

# The primary carbon and the formation of carbon species in terrestrial magmas

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## Problems

There is general agreement that primary carbon and redox state of mantle play an important role in the formation of carbon species in the terrestrial basalts as well as in the composition of gases, evacuated by these liquids to the upper layers of the Earth. It is expected, that interaction between primary carbon and production of partial melting of the upper mantle:  $C(\text{graphite, diamond}) + O^{2-}(\text{melt}) + O_2 = CO_3^{2-}(\text{melt})$  (1) leads to the formation of  $CO_3^{2-}$  (carbonate ion) in melt (Holloway, J.R. *et al.*, 1992; Kadik and Shilobreeva 1994). Eq.(1) shows, that  $CO_3^{2-}$  or  $CO_2$  content in melt in equilibrium with graphite is a function of oxygen fugacity. Next mechanism, that may control the presence of free carbon and the formation of C-bearing components in magmas, is the carbon solubility in minerals under mantle conditions by participating in point defect equilibria (Freund 1981; Watson, 1986)

## Carbon and carbon-saturated fluid in upper mantle

Data on the oxygen fugacities ( $f_{O_2}$ ) recorded by mantle rocks show that the primitive and less modified spinel lherzolites may be in equilibrium with free carbon (Balthaus 1993; Bryndzia and Wood 1990; Kadik 1990). Electrochemical measurements of the intrinsic  $f_{O_2}$  of coexisting minerals (Ol, OPx, CPx, Spl, Gar) of mantle peridotite xenoliths from Mongolia and the Baikal region (central Asian) indicate that the evolution of the upper mantle beneath continental rift systems is characterized by a wide range of redox conditions mainly in the range between the wustite-magnetite (WM) and the iron-wustite buffer (IW). Main part of slightly depleted lherzolite are moderately reduced (around WM and WM-2). At 800–1200°C, 10–20 kbar the range of oxygen fugacities corresponds to the complete spectrum of C-O-H fluid saturated by carbon. This conclusion is confirmed by the presence of rare and extremely fine-grained crystals in minerals and carbon dissolved in olivines and pyroxenes (5–100 ppm)].

The observed evolution of oxygen fugacities is

closely linked to the distribution of volatile species.  $H_2O$  and  $CO_2$  would be dominant volatiles for more depleted and oxidized peridotites and  $CH_4$  for more reduced and less modified part of peridotites. We interpret highly reduced peridotites as a relict from earlier lower- $f_{O_2}$  regime in the outer layers of primitive Earth. By comparing the measured  $f_{O_2}$  with carbon- $CO$ - $CO_2$ -carbonate equilibria we find the data not to be consistent with hypothesis that oxidation state of the upper mantle is buffering by C-O fluid in equilibrium with elemental carbon. Our data support that oxygen fugacity of the fertile upper mantle is weakly buffered by ferric/ferrous redox equilibria. Correlation between  $f_{O_2}$  of minerals and the composition of the spinel lherzolites (Mongolia) in terms of degree of extraction of the basaltic component indicates decreasing of  $f_{O_2}$  during partial melting. It is expected, that redox state of primary melt has been controlled by reactions:  $C(\text{graphite}) + 2Fe_2O_3(\text{melt}) + O^{2-}(\text{melt}) = CO_3^{2-}(\text{melt}) + 4FeO(\text{melt})$ .

## Interaction between carbon, crystals and melt

The experiments were made on C(graphite)-melt-crystals equilibria for C + basaltic melt, C + basaltic melt + CPx at 15–30 kbar and 1350–1400°C and on C +  $Mg_2SiO_4$ , C +  $Mg_2SiO_4$  + melt, C +  $Mg_2SiO_4$  + (CO- $CO_2$ ) vapour + melt for CaMgSi<sub>2</sub>O<sub>6</sub>- $Mg_2SiO_4$  composition at 25–40 kbar, 1400–1700°C. The solubility of carbon in crystals and silicate melts was determined by registration of the beta activity from <sup>14</sup>C and by the infrared determinations of species in glasses. Experiments show, that carbon may be soluble in forsterite and pyroxene on concentration of 10–100 ppm and reactions with graphite lead to formation in melt 400–4000 ppm of  $CO_2$ . The coefficient of distribution  $D = (C \text{ in melt} / C \text{ in crystal})$  equals about 10–100. Thus carbon is incompatible element in the melt + crystals equilibria and during the fluid-absent partial melting magma will be enriched in carbon in comparison with crystalline rest. Fig. 1 shows results of experimental examinations of solubility carbon in basaltic melt with initial amount of  $H_2O$

