THE INFLUENCE OF VARIABLE TiO₂ CONTENTS AND OXYGEN FUGACITY ON THE TEMPERATURES AND DEPTHS OF MELT GENERATION OF LUNAR HIGH-Ti ULTRAMAFIC GLASSES. M. E. Guenther¹, S. M. Brown¹ and T. L. Grove¹, Massachusetts Institute of Technology, Department of Earth, Atmospheric and Planetary Science, 77 Mass Ave, 02139, MA (megang@mit.edu, brownsm@mit.edu, tlgrove@mit.edu).

Introduction: The lunar high-TiO₂ ultramafic glasses are among the most unusual ultramafic magmas found in our solar system [1]. With FeO + MgO at 30 - 37 wt. %, TiO₂ from 9 - 16.4 wt. % and SiO₂ at 34 - 37 wt. % these exotic glasses erupted from lunar fire fountains at temperatures between 1350 and 1500 °C. They are found distributed in lunar regolith at all of the Apollo landing sites. They are generally thought to represent melting of a lunar magma ocean cumulate source region that contained a late-stage cumulate mineral containing high TiO₂; possibly ilmenite. Previous experimental studies have determined the high-pressure, high-temperature near liquidus phase equilibria [2,3]. Here we report new experimental constraints on the high-pressure near-liquidus phase relations for the Apollo 14 Black (14B, 16.4 wt. % TiO₂), the Apollo 15 Red (15R, 13.8 wt. % TiO₂) and the Apollo 17 Orange (17O, 9.0 wt. % TiO₂) ultramafic glasses. Experiments by Krawczynski and Grove [3] showed that the near-liquidus, high-pressure phase relations of lunar high- and moderate-Ti ultramafic glasses were very sensitive to the sample container used (iron vs. graphite capsules). Krawczynski and Grove [3] quantified the effect on oxygen fugacity (fO₂) imposed by iron capsule vs. graphite containers. Iron capsules fix fO₂ at iron-wüstite-2, (IW–2), and graphite capsules fix fO₂ at IW+2. These different fO₂ conditions strongly influence the pressure and temperature of phase appearance. The major effect is to stabilize olivine as the liquidus phase to higher pressures, moving the point where the liquid is multiply saturated with olivine (oliv) + orthopyroxene (opx) to higher pressure and temperature. We have redone and refined the phase relations for the 14B, 15R and 17O glasses in both iron and graphite. The justification for revisiting these phase relation is that earlier studies were carried out using only one capsule material (e.g., graphite 14B [2]) or the higher pressure liquidus phase relations were not explored in sufficient detail [3] to locate the oliv + opx saturation point in pressure – temperature space.

Experiments: High-pressure experiments (1.4 to 4.0 GPa) were performed in a 0.5” piston cylinder device [5] using iron and graphite capsules. The starting materials were the same as those used by our MIT laboratory in previous experimental studies on these three glass compositions [2,3]. Experimental procedures are similar to those described in [3,4]. Mineral and quenched melt compositions were analyzed using methods discussed in [3,4] using the MIT JEOL 8200 Superprobe. For all the compositions we reproduced the pressure-temperature of oliv + opx multiple saturation in both iron and graphite capsules.

Effects of fO₂ on Phase Equilibria: For the Apollo 14B glass the oliv + opx multiple saturation point is at 1420 °C at 1.4 GPa in graphite capsules and 1530 °C and 4 GPa in iron capsules. For the Apollo 15R glass multiple saturation with oliv + opx occurs at 1350 °C at 1.2 GPa in graphite capsules and 1490 °C and 2.8 GPa in iron capsules. The Apollo 17O glass is multiple saturated with oliv + opx at 1530 °C at 2.5 GPa in graphite capsules and 1570 °C and 3.3 GPa in iron capsules. Figure 1 summarizes the change in multiple saturation pressure and temperature for these three high-TiO₂ glasses and include the change in multiple saturation pressure found by Brown and Grove [4] in the intermediate TiO₂ Apollo 14 Yellow glass (14Y, 4.5 wt. % TiO₂). Initially [3] proposed that the change in multiple saturation point pressure with changing fO₂ (AMSP) might be most sensitively controlled by melt TiO₂ content which, in turn, might be influencing speciation of Fe and Mg in the melt. This effect is to make the melt more olivine-normative at the low fO₂ imposed by the iron capsule. While the effect of TiO₂ content on AMSP is clearly an important influence with ΔMSP = 2.6 GPa for the 14B glass at 16.4 wt. % TiO₂, and ΔMSP = 1.6 GPa for the 15R glass at 13.8 wt. % TiO₂, the effect is not a simple linear function of TiO₂ content as the 17O at 9 wt. % TiO₂ has a ΔMSP = 0.8 GPa and the 14Y at 4.5 wt. % TiO₂ has a ΔMSP = 0.6 GPa.

In an effort to systematically explore the effect of fO₂ and melt TiO₂ content, Brown and Grove [4] proposed that the effect of fO₂ in changing the multiple saturation pressure was to create an armalcolite-like melt component through an exchange reaction in the melt:
\[ \text{Mg}_{0.5}\text{Ti}_{1.5}^{4+}\text{Ti}_{0.5}^{3+}\text{O}_5 + \text{FeO} = \text{Fe}_{0.5}\text{Ti}_{1.5}^{4+}\text{Ti}_{0.5}^{3+}\text{O}_5 + \text{MgO} \]
We are currently exploring this melt exchange reaction now that we have quantitative constraints on the influence of variable $f_{O_2}$ on the phase equilibria for these four lunar glass compositions. Other trivalent cations in the melt (e.g. Cr$^{3+}$ and Al$^{3+}$) could also play a role in stabilizing this melt component.

Figure 1. Changes in the pressure and temperature of olivine + orthopyroxene multiple saturation for high-TiO$_2$ ultramafic glasses. Intermediate TiO$_2$ Apollo 14 Yellow glass data from [4]. Circles indicate $f_{O_2}$ imposed by graphite capsules. Squares indicate $f_{O_2}$ imposed by iron capsules.

Depth of origin of high-Ti glasses and late stage cumulate overturn: Late stage lunar mantle overturn is the expected result of lunar magma ocean solidification [6]. The high-TiO$_2$ late stage cumulates of lunar magma ocean solidification would have formed at shallow depths (50-60 km, [7]). To explain the multiple saturation depths of the high TiO$_2$ lunar ultramafic glasses therefore requires that these high-TiO$_2$ cumulates sank into the lunar interior where remelting and mixing of the melts of diverse cumulate components gave rise to the lunar ultramafic magmas. If the $f_{O_2}$ values of these high TiO$_2$ ultramafic magma source regions were near metal saturation, then the depth of melting could be very high > 900 km. This implies a significant overturn and stirring event that delivered the diverse cumulate components to great depths.