**Introduction:** Calculation of oxygen fugacity in high pressure and temperature experiments in metal-silicate systems is usually approximated by the ratio of Fe in the metal and FeO in the silicate melt: \( \Delta \text{IW} = 2 \log(X_{\text{Fe}}/X_{\text{FeO}}) \), where IW is the iron-wüstite reference oxygen buffer. Although this is a quick and easy calculation to make, it has been applied to a huge variety of metallic (Fe-Ni-S-C-O-Si) systems and silicate liquids (\( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \), \( \text{TiO}_2 \), FeO, MgO, CaO, Na\(_2\)O, K\(_2\)O systems). This approach has surely led to values that have little meaning, yet are applied with great confidence, for example, to a terrestrial mantle at "IW-2". Although \( \text{O}_2 \) can be circumvented in some cases by consideration of Fe-M distribution coefficient, these do not eliminate the effects of alloy or silicate liquid compositional variation, or the specific chemical effects of \( \text{S} \) in the silicate liquid, for example. In order to address the issue of what the actual value of \( \text{O}_2 \) is in any given experiment, we have calculated \( \text{O}_2 \) from the equilibria \( 2\text{Fe (metal)} + \text{SiO}_2 \) (liq) + \( \text{O}_2 \) = \( \text{Fe}_2\text{SiO}_4 \) (liq).

**Calculations:** Modeling this equilibria at high PT conditions requires satisfactory a-x relations and thermodynamic or equation of state (EOS) data. We utilize activities of Fe in the FeNi alloy [1,2] and in the FeNiS system [3], and activities of \( \text{SiO}_2 \) and \( \text{Fe}_2\text{SiO}_4 \) in the silicate melt [4]. EOS data for FeNi alloy [5] up to 30 GPa are used, as is the EOS for silicate melt [4]. The position of the IW buffer also changes with P and T, and is calculated from recent work [6].

**Calculations along hypothetical adiabats and for specific experiments:** To illustrate the potential differences between a basaltic melt and a peridotite melt, we can first calculate \( \text{O}_2 \) for two hypothetical melt compositions along an adiabat (0.3 K/km gradient) between 1 bar and 50 GPa. Calculations have been carried out for a few specific experiments from the literature chosen to represent certain extremes of composition or PT conditions. For example, high T runs from [7] and [8] are chosen to investigate the effect of very high T (2873-3000 K at 25-26 GPa). Sulfur-rich melts of [9] and [10] were chosen at very low and very high pressures (0.8 vs. 25 GPa). And several high PT experiments from [11,12] were chosen for additional comparisons.

**Results:** We can compare the actual calculated values to those calculated using the ratio approximation approach. In general, the calculated values are 1 to 2 log \( \text{O}_2 \) units higher than those using the ratio approximation. The difference becomes higher at high pressures (>25 GPa) for the peridotite (Fig. 1). The difference stays relatively low for the basalt, but the EOS for basalt is more uncertain at higher pressures due to the role of alkalis. These results suggest that calculated \( \text{O}_2 \) from the ratio approximation could be too low, and the offset becomes even higher at the high PT conditions estimated for core formation. As a result this should be considered in detailed modeling efforts for a complete understanding of metal-silicate equilibria.

**References:**