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Conditions for the origin of oxidized carbonate-silicate melts: Implications for mantle metasomatism and diamond formation

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ABSTRACT

An experimental study on the origin of ferric and ferrous carbonate-silicate melts, which can be considered as the potential metasomatic oxidizing agents and diamond forming media, was performed in the $(Ca,Mg)CO_3$-SiO_2-Al_2O_3-$(Mg,Fe)(Cr,Fe,Ti)O_3$ system, at 6.3 GPa and 1350–1450 °C. At 1350–1450 °C and fO_2 of FMQ + 2 log units, carbonate–silicate melt, coexisting with Fe^{3+}-bearing ilmenite, pyrope-almandine and rutile, contained up to 13 wt.% of Fe_2O_3. An increase in the degree of partial melting was accompanied by decarbonation and melt enrichment with CO_2, up to 21 wt.%. At 1550–1650 °C excess CO_2 segregated as a separate fluid phase. The restricted solubility of CO_2 in the melt indicated that investigated system did not achieve the second critical point at 6.3 GPa. At 1350–1450 °C and fO_2 close to CCO buffer, Fe^{2+}-bearing carbonate–silicate melt was formed in association with pyrope-almandine and Fe^{3+}-bearing rutile. It was experimentally shown that CO_2-rich ferrous carbonate-silicate melt can be an effective waterless medium for the diamond crystallization. It provides relatively high diamond growth rates (3–5 μm/h) at P,T-conditions, corresponding to the formation of most natural diamonds.

1. Introduction

Modern models predict that the subcratonic lithospheric mantle becomes increasingly reduced with depth (Luth et al., 1990; McCammon and Kopylova, 2004; Woodland and Koch, 2003). However, variations of Fe^{2+}/Fe^{3+} ratios, revealed by the study of some xenoliths, suggest that redox conditions in the mantle conform to more complex patterns. Particularly, mantle xenoliths from Kimberley kimberlites are strongly oxidized and do not agree with the trend of oxygen fugacity decrease with depth. According to data of Creighton et al. (2009) and Woodland and Koch (2003), oxygen fugacity values in the most oxidized "MARID metasomatized" (Mica-Amphibole-Rutile-Ilmenite-Diopside) xenoliths can reach FMQ + 1 log unit. Findings of strongly oxidized rocks confirm the assumption that part of the lithospheric mantle is altered by mobile oxidized fluids/melts at fO_2 values out of diamond or graphite stability field (Creighton et al., 2009; Woodland and Koch, 2003).

Oxygen fugacity in the mantle rocks is dominated mainly by Fe^{2+}/Fe^{3+} equilibrium between minerals and by equilibria involving carbon-bearing phases (Luth, 1999). The evaluation of the effect of different equilibria on the oxidation state of a "closed-system" mantle volume can be performed using buffering capabilities of the different equilibria, which can be represented by the amount of excess oxygen the different equilibria have to offer. The analysis of distribution and concentrations of Fe^{2+}, Fe^{3+} and C in various types of mantle rocks (Canil et al., 1994; Javoy, 1997; Luth, 1999; Trull et al., 1993), shows that all amount of C^0 can be oxidized by Fe^{3+} to CO_2 or carbonates only in rocks depleted with carbon. According to Navon (1999), in peridotites from the carbon-rich regions of diamond formation, buffer capacity of the mantle carbon is close to that of reactions, involving Fe^{2+} and Fe^{3+}. Oxygen potential in eclogites is controlled most probably by carbon-containing fluid (Poli et al., 2009). Experimental data, obtained in recent decades, show that at pressures higher than 7 GPa, the influence of Fe^{3+} concentration in rocks on the redox potential of the medium decreases. Experiments, performed by Rohrbach et al. (2011) in a model peridotite composition showed, that at $P > 7$ GPa subcalcic pyroxene and majoritic garnet incorporated appreciable amounts of ferric iron, even though at the experimental conditions they were in redox equilibrium with metallic iron. Thus, as a result of stabilization of high-density Fe^{3+}-bearing silicates, redox reactions, involving Fe^{2+} and Fe^{3+} shift to more reduced region, close to fO_2 values at IW buffer (Rohrbach et al., 2011, Rohrbach et al., 2007; Ryabchikov, 2009; Wood et al., 1990). Accordingly, potential regions for the generation of oxidized metasomatic agents should be present in the lithosphere and contain enough Fe^{3+} to oxidize all elemental carbon.

