Shock-induced melting of MgSiO₃ perovskite and implications for melts in Earth’s lowermost mantle

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[1] New shock wave equation of state (EOS) data for enstatite and MgSiO₃ glass constrain the density change upon melting of Mg-silicate perovskite up to 200 GPa. The melt becomes denser than perovskite near the base of Earth’s lower mantle. This inference is confirmed by shock temperature data suggesting a negative pressure-temperature slope along the melting curve at high pressure. Although melting of Earth’s mantle involves multiple phases and chemical components, this implies that the partial melts invoked to explain anomalous seismic velocities in the lowermost mantle may be dynamically stable. INDEX TERMS: 3919 Mineral Physics: Equations of state; 3944 Mineral Physics: Shock wave experiments; 8124 Tectonophysics: Earth’s interior—composition and state (1212). Citation: Akins, J. A., S.-N. Luo, P. D. Asimow, and T. J. Ahrens (2004), Shock-induced melting of MgSiO₃ perovskite and implications for melts in Earth’s lowermost mantle, Geophys. Res. Lett., 31, L14612, doi:10.1029/2004GL020237.

[2] The perovskite (pv) structure of (Mg, Fe)SiO₃ is considered to be the most abundant phase in the lower mantle, which makes its high-pressure, high-temperature behavior a matter of some interest. Of particular importance, given seismic ultra-low velocity zones (ULVZs) [Williams and Garnero, 1996] above the core-mantle boundary, are constraints on the phase relations and density contrasts among mantle solids, mantle melts, and the core that may explain the presence and stability of partial melting at the very base of the mantle [Montague and Kellogg, 2000; Namiki, 2003; Zhong and Hager, 2003].

[3] The thermal EOS of MgSiO₃ pv has been constrained by numerous static experiments and computational studies [Wang et al., 1994; Utsumi et al., 1995; Funamori et al., 1996; Saxena et al., 1999; Fiquet et al., 2000; Karki et al., 2001; Marton et al., 2001; Brodholt et al., 2002]. Previous dynamic pressure-density-internal energy (P-v-E) data for MgSiO₃ composition are compiled in [Marsh, 1980] and Simakov and Trunin [1973]. We obtained new P-v-E Hugoniot data to 206 GPa on initial MgSiO₃ synthetic glass and natural Sri Lankan enstatite (en) (Table 1 of auxiliary material (electronic data supplement (EDS))) [Akins, 2003]. Interpretation of these data are complemented by our recent shock temperature (T) results to 180 GPa [Luo et al., 2004]. Shock T constrains the thermal EOS of the high-P phases and can also indicate melting, since shock T in melts is typically lower than the extrapolation of solid Hugoniots. Here we compare the melting behavior of MgSiO₃ on the Hugoniots of three starting materials: an ultraporous equimolar mixture of MgO+SiO₂ (starting density ρ₀ = 1.58 g/cm³) [Marsh, 1980], MgSiO₃ glass (ρ₀ = 2.73 g/cm³) and en (ρ₀ = 3.22 g/cm³). We also combine diamond-anvil cell (DAC) and shock T data to define the melting curve of MgSiO₃ pv to 200 GPa and to examine the relative buoyancy of solids and melt of this composition.

[4] The phase in the shock state is not determined in most shock wave experiments. Whether fully-ordered crystalline high-pressure phases (H.P.P.) form during shock compression remains unknown but the advent of ultrafast x-ray [d’Almeida and Gupta, 2000] and electron [Stivick et al., 2003] diffraction promises to resolve this issue soon. For now, interpretation of shock data is guided by calculations of theoretical Hugoniot curves for candidate H.P.P. based on a Mie-Grüneisen offset from 3rd order Birch-Murnaghan isentropes (details are given in EDS and by McQueen et al. [1963]). Selected elastic and thermodynamic parameters of MgSiO₃ akimotoite, pv, and melt with low-pressure properties (L.P.P. melt) are listed in Table 2 of the EDS. Many Hugoniot data can be assigned to one of these phases, but the highest-P experiments on en require a new phase or a drastic change in EOS. Although an orthorhombic (Cmcm) postperovskite phase ~1.0–1.5% denser than pv has been reported [Murakami et al., 2004; Shim et al., 2004] (calculated thermodynamic parameters in EDS Table 2 from T. Tsuchiya et al. (Phase transition in MgSiO₃ perovskite in the Earth’s lower mantle, submitted to Science, 2004, hereinafter referred to as Tsuchiya et al., submitted manuscript, 2004)), it is not dense enough to explain the highest-P data; we argue that these require a H.P.P melt even denser than postperovskite. We estimate the parameters of a candidate EOS for this melt consistent with our data: ρ₀ = 3.68 g cm⁻³; K₀ₚ = 125 GPa; K’ = 4.0; γ = 2.4(V'/V)¹; Er = 2.4 MJ/kg relative to en; and Cᵥ = 0.92×3nR, where R is the gas constant.

