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Reducing role of sulfides and diamond formation in the Earth's mantle

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Abstract

Sulfides are abundant inclusions in diamond, but their role in the diamond genesis is still debatable. To address this issue, experimental modeling of natural diamond-forming processes with the participation of sulfides has been performed with the $MgCO_3$–SiO_2–Al_2O_3–FeS system at 6.3 GPa in the temperature range of 1250–1800 °C, using a multi-anvil high pressure apparatus of the "split-sphere" type. As a result of redox reactions involving carbonate, oxides and sulfide, diamond and/or graphite are produced in association with garnet, orthopyroxene, coesite and sulfides (pyrite, pyrrhotite). Diamond crystals, formed from the carbon of initial carbonate, are found to contain nitrogen impurity with total concentration of approximately 1500 ppm, and defects related to hydrogen impurity. Based on the experimental data and thermodynamic calculations, the processes of the carbonate–oxide–sulfide interaction are reconstructed, revealing the role of sulfides as a reducing agent for CO_2-fluid. It is established that pyrrhotite acts as the reducing agent irrespective of its aggregate state (solid or melt). At temperatures below melting, pyrrhotite is enriched with sulfur and depleted with iron from FeS to $Fe_{0.85}S$. At higher temperatures, sulfide melt is enriched with sulfur and crystallizes as pyrite and pyrrhotite during quenching. The medium in which diamond and/or graphite crystallize is a CO_2-dominated fluid containing dissolved carbon, silicates, oxides and sulfides. The investigated processes and mechanisms of diamond crystallization can be considered as a possible model of the diamond formation in sulfide-bearing paragenesis in mantle metasomatism or UHP metamorphism of crustal material.

Keywords: diamond formation; sulfides; carbonates; silicates; fluid; redox reactions; mantle; HPHT experiments

1. Introduction

The modern models of diamond genesis are based, mainly, on the results of investigations of mineral and fluid inclusions in diamonds, as well as on experimental data on diamond formation in various media. Among the mineral inclusions in diamond, silicates, sulfides and oxides dominate (Sobolev, 1977; Meyer, 1987; Harris, 1992). Fluid inclusions in diamonds have been actively studied since recent time, because it is fluid inclusions that give an exceptionally significant information for the reconstruction of diamond-forming media (Navon et al., 1988; Schrauder and Navon, 1993, 1994; Izraeli et al.,

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2001). Of particular interest are micro- and nano-inclusions, characteristic of diamonds of both mantle (Klein-BenDavid et al., 2006; Tomlinson et al., 2006) and UHP metamorphic origin (Dobrzhinetskaya et al., 2003; Hwang et al., 2005). A comprehensive body of data accrued from the inclusion studies demonstrates the complexity and heterogeneity of the natural diamond-forming environment. This stimulates experimental investigations aimed at determining the role of specific components of the environment in nucleation and growth of diamond. Since, most of the models associate the origin of diamond with oxidation–reduction reactions (Haggerty, 1986; Sobolev and Shatsky, 1990; Deines and Harris, 1995; Ogasawara et al., 1997; Luth, 1999) and mantle metasomatism (Boyd et al., 1994a,b; Taylor and Anand, 2004; Shatsky et al., 2005), experimental studies into these reactions and processes are of interest.

