamori, 2008). Therefore, it may be valid to estimate densities at high pressures with the equation of state for each amorphous phase. In GeO_2, the density of glass may exceed that of a crystal with the α-PbO_2-type structure at 45–50 GPa. This may be related to the transition from a sixfold-coordinated α-PbO_2-type to an eightfold-coordinated pyrite-type at 65–85 GPa, accompanied by a relatively large volume decrease of 4–5%. These observations support the view on the density crossover discussed in the previous section. Reversely, these observations may suggest that discussions of the compression behavior of melts can be made based on that of glasses, although details are definitely different.

Melting curves of SiO_2, $MgSiO_3$, and MgO are shown in Fig. 1b. In $MgSiO_3$, the data of static-compression experiments from two different groups ZB and SL agree well with each other. It is worth pointing out that experimental details, for example, the wavelength of laser for heating, sample assembly, and melting criteria, of the two