

# Formation of Carbon and Hydrogen Species in Magmas at low Oxygen Fugacity

Arnold Kadik (kadik@geokhi.ru)<sup>1</sup>, Francoise Pineau (fpi@ccr.jussieu.fr)<sup>2</sup>, Yuri Litvin (litvin@iem.ac.ru)<sup>3</sup>,  
Natalie Jendrzewski<sup>4</sup>, I. Martinez<sup>4</sup> & Marc Javoy<sup>4</sup>

<sup>1</sup> V.I. Vernadsky Institute RAS, Moscow, Kosygina str., 19, Russia

<sup>2</sup> Laboratoire de Geochimie des Isotopes Stables, Universite Paris 7 Denis Diderot, IPGP, 2 Place Jussieu, 75 251 Paris Cedex 05, France

<sup>3</sup> Institute of Experimental Mineralogy RAS, Chernogolovka, Russia

<sup>4</sup> Laboratoire de Geochimie des Isotopes Stables, France

A variety of evidence exists to support the idea that at least part of the upper mantle is reduced enough to stabilize carbon, CH<sub>4</sub> and H<sub>2</sub> at depth (Ballhaus, 1993; Kadik, 1997) and that the Earth's mantle was originally very reduced and has become progressively more oxidized, resulting perhaps in the multi-stage mechanism of accretion production of the upper mantle oxidized iron via the auto-redox process (Allègre et al, 1995; Javoy, 1995). Accretional models imply the depletion of the original volatiles of the Earth. Within the framework of these representations the presence of a primary fluid phase in mantle is rather doubtful. Although this area is still one of the active debate and inquiry, it seems likely that the range of oxidation states from relatively oxidized (fO<sub>2</sub> ~FMQ) to reduced (fO<sub>2</sub> ~IW) is applicable to the 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; Kadik, 1997). Our major concern is to demonstrate that carbon and hydrogen solubility in the melt may have important implication for the upper mantle evolution and the formation of carbon and hydrogen species in the terrestrial magmas during the early differentiation of the Earth. Our further purpose is to elaborate the role of fluid-absent melting in the generation of the oxidized C-O-H volatiles from reduced carbon-bearing upper mantle source. The iron-bearing silicate melt (ferro-basalt) + iron metallic phase + graphite + hydrogen equilibrium have been considered in this study. Experiments were carried out in an anvil-with-hole apparatus at 3.7 GPa, 1520-1600 °C. The researched substance was isolated from the walls of Pt capsule with the tungsten foil. This technique relies on the diffusion of H<sub>2</sub> through Pt to achieve equal chemical potentials of H<sub>2</sub> in the inner Pt capsule and outer furnace assembly. The fO<sub>2</sub> for silicate melt - iron equilibrium yields fO<sub>2</sub> of 2,5x0.1 log units below IW. The reduction of FeO in melt with the formation of Fe alloy leads to liberation of oxygen that reacts with H<sub>2</sub> diffusing into the capsule from the buffer assemblage and with graphite inside of capsule forming carbon and hydrogen species in silicate liquid at low oxygen fugacity. Pyrolysis/gas chromatographic analyses give dissolved C contents of 1000-2000 ppm (wt). Ion probe analysis of 1H<sup>+</sup> / <sup>30</sup>Si<sup>+</sup> ratio in the glasses corresponds to

1.8 wt% of H<sub>2</sub>O. The melt has a strong preference for dissolved H over C under reduced conditions. Infrared spectroscopic investigations of glasses, quenched from 3.7 GPa, establish that general reduction of a silicate network and FeO with liberation of oxygen is the dominant process of C and H solubility in iron bearing silicate melts. The main part of liberated oxygen was spent on the formation of "oxidized" forms of carbon and hydrogen in melt, such as H<sub>2</sub>O, OH- and CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>. There is no spectroscopic evidence for the presence of the dissolved molecular CH<sub>4</sub> and other C-H groups. The spectroscopic constraints greatly limit the choice of a reduced component. It is suggested that the most likely candidates are the network units containing Si-C bonds and non-stoichiometric network component containing units having O/Si ratio less than 2. It is supposed also, that a part of carbon and hydrogen could be dissolved in the atomic form. The interaction of carbon and hydrogen with silicate melts at low fO<sub>2</sub>'s has a number of features, which could play a key role in CO<sub>2</sub> and the H<sub>2</sub>O formation at the early stages of mantle evolution. We argue that fluid-absent partial melting of the reducing carbon-bearing planetary mantle will form magmas that yield the "oxidized" forms of carbon and hydrogen in melt that should be more oxidizing than the mantle source. The transport of primary magmas from the planetary interiors to the surface provides the primary supply of H<sub>2</sub>O and CO<sub>2</sub> of volcanic gases. It is supposed, that the major factor controlling transport of oxygen in the large-scale melting zone at low fO<sub>2</sub> should be the auto-redox process that would release O to oxidize the proto-mantle (Allègre et al, 1995; Javoy, 1995).

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