

PECULIARITIES OF DIAMOND FORMATION IN THE MANTLE CARBONATE-SILICATE-SULPHIDE MELTS BY EXPERIMENTAL EVIDENCE

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Chemical composition of parental diamond-forming media is of great importance for the problem of diamond origin. The version that the main parental media of natural diamonds are represented by carbonatite melts is most probable. The media consist mainly from carbonate and silicate components and contain small quantities of sulphides, phosphates, haloids, oxides, CO₂, H₂O, and other admixed components. Experiments at high pressure demonstrate that both the main and admixed components are effective for diamond nucleation. Spontaneous crystallization of diamond is experimentally realized in carbonate-silicate-carbon [1, 2], sulphide-carbon [3], chloride-carbon [4] melt-solutions, water-carbon and CO₂-carbon fluids [5]. It means that "experimental criterion" based on diamond syntheses in one or another media is necessary but is insufficient in an estimation of a chemical composition of parental diamond-forming media. So, we should look for the unequivocal solution of the problem of the parental media using the complex approach. We have to formulate this task as a clarification of chemical and phase compositions of the parental media at a wide range of mantle pressures and temperatures. The compositions have to be in agreement with the second experimental criterium according to which diamonds and syngenetic solid, melted and fluid inclusions can simultaneously form in them. Therefore, experimental study should be focused on searching parental media which are primary both for diamonds and for their syngenetic inclusions.

The carbonatite model is compatible with experimental results on spontaneous and seeded diamond formation and mineralogical data for syngenetic inclusions of minerals, melts and fluids in mantle-derived diamonds [6 - 8]. It is experimentally revealed that sulphide melts with the dissolved carbon are effective for spontaneous nucleation and growth of diamond [3, 9]. Capability of sulphide melts to syngenetic formation of diamonds with primary silicate and carbonate inclusions is not yet clear.

We have studied phase relations of the system CaCO₃ - pyrope (Mg₃Al₂Si₃O₁₂) - pyrrhotite (FeS) which representatively models the compositions of natural diamond-forming media. CaCO₃ is one of major components of deep carbonatites and fluid-carbonatite inclusions in diamonds; pyrope Mg₃Al₂Si₃O₁₂ is an indicative component a garnet-peridotite mantle; pyrrhotite FeS belongs to sulphide minerals associated closely with mantle xenoliths and diamonds. Along with it, phase relations of binary boundary systems have been investigated: CaCO₃ - pyrope, pyrope - pyrrhotite and CaCO₃ - pyrrhotite. The goal of the work consists in an experimental investigation of phase equilibria at the melting of model systems at PT-parameters of thermodynamic stability of diamond (P = 7.0 ГПа, T = 1000-2000°C). The main goals are connected with quantitative studies of phase relations of sulphide minerals and melts with silicate and carbonate ones and, especially, on solubility of components in the melts formed.

It is found that carbonate and silicate melts are completely miscible at the melting of the carbonate-silicate system. Carbonate-silicate melts form dendrite or fine-grained aggregates (fig. 1) at quenching. Garnet of pyrope-grossular composition and Ca-Mg-carbonate are formed. The occurrence of Ca-Mg-phases is fixed at all range of experimental temperatures (1150 - 1650°C).

Microprobe analyses of experimental phases are presented in the table 1: Ca- and Mg-components are determined in all products of crystallization of uniform carbonate-silicate melt.

The system $\text{CaCO}_3 - \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ is pseudobinary at high pressure due to the boundary components interaction and formation of Mg-Ca-carbonate and pyrope-grossular garnet in subsolidus. Sulphide melt forms large and fine round drops in carbonate melt (fig. 2) at the melting of the carbonate-sulphide system $\text{CaCO}_3 - \text{FeS}$. Similar quenching configurations of samples denote immiscibility of the melts.

Microprobe analyses of carbonate and sulphide melts has revealed small amounts of Ca in sulphide melt (table 2) and Fe in carbonate melt (table 3). But S was not found in the latter.

The following reactions may responsible for a Fe/Ca exchange between sulphide and carbonate melts:

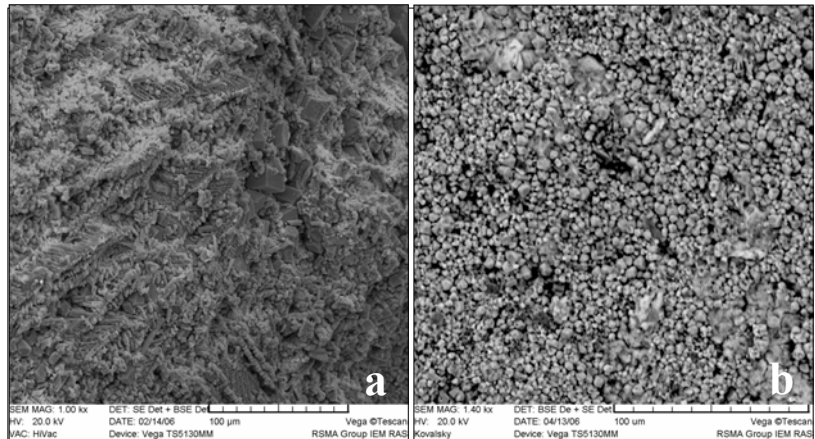
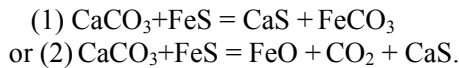