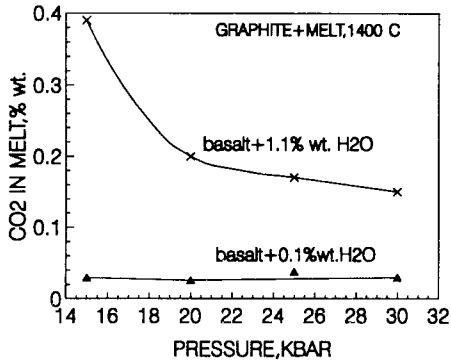


FIG. 1.

= 0.1 % and 1.1 % wt. at 1–30 kbar and 1250–1400°C. It was found that structural sites of dissolved carbon is determined by formation of carbonate ionic complex  $\text{CO}_3^{2-}$ . The reaction between graphite and basaltic melt leads to the formation of 0.04–0.40 % wt.  $\text{CO}_2$  in melt at high pressure (15–30 kbar, 1350–1700°C). In the presence of ( $\text{CO}$ ,  $\text{CO}_2$ ) vapour at low pressure (1–5 kbar, 1250°C) the reactions between graphite and basaltic melt lead to formation of 0.01–0.03 wt.%  $\text{CO}_2$ . It was found influence of dissolved  $\text{H}_2\text{O}$  on the carbon concentration in melt. It increases with increasing of  $\text{H}_2\text{O}$  content in system (Fig.1). We expect reaction between carbon and melt species relating with molecular water, hydroxyl and carbonate groups:  $\text{C}(\text{graphite}) + 2\text{OH}^-(\text{melt}) + 2\text{O} = \text{H}_2\text{O}(\text{melt}) + \text{CO}_3^{2-}(\text{melt})$  (2), where O represent a distinguishable reactive oxygen species e.g. bridging, non-bridging or free. According to Eqn.(2) melt with higher ratio of species  $\text{OH}^-$  to molecular water would have a higher concentration of carbonate ion in melt.

#### Fluid-absent melting

It may be suggested, that the carbon-melt-crystal reactions during 1) fluid-absent melting in presence some amount of free carbon (carbon saturated equilibrium of melt + crystals + graphite) and 2) fluid-absent melting of carbon-bearing minerals (carbon unsaturated equilibrium of melt + carbon-bearing minerals) may be reason of the carbon-species formation in basaltic

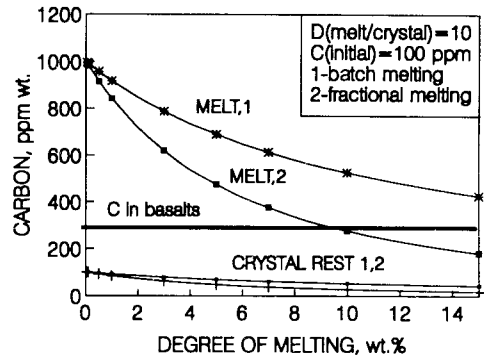


FIG. 2.

magma. The reaction between graphite and basaltic melt in the presence some amount  $\text{H}_2\text{O}$  may lead to formation in magma 0.1–0.5 % wt.  $\text{CO}_2$ , observed generally in basaltic glasses (first case). And  $\text{CO}_2$  content in melt during partial melting of carbon-bearing minerals in the absence of the free carbon (second case) may be enough high (several hundred ppm) (Fig.2). At the same time we see, that the melting must have depleted the concentration of the carbon in the crystalline rest.

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