

THE HIGH-PRESSURE, HIGH-TEMPERATURE DENSITY OF PRIMITIVE LUNAR MELTS.

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Introduction: Picritic glass beads, thought to have formed in fire fountaining eruptions, represent the most primitive lunar magmas sampled to date [1,2] and are prime candidates for studies of the petrological and geochemical evolution of the lunar interior. The glasses have a very broad range in titanium content, which can be as high as 16.4 wt% TiO₂. Various researchers suggested that the relatively high density of high-titanium lunar basalts could have made it impossible for them to erupt from their depth of origin without additional external aid such as the presence of volatiles [3,4]. Quantitative models for the transport of lunar picritic glass compositions from source to surface require the availability of accurate estimates of their high-pressure (P), high-temperature (T) densities.

Here we present new molecular dynamics (MD) simulations of the high-pressure, high-temperature density of three molten lunar glass compositions (Apollo 15 Green C with 0.3 wt% TiO₂, Apollo 17 74220 Orange with 9.1 wt% TiO₂, and Apollo 14 Black with 16.4 wt% TiO₂) and provide a synthesis and comparison with earlier calculations and *ex situ* and *in situ* measurements. Our aim is to assess the remaining uncertainties in lunar melt density models, and aid future thermo-chemical models of lunar magmatic differentiation.

Computational methods: Melt densities were calculated using classical molecular dynamics (MD) after Guillot et al. [5,6]. A simple force field is used to describe the silicate melt structure of the main oxide components SiO₂, TiO₂, Al₂O₃, FeO, MgO, CaO, Na₂O, and K₂O - the contributions of the minor components Cr₂O₃ and MnO were not included. For the simulations we used ~1000 atoms, tracked over a typical time scale of 1 ns (corresponding to 10⁶ MD steps).

A series of MD simulations in the isothermal-isobaric (NPT) ensemble were performed to assess melt density evolution with P in the range 0-10 GPa along 1723 K, 2073 K, and 2423 K isotherms. Each composition was first equilibrated at $P=0$ GPa at high T . All data points were independent from one another and have been equilibrated in the NPT ensemble at chosen P - T . NPT ensemble calculations were cross-checked with microcanonical (NVE) ensembles to evaluate statistical uncertainties, using production runs of 0.1–1 ns. Statistical fluctuations during the runs were ± 0.5 GPa for P (when density is fixed), $\Delta T/T = \pm 1\%$ and $\Delta p/p = \pm 1\%$ (when pressure is fixed). Resulting pressure-temperature-density data were fit-

ted using a third-order Birch–Murnaghan equation of state (EOS) to obtain thermoelastic parameters for each composition.

Results: Computed densities are shown as symbols in Fig. 1 below, with best-fit EOS given by solid curves and EOS parameters listed for each composition..

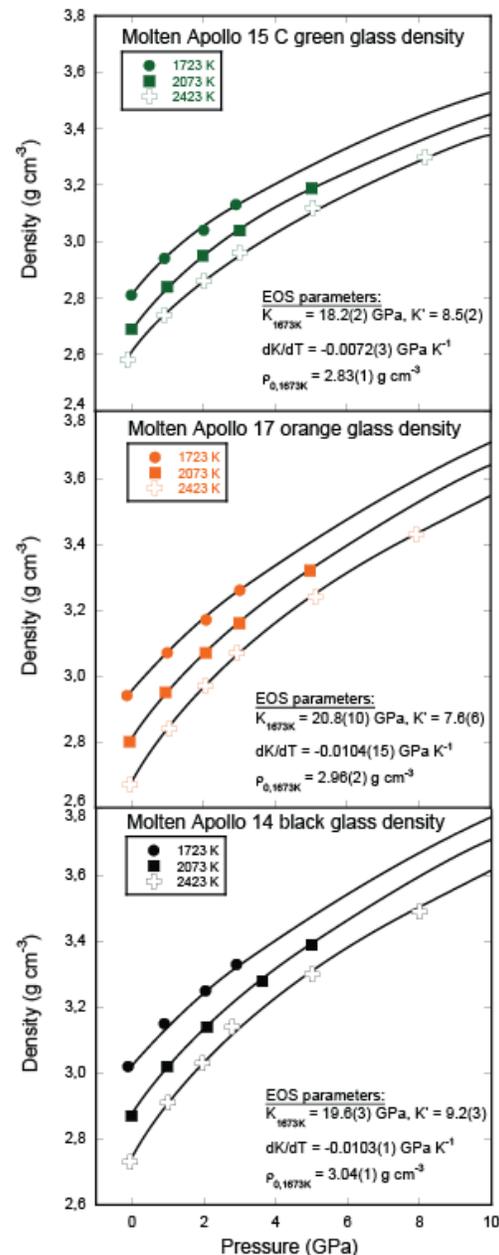


Figure 1. Density calculations of molten Apollo glasses.

