Influence of variable fO_2 and TiO_2 on the high pressure phase equilibria of lunar ultramafic glasses

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Pressure-temperature conditions of multiple saturation with olivine and orthopyroxene of intermediate and high titanium Apollo ultramafic glasses strongly depend on fO_2. Piston cylinder experiments conducted in both graphite capsules (IW+2) and iron capsules (IW-2) bracket the expected range of fO_2 involved in lunar petrogenesis. The pressure of multiple saturation increases by 1 GPa (~200 km) for the Apollo 15 red glass (13.5 wt% TiO_2), and by 0.5 GPa (~100 km) for both the Apollo 17 orange glass (8.8 wt% TiO_2) and the Apollo 14 yellow glass (4.5 wt% TiO_2). The change in multiple saturation (ΔMSP) is not linear with TiO_2 but with TiFe# = molar (Fe+Ti)/(Fe+Ti+Mg). We find that the melt activity coefficient ratio of FeO to MgO, or $(\Upsilon_{FeO}/\Upsilon_{MgO})^{melt}$, decreases at low fO_2, suggesting that melt speciation of Fe changes with variable fO_2.

These two observations limit the nature of melt behavior at low fO_2. One reaction to describe a melt component oxidation-reduction reaction that explains the observed behavior is:

$$(\mathrm{Fe,Mg})\mathrm{Ti}_2^{4+}\mathrm{O}_5 + \mathrm{x}(\mathrm{Fe,Mg})\mathrm{Ti}^{4+}\mathrm{O}_3 \rightleftharpoons (\mathrm{Fe,Mg})_{1-\mathrm{x}}\mathrm{Ti}^{4+}_{2-\mathrm{x}}\mathrm{Ti}^{3+}_{2\mathrm{x}}\mathrm{O}_5 + 2\mathrm{x}(\mathrm{Fe,Mg})\mathrm{O} + \mathrm{xO}_2.$$

Armalcolite and ilmenite melt components are in equilibrium at higher fO_2. At lower fO_2, some Ti^{4+} reduces to Ti^{3+}. The ilmenite melt component dissociates and donates Ti^{3+} to the modified more-Ti rich armalcolite melt component. To satisfy charge balance, (Fe,Mg)O is ejected into the melt, along with (Fe,Mg)O from the ilmenite melt component. Increasing the available FeO+MgO for the remaining melt components explains the deepening ΔMSP. The reduced armalcolite melt component is most stable at higher Ti+Fe contents, illustrated by the melt component exchange reaction (x=0.5):

$$\mathrm{Mg}_{0.5}\mathrm{Ti}^{4+}_{1.5}\mathrm{Ti}^{3+}\mathrm{O}_5 + \mathrm{FeO} \rightleftharpoons \mathrm{Fe}_{0.5}\mathrm{Ti}^{4+}_{1.5}\mathrm{Ti}^{3+}\mathrm{O}_5 + \mathrm{MgO}.$$

The reaction proceeds to the right as the FeTi# increases, explaining both the reduction in $(\Upsilon_{FeO}/\Upsilon_{MgO})^{melt}$ and the ΔMSP – FeTi# linear relationship.