THE EFFECT OF TITANIUM ON LUNAR MAGMA COMPRESSIBILITY AT HIGH PRESSURE

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Introduction: Knowledge of the density, compressibility and other physical properties of magmas at high pressure is required in order to understand the differentiation of planetary interiors. Here we report new experimental data on the effect of TiO_2 on the physical properties of ultramafic mantle melts as represented by the lunar picritic glasses. Lunar picritic glasses are thought to be pristine igneous samples derived directly from the deep lunar interior. The glass beads have distinctive colors that correspond to TiO_2 content. For example, Apollo 14 "black glass" has the highest TiO_2 content with 16.4 wt%, Apollo 17 "orange glass" is intermediate with 9.1 wt% TiO_2, and Apollo 15 "green glass" is lowest with 0.26 wt% [1]. These glasses all have high FeO contents and their melt densities are among the highest found on terrestrial planets. The densest melt of all the samples, and to our knowledge the densest known magma in the solar system, is Apollo 14 black glass with 24.5 wt% FeO and calculated 1-bar liquidus density of ~3.13 gcm^{-3}. These facts led Delano [1] to predict that high-TiO_2 black glass melt would be neutrally buoyant relative to coexisting liquidus olivines and pyroxenes at a depth of approximately 500 km in the lunar mantle. He pointed out that lunar magmas with higher TiO_2 than black glass may be absent from the lunar surface because they were too dense to rise from their mantle source regions. Circone and Agee [2] carried out high pressure sink/float density measurements on molten black glass and confirmed Delano's original idea. They found that molten black glass was the most compressible mantle silicate melt yet studied and that it would be negatively buoyant relative to an olivine-pyroxene source rock at depths >400 km. Thus fire fountain eruptions of black glass magma are an enigma, since this dense melt should sink deeper into lunar mantle from its source at >400 km, and not rise to the surface.

Orange Glass: We recently reported sink/float experiments on molten orange glass up to 8.5 GPa using piston cylinder (PC) and Walker style multi anvil (MA) devices performed in the High Pressure Lab at the University of New Mexico [3]. These data predict a density crossover for the molten orange glass composition with equilibrium orthopyroxene at ~2.8 GPa, equivalent to a depth of ~600 km in the lunar mantle and density of 3.25 gcm^{-3}. This crossover depth is close to the orange glass multiple saturation point, possibly posing constraints on the buoyant rise of molten orange glass. A density crossover with equilibrium olivine is predicted to fall outside the lunar pressure range (>4.7 GPa), indicating that the orange glass is less dense than its equilibrium olivines. We noted that the compression curve for molten orange glass appeared to have a steeper slope, especially above 3 GPa, than that of black glass, suggesting a compositional effect on compressibility. Here we report new additional sink/float experiments that place narrower brackets on orange glass density in this pressure range. We recently observed the floating of garnet crystals with composition Py63.4-Al33.5-Gr2.6 at 8 GPa and 2223K and sinking of corundum crystals at 6 GPa and 2153K. All our sink/float experiments to date are summarized in figure 1.

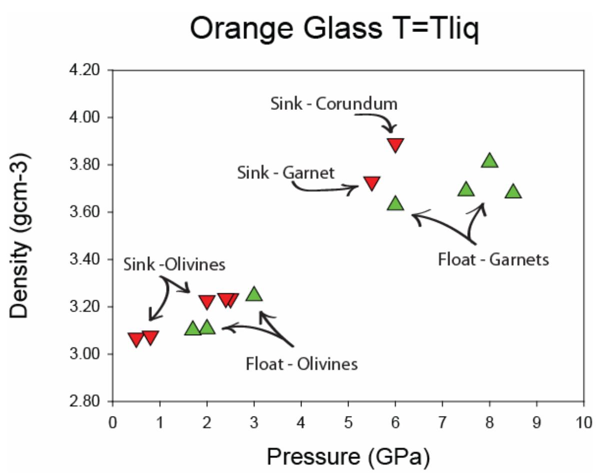

Figure 1. Density brackets for molten orange glass along the liquidus. Red down-triangles represent buoyancy marker sinks, green up-triangles are floats. The buoyancy markers are olivines at lower pressures, and garnets and corundum at higher pressures. The highest experimental temperatures were 2223 K at 8-8.5 GPa and the lowest temperature was 1724 K at 0.5-0.8 GPa. The density of molten orange glass at T=Tliquidus falls between the red and the green triangles. The density is very well constrained up to ~2.5 GPa, while more measurements are needed to tighten the bounds at P>6 GPa (currently underway).

Experimental: The starting material was a reagent mix synthesized by Mike Krawzynski (MIT) and is nearly identical in major element composition to Apollo 17 orange glass. This starting material was packed into a Mo^0 capsule with two, gem quality, density marker spheres; one placed at the top and one at the bottom of the capsule. The sample was brought to target pressure first and then rapidly heated at 250-

400 K per minute to super liquidus temperatures and held for 30-45 s (1720-2225 K, depending on target pressure and orange glass liquidus). See [3] for experimental details.