The 1 bar densities at 1673 K are 2.83 ± 0.01 , 2.96 ± 0.02 and 3.04 ± 0.01 g cm⁻³ for molten green, orange and black glass respectively. Thermo-elastic parameters vary slightly with composition, with isothermal bulk moduli K_{1673K} , ranging from 18.2 ± 0.2 GPa for the green glass composition, 20.8 ± 1.0 GPa for molten orange glass and 19.6 ± 0.3 GPa for molten black glass at 1673 K. Pressure derivatives, K' were found to be 8.5 ± 0.2 for green, 7.6 ± 0.6 for orange and 9.2 ± 0.3 for the black glass composition. Values for dK/dT are identical for orange and black glass compositions at -0.0104 ± 0.0015 and -0.0103 ± 0.0001 GPa K⁻¹ respectively, while for green glass composition the value is significantly lower at -0.0072 ± 0.0003 GPa K⁻¹.

Comparison with previous data: Fig. 2 shows a comparison between our new results (solid curves including propagated errors) and previously published density determinations using a range of techniques.

Extrapolation from room pressure density models: Delano [7] estimated the densities of molten lunar glass compositions using extrapolations from room-pressure melt density measurements. Comparing his calculated 1 bar liquidus densities to the values obtained here using MD we find that molten green glass values are comparable, whereas orange and black glass values obtained by MD are 1.5 and 1.8% lower, respectively, than the Delano [7] estimates. His calculated EOS parameters are very close to our new results, leading to a nearly identical predicted pressure evolution of melt density for all three compositions (dashed curves in Fig. 2).

Ex situ experimental results: Ex situ high-pressure, high-temperature sink/float experiments were previously performed on synthetic analogues of all three compositions [3,8,9]. Tight constraints on melt densities were obtained at a limited number of pressure-temperature conditions, shown as symbols in Fig. 2. Within the lunar pressure regime these results agree with our MD data to within 1.3% for the green glass composition, 0.7% for the orange glass composition, and 2.8% for the black glass composition.

In situ experimental results: Sakamaki et al. [10] presented the first *in situ* density measurements on a synthetic equivalent of the black glass composition at superliquidus conditions using the synchrotron X-ray absorption technique [11-13], obtaining data at pressures between 0.8 and 4.7 GPa, and temperatures between 1700 and 2100 K. They derived a BMEOS at 1700 K with $K_{1700} = 9.0 \pm 1.2$ GPa, $K' = 16.0 \pm 3.4$ and $dK/dT = -0.0030 \pm 0.0008$ GPa K⁻¹, indicating a significantly more compressible liquid than predicted by our simulations and by the *ex situ* experiments of [3]. Den-

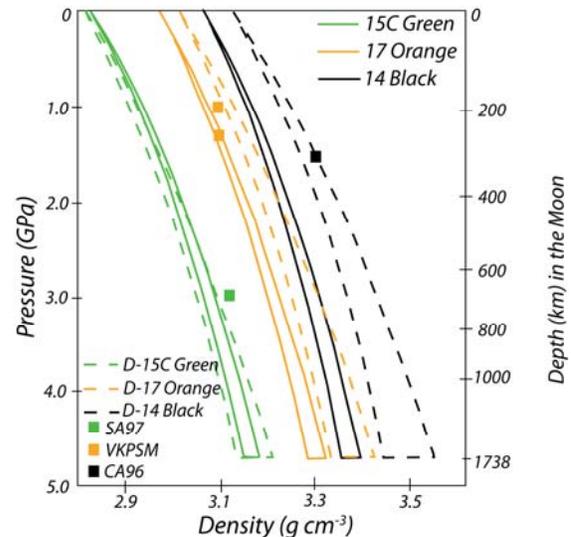


Figure 2. Synthesis of molten lunar glass density measurements. Solid curves: this study; dashed curves: ref.[7]; SA97:ref.[8]; VKPSM:ref.[9]; CA96:ref.[3].

sities obtained by MD are all lower compared to these *in situ* results, with density differences up to 5.9%.

Implications for lunar magma density modeling: Within the lunar *P-T* range, the differences in thermo-elastic parameters obtained using the different methods for both orange and black glass compositions result in only minor differences in predicted densities in the lunar interior. A primary reason for the melt density differences shown in Fig. 2 is related to the 1 bar reference density points. Uncertainties in these values are partly related to uncertainties in the partial molar volume of TiO₂. These uncertainties can be related to the variable coordination states of Ti in silicate melts. Coordination states of both Ti and Fe are currently both unknown for natural picritic lunar magmas. Further reduction of the uncertainties depicted in Fig. 2 requires determination of these parameters.

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