

SULFIDE-SILICATE-CARBON SYSTEMS: MINERAL EQUILIBRIA, DIAMOND FORMATION, NATURAL RELATIONS

Shushkanova A.V., Litvin Yu.A.

Tel: (096)5246205.

nastashushkanova@newmail.ru

Sulfides are the abundant minerals of the Earth's mantle. Sulfide minerals are associated with the mantle peridotites and eclogites including the diamond-bearing varieties as well with diamonds as both primary inclusions [1, 2] and contacts covers [3]. Study of the mantle mineral systems with sulfides is of interest for the mantle mineralogy and petrology and an understanding of the processes of natural diamond formation.

The detection of sulfides in the centers of diamond nucleation is a base for the sulfide version of diamond formation. Under this version, sulfide substances are the natural diamond-forming media [4]. Silicate minerals may be included together with sulfides in the same diamond crystal (fig. 1, 2) that is an evidence of a syngeneses of diamond, sulfide, and silicate minerals

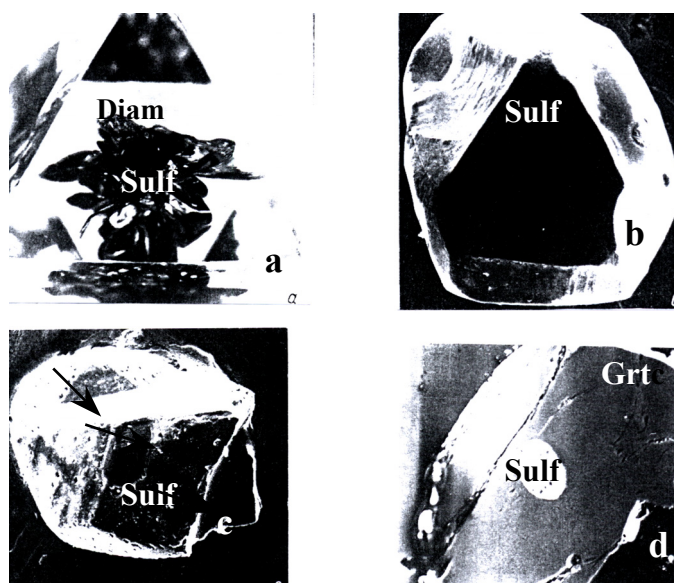


Fig. 1. Primary sulfide inclusions [4]: a) sulfide in diamond; b) sulfide (the inclusion is withdrawn from diamond); c) garnet in sulfide (the inclusion is withdrawn from diamond); d) sulfide in garnet (the inclusion is withdrawn from diamond).

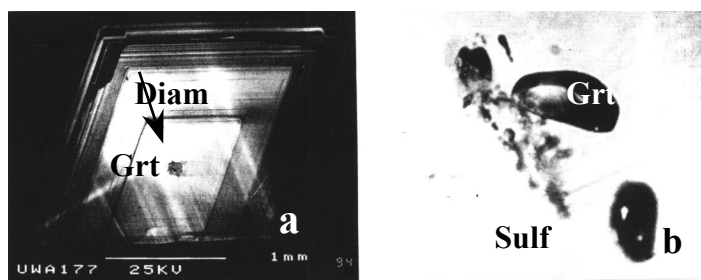


Fig. 2. Inclusions of silicate (a) and sulfide (b) in the growth center of diamond [5].

Experimental data demonstrate that silicate melts do not dissolve carbon and are not effective for the processes of diamond formation [6] in contrast to the melts with chemistry of natural parental media such as the carbonate-silicate-carbon [7] and sulfide-carbon [8] ones.

The assumption that diamonds containing simultaneously syngenetic silicate and sulfides inclusions were crystallized from hybrid sulfide-silicate melts is not in agreement with liquid immiscibility of sulfide with both silicate and carbonate melts which is observed in natural and experimental conditions (fig. 3).