[5] Consider first the Hugoniot data for ultraporous MgO+SiO₂ (Figure 1a) [Marsh, 1980]. Up to 21 GPa the density is similar to the Hugoniot of normal en [Simakov and Trunin, 1973; Marsh, 1980]. The datum at 31 GPa and 4.2 g/cm³, however, is substantially denser than the crystal Hugoniot. Calculations of possible H.P.P. indicate a reasonable fit for pv; other possibilities (e.g., periclase plus stishovite) cannot account for the density. We presume that conversion to pv is kinetically easier along the high-T porous-material compression path. The estimated shock T
at 31 GPa, 4000 K, is above the melting curve of MgSiO₃ (Figure 2), but superheated solid shock states are common for shocks that overdrive the melting curve by less than ~30% [Luo and Ahrens, 2003]. The next datum, at 34 GPa, exhibits an abrupt decrease in density of ~10% that we propose is due to melting [Akins, 2003]. A calculated Hugoniot for ultraporous MgO+SiO₂ shocked to L.P.P. melt (EDS Table 2) agrees with the $P$-$\rho$ data at 34 and 41 GPa (Figure 1a). The calculated $T$ at 34 GPa, 4000 K, is an upper bound on the melting curve (Figure 2). At ~34 GPa, therefore, MgSiO₃ $pv$ melts with a large positive $\Delta V_m$ to a low-density liquid presumably dominated by four-fold coordination of silicon.

[6] The MgSiO₃ glass data show a different behavior. Our 47 GPa point and existing data on ceramic materials of similar $\rho_0$ [Marsh, 1980] are consistent with a mixed phase region (M.P.R.) of $en$ and H.P.P., perhaps mostly majorite. Our 87 and 110 GPa data are consistent with solid $pv$ (Figure 1b). The lower-precision $P$-$\rho$ estimates from time-resolved shock $T$ experiments at 117 and 121 GPa [Luo et al., 2004] suggest density perhaps slightly lower than the extrapolation of the $pv$ Hugoniot, but the difference is within error. However, the measured shock $T$ at 117 GPa is ~1000 K lower than the calculated $T$ for MgSiO₃ glass shocked to $pv$ (Figure 2). Our interpretation is that the MgSiO₃ glass yields superheated $pv$ up to 110 GPa and 6200 K followed by melting with negligible $\Delta V_m$ and a $T$ drop of ~700 K to a dense melt by 117 GPa.

[7] The $en$ crystal Hugoniot follows a still lower-$T$ path and displays a third melting behavior (Figure 1c). First, the data at 68 and 88 GPa are too dense to still be $en$ and show a steep slope consistent with a single-phase regime, yet are not dense enough to be $pv$ (compare to the higher density of a laser-heated DAC XRD measurement on $pv$ at 2900 K and 67 GPa [Fiquet et al., 2000], ~1300 K hotter than the shock state at 68 GPa). After examining all candidate phases, we conclude that akimotoite is attained between 70 and 90 GPa on the $en$ Hugoniot [Akins, 2003]. At 110 to 150 GPa the calculated Hugoniot for $en$ going to $pv$ fits the data. The data between 57 and 140 GPa of Gong et al. [2004] on slightly porous natural orthopyroxene with Mg/(Mg+Fe) = 0.92 also show densities consistent with $pv$; no akimotoite regime can be seen in their data, perhaps due to experimental scatter, initial porosity, or differences in phase relations due to Fe.

