# A COMPARISON OF MELT DENSITY AND COMPRESSIBILITY OF THE GREEN, YELLOW, AND ORANGE APOLLO GLASSES AS A FUNCTION OF $TiO_2$ CONTENT.

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**Introduction:** Lunar mare volcanism is hypothesized to have lasted about 2 Ga with the two main episodes of concern for this study occurring between 3.16-3.4 Ga (low and very-low-Ti basalts) and 3.6-3.9 Ga (high-Ti basalts) [1]. Due to their wide range in major-element compositions, particularly $TiO_2$, the mare volcanics are most likely produced by partial melting of a highly differentiated mantle source created in part by crystallization of the lunar magma ocean (LMO) [1]. The eruption products of concern for this study are the lunar glasses which are believed to be the result of rapid quenching of lunar fire fountain eruptions [2]. Found amongst mare basalts, lunar picritic glasses are thought to be pristine igneous samples derived directly from the deep lunar interior making them a prime candidate for experimental studies [2]. The glass beads have distinctive colors that correspond to $TiO_2$ content. For example, the $TiO_2$ content of Apollo 15 green glass is very low with 0.26 wt%, Apollo 14 yellow glass is low with 4.58 wt%, and Apollo 17 orange glass has a high $TiO_2$ content of 9.12 wt% [2]. These glasses all have high FeO and MgO contents, low $Al_2O_3$, CaO, and $Na_2O$ contents, and their 1 bar melt densities are among the highest found on the terrestrial planets. The densest melt of all the samples, and to our knowledge the densest known magma in the Solar System, is the Apollo 14 black glass with 24.5 wt% FeO, 16.4 wt% $TiO_2$ and calculated 1-bar liquidus density of ~3.13 $gcm^{-3}$ [3].

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. Since the lunar glasses are thought to be the most primitive material from the Moon, determining if there is a direct correlation between $TiO_2$ content with density and compressibility will aid in the constantly improving physical models of lunar differentiation [4-6]. The goal of this study is to determine the effect of $TiO_2$ on lunar magma density and compressibility for the green, yellow, and orange Apollo glasses representative of very low, low, and high $TiO_2$ contents, respectively.

**Methods:** *Experimental.* The starting material for the orange glass was a reagent mix synthesized by Mike Krawzynski (MIT) whereas the starting material for the green glass and yellow glass were synthesized by the authors (UNM). These mixes were made to match the major element composition as defined by [2]. For each experiment the starting material is packed into a $Mo^0$ capsule with two mineral spheres, which serve as density markers, placed at the top and bottom. All density markers used are spherical crystals with a diameter of 300-600 µm created in a Bond Air Mill. For the piston cylinder (PC) experiments, forsterite-rich olivine spheres are used whereas garnets are used for the MA experiments. For both techniques, the sample is pressurized and rapidly heated at 200-300 K per minute to super-liquidus temperatures. The experiments are held at the elevated P-T conditions for at least 30 seconds to allow the synthetic powder adequate time to melt and for the spheres to be driven up or down in the capsule by buoyancy forces. Experiments are limited to these short run durations to prevent dissolution of the spheres into the melt, which would drive the melt composition from the target composition being investigated. The sample is quenched by shutting off the power to the furnace and allowing the run to decompress gradually. The average rate of cooling is approximately 95°/s. See [7] for full experimental details.

*Analytical.* The run products are set in one-inch diameter mounts using Petropoxy and allowed to harden over night. They are ground using various grit sizes of sand paper and polished to 0.3 µm to reveal the final location of the spheres. However, the result of each experiment does not provide a direct measurement of the density of the liquid at the experimental conditions but rather gives an open ended bracket on the density. The precise density of the liquid is best defined by a neutral buoyancy bracketed by a sink and float at slightly lower and higher pressures, respectively. The densities of the mineral markers in each experiment are calculated using the Birch Murnaghan equations of state. All polished run products, including quenched materials and mineral spheres, are carbon coated and analyzed by electron probe microanalysis (EPMA) at the University of New Mexico with an accelerating voltage of 15 kV and beam current of 20 nA. A broad beam (10-20 µm) is used for glass analyses whereas a focused beam (~1 µm) is used for the analyses of the mineral density markers.

**Results:** Here we report new sink/float experiments for the green and orange lunar glasses. Figures 1 and 2 show the current experimental data for these two compositions. For the green glass, a density bracket has been constructed with a sink and float of a garnet sphere with composition $Py_{49}Al_{31}Gr_{18}$ at 7 and 9 GPa, respectively. This bracket is further constrained with a sink of a garnet sphere with composition $Py_{63}Al_{24}Gr_{12}$ at 8.5 GPa. Lower pressure data is from [8]. We also recently observed the sinking of garnet spheres with a composition of $Py_{35}Al_{60}Gr_5$ and $Py_{49}Al_{31}Gr_{18}$ at 8 and 10 GPa, respectively in the orange glass further constraining the compression curve. Lower pressure data is from [7].

