Unveiling the Nature of the Bonded-to-Atomic Transition in Liquid SiO_2 to TPa Pressures

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SiO_2 is an important compound for theory, basic science, and technology, including as a laboratory standard for high-energy-density experiments. As a key constituent of Earth, terrestrial, and even giant planets, the response of SiO_2 to dynamic compression helps to determine (1) how planets form through giant impacts and (2) the high pressure–temperature material properties that control, for example, how the deep interiors of planets evolve.

Laser and magnetically driven experiments and first-principles calculations over the past two decades[1–12] have provided important constraints on the high-temperature phase diagram and properties of SiO_2 and established it as a standard for impedance matching at up to 1.2 TPa. Questions remain, however, about the liquid structure of SiO_2 at extreme conditions,[8,13–15] the understanding of which not only helps to clarify phase transitions and metallization that generally occurs in materials under significant compression but can also shed light on material transport properties (e.g., electrical and thermal conductivity) critical to modeling the dynamics of the magma ocean and magnetic-field generation in early Earth and super-Earth exoplanets, as well as for numerical simulations of giant impacts.

We have performed extensive simulations from first principles and in-depth analysis of the structure, electron density, and thermodynamic properties of liquid SiO_2 to gain insights into the nature of the bonded-to-atomic transition. Our results show that a heat capacity anomaly happens at 2 to 3×10^4 K (1.5 to 2.5 eV) over the pressure range of 0.1 to 1 TPa, coinciding with conditions where the lifetime of Si–O bonds equals 50 fs. This corresponds to bonded-to-atomic liquid transition temperatures that are lower and more sensitive to pressure than previous estimates based on laser-driven Hugoniot measurements (black line with diamonds versus gray dashed curve in Fig. 1). These results render a new bonded-to-atomic boundary of liquid SiO_2 that overlaps with the conditions of interest to giant-impact simulations, which indicates more-complex variations (i.e., a decrease and then an increase with temperatures) in heat capacity than that considered previously. This can rebalance the dissipation of irreversible work into temperature and entropy in events of giant impact, necessitating reconsideration of predictions by simulations that are based on empirical equation-of-state (EOS) models.

Furthermore, our calculated Hugoniots show overall agreement with experimental ones (see Fig. 1) and are similar to previous calculations using similar methods.[4,8,9,14] The discrepancies between theory and experiment in the stishovite temperature–pressure Hugoniot near melting, together with the previously shown inconsistencies at 1.0 to 2.5 TPa, emphasize the need for further development in both numerical simulations and dynamic compression experiments to improve constraints on the phase diagram, EOS, and properties of SiO_2 in regions off the Hugoniots of α-quartz and fused silica and elucidate the exotic behaviors affecting matter at extreme conditions. These include simulations that overcome the increased limitations of pseudopotentials and computational cost for reaching convergence at the high density/temperature conditions or go beyond LDA/GGA (local density approximation/generalized gradient approximation) for the exchange-correlation functional, as well as more in-depth experimental

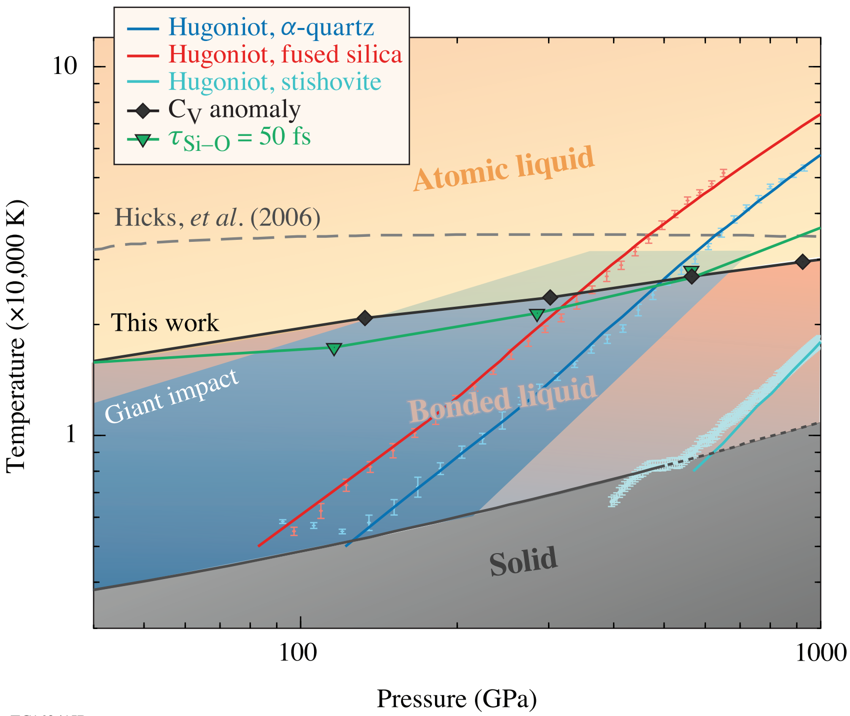

Figure 1
Phase diagram of SiO_2 featuring the bonded-to-atomic liquid transition determined in this work (black curve with diamond symbols) as compared to a previous estimation (Hicks *et al.*,[1] gray dashed curve). Also shown are the conditions for Si–O bond lifetime equaling 50 fs (green line with triangles), Hugoniots from this work (solid curves in red, blue, and turquoise for fused silica, α-quartz, and stishovite, respectively) in comparison to experiments[1,2] (lighter-colored symbols), the melting curve (solid dark-gray curve: measured; dashed dark-gray curve: extrapolated) from Millot *et al.*,[2] and the conditions of interest (blue shaded area) to giant impacts.[16]

studies, currently lacking benchmarking u_s–u_p data for stishovite between 0.2 and 1.2 TPa and relying on pyrometry and a gray-body approximation for temperature estimation.

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