

**EXPERIMENTAL INVESTIGATION OF  $fO_2$  EFFECTS ON APOLLO 17 ORANGE GLASS PHASE EQUILIBRIA.** M. J. Krawczynski<sup>1</sup> and T. L. Grove<sup>1</sup>, <sup>1</sup>Massachusetts Institute of Technology, Dept. of Earth, Atm. And Planetary Sciences. Cambridge, MA 02139 ([kraw@mit.edu](mailto:kraw@mit.edu), [tlgrove@mit.edu](mailto:tlgrove@mit.edu)).

**Introduction:** The Apollo 17 orange glass represents one of the high-titanium (hi-Ti) compositions (9.1 wt %  $TiO_2$ ) in the spectrum of pristine ultramafic glasses returned from the moon [1]. The hi-Ti ultramafic glasses provide us with evidence of lunar mantle processes that led to the melting of magma ocean cumulates nearly one billion years after the magma ocean solidified. Estimates of two phase multiple saturation points have been used to constrain the depth, temperature, and melting processes that produce hi-Ti glasses and thus understand the nature of magma ocean processes.

Green et al. [2] investigated the high-pressure phase relations of the Apollo 17 orange glass (17O) using mild steel capsules, and determined the minimum pressure of olivine + orthopyroxene (oliv + opx) multiple saturation on the liquidus at about 2.1 GPa.

There are several reasons to revisit the phase equilibria of the 17O glass. The run times of Green et al. [2] (5 mins – 1 hour) are too short to ensure equilibrium has been reached. In addition the carbon in mild steel causes changes to the silicate melt bulk composition of an experiment by reducing FeO to Fe-metal. This would lead to an underestimate of the oliv + opx multiple saturation pressure. Furthermore, the study of Green et al. [2] does not report any information on pressure calibration or pressurization techniques [3]. Lastly, and perhaps the most important reason, the high amount of  $TiO_2$  and FeO in the hi-Ti magmas also make the phase relations more sensitive to changes in the oxidation state of the source region. We have previously investigated this effect in the Apollo 15 red glass [4].

**Experimental Techniques:** Experiments were carried out in a piston cylinder apparatus using both graphite and spec-pure Fe-metal capsules. The starting material is a mixture of synthetic oxides, combined in correct proportions to recreate the bulk composition of 17O [1] and conditioned at iron-wüstite (IW) oxygen fugacity conditions. It has previously been shown that experiments in Fe-metal capsules buffer at a lower oxygen fugacity (IW-2) than that of graphite capsules (IW+1.2) [4].

**Phase equilibria of orange glass:** The graphite capsule experiments are multiply saturated with olivine and orthopyroxene on the liquidus at a minimum pressure of 2.5 GPa (Fig. 1). This pressure corresponds to a depth of ~475 km in the moon, and is deeper than that predicted by Green et al. [2]. Ti-rich chromite also appears ~60 °C below the liquidus, and none of

our experiments have reached saturation with ilmenite or armalcolite.

The Fe-metal capsule experiments are multiply saturated with oliv + opx on the liquidus at a pressure of 3.0 GPa (Fig. 2), which corresponds to a lunar depth of ~590 km. This is the deepest multiple saturation point found for any of the hi-Ti glasses. Orthopyroxene reacts out with decreasing temperature, and is replaced by a subcalcic augite (cpx). At higher pressures opx and cpx appear to both be liquidus phases, which is consistent with the Green et al. [2] results. We are currently investigating the appearance of garnet and other Ti-rich phases.

**Discussion:** The difference in multiple saturation point pressure ( $\Delta MS$ ) between the low  $fO_2$  and high  $fO_2$  experiments on 17O is ~0.5 GPa. This translates to a 100 km depth difference in the moon. This difference is smaller than that found in the Apollo 15 red glass (15R,  $\Delta MS$  ~0.75 GPa) [4]. However, even the high  $fO_2$  experiments on 17O produce an absolute depth of a multiply saturated liquidus that is deeper than the low  $fO_2$  Apollo 15 red glass experiments [4].

