THE EFFECT OF CO$_2$ ON DENSITY OF MOLTEN APOLLO 14 BLACK GLASS AT HIGH PRESSURE.

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Introduction: Knowledge of the density, compressibility and other physical properties of magmas at high pressure are required in order to understand the differentiation of the lunar interior. We present here the first experiments to determine the effect of dissolved volatiles 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. As probes of the lunar interior, picrite glasses are unique in that they are quenched near-primary liquids that originated at greater depths in the Moon compared to dominantly crystalline mare basalts. They are found as beads in lunar soils and are likely formed during rapid cooling and quenching of fire fountain eruptions on the Moon, probably during the period of peak lunar magmatism, and their compositions span the range of nearly all lunar basalts [1]. 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 8.6 wt% TiO$_2$, and Apollo 15 "green glass" is lowest with 0.26 wt% [2]. These glasses all have high FeO contents and their melt densities are among 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 [3] of ~3.13 gcm^{-3}. This fact led Delano [4] 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 [5] carried out high pressure sink/float density measurements on molten black glass and confirmed Delano's original idea. They found that molten black glass is 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. On the other hand, buoyant rise could be explained by the presence of a density-lowering propellant such as volatile compounds in the black glass source region. Volatiles that include carbon and sulfur compounds,

H$_2$O, Cl, and F occur in extremely low concentration levels in lunar glasses however it is conceivable that these have been efficiently degassed and lost to space during eruption. Indeed, studies by Dixon [6] and others show a strong positive pressure dependence on the solubility of H$_2$O and CO$_2$ in terrestrial magmas. These studies indicate that CO$_2$ is significantly more volatile than H$_2$O, hence recent detection of trace amounts of water in lunar glasses [7] encourages the notion that CO$_2$ or CO could also have been present in the source region, but was completely lost during decompression degassing. Fogel and Rutherford [8] proposed that oxidation of a modest amount of graphite in the lunar basalt source region through a reaction such as FeO + C → Fe + CO could produce the required fire fountain propellant.

Our understanding of the solubility limits of CO, CO$_2$, or CO$_3^{-2}$ in lunar melts is at best fragmentary. We are unaware of any data on the solubility of carbon dioxide in lunar basalt compositions at high pressure, and the terrestrial database contains nothing comparable to high-Ti compositions such as black glass. Therefore we are carrying out a systematic experimental study of the effect of pressure on the solubility of carbon in a synthetic Apollo 14 black glass melt. The experiments also allow the determination of the effect of carbon solubility on the density of the molten black glass material, and work is underway up to pressures that include the entire lunar interior (~4.7 GPa).
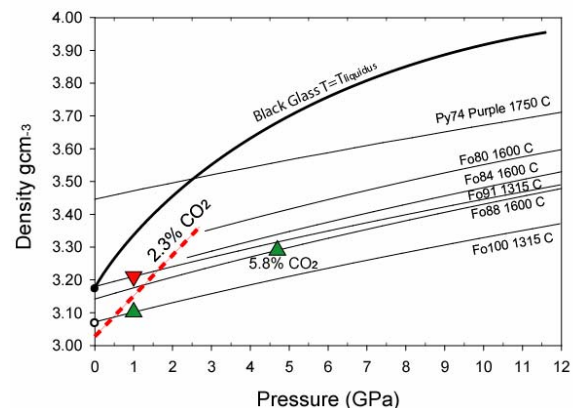

Figure 1. The effect of CO$_2$ on density of molten black glass as a function of pressure (determined by sink/float bracket). Bold curve is the compression of molten black glass from Circone and Agee [5]. Green up-arrows indicate "float" and red down-arrow indicate "sink" of mineral marker spheres in carbonated black glass. Shown also is an array of mineral marker compression curves suitable for bracketing the density of carbonate black glass in planned experiments.