[8] At 170 GPa our $en$ data show a jump in density of ~5%. Figure 1c includes a calculated Hugoniot for conversion to the postperovskite solid [Murakami et al., 2004; Shim et al., 2004; Tsuchiya et al., submitted manuscript, 2003; Presnall et al., 2004; Presnall et al., 2005] and displays a third melting behavior (Figure 1c). First, the $en$ crystal Hugoniot follows a still lower-$T$ path and displays a third melting behavior (Figure 1c). First, the data at 68 and 88 GPa are too dense to still be $en$ and show a steep slope consistent with a single-phase regime, yet are not dense enough to be $pv$ (compare to the higher density of a laser-heated DAC XRD measurement on $pv$ at 2900 K and 67 GPa [Fiquet et al., 2000], ~1300 K hotter than the shock state at 68 GPa). After examining all candidate phases, we conclude that akimotoite is attained between 70 and 90 GPa on the $en$ Hugoniot [Akins, 2003]. At 110 to 150 GPa the calculated Hugoniot for $en$ going to $pv$ fits the data. The data between 57 and 140 GPa of Gong et al. [2004] on slightly porous natural orthopyroxene with Mg/(Mg+Fe) = 0.92 also show densities consistent with $pv$; no akimotoite regime can be seen in their data, perhaps due to experimental scatter, initial porosity, or differences in phase relations due to Fe.
2004), but this explains only about half the density jump observed. A similar jump is observed along the quartz Hugoniot at 115 GPa. In the SiO$_2$ system this corresponds to a drop in longitudinal sound speed to the bulk sound velocity [Chhabildas and Miller, 1985; McQueen, 1991] and a 2000 K drop in $T$ [McQueen and Fritz, 1982; Lyzenga et al., 1983; Boslough, 1988]. In SiO$_2$, these observations demand a transition from superheated solid to high-density liquid. We propose that the $en$ Hugoniot undergoes a similar transition at 170 GPa from pv solid to H.P.P. melt with an increase in density [Akins, 2003]. The $P$-$p$ data inferred from radiance duration in shock $T$ experiments [Luo et al., 2004] are consistent with this interpretation within their error bars. Moreover, the shock $T$ measured at 142 and 165 GPa is within error of calculated $T$ along the en-to-pv Hugoniot, whereas the $T$ datum at 183 GPa is at least 500 K below the calculation, which again suggests a melt as the H.P.P. (Figure 2). Calculated shock $T$ for en-to-postperovskite phase (Tsuchiya et al., submitted manuscript, 2004) at 183 GPa does not fit the data (Figure 2). However, definitive confirmation that the $en$ Hugoniot passes into a dense melt rather than a dense solid will require longitudinal sound speed measurements across the transition.

Because the H.P.P. melt Hugoniot state is at lower $T$ than the superheated extrapolation of the en-to-pv Hugoniot, it is necessary to examine how much of the 5% density jump along the Hugoniot is due to $T$ rather than the $\Delta V_m$ between melt and solid on the melting curve. In order for $\Delta V_m$ to be positive, a 5% increase in pv density upon cooling from the extension of the pv Hugoniot to the H.P.P. melt Hugoniot requires a thermal expansion coefficient ($\alpha$) $\geq 6.0 \times 10^{-5}$ K$^{-1}$ [Akins, 2003]. Fiquet et al. [2000] provide thermal EOS data for pv with $\alpha = 2.7 \times 10^{-5}$ K$^{-1}$ at 5000 K and room $P$; fitting their data to an Anderson-Grueneisen form [Anderson, 1995] yields a predicted $\alpha = 1.0 \times 10^{-5}$ K$^{-1}$ at 170 GPa. With this value and a $\Delta T$ of $-730$ K from comparison of our pv and H.P.P. melt Hugoniots we find that $\Delta V_m$ is indeed negative and that the melt is 3.2% denser than the solid on the melting curve at 170 GPa and 5000 K (details in EDS, Table 3).