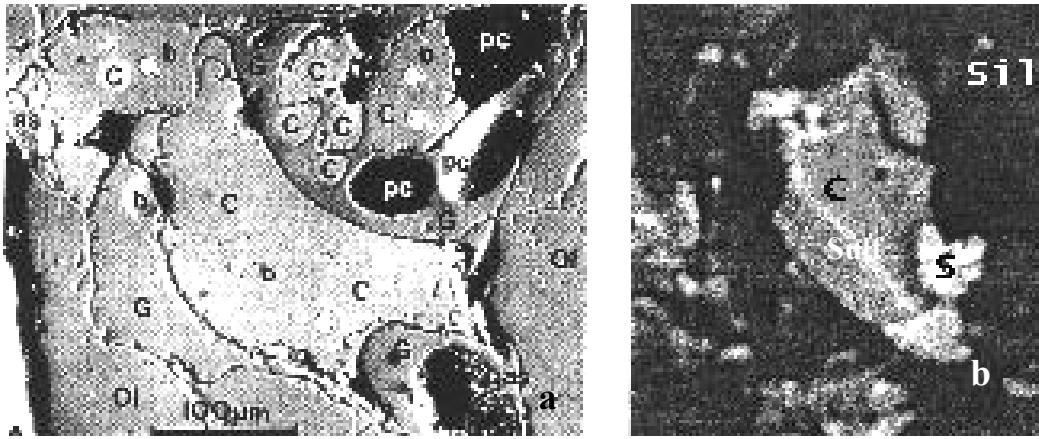


Fig. 3. Liquid immiscibility of sulfide melts with the silicate and carbonate ones: (a) by natural evidence [9]; (b) in experiment at 7 GPa [10].

The main objective of the experimental study is checking of a possibility of the syngenetic crystallization of diamond and silicates from sulfide melts.

The silicate–sulfide system, which was chosen for realization of the goal consists of natural garnet (Grt) from Udachnaya pipe (Yakutiya) and pyrrhotite (Po). Garnet composition: SiO_2 – 39.16, TiO_2 – 64, Al_2O_3 – 21.05, Cr_2O_3 – 0.03, FeO – 21.86, MnO – 0.44, MgO – 8.55, CaO – 8.50, Na_2O – 0.09 (wt. %). Pyrrhotite composition: S – 38.96, Fe – 60.74, Co – 0.06, As – 0.04 (wt. %).

Powdered mixtures of the minerals in the ratios of 50:50, 75:25, and 25:75 were placed in graphite ampoules and subjected to pressure of 7 GPa and temperatures of 1200 – 2000 °C in the anvil-with-hall apparatus with the cell made from lithographic limestone [11]. The accuracies of pressure and temperature estimations are ± 0.1 GPa and $\pm 20^\circ\text{C}$, respectively. Experimental samples were studied by the methods of scanning electron microscopy and electron microprobe with the use of electron microscope Tescan Vega TC 5130 MM with the analyzer Link inca Energy (IEM RAS, with assistance of A.N. Nekrasov).

Experimental studies of the garnet – pyrrhotite system (fig. 4) point to a formation of two-phase subsolidus assemblage Grt + Po with compositions of the boundary phases of the system – natural pyrope – almandite – grossularite garnet and pyrrhotite Fe_{1-x}S (without any indications of formation of sulfide – silicate solid solutions). When the subsolidus assembly melts completely, sulfide and silicate melts in a state of complete liquid immiscibility are formed. A phase diagram for the mantle sulfide – silicate system is first constructed and belongs to the type of that for the systems with components which crystallize from their own melts [12].

