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EVIDENCE FOR A PHASE TRANSITION IN SILICATE MELT AT EXTREME PRESSURE AND TEMPERATURE CONDITIONS

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ABSTRACT

Laser-driven shock compression experiments reveal the presence of a phase transition in $MgSiO_3$ over the pressure-temperature range 300-400 GPa and 10,000-16,000 K, with a positive Clapeyron slope and volume change of ~6.3 (± 2.0) percent. The observations are most readily interpreted as an abrupt liquid–liquid transition in a silicate composition representative of terrestrial planetary mantles, implying potentially significant consequences for the thermal–chemical evolution of extra-solar planetary interiors. In addition, the present results extend the Hugoniot equation of state of $MgSiO_3$ single-crystal and glass to 950 GPa.

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Crystallographic phase tranformations in the mineral phases constituting the terrestrial mantle have long been recognized for their role in governing the structure and geodynamic evolution of Earth's interior [1-4]. Here we present direct experimental evidence that similar, pressure-induced phase changes can occur in silicate liquids (magmas) at the extreme conditions characteristic of the interiors of several Earth-mass extra-solar planets (super-Earths) and the type of giant impact events inherent to planetary formation (pressures of many hundred GPa and temperatures exceeding 1 eV ≈ 11,000 K). Experimental observations of such "first-order" liquid-liquid transitions are so far limited to few cases, notably that of phosphorous [5-7]. Because of the key role that melts play in planetary evolution, pressure-induced liquid-liquid phase separation in silicate magmas may represent a previously unrecognized but important mechanism for global-scale chemical differentiation, and may also influence the thermal transport and convective processes that govern the formation of a mantle and core early in planetary history.

Experiments were carried out at the Janus and OMEGA laser facilities (Lawrence Livermore National Lab, and University of Rochester Laboratory for Laser Energetics). A 1-2 ns laser pulse of intensity ~10^{13} W/cm^2 was used to generate optically-reflecting, decaying shock waves in $MgSiO_3$ glass and crystalline (enstatite) samples. As the wave decays in time, a continuum of pressure-temperature shock states can be documented in a single experiment. Spatially and temporally resolved (~10 μm/pixel and 100 ps, respectively) velocity interferometry [8, 9] and optical pyrometry [10, 11] were used to characterize the evolution of shock velocity (U_S) and temperature (T) (Fig. 1). Similarly, optical reflectivity at 532 nm (R) was obtained from the interferometry data by comparison with an unshocked Al reference. Because conservation of mass, momentum and energy are obeyed at the shock front, pressure (P) and specific volume (V), can be determined from the shock velocity using the Rankine-Hugoniot equations [12]. We thus derive the pressure–density equation of state (EOS), and corresponding temperature and specific heat of our sample, over a broad range of pressure (see supporting online material, [13]). Simultaneous pressure-temperature data were collected in this manner up to nearly 500 GPa (Fig. 2). Additional equation-of-state measurements at pressures above the proposed phase transition, to 950 GPa, use impedance matching with an α-SiO_2 standard of known EOS (Fig. 2, inset and Table S2).

In a given experiment, the arrival of the shock in the sample brings it to an initial high-pressure, high-temperature state. As the shock decays, shock velocity and thermal emission initially decrease with time before undergoing a brief reversal as the Hugoniot transits what we interpret as a liquid-liquid phase boundary (Fig. 1). Similar anomalies in thermal emission have been documented in other materials under shock loading, and can indicate a release (and/or absorption) of internal energy or a change of optical properties in the sample [14-16]. The unique observation in the present case is that the decay in shock-velocity and thermal emission *both* reverse themselves during the same time interval. The rise in U_S (~0.7 km/sec in Fig. 1) corresponds to a significant volume change in the material, as dictated by the Rankine-Hugoniot relations.

Similar evidence was repeatedly observed in experiments with both crystalline and glass starting materials. In both cases, the burst in thermal emission documented by pyrometry is coincident with the change in shock velocity (hence, change in volume) documented by velocity interferometry. The glass starting material has a lower initial density (2.74 g/cc) relative to the single-crystal (3.22 g/cc), and thus achieves higher temperatures for a given shock pressure. Experiments on the glass therefore document the observed transition at higher P/T conditions; together with the single-crystal data, we can thus define a Clapeyron slope, dP_{tr}/dT, for the apparent phase boundary (Fig. 2).