For a univariant reaction such as the congruent melting of a pure phase, the volume change of the reaction is related to its slope in P-T space by the Clausius-Clapeyron equation,

$$dT/dP = \Delta V_m/\Delta S_m,$$  

where $\Delta S_m$ is entropy of fusion. $\Delta S_m$ should be positive and a weak function of $P$, even if disorder contributes somewhat to the entropy of shocked solids. Hence the slope of the melting curve is roughly proportional to $\Delta V_m$ and, in particular, $\Delta V_m < 0$ implies a negative slope. The shock $T$ data of [Luo et al., 2004], which place the melting curve at 5500 K at 110 GPa and 5000 K at 170 GPa, are therefore consistent with the negative $\Delta V_m$ that our EOS data require at 170 GPa.

At 32 GPa, where we observe a $\sim 10\%$ increase in volume along the Hugoniot upon melting of ultrapressured MgO+$\text{SiO}_2$, the melting curve of pv is directly constrained by multianvil and DAC studies. It has a slope of 50 K/GPa, which is consistent with the $\Delta V_m$ and $\Delta S_m$ between our derived equations of state for L.P.P. melt and pv. We fitted the melting curve of pv in the H.P.P. regime to a Lindemann law [Anderson, 1995],

$$T_m = T_m(\frac{p}{p_m})^{2/3} \exp\left\{\frac{2\alpha r}{q} \left[ 1 - \left(\frac{p}{p_m}\right)^q \right]\right\},$$  

where the volume dependence of the Grueneisen parameter of pv is constrained by static high-T EOS and shock data and the fictive melting $T$ of pv to H.P.P. melt at zero $P$, $T_{mono}$, is a free parameter. Choosing $T_{mono} = 3100$ K results in a curve that merges with the upper end of the DAC melting points [Shen and Lazor, 1995; Sweeney and Heinz, 1998; Boehler, 2000] around 50 GPa and agrees with the melting $T$ at 110 GPa inferred from shock data. The Lindemann melting curve slope of 10 K/GPa at 110 GPa and a $\Delta V_{en}$ of $+0.8\%$ estimated from our shock EOS data on MgSiO$_3$ glass leads to $\Delta S_m = 0.4$R. If this value applies also at 170 GPa, then our inferred $\Delta V_m$ of $-3.2\%$ implies that the slope of the melting curve should be $-35$ K/GPa at 170 GPa (Figure 2). We estimate that melting of MgSiO$_3$ pv at the core-mantle boundary, 135 GPa, occurs at $T = 5300$ K, a volume change of $-0.2\%$ and a Clapeyron slope of $-3$ K/GPa. If the postperovskite phase is stable on the liquidus at these conditions, $T$ will be slightly higher and the volume change and Clapeyron slope will be positive; however, the positive Clapeyron slope suggested for the pv-postperovskite phase boundary suggests that even if the adiabatic geotherm crosses into the postperovskite field at the top of D"{O}, the base of the conductive core-mantle boundary layer may be hot enough to cross back into the pv stability field.

In conclusion, shock wave EOS data on various phases of MgSiO$_3$, supplemented by shock $T$ measurements [Luo et al., 2004], suggest that MgSiO$_3$ melt increases substantially in density with increasing $P$ across the pv stability field. The initially very steep slope of the melting curve seen in DAC experiments is consistent with a low-density melt similar in structure to that seen at ambient $P$, but by $\sim 120$ GPa the melt approaches the density of solid pv. Although this H.P.P. melt must be dominated by six-fold coordination, its compressibility remains larger than that of pv and by 170 GPa the melt exceeds the density of pv. This result by itself is insufficient to describe the dynamics of the lowermost mantle, where other components are significant contributors. However, the existence of a melt denser than the most abundant dense silicate is provocative. It suggests that small degree partial melts may be neutrally buoyant and stable for long times in the D"{O} layer, and that silicate melts may also accumulate to high degrees of melting just above the core mantle boundary and explain the existence of ULVZs. The implications for chemical evolution of the mantle, the dynamics and chemical signatures of deep mantle plumes, and possible ongoing interactions between core and mantle remain areas for further work.

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**References**


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