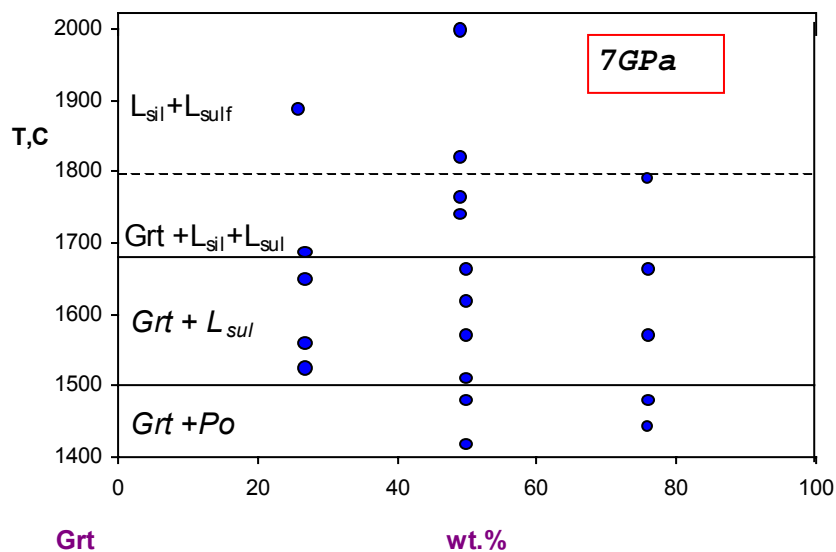


Fig. 4. Phase diagram of the experimental garnet – pyrrhotite system at 7 GPa.

By the microprobe analyses of experimental phases, a mutual solubility of the components is absent at the melting temperature of the more refractory components and higher temperatures. It is found that garnet is not practically capable to dissolve in sulfide melt. The mapping of distribution of chemical elements (fig. 5) supports the result.

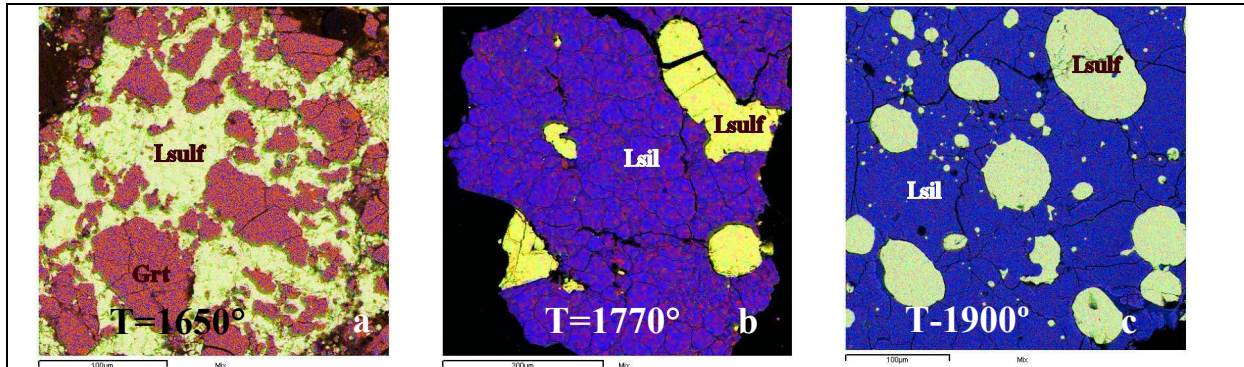


Fig.5. Maps of chemical elements (S, Fe, Al) from different fields of phase diagram

By the experimental evidence, silicate minerals can not crystallize from sulfide melts. This argues for an impossibility of a syngensis of diamond and silicate minerals in sulfide melts.

The system under study is first successfully used for diamond synthesis. For this, graphite was added to the starting materials as the carbon source. Scanning electron microscope images of diamonds in situ in the pyrrhotite – carbon and garnet – pyrrhotite – carbon systems are given on the figs. 6, a and 6, b, respectively. The experimental conditions are 8.5 GPa and 1600 - 1700 °C. Diamond crystallization proceeded in sulfide – carbon melts with dissolved carbon in the state of labile over saturation to diamond.