Given our measured pressure-density (Hugoniot) relations for the two starting materials over different temperature ranges (Fig. 2, inset), we can estimate thermal expansion coefficients for the two phases [13]. In combination with the inferred Clapeyron slope ($1.4\pm2.5 \times10^7$ Pa/K, Fig. 2), this enables us to determine the change in volume (ΔV) and entropy (ΔS) on transformation from the low-pressure to the high-pressure phase at constant pressure and temperature. We find $\Delta V = -6.25 \pm 2.2\%$ and $\Delta S = -2.9 \pm 0.6$ J/K·mol of atoms [17]. With increasing pressure, the material therefore undergoes an abrupt phase transformation to a high-pressure phase with a smaller volume and decreased entropy.

We infer that the apparent heat release observed under decaying shock conditions results from time-dependence (or "kinetic hindrance") of the transition relative to the time-scale of the experiments. Although this may at first seem surprising for a liquid at temperatures above 10,000 K, the situation is analogous to that for solid-solid transformations along the Hugoniot, which are also seen to be kinetically hindered despite the fact that the sample is responding mechanically as a fluid (i.e. well above the Hugoniot elastic limit) [18, 19]. The large ΔV may also hinder the transition, as viscous flow is required to accommodate the resulting strain in the sample [20]. The phase line that we identify (Fig. 2) is thus likely to be an upper bound for the equilibrium transition.

Given the paucity of data for super-solidus transitions of this nature, we have considered the possibility that our data represent either a dissociative or liquid-solid transition. These are not our preferred interpretations for several reasons. First, we infer that our data are entirely in the molten phase, based on previous studies in which shock melting was determined at lower temperatures (albeit also at lower pressures [21-23]), and based on the fact that our observations fall above the known (or expected) melting points of the oxide components, SiO_2 and MgO [14, 15, 24]. An increase in melting temperature from below ~5000 K at 100-200 GPa (as determined by previous theory and experiment: Fig. 2) to the 10,000-16,000 K at 300-400 GPa of the transition documented in our experiments would require a radical change in the melting curve and the presence of a new crystalline phase of $MgSiO_3$ for which there is no other evidence, either theoretically or experimentally. Second, the absolute magnitudes of entropy change and volume change are respectively much smaller and much larger than is characteristically found for melting transitions at high pressure, with $\Delta S \sim R = 8.3$ J/K·mol of atoms and $\Delta V \sim$ 1-2% being typical [25, 26]. Indeed, because the high-pressure phase is seen to have lower entropy, the transition is not likely attributable to dissociation. Dissociation of $MgSiO_3$ is expected to result in a volume change several times smaller than what we observe, and with a Clapeyron slope opposite to that documented by our experiments [27]. We thus conclude that the transition is between two liquid states, with distinct densities and entropies.

In addition, our optical reflectivity measurements document a change in bonding character that is distinct from the phase transition discussed thus far [28]. Changes in the optical properties of the shocked material serve as a probe of the electronic properties at the atomic scale. Reflectivity was measured for all experiments and reveals a gradual change commensurate with the onset of metallic-like behavior above ~12-15,000 K, and for which temperature plays a greater role than pressure (Fig. 3). DC conductivities are extracted from our data using a Drude semiconductor model and range from ~2500-5000 ohm-cm^{-1} with increasing temperature, well-exceeding minimum metallic conductivity [13]. Similar trends have been observed in other materials, including SiO_2, where reflectivity of more than a few percent is indicative of metallization [15, 29].

It is notable that the combined high densities and temperatures required to metallize $MgSiO_3$ are easily achieved during "late-stage" giant impacts, such as the one that formed the Earth's moon [30]. In the aftermath of such an event, and during the magma-ocean stage expected to follow, the possibility of liquid-liquid phase separation between highly conductive states may have significant implications for planetary differentiation. In particular, other chemical elements are expected to be preferentially drawn into one liquid phase relative to the other (partitioning), thus providing an efficient means of chemical separation. Because convective liquid motions in a magma ocean are expected to be rapid, spanning global distances (~10^4-10^7 m) on relevant planetary dynamic timescales (~10^9-10^{15} s), the observed transition offers a means of dramatically influencing geochemical differentiation, and altering the bulk chemical composition of large fractions of a planet early in its history.

Latent-heat and buoyancy effects suggested to dictate the convective dynamics across solid–solid transitions of Earth's mantle could play a similar role during liquid-liquid phase separation, stabilizing convective layering and compositional stratification [4], though in a very different convective regime than for present-day mantle convection (i.e. much higher Rayleigh number [31]). In addition, silicate and metallic (iron-alloy) constituents are typically treated as being distinct in planetary accretion models; however, our observation of metallic silicate melt suggest that this distinction may be more subtle during the formation and early evolution of a terrestrial planet. Indeed, the presence of conductive silicate melt may influence partitioning of elements into the core during its formation, as well as the generation and sustenance of planetary magnetic fields. Though such effects may have only been transient in the case of the Earth, they may continue to be relevant today in the interiors of "super-Earth" exoplanets.

