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Solubility of H and C in reduced melts at fO₂'s in area of the Fe-Si alloy stability

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It is generally accepted that most part of the present-day upper mantle is moderately oxidised and well above metal saturation. Fluids identified in mantle samples are also oxidised, and consist mainly of $CO_2 + H_2O$. However, it is supposed that the mantle was reduced at early stages of the Earth's evolution and was in chemical equilibrium with metallic iron and the Earth's metallic core. If the average composition of olivine of the upper mantle was Fo91, fO_2 in the mantle was at least five logarithmic units lower than that of present-day lithospheric and asthenospheric layers ($\Delta \log fO_2(IW) = -2$). The proto-Earth formed from enstatite chondries would have been very reduced ($\Delta \log fO_2(IW)$ from -3 to -5) (Javoy, 1997). CH₄ and H₂ in equilibrium with iron and free carbon (graphite and diamond) must be dominant volatile components of the ancient upper mantle. Volatiles in the reduced part of the system C-O-H may therefore be of considerable importance in igneous petrogenesis (Taylor and Green, 1987; Ballhaus 1993; Holloway and Jakobsson; 1996; Javoy, 1995; 1997; Kadik, 1997; Kadik et al., 2004).

The transport of volatile constituents from planetary interiors to surfaces provides the primary supply of material for the upper layers of the Earth and atmospheres. The major factor controlling this transport is the solubility of volatile species in magmas and the oxidise-reduction evolution of the magma relative to their mantle sources.

Studies of the iron-bearing silicate melt (ferrobasalt) + molten Fe-Si alloy (1-12 wt % of Si) + graphite + hydrogen equilibria show that large scale melting of growth Earth could be associated with melts containing an oxidised form of hydrogen, although the early Earth was likely a reducing environment. Melt should be more oxidising than

the mantle source (Kadik et al., 2004)

In a series of experiments conducted at 4 GPa and 1550-1600°C, we have characterised the nature (oxidised versus reduced) and quantified the abundance's of C- and Hcompound dissolved in an iron bearing silicate. The fO₂ for silicate melt-iron alloygraphite-hydrogen equilibrium was 2.3 log (Kadik et al., 2004) and 3.5.5-6.0 log units below iron-wüstite (IW). The speciation of the C- and H- components dissolved in the glass has been determined by Infrared and Raman spectroscopy. It was established that that the main part of the liberated oxygen was used at $\Delta \log fO_2(IW) = -2.3$ and at $\Delta \log fO_2(IW) = -(3.5-6.0)$ to form mainly OH⁻, traces of H₂.⁻ Dissolved carbon is mainly present as atomic carbon. The Raman spectra also suggest that the network units may contain Si-C bonds and a non- stoichiometric network component containing units having O/Si ratio less than 2. Dissolved molecular $\tilde{N}H_4$ and C=O bond were noted in melt at $\Delta \log fO_2(IW) = -(3.5-6.0)$. Iron-bearing silicate melt has a strong preference for dissolved H over C under reduced conditions.

Recent physical theories of planetary evolution propose that Earth and possibly other "terrestrial" bodies have experienced high-temperature conditions during their formation. It is suggested that the mantle of the Earth was partially or completely molten, and molten Fe-alloy and molten silicate underwent gravitational migration. In the light of experimental data, it appears that a large scale melting of growth Earth could be associated with melts containing an oxidised form of hydrogen, although the early Earth was likely a reducing environment.

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