3.5.P05

On the saturation surface and oxidation state of C-H-O-S-silicate melt systems

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The equilibrium between a H_2O–CO_2–SO_2–H_2S gas phase and silicate melts is investigated by means of thermochemical calculations which join homogeneous reactions in the gas phase and heterogeneous gas–melt saturation modeling based on classical sub-regular multicomponent mixing and Toop-Samis polymeric approach. Sulfur in the melt phase is assumed to be present in two different oxidation states (sulfide and sulfate ions). The thermodynamic model is an extension of that presented in Moretti et al. [1] to account for iron speciation at high pressure with variable dissolved water contents. The consequences on the equilibrium conditions of different assumptions on the effective redox buffer in magma are examined for melts of basaltic and rhyolitic composition, determining the equilibrium conditions on the basis of i) constant Fe^{II}/Fe^{III}, ii) constant fH_2S/fSO_2, and iii) constant relative fO_2, expressed as difference in log-units to a solid buffer. The first two buffers are expected to be effective in basaltic and andesitic-rhyolitic magmas, respectively, according to the most abundant reservoir of redox couples. Furthermore, for each assumed redox buffer the pressure dependence of phase composition and oxidation state of the system shows strongly non-linear trends. The largest compositional differences are shown by sulfur species, however, the concentrations of H_2O and CO_2 in the two phases at equilibrium also show non-negligible dependence on the redox conditions. For each assumed redox buffer, sulfur dioxide in the gas phase, and sulfate ions in the liquid phase, are found to be present in appreciable quantities or represent the dominating sulfur species. The more reliable redox buffers represented by constant Fe^{II}/Fe^{III} for basalt, and constant fH_2S/fSO_2 for rhyolite, show that oxygen fugacity paths during magma depressurization strongly deviate from those related to a solid buffer plus or minus a constant.

Results here presented, although not yet accounting for the separation of S-bearing solid or liquid phases, may furnish insights on the composition of gases separated from magmas originated in various geodynamic settings, under different redox conditions.

Reference

[1] Moretti R., Papale P. and Ottonello G. (2003) In: *Volcanic Degassing* (Oppenheimer C., Pyle D. and Barclay J., eds.) Geol. Soc. London Spec. Publ., **213**, 81-101.

3.5.P06

Solubility of H and C in reduced melts at fO_2's in area of the Fe alloy stability

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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. CH_4 and H_2 in equilibrium with free carbon (graphite and diamond) must be dominant volatile components of the ancient upper mantle.

Studies of the iron-bearing silicate melt (ferrobasalt) + molten Fe-Si alloy (1-9 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., 2003)

In a series of experiments conducted at 4-7 GPa and 1520-1700°C, we have characterised the nature (oxidised versus reduced) and quantified the abundance's of C- and H-compound dissolved in an iron bearing silicate. The fO_2 for silicate melt-iron alloy-graphite-hydrogen equilibrium was 2.3 log and 4.5-6.5 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)= -(4.5-6.5) to form mainly OH^-, traces of H_2 and CO_3^{2-}.$^-$ Dissolved carbon is mainly present as atomic carbon or amorphous 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 methane or other hydrocarbon groups such as $-CH_3$ or $-CH_2-$ are expected at $\Delta\log fO_2$ (IW)= - (4.5-6.5)

We argue that magma generation in reduced environment at fO_2's in area of the Fe alloy stability and at pressures of the order of 100-150 km depth could form melts containing dissolved both oxidised, and reduced components of hydrogen and carbon species.

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