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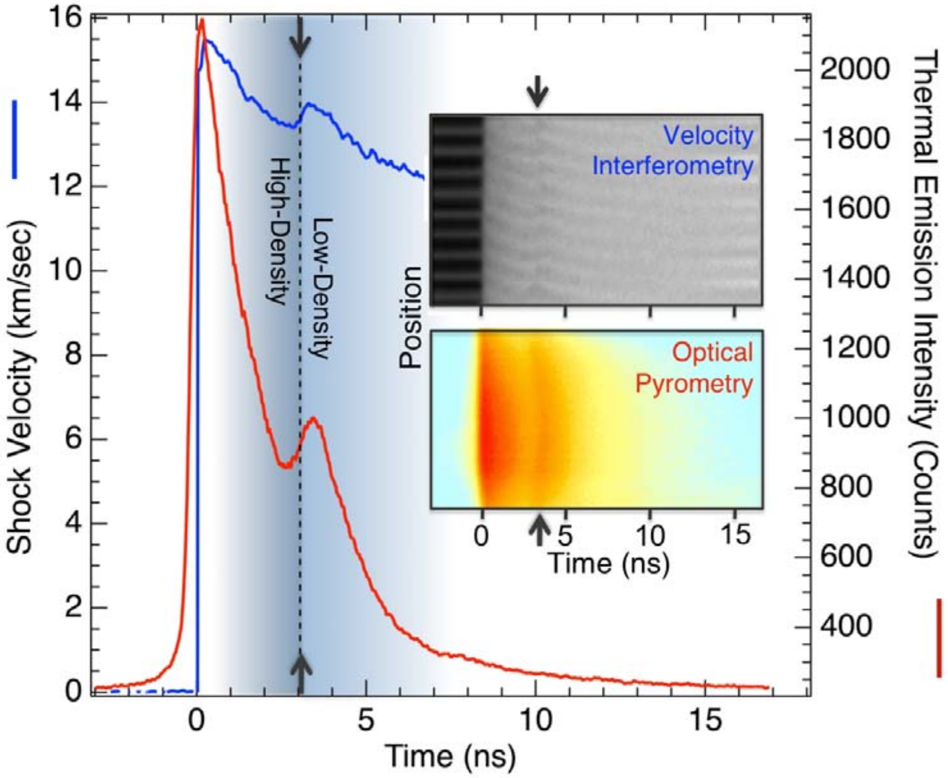

FIG. 1 (Color). Example of data from a single experiment performed with crystalline starting material shows simultaneous reversals in shock velocity and temperature as a function of time as the Hugoniot crosses the phase transition (visible between 2 and 4 ns, as indicated by arrows and dashed line). Inset: Arrows indicate the transition in the raw data images, from which the profiles in the main figure are extracted.