At the opening stage of the experimental modeling of the diamond genesis, various non-metallic solvents have been investigated for the capability of diamond synthesis. These include melts of alkaline (Akaishi et al., 1990; Litvin et al., 1997; Pal'yanov et al., 1999) and alkaline–earth carbonates (Akaishi et al., 1990; Taniguchi et al., 1996; Pal'yanov et al., 1998; Sato et al., 1999), carbonate–silicate systems (Arima et al., 1993; Litvin and Zharikov, 2000; Shatsky et al., 2002), sulfide melts (Litvin et al., 2002; Palyanov et al., 2006) and sulfur (Sato and Katsura, 2001; Pal'yanov et al., 2001). Since fluids are believed to play an important role in diamond formation processes, diamond crystallization has been studied in C–O–H system (Yamaoka et al., 1992; Akaishi et al., 2000; Sokol et al., 2001), silicate–fluid (Sokol et al., 1999; Pal'yanov et al., 2005a) and carbonate–fluid systems (Pal'yanov et al., 1999, 2002a; Sokol et al., 2004). Recently, experimental studies focusing on diamond formation through oxidation–reduction reactions have started to appear. To date it has been experimentally demonstrated that diamond can form as a result of redox reactions involving carbonates and Si, SiC or silicon-bearing metal (Arima et al., 2002; Siebert et al., 2005), or carbonates and reduced fluids (Pal'yanov et al., 2002b; Yamaoka et al., 2002; Pal'yanov et al., 2005b).

One of the challenging questions is unrevealed role of sulfides in the origin of diamond. As is known, sulfides are among the most common inclusions in diamonds (Sharp, 1966; Harris and Gurney, 1979; Efimova et al., 1983; Bulanova et al., 1993; Pearson et al., 1998; Richardson et al., 2004). A considerable amount of sulfide micro-inclusions were revealed in diamonds from kimberlites from Canada and Siberia (Klein-BenDavid et al., 2003, 2006) as well as in metamorphic diamonds from Erzgebirge (Hwang et al., 2001) and Kokchetav Massif (Hwang et al., 2003). Two models have been proposed, which account for the involvement of sulfides in diamond genesis. First one supposes diamond crystallization from sulfide melt saturated with carbon (Haggerty, 1986), in a manner similar to diamond synthesis from carbon solution in transition metals melt. This model has been developed in a number of studies (Bulanova et al., 1993; Bulanova, 1995; Spetsius, 1999). Experiments on the interaction between graphite and sulfide melts of FeS and $(Fe,Ni)_9S_8$ compositions, performed over a wide range of *P–T* parameters, showed that the minimal pressure required for diamond nucleation from carbon saturated sulfide melt is 7.5 GPa (Palyanov et al., 2006). Another idea was first proposed by Marx (Marx, 1972), who suggested that diamond could form via the reaction $2FeS+CO_2=2FeO+S_2+C$. Experimental investigation of this or similar reactions, however, represents a formidable task due to methodical complexity. First study along this line is the experimental investigation of magnesite reduction in the presence of a eutectic-composition $Fe_{70}S_{28}O_2$ melt (Gunn and Luth, 2006). As a result of carbonate reduction by Fe^0-rich sulfide melt metastable graphite was produced in the experiments.

In the present study, we have investigated carbonate–oxide–sulfide interaction in the $MgCO_3$–SiO_2–Al_2O_3–FeS system under mantle *P–T* parameters. Based on the experimental data and thermodynamic calculations an

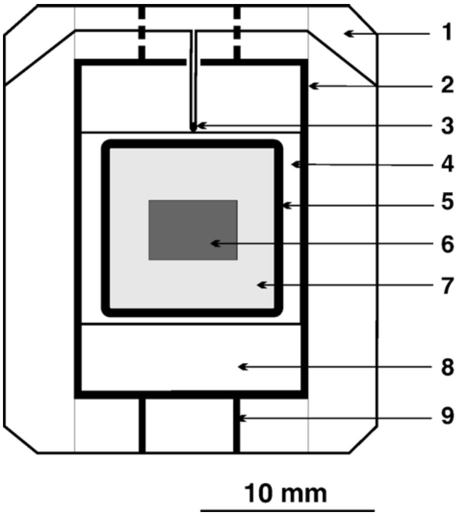

Fig. 1. The high pressure cell used in the present study: 1 — ZrO_2 container; 2 — cylindrical graphite heater; 3 — $PtRh_6/PtRh_{30}$ thermocouple; 4 — MgO sleeve; 5 — graphite sleeve; 6 — FeS; 7 — $MgCO_3+Al_2O_3+SiO_2$ ampoule; 8 — ZrO_2; 9 — Mo leads.