The distribution of trace elements in minerals from xenoliths indicates that potential metasomatic agents at the upper mantle conditions are mobile carbonatitic melts/fluids (Kogarko, 2006). There is very limited experimental evidence on the mechanism of generation

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of these melts. According to Foley (2010), partial melting processes, involving selective dissolution of fluid components, play an important role in the formation of carbonatitic melts. In addition, during partial melting of the mantle rocks Fe^{3+} is more incompatible than Fe^{2+} (Arculus, 1994). As a result, newly formed melt is more oxidized and has higher $Fe^{3+}/\Sigma Fe$ ratios, than its mantle source. The separation of oxidized melt causes depletion of the parent rock in iron and considerable lowering of its buffer capacity (Rohrbach et al., 2011). Penetration of such oxidized melts/fluids into reduced mantle rocks causes metasomatic oxidation and can result in the increase in oxygen fugacity in local mantle domains to 3–4 orders of magnitude (Woodland and Koch, 2003), and finally in total oxidation of diamond in these regions. In this general scenario, the genesis and composition of oxidized melts/fluids are of great interest.

In the MgO-Al_2O_3-SiO_2-CO_2 and MgO-Al_2O_3-SiO_2-FeO-CaO-Na_2O model systems, at lithospheric pressures and fO_2 values close to CCO buffer, carbonatitic melts are formed at temperatures slightly higher than solidus (Dalton and Presnall, 1998; Dasgupta et al., 2004; Grassi and Schmidt, 2011; Hammouda, 2003; Yaxley and Brey, 2004). As the temperature increases, the composition of the generated melt is found to change from nearly pure carbonate ($SiO_2 \approx 5$ wt.%) to kimberlitic ($SiO_2 > 25$ wt.%, at 70–100 °C above the solidus) (Dalton and Presnall, 1998). In the subsolidus region at fO_2 values above CCO buffer, the boundaries of the stability field of carbonates and CO_2 are determined by decarbonation reactions (Eggler, 1976; Knoche et al., 1999; Luth, 1999; Newton and Sharp, 1975; Wyllie et al., 1983). Redistribution of Fe^{3+} between a melt and solid phases at partial melting and change of fO_2 caused by migration of Fe^{3+} containing oxidized melts previously were not adequately examined at the mantle P,T-parameters.

Here we present an experimental study of the generation of oxidized mantle carbonate-containing melts/fluids and formation of Fe^{3+} bearing mineral phases - indicators of oxidized mantle metasomatism processes.

2. Experimental methods

Experimental investigation was performed in the ilmenite-containing $(Ca,Mg)CO_3$-SiO_2-Al_2O_3-$(Mg,Fe)(Cr,Fe,Ti)O_3$ system. Experiments were carried out at 6.3 GPa in the temperature range of 1350–1650 °C using a multi-anvil high-pressure apparatus of a "split-sphere" type. Details of the pressure and temperature calibration in the high-pressure cell have been presented elsewhere (Palyanov et al., 2010). Scheme of the reaction ampoule assembly (Fig. 1a), used in the present work and the methodical approach were developed in Palyanov et al. (2007). In the present study this scheme was used to create conditions for the formation of coexisting oxidizing melt and CO_2-fluid in a rather simple silicate-oxide-carbonate assemblage. The simplicity of the system was a very important factor to enable the adequate interpretation of experimental results. The starting materials were 99.9% pure SiO_2 and Al_2O_3, natural magnesite and dolomite (Chelyabinsk region, Russia) with impurity content of 0.3 wt.% and natural picroilmenite (kimberlite pipe Udachnaya, Yakutia). The initial mixture of carbonates and oxides, reacting completely under run conditions, would produce pyrope garnet and CO_2 fluid via decarbonation (Pal'yanov et al., 2005a, 2005b). Ilmenite, being an important Fe^{2+} and Fe^{3+}-bearing mineral phase in the upper mantle (Green and Sobolev, 1975; Sobolev, 1977; Sobolev and Yefimova, 2000), and one of the principal phases in strongly oxidized MARID suite, was used as the source of ferric and ferrous iron. Reacting under run conditions, picroilmenite would interact with CO_2 via carbonation reaction into rutile and Fe-magnesite, or decompose into rutile and Ti-magnetite assemblage. In both cases, in the course of partial melting processes, Fe^{3+}-content of ilmenite would be redistributed into rutile and melt, providing the internal buffer (ilmenite-rutile-magnetite buffer). The composition of picroilmenite and bulk composition of the starting mixture are presented in Table 1. Mass concentrations of Fe^{2+} and Fe^{3+} in initial picroilmenite were measured using Mössbauer spectroscopy. Mössbauer spectra of the powder samples of picroilmenite were measured using a conventional constant acceleration spectrometer NZ-640 with the velocity reverse, in the regime of moving $^{57}Co/Rh$ source, at room temperature. The isomer shifts of the spectra were calibrated using reference spectrum of the α-Fe. Spectra were fitted using an original program of Lorentzian line shape approximation.