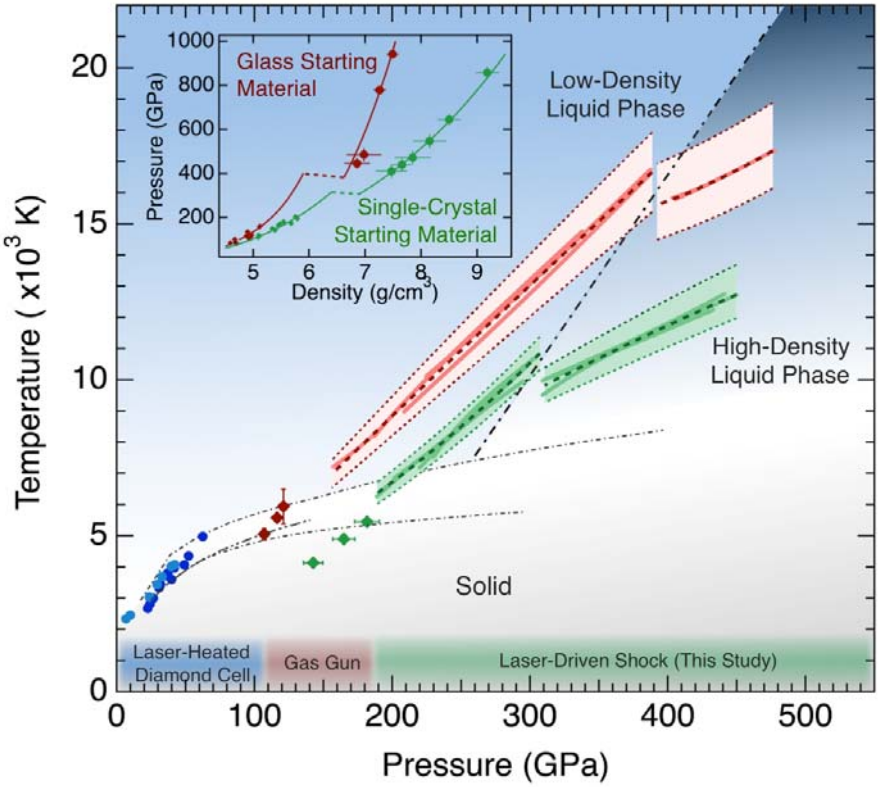

FIG. 2 (Color). Decaying shock measurements on samples of initially single-crystal (green) and glass (red) $MgSiO_3$ identify a phase boundary with positive Clapeyron slope between low- and high-density liquid phases (dot-dash line). Results from 3 experiments on each material are plotted, with temperature uncertainties indicated by the colored bands: these are consistent with previous shock-wave data for single-crystal and glass samples (green and red diamonds, respectively [21, 22]). Theoretical predictions of melting temperatures are shown as thin, dotted curves [33-35]. Experimental melting points from laser-heated diamond-cell experiments are shown as blue circles [36, 37]. Inset: Hugoniot equation-of-state data were collected between 400 and 950 GPa in the present study. The density discontinuities near 6.5 g/cm^3 correspond to the change documented by velocity interferometry in Fig. 1 and the *P*/*T* discontinuities in the main figure (see also Supporting Material, [13]). EOS data below 200 GPa are from refs. [21-22].

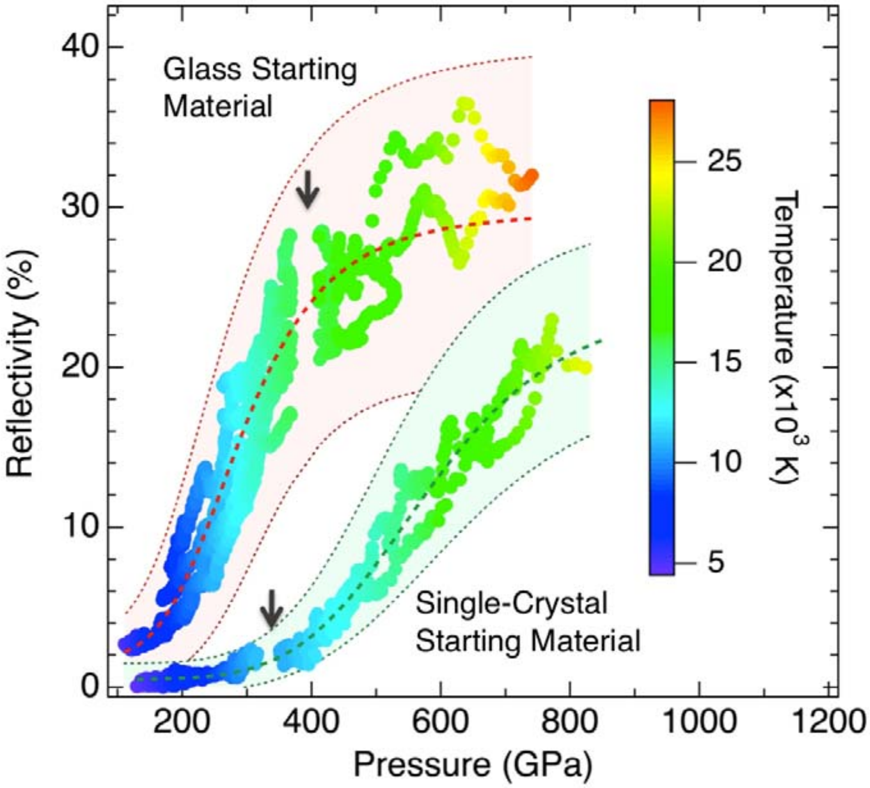

FIG. 3 (Color). Optical reflectivity extracted from velocity interferometry data (532 nm wavelength) documents the onset of metallization: reflectivities exceeding 5-10% indicate a gradual change in bonding character that is predominantly temperature-driven. Onset of metallization is thus distinct from the liquid-liquid phase transition (indicated by grey arrows).

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hindrance allowing compression beyond the equilibrium pressures (hence temperatures) of this phase. At higher pressures, volume contraction across the transition greatly reduces the strain experienced in the high-pressure phase, thereby significantly reducing the Hugoniot temperature. That is, the effect of the large ΔV across the (overdriven) transition is to reduce the observed shock temperature more than the opposing contribution from increasing entropy along the Hugoniot. Though such kinetic hindrance might suggest a glass transition, we find that this is not likely based on comparisons of estimated shock rise-times with available viscosity data for silicate compositions [32].

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