

Magmatic transport of nitrogen, hydrogen and carbon constituents from reduced planetary interiors

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In theories of the Earth's formation, the composition of gases extracted by primary planetary magmas is accounted for the large-scale melting of the early mantle in the presence of the metallic Fe phase. The melting should have been accompanied by the formation of volatile compounds, which composition was controlled by the interaction of N, H and C with silicate and metallic melts.

In a series of experiments in the system Fe-bearing melt + molten Fe rich metallic phase (0.1-12 % Si) + H₂ carried out at 4 GPa and 1520-1600°C and log fO₂ (oxygen fugacity) = 2 -5 below IW, we have characterised the nature (oxidised versus reduced) and quantified the abundance of C, H and N-compound dissolved in an iron bearing silicate melt. The speciation of components dissolved in the glass has been determined by Infrared and Raman spectroscopy.

The solubility of Si in liquid metal increases with decreasing fO₂ from 0.1-0.55 wt % at $\Delta\log fO_2(IW) = -(2-3)$ to 10-12 wt % at $\Delta\log fO_2(IW) = -(4-5)$. Carbon content in iron-rich globules to be fixed between 3 and 6 wt %. The amount of H (as H₂O, OH, H₂, CH₄) and C (as CO₂, CO₃²⁻, CH₄, Si-C) dissolved in the glasses was measured by ion microprobe and by CNH analysis. Hydrogen content decreases with decreasing fO₂ from 0.3-0.4 wt % at $\Delta\log fO_2(IW) = -(2-3)$ to 0.1-0.2 wt % at $\Delta\log fO_2(IW) = -(4-5)$ as a result of decreasing of H₂O in melt. Carbon content increases with decreasing fO₂ from 0.2-0.5 wt% at $\Delta\log fO_2(IW) = -(2-3)$ to 1-2 wt % at $\Delta\log fO_2(IW) = -(4-5)$ as a result of increasing of CH₄. The nitrogen solubility (as N₂, N³⁻) reaches 2-3 wt % at $\Delta\log fO_2(IW) = -(2-4)$.

In the light of experimental data we argue that magma in reduced environment in area of the Fe-Si alloy stability could form melts containing dissolved both oxidized, and reduced components of hydrogen and carbon species. We assume that core growth took place under reduced conditions imposed by the pristine terrestrial materials and was accompanied by the emission of CH₄, H₂, N₂ and NH₃ and minor H₂O into the atmosphere.

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Colloid formation in aerated Fe(II) containing water: Effect of phosphate, silicate and Ca on morphology and structure

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The biogeochemical cycling of nutrients and pollutants is strongly influenced by the formation and presence of colloids. In this study we focused on the microscopic analysis of colloids formed due to iron oxidation and hydrolysis in synthetic carbonate-buffered groundwater (pH 7, 2-30 mg/L Fe(II)). We investigated the influence of phosphate (2-20 mg/L P), silicate (2-20 mg/L Si), and Ca (2.5 mM Ca- or 8 mM Na-bicarbonate) on colloid formation. The morphology, chemistry and crystallography of the colloids were characterized using HR-TEM (high resolution transmission electron microscopy), TEM-EDX (energy dispersive x-ray analysis) and SAED (selected area electron diffraction).

When Fe(II) is added to a Na-bicarbonate-buffered water, idiomorphic lepidocrocite (Lp) crystallizes, as confirmed by SAED. Individual sheet-like crystals are between 100 - 200 nm long and a few nm thick. These crystals agglomerate to 'spherical' entities with a diameter of up to 500 nm. Several of these 'spherical' entities agglomerate again to fractal-like aggregates.

At high Si/Fe ratio, the crystallization of Lp is suppressed and ferrihydrite (Fh) forms instead. The Fh crystals are platelets of ~5 nm showing lattice fringes in HR-TEM images. The individual Fh agglomerate to spheres of ~200 nm and form fractal-like aggregates. SAED images of aggregates show two distinct rings at distances of 0.15 and 0.25 nm, indicative of 2-line Fh.

At high P/Fe ratios, a Fe-phosphate (Fe-P) forms. The Fe-P appears as spherical particles of ~100 nm in diameter, but no primary crystals can be observed. However in the SAED pattern, a faint ring at a distance of ~0.29 nm is observed, in agreement with XRD patterns from amorphous Fe-P references.

At lower Si/Fe or P/Fe ratios, depletion of Si or P due to precipitation of Fh or Fe-P results in the subsequent formation of Lp. The presence of Ca in solutions containing Si and P enhances Fe(III)-colloid coagulation due to a reduction of the electrostatic repulsion. Based on our microscopic investigations, it is not clear, yet, whether Ca is also directly incorporated into the colloid structures.

Despite the varying chemistry, the morphologies of all colloids are very similar. The formation can be described with the following three steps: 1. rapid formation of primary particles (Fh, Lp, Fe-P), 2. formation of 'spherical' entities and 3. agglomeration to fractal-like aggregates.