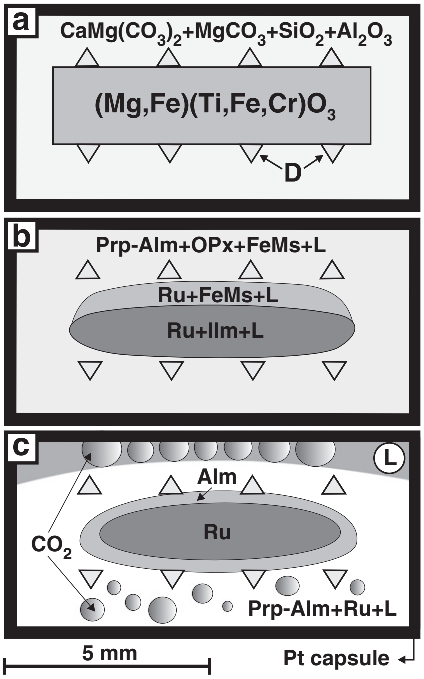

Fig. 1. Initial ampoule assembly (a) and schemes of carbonate-oxide interaction at fO_2 buffered by decomposition of Fe^{3+}-bearing ilmenite (b — at 1350–1450 °C, c — at 1550–1650 °C).D — diamond seed crystals; Prp-Alm — pyrope-almandine; OPx — orthopyroxene; FeMs — Fe-magnesite; Ru — rutile; Ilm — ilmenite; Alm — almandine; L — CO_2-rich Fe^{3+}-containing carbonate–silicate melt.

The mixture of Al_2O_3, SiO_2, $CaMg(CO_3)_2$ and $MgCO_3$ (total mass of 300 mg) was placed in the Pt capsule with a diameter of 10 mm. A picroilmenite pellet (150 mg) was put inside the carbonate-oxide mixture. Relatively large volume of picroilmenite was conditioned by its role as a source for buffer reaction. Filled capsules were sealed by arc welding. The height of the sealed capsules varied from 3.5 to 4.0 mm. This scheme on the one hand allowed us to use the redox reaction, involving decomposition of ilmenite to estimate fO_2 in ampoules, and on the another hand enabled the investigation of partial melting and decarbonation processes, with minimal interaction between Pt capsule and Fe-containing phases. The presence of Fe^{3+}(Fe_3O_4 content) in initial picroilmenite permitted effective fO_2 buffering, even in case of spontaneous diffusion of hydrogen through the walls of Pt capsule.

The oxygen fugacity (fO_2) values for the reaction (Fig. 6)

$$3FeTiO_3 + 0.5O_2(g) = Fe_3O_4 + 3TiO_2 \quad (1)$$

were calculated in the temperature range of 1000–1850 °C and pressure of 6.3 GPa, using thermodynamic constants for $FeTiO_3$, Fe_3O_4 and TiO_2 from H-Holland98 database (Holland and Powell, 1998), for O_2 (g) from g-reid database (Reid et al., 1977), and calculation module of "Selector-Windows" program complex (Chudnenko, 2010).

In an additional series of experiments, a cylindrical graphite container, filled with the powdered picroilmenite, homogenized with initial carbonate-oxide mixture, in the same proportions as mentioned above, was placed in the Pt capsule. The use of Pt + graphite capsule provided fO_2 values at CCO buffer. In both series of experiments cubo-octahedral synthetic diamond seed crystals (0.5 mm in size) were placed in the ampoule. It allowed us to define, if redox conditions in the ampoule corresponded to the diamond/graphite stability field.