ORIGIN OF THE APOLLO 14 BLACK GLASSES: NEW EXPERIMENTAL CONSTRAINTS ON THE INFLUENCE OF VARIABLE OXYGEN FUGACITY ON THE DEPTH OF MULTIPLE SATURATION AND IMPLICATIONS FOR LATE-STAGE MAGMA OCEAN CUMULATE OVERTURN.

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Introduction: The lunar ultramafic glasses show extraordinary compositional variability ranging from 0.25 to 16.4 wt. % TiO_2 [1]. High pressure experimental studies on the high-Ti end member, the Apollo 14 black glass, were performed by [2] using graphite capsules as sample containers. Subsequently, experiments by [3, 4, 5] 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). Using an iron capsule instead of a graphite container imposes very different oxygen fugacity (f_{O2}); iron-wüstite-2, (IW–2) in iron, and IW+2 in graphite. These different f_{O2} conditions influence the pressure and temperature of phase appearances. 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. Here we report phase equilibrium experiments in iron capsules to explore the influence of variable f_{O2} on the Apollo 14 black glass.

Experiments: High pressure experiments (1.4 to 3.7 GPa) were performed in a 0.5" piston cylinder device [6] using iron and graphite capsules. The Apollo 14 black glass starting material was the same as that used by [2]. Experimental procedures are similar to those described in [4, 5]. Mineral and quenched melt compositions were analyzed using methods discussed in [4, 5] using the MIT JEOL 8200 Superprobe. Figure 1 shows the experimental results from this study (right) and the work of Wagner and Grove (left) [2]. We repeated two experiments in graphite near the conditions of multiple saturation reported by [2] and the same phase assemblage was obtained. The phase relations in graphite capsules (as reported in [2]) show oliv + spinel (sp) as liquidus phases at pressures below 1.4 GPa, multiply saturated liquids (oliv + opx + sp) at 1.4 and 1.7 GPa, and then opx + sp as liquidus phases at 2.2 GPa.

The phase relations of the Apollo 14 black glass composition are extremely sensitive to the oxidation state imposed by the sample container. The effects of

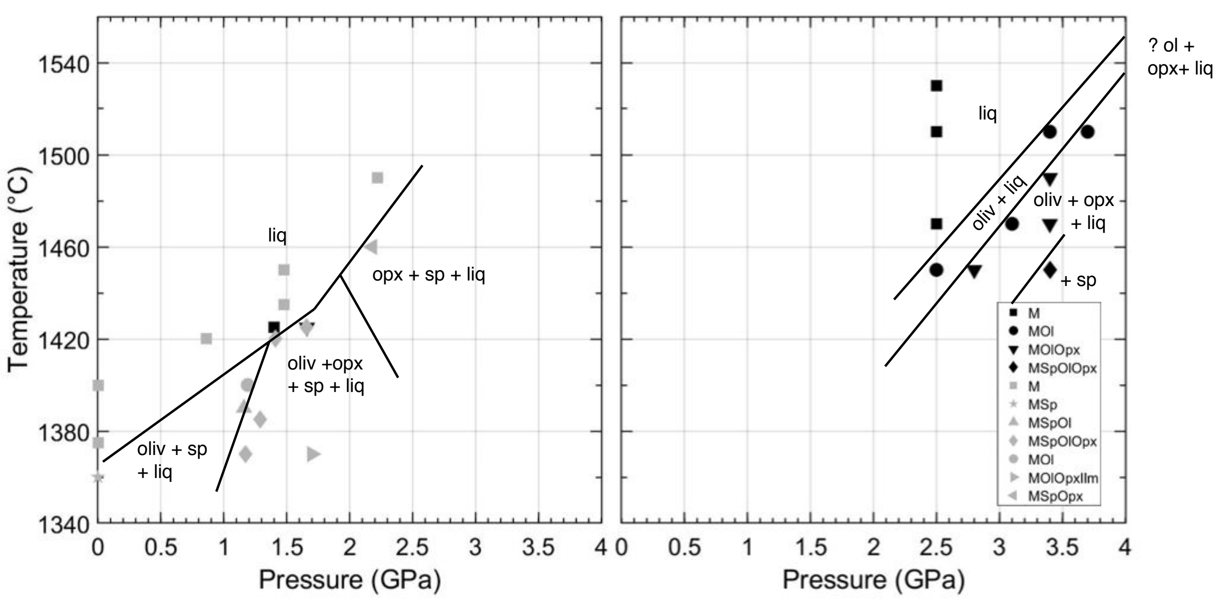

Figure 1. Ap 14 black glass experiments in graphite (left) and iron (right) capsules. Legend: M = liq, MOl = liq + oliv, MOlOpx = liq + oliv + opx, MSpOlOpx = liq + sp + oliv + opx, MSpOpx = liq + sp + opx, Ilm = + ilmenite. Gray symbols = study [2], Black symbols = this study.