Experimental: Experiments were performed in the piston-cylinder apparatus (Quickpress) and Walker-style multi-anvil device at the Institute of Meteoritics, University of New Mexico. The density of molten black glass was determined using the sink/float technique [9]. Starting materials were mixtures of reagent grade oxide powders, with 5 wt% CO_2 added in the form of $CaCO_3$. Figure 1 shows our initial results in which we observed the floating of Fo100 spheres and sinking of Fo91 spheres at 1 GPa and 1315ºC, and the floating of Fo88 spheres at 4.7 GPa and 1600ºC. Grinding and sectioning of the run products revealed the final position of the mineral buoyancy markers. In the 1 GPa experiments we also observed the presence of a quenched CO_2 fluid phase coexisting with the silicate melt. Electron microprobe analyses of the 1 GPa run products confirmed supersaturation conditions and detected 2.4±.2 and 2.2±0.2 wt% CO_2 (total) dissolved in the quench silicate melts respectively. We observed no CO_2 fluid phase in the 4.7 GPa run product and electron microprobe analyses showed 5.8±0.9 wt% CO_2 (total) dissolved in the quench silicate melt. Thus these experiments give the effect of pressure on both density of carbonated silicate melt and the solubility of CO_2 in silicate melt. The sink and float at 1 GPa and 1315ºC, bracket the density of experimental carbonated molten black glass at 3.16±0.6 gcm^{-3}, compared to 3.31 gcm^{-3} for the non-carbonated black glass at the same conditions calculated from Circone and Agee [5].

The Effect of Pressure on CO_2 in Molten Black Glass: Up to now, no data existed on the solubility of CO_2 in high-TiO_2 silicate melts or on the density of carbonated high-TiO_2 silicate melts at any pressure. Our preliminary results here show that CO_2 decreases the density of molten black glass as expected from earlier work on carbonated low-TiO_2 silicate melts. How this density difference changes with pressure requires additional experiments which are currently underway. Our data show evidence for a relatively high solubility of CO_2 in black glass even at modest pressure (1 GPa). This is agreement with work on low silica melts [6, 10], however more work is needed to better understand the role of Ti^{+4} on CO_2 solubility and on melt polymerization.

Buoyancy of Carbonated Magma in the Lunar Mantle: Figure 2 illustrates that the density cross-over between molten black glass and a proposed lunar mantle density-depth profile occurs at a pressure of 0.9 GPa or ~200 km in the Moon. This pressure is significantly less than the experimentally determined olivine-pyroxene-melt multiple saturation point, which defines the minimum depth of origin for black glass by partial melting of its mantle source region [11]. Thus a simple, single-stage melting scenario produces a black

glass magma that is denser than its surrounding mantle. Figure 2 shows that addition of CO_2 significantly lowers the molten black glass density, which provides a mechanism for buoyant rise and eruption of this magma as observed in recovered spherules from the Apollo 14 landing site.
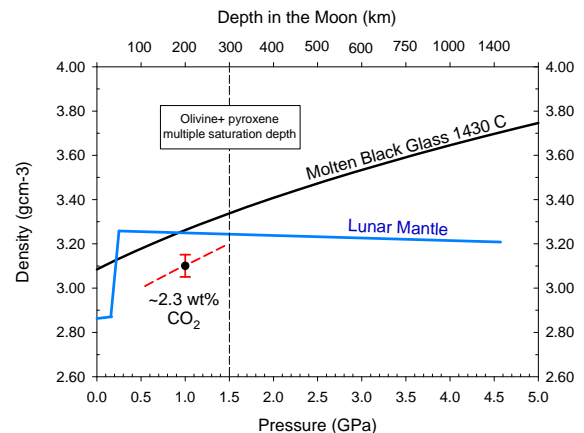

Figure 2. Density of molten black glass as a function of pressure from [5] compared to a density-depth profile of the lunar mantle from [12]. Molten black glass with 2.3 wt% CO_2 is shown as the data point with red error bars.

Conclusions: The results presented here give new data on (1) the carbon carrying capacity of high-Ti melts in the deep lunar interior, (2) the level of neutral buoyancy in the lunar interior for CO_2-bearing molten black glass, and (3) the effect of pressure on the partial molar volume of CO_2 in a high-Ti silicate melt. After this first phase of study, which will include more sink/float measurements at multiple pressures, we envisage a complementary campaign to determine the effects of H_2O, F, and Cl on molten black glass density and compressibility. We will also undertake comparison experiments on orange and green glass [13] compositions to pin down the effect of volatiles on intermediate and low Ti lunar magmas.

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