

## The effect of pressure and oxygen fugacity on the ferric-ferrous ratio of silicate melts

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The oxygen fugacity at which a silicate melt has equilibrated can be determined from its ferric/ferrous iron ratio. This relationship has a pressure dependence, however, and a basaltic melt that initially equilibrated during partial melting in the mantle source region will have a lower oxygen fugacity as it rises towards the surface if the ferric/ferrous ratio remains constant. This can be attributed to the positive volume change of the melt component equilibrium  $\text{FeO} + 1/4\text{O}_2 = \text{FeO}_{1.5}$ . Similarly if the equilibrium oxygen fugacity for a silicate melt is buffered at some relative level, the melt ferric/ferrous ratio will decrease with increasing pressure, as depths approach the basalt source region. However, the iron melt components should also have relatively high compressibilities and it is possible that at pressures greater than the basalt source region, the ferric/ferrous ratio of silicate melts may start to increase with pressure at a constant relative oxygen fugacity, as has been found for redox equilibria involving mineral phases.

In this study we have examined the ferric/ferrous ratio of silicate melts at a fixed relative oxygen fugacity as a function of pressure in quenched experiments performed in a multianvil press. We have equilibrated an andesitic melt with a coexisting Rh-RhO<sub>2</sub> buffer between 5 and 24 GPa. Further experiments were performed on the same melt in equilibrium with iron metal. The recovered melts, which generally crystallise on quenching, were then analysed using Mössbauer spectroscopy to determine the ferric/ferrous ratio. The results show that for melts in equilibrium with the Rh-RhO<sub>2</sub> buffer at lower pressures, the ferric iron content decreases with pressure. However, above 15 GPa this trend apparently reverses and the ferric iron content increases with pressure. The likely explanation for this is that the ferric iron component although having initially a larger volume than the ferrous iron component, is more compressible and the volume change of the iron melt component equilibrium becomes negative. However, in order to model the volumes and compressibilities of the iron components an accurate determination for the oxygen fugacity of the Rh-RhO<sub>2</sub> buffer at high pressure and temperature is required. To this end, we have performed in situ x-ray diffraction measurements on Rh and RhO<sub>2</sub> in the multianvil press installed at the APS synchrotron facility. The results allow the equations of state of the buffer phases to be determined and also demonstrate that several phase transformations take place in RhO<sub>2</sub>, which have important effects on the determination of the oxygen fugacity for this buffer.

During the formation of the Earth one or more phases of global melting likely formed a magma ocean with a depth that may at times have extended into the lower mantle. Such an ocean would have facilitated the separation of core forming iron metal from silicates. If silicates equilibrated with core forming metal at the base of this ocean, then the redox state would have been below the iron-wüstite oxygen buffer, at least at its base. The proposed change in the sign of the melt iron equilibrium, however, would drive the oxygen fugacity of a deep magma ocean with a fixed ferric/ferrous ratio down with increasing depth, creating a redox gradient. As a result the magma ocean could potentially be in equilibrium with metallic iron at its base but more oxidised in its shallower regions. Crystallisation of this magma ocean could render an upper mantle oxygen fugacity similar to that in the Earth's accessible mantle today, which is approximately 4 orders of magnitude higher than normally expected during core-mantle equilibration.

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