The melt species most sensitive to changes in  $fO_2$  are  $Ti^{4+}/Ti^{3+}$  and  $Fe^{3+}/Fe^{2+}/Fe^0$ . 17O and 15R have almost identical FeO\* contents, therefore we infer that the  $\Delta MS$  difference between the Apollo 15 red and Apollo 17 orange glasses is due mainly to differences in the  $TiO_2$  content (15R has 35% more  $TiO_2$  than 17O). Furthermore, there is almost no  $Fe^{3+}$  in our experiments and the solubility of  $Fe^0$  in silicate melt is also very small. This is consistent with the oxidation state of Ti exerting a larger control on phase equilibria than Fe. This is a testable conclusion, as we would predict that the Apollo 14 black glass would have the highest  $\Delta MS$ , and also that the saturation of ilmenite (a  $Ti^{4+}$  bearing phase) will be a strong function of  $fO_2$ .

**Origin of the orange glass:** The experiments we are conducting in Fe-metal and graphite capsules may represent the extremes in  $fO_2$  conditions present in the lunar mantle. For the orange glass source region,  $fO_2$  is estimated to lie in between these two end-member states at about  $\Delta IW$ -0.6 [5,6]. This leads us to conclude that an appropriate multiple saturation depth would be between 475-590 km. Even at the shallowest depths of our results, a 475 km depth of origin is unlikely because melts as Ti-rich as 17O are so compressible, that they could not buoyantly ascend, because this multiple saturation depth is deeper than the liquid-crystal density cross-over of 400 km as determined by Agee [7]. Thus, the 17O glass should not be eruptible

on the lunar surface, but should instead sink into the deep lunar mantle. The high temperature of the orange glass (the highest of all lunar hi-Ti glasses, see fig. 1 and 2), and the distance it must traverse through the shallow lunar mantle make assimilation an unavoidable consequence. The negative buoyancy and extreme temperatures in addition to the lack of any Ti-rich phase near the liquidus lead us to conclude that the orange glass is most likely the end product of polybaric melting and assimilation of magma ocean cumulates, and that interaction with and assimilation of a Ti-rich phase occurred at shallower depths than initial magma generation.

Sato M. (1976) *PLSC7*, 1323-1344. [6] M. Nicolis pers. comm. [7] Agee C. (1998) *PEPI*, 107, 63-74.

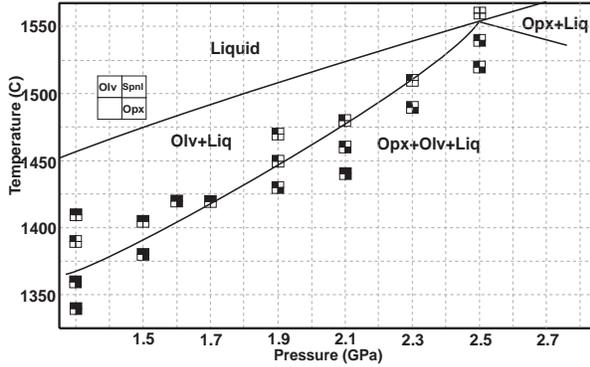


Figure 1: Phase diagram for graphite capsule experiments on the Apollo 17 orange glass. Note that even in our more oxidizing environment, the multiple saturation point is higher than that of [2].

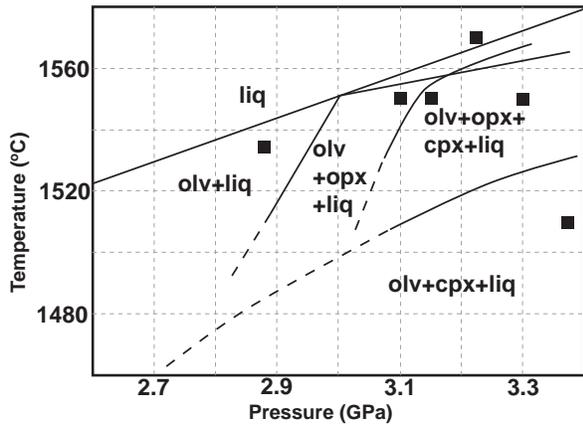


Figure 2: Phase diagram for spec-pure Fe-metal capsule experiments with Apollo 17 orange glass starting material. Oliv + opx saturation on the liquidus is about 3.0 GPa.

**References:** [1] Delano J.W. (1986) *JGR*, 91, D201-D213. [2] Green D.H. et al. (1975) *PLSC6*, 871-893. [3] Johannes et al. (1971) *CMP*, 32, 24-38. [4] Grove T.L. et al. (2007) *LPS XXXVIII*, #1236. [5]