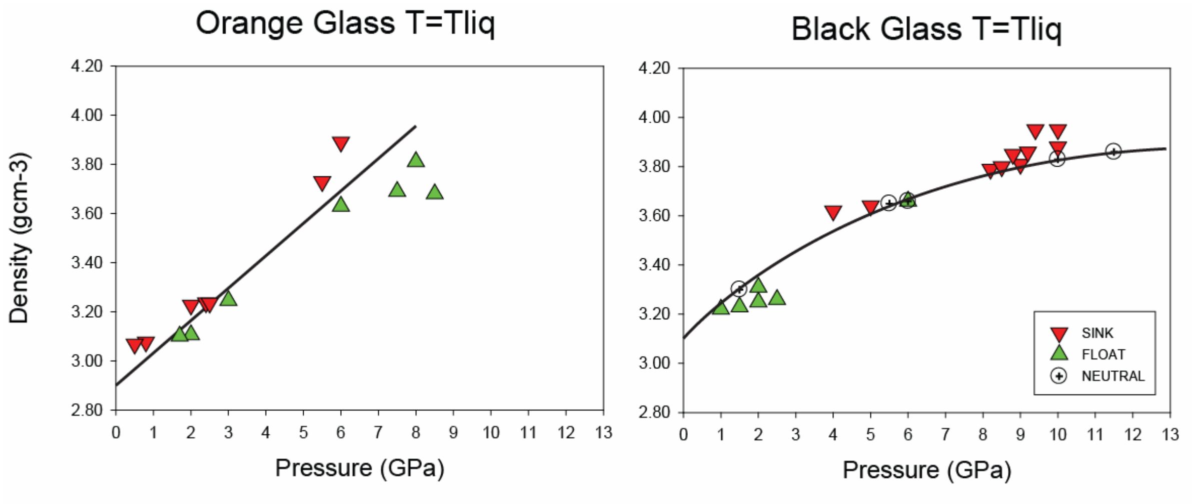

Figure 2. Comparison of high pressure density measurements of molten orange glass (this study and [3]) and molten black glass [2]. The compression curves for the two lunar magmas are markedly different. Orange glass density can be approximated by a linear compression curve, although above 6 GPa curvature may be present.

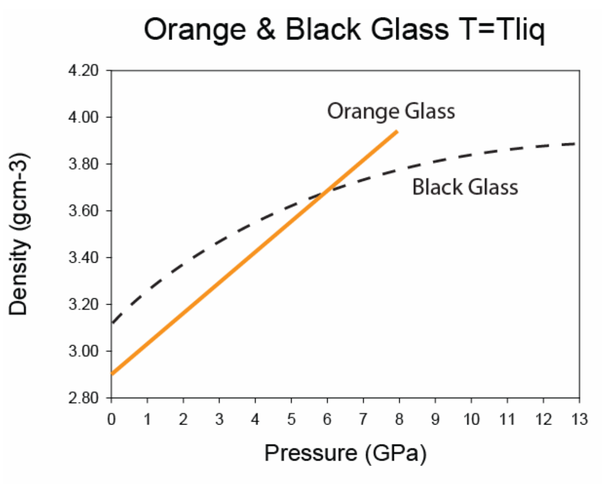

Figure 3. Comparison of compression curves for molten black glass [2] (dashed curve) and orange glass (solid orange line). Note that the molten orange glass becomes denser at around 6 GPa. Although the maximum pressure in the Moon is ~4.7 GPa, higher experimental pressures are important for determination of melt bulk modulus and detecting and revealing such factors as compositional effects on melt compressibility.

Discussion: Figure 2 illustrates the marked difference between compression curves of molten orange glass and black glass. Our latest sink/float observations at 6 and 8 GPa confirm that the orange glass compression curve can be approximated by a straight line at liquidus temperatures, while black glass shows strong decrease in slope with pressure, especially above 3 GPa. In fact, the differences in slope produce a density crossover between molten orange glass and black glass at approximately 6 GPa (figure 3). Why the marked difference between orange and black compression curves? The most likely explanation for the apparent difference in compressibility is that they have different TiO_2 contents which is the biggest compositional difference between orange and black glass. Since the densities of silicate melts are largely governed by the geometrical packing and coordination of their network forming ions, the capacity of Ti^{4+} to shift coordination will strongly affect the densities. Thus it is possible that silicate melts with high TiO_2 contents will show unusual compressibility changes as coordination in the melt shifts to higher values with increasing pressure. Indeed, the pronounced flattening of the molten black glass compression curve at P>3GPa could be reflecting the completion of the coordination change to 6-fold in a large number of Ti-sites. If so, then one would expect to see a compressibility decrease as melt density experiences little or no boost from coordination change with higher compressions. In the case of molten orange glass, with less TiO_2, we see less compression curve flattening, however more experiments in the range 6-12 GPa are required in order to make a full comparison with black glass, as well as experiments on very low TiO_2 melts such as Apollo 15 green glass [4].

References: [1] Delano (1986) *Proc LPSC 16*, D201-212. [2] Circone S. and Agee C. B. (1996) *GCA*, *60*, 2709–2720. [3] van Kan-Parker et al. (2011) *GCA*, *in press*. [4] Smith J. R. and Agee C. B. (1997) *GCA*, *61*, 2139-2145.