decreasing f_{O2} imposed by the iron capsule (Figure 1, right) are to increase the oliv liquidus volume up to the maximum pressure investigated (3.7 GPa) and to remove Cr-spinel from the liquidus. At this pressure a small oliv liquidus phase volume is present and oliv + opx appear ~ 20 ^{o}C below the liquidus. We infer that the oliv + opx multiple saturation point will occur at 4 GPa and ~1550 ^{o}C. Experiments are currently in progress to determine the multiple saturation pressure.

Effects of f_{O2} on Phase Equilibria: The first realization that the capsule material enclosing the lunar glass sample might influence phase relations came when Krawczynski and Grove [4] carried out melting experiments on the Apollo 14 red glass and obtained multiple saturation with oliv and opx at pressures much lower than those obtained by Delano [3] in his iron capsule experiments. This led to the realization that the f_{O2} imposed by the capsule must be changing the species present in the melt, and thereby affecting the phase assemblage that is stable at a given temperature and pressure. Moreover, there is no observed effect of f_{O2} on the high pressure phase relations obtained with low-Ti ultramafic glasses equilibrated in graphite and iron capsules [7]. This led Krawczynski and Grove [4] to propose that the TiO_2 content of the melt and f_{O2} were the major controls on phase stability at high temperatures and pressures. In an effort to systematically explore the effect of f_{O2} and melt TiO_2 content, Brown and Grove [6] determined the high pressure phase relation of the intermediate TiO_2 yellow glasses. They found that the effect of f_{O2} on phase relations in these lower TiO_2 glasses (~4 wt. % TiO_2) was as great as it was for ultramafic glasses with more than two times the TiO_2 content (e.g. the Apollo 17 orange glass [5]), which they argued was caused by the high FeO content of the Apollo 14 yellow glasses. Both [4] and [5] predicted the change in multiple saturation pressure, ΔMSP, to be ~1-1.1 GPa for the black glass.

This effect of f_{O2} in changing the multiple saturation pressure is summarized in Figure 2 for all the ultramafic glasses that have been experimentally studied in both iron and graphite. It is apparent that TiO_2 exercises an important control on the multiple saturation points and the effect is greatest for this highest TiO_2 Apollo 14 black glass; twice the magnitude that is found for the Apollo 14 red glass. The observed ΔMSP (~2.2 GPa) is also twice as large as predicted (~1.1 GPa) suggesting that melt speciation at low f_{O2} is more complex than envisioned by [5], possibly influenced by the multivalent cation Cr.

Implications for magma ocean overturn: If the f_{O2} of the Apollo 14 black glass source region is near metal saturation, then the depth of melting indicated by the Apollo 14 black glass is > 800 km, which implies a significant overturn event that delivered the high-Ti component to great depths, possibly mixing to depths greater than the original base of the primordial lunar magma ocean, which now seems most likely to have been ~ 600 km [8].

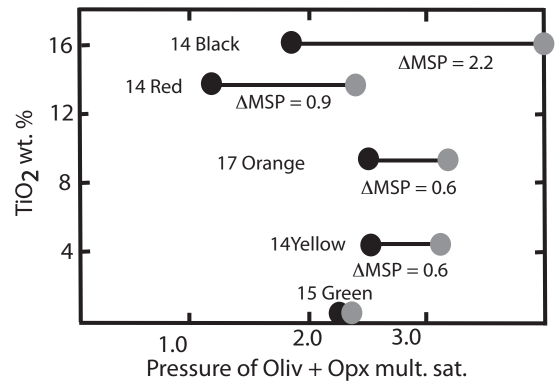

Figure 2: Summary of MSP data for lunar ultramafic glasses. Black = experiments in graphite capsules, gray = experiments in iron capsules.

References:

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