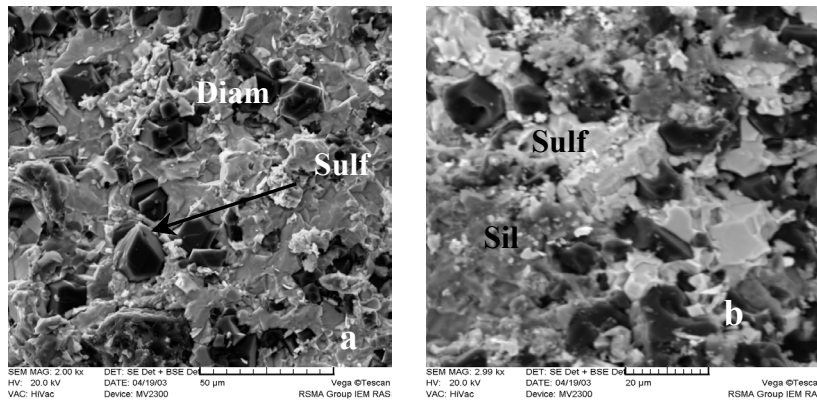


Fig. 6. Diamonds synthesized in the systems:

- a) pyrrhotite – carbon (smpl. 1/879);
- b) garnet – pyrrhotite – carbon (smpl. 1/880).

Thus, the studies allow definite conclusions:

(1) Phase equilibria of the garnet - pyrrhotite silicate – sulfide system at the parameters of diamond stability (7 GPa, 1400 – 2000 °C) on the carbon phase diagram [13] is first studied.

(2) The type obtained for phase diagram for the Grt – Po join declines a possibility of the syngenetic formation of diamond and garnet from sulfide – carbon melts. This may be evidence that natural diamonds with the coexisting sulfide and silicate inclusions were formed in carbonate – silicate – carbon melts with high contents of admixed sulfides. As this takes place, the episodes when sulfide-carbon melts became parental media are not excluded.

(3) Spontaneous crystallization of diamond in the Po - C and Grt – Po – C at 8.5 GPa and 1600 – 1700 °C is first realized.

References:

1. Sharp W.E. // Nature, 211, 5047, 402-403 (1996).

2. *Bulanova G.P., Shestakova O.E., Leskova N.N.* // *Zap. Vses. Miner. Ob-va*, 111, 5, 557-562.
3. *Spetsius Z.V.* // *Proc. VII Int. Kimberlite Conf., Cape Town*, p. 823-828 (1998).
4. *Efimova E.S., Sobolev N.V., Pospelova L.N.* // *Zap. Vses. Miner. Ob-va*, 112, 3, 300-309 (1983).
5. *Bulanova G.P., Griffin W.L., Ryan C.G.* // *Mineral. Mag.*, 62, 3, 409-419 (1998).
6. *Borzdov Yu.M., Sokol A.G., Palyanov Yu.N. et al.* // *Doklady Ac. Sci.*, 366, 4, 530-533 (1999).
7. *Litvin Yu.A., Zharikov V.A.* // *Doklady Ac. Sci.*, 372, 6, 808-811 (2000).
8. *Litvin Yu.A., Butvina V.G., Bobrov A.V., Zharikov V.A.* // *Doklady Ac. Sci.*, 382, 1, 106-109 (2002).
9. *Kogarko L.N., Henderson C.M.B., Pacheke H.* // *Contrib. Mineral. Petrol.*, 121, 267-274 (1995).
10. *Litvin Yu.A., Jones A.P., Beard A.D. et al.* // *Doklady Ac. Sci.*, 381, 4, 528-531 (2001).
11. *Litvin Yu.A.* Physicochemical Study of the deep-seated Earth's substance melting // *Moscow: Nauka*, 1991. 311 p.
12. *Zakharov A.M.* Phase diagrams of binary and ternary systems. *Moscow: Metallurgy*, 1990.
13. *Kennedy C.S., Kennedy G.S.* // *J. Geophys. Res.*, 81, 14, 2467-2470 (1976).

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21) 2003
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003
 URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/term-6e.pdf
 Published on July 15, 2003

© Department of the Earth Sciences RAS, 1997-2003
 All rights reserved