Redox gradients in metal-saturated magma oceans

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Crucial planetary differentiation occurs in magma oceans (MOs), as metal separates from molten silicate and volatile species are degassed (or ingassed) at the magma ocean-atmosphere interface. Both mass transfer processes are affected greatly by oxygen fugacity, which determines core/mantle element partitioning and the solubility and speciation of volatiles in the magma and overlying atmosphere. Redox conditions are set by equilibration between FeO-bearing silicate liquid and core-destined alloy. Yet, the large span of pressures prevailing in planetary magma oceans can produce gradients in f_{O2} between the shallow magma-vapor and (on average) deep magma-alloy loci of equilibration. In a metal-free MO, conditions may be more or less reducing at the surface, depending on the competing effects of *P* on Fe^{2+} and Fe^{3+} in the melt (Hirschmann, 2012). There also may be effective redox gradients in a MO in which metal droplets are kept suspended by vigorous convection, owing to the differences between the *P* and *T* dependence of the solid iron-wüstite (IW) reference buffer and that of coexisting molten alloy and FeO in silicate liquid (Righter and Ghiorso, 2012a). Detailed evaluation of the latter should incorporate an adequate equation of state of Fe in the magma, but attempts to do so thus far displayed extreme dependence on silicate composition, suggesting interference of model artifacts (Righter and Ghiorso, 2012a, 2012b). Direct experimental constraints include low *P* equilibration of melt with metal at known f_{O2} and high pressure (14-33 GPa) melts saturated with ferropericlase (fp). The former allows calculation of activity coefficients (and their uncertainties) of liquid FeO in low *P* silicate melt, and the latter allows direct correlation of the composition of high *P* melt to the IW buffer, subject to constraints on the mixing properties of fp solid solution. For a metal-saturated MO with 8 wt.% FeO along a MO adiabat, f_{O2} would be IW-2.0±0.1 at 25 GPa, but IW-2.6±0.3 at the surface. A key influence is that the IW solid buffer occurs at higher relative f_{O2} at low *P*, owing to non-stoichiometry of $Fe_{1-x}O$ at low *P* but not at high. Thus, contrary to the conclusion of Righter and Ghiorso (2012a), a metal-saturated MO is more reduced compared to IW at its surface than at its base, meaning that the overlying atmosphere would have high H_2/H_2O, with C and N chiefly as CO and NH_3, respectively.