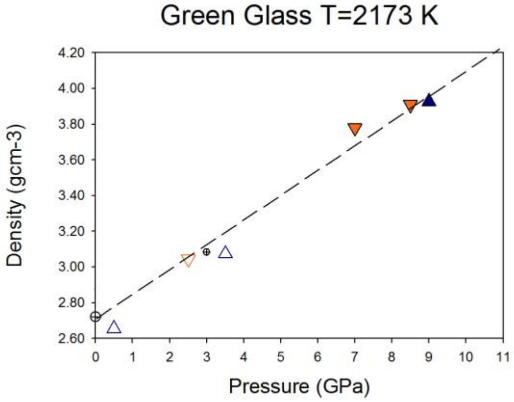

**Figure 1. Graphical representation of experimental data for the Apollo 15 green glass.** The orange triangles are sinks, the circles are neutral buoyancies, and the blue triangles are floats. The empty symbols are from [3] whereas the filled symbols are from this study. More data is needed to place better constraints on the density of the green glass particularly between 4 and 8 GPa. The black dotted line shows the ideal compression curve for this composition. This line shows there is no compression curve flattening up to 9 GPa for the green glass.

**Discussion:** Currently, the green glass compression curve can be estimated by a straight line. More experimental data is needed to place better constraints on this line. Previous experimental data has concluded the compression curve for the orange glass can be approximated by a straight line [7, 9]. However, the new experimental data reported here at higher pressures indicate the orange glass density curve is best estimated by a Burch-Murnaghan equation of state with K' = 7.6, K = 9.5 GPa, when T = 2173 K. Figure 3 shows a comparison of the density studies done on the lunar glasses to date [3, 7-9]. The difference in compressibility between the green, yellow, orange, and black glasses is attributed to their vastly different $TiO_2$ contents from 0.24-16.4 wt%. Work is ongoing to further investigate this interpretation. Previous studies have shown that the density of silicate melts is largely governed by the geometric packing and coordination of their network forming ions [10]. Furthermore, the capacity of $Ti^{4+}$ to shift coordination from 4-fold through 6-fold has a large impact on melt density [10]. Therefore, the lack of compression curve flattening in the green and yellow glasses compared to the slight compression curve flattening in the orange glass and increased flattening of the black glass compression curve around 3 GPa could be due to the melt density experiencing little or no boost from coordination change with higher pressures. This is also seen above 8 GPa, where the green glass is the densest and the black glass is the least dense with the yellow and orange glasses falling in between in order of $TiO_2$ content.

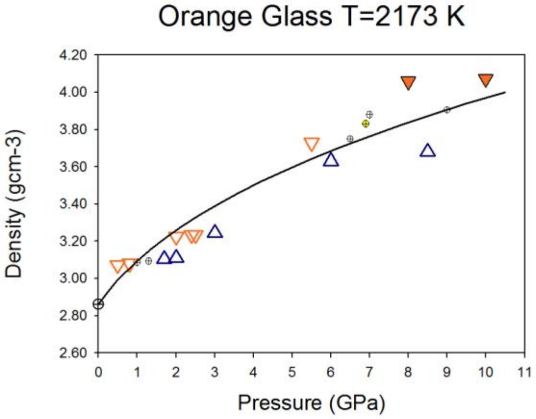

**Figure 2. Graphical representation of experimental data for the Apollo 17 orange glass.** Flattening of the orange glass compression curve is observed around 7-8 GPa compared with the green glass in Figure 1 which displays no compression curve flattening. Symbols are the same as in Figure 1. The empty symbols are from [4] whereas the filled symbols are from this study. The black line is the best fit using the Birch-Murnaghan equation of state with parameters as discussed in the text.

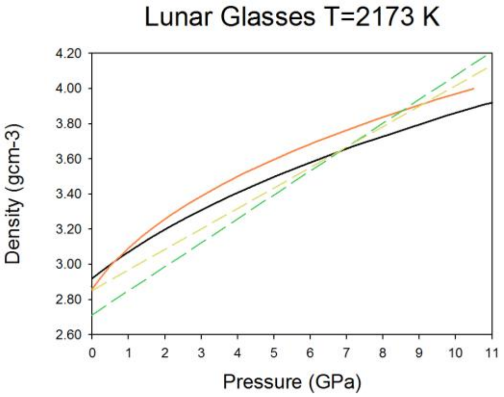

**Figure 3. Comparison of compression curves for molten green, yellow, orange, and black [3] glass.** The green glass becomes denser than the black around 7 GPa where there is also a crossover with the yellow glass. The yellow line is preliminary data for the yellow glass based on a sink and neutral buoyancy of $Fo_{100}$ spheres at 1 and 2 GPa, respectively. The orange glass becomes denser than the black glass almost immediately. The black line is the best fit for the black glass using the Birch-Murnaghan equation of state with K'=5.2, K=17.3 GPa, and T=2173 K. The green and orange lines correspond to the lines in Figures 1 and 2.

**References:** [1] Shearer et al. (2006) RIMG, 60, 365-518 [2] Delano, J. W. (1986) Proc. Lunar Planet. Sci. Conf., 17, D201-D213. [3] Circone S. and C. B. Agee (1996) GCA, 60, 2709-2720. [4] Mysen, B. O. (1987) The Geochemical Society, Special Publication No. 1. 357-399. [5] Longhi, J. (1980) Proc. Lunar Planet. Sci. Conf, 11, 289-315. [6] Warren, P. H. (1992) EPSL, 112, 101-116. [7] van Kan Parker et al. (2011) GCA 75, 1161-1172. [8] Smith J.R. and Agee C.B. (1997) GCA, 61, 2139-2145. [9] Vander Kaaden et al. (2011) LPSC XXXXII, Abstract #1295. [10] Liu Q. and Lange R. A. (2001) *GCA*, 65(14), 2379-2393.