Fig.1. Carbonate-silicate melts after quenching.

a) Sample 1/1126: starting materials-

$\text{Prp}_{50}(\text{CaCO}_3)_{50}$, $T=1400^\circ\text{C}$, $P=7\text{GPa}$, duration - 60 min.

b) Sample 1/1123: starting material- $\text{Prp}_{50}(\text{CaCO}_3)_{50}$.
 $T=1250^\circ\text{C}$, $P=7\text{GPa}$, duration - 60 min

Table 1. Microprobe phases' analyses ϕa_3 (weight % of elements' oxides) formed at quenching of carbonate-silicate melt

MgO	Al_2O_3	SiO_2	CaO
silicate phases			
24.90	25.81	45.94	8.37
21.82	24.34	44.44	11.46
20.20	23.35	41.03	15.38
17.47	19.66	35.06	8.97
carbonate phases			
22.35	1.63	0.89	30.18
2.02	1.13	0.99	48.39
17.67	4.61	1.82	30.11

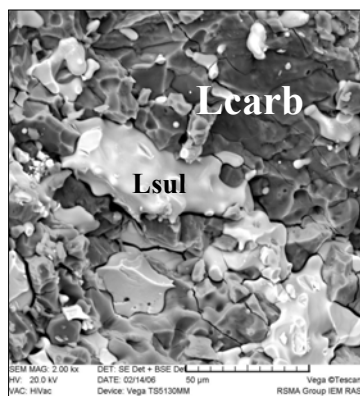


Fig.2. Equilibrium sulphide and carbonate melts.
 Sample № 1/1128. Starting proportions $\text{FeS}_{50}(\text{CaCO}_3)_{50}$; $T=1405^\circ\text{C}$; $P=7\text{GPa}$; duration – 60 min.

Ca-component in sulphide melt is represented with CaS-sulphide, and Fe-component in carbonate melt as FeCO_3 carbonate or FeO oxide.

Earlier we studied the sulphide-silicate system pyrrhotite - garnet and its boundary section pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{FeS}$ [9.] Microprobe analyses of experimental phases and SEM images demonstrated some irregularity of distribution of the dissolved sulphide components in silicate melts. The solubility is about

Table 2. Microprobe analyses of quenched sulphide phases (weight %)

S	Fe	Ca
36.76	62.28	<2 σ
36.45	62.09	0.18
36.09	62.10	0.47
37.47	61.70	0.21

Table 3. Microprobe analyses of quenched sulphide phases (weight %)

O	S	Ca	Fe
14.77	<2 σ	36.49	0.27
14.76	<2 σ	36.43	0.40
14.93	<2 σ	37.08	0.29
14.63	<2 σ	36.21	0.25

0.5 - 0.8 % FeS. At the same time, solubility of garnet components in sulphide melts have appeared below of detection limit (for Si and Al 0.16 - 0.50 and 0.18 - 0.40 % respectively). This is independent on garnet component source – solid, partial or complete melt phases.

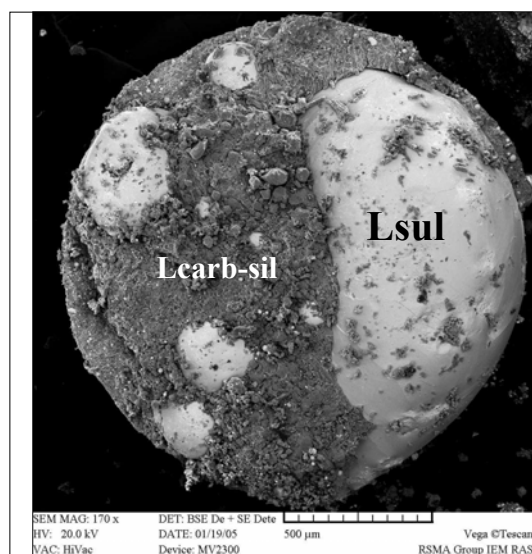


Fig.3. Equilibrium sulphide and carbonate-silicate melts. Sample № 1/1088. Starting proportions $[(\text{MgCO}_3)_{50}\text{Prp}_{50}]_{50}\text{FeS}_{50}$; $T=2400^\circ\text{C}$; $P=7\text{GPa}$; duration – 2 min

Table 4. Microprobe analyses of carbonate-silicate phases (weight %)

MgO	Al ₂ O ₃	SiO ₂	SO ₃	CaO	FeO
18.81	24.35	40.23	0.03	10.64	5.22
19.69	23.38	42.70	<2σ	8.85	4.86
21.63	25.04	46.64	<2σ	10.11	5.63
21.33	23.57	43.22	<2σ	8.89	4.18

Table 5. Microprobe analyses of sulphide phases (weight %)

S	Ca	Fe	O
37.80	0.21	59.67	1.83
38.23	0.23	60.33	1.61
36.80	<2σ	59.30	1.59
36.55	0.17	59.60	3.18

Experiments on melting of the ternary system have revealed practically complete immiscibility of sulphide and homogeneous silicate-carbonate melts. Sulphide melt forms drops in carbonate-silicate one (fig. 3).

Effect of solubility of silicate and carbonate components in sulphide melt is not found out (tables 4, 5). For the ternary system, Fe was found in uniform carbonate-silicate melt (in S absence) and S and extra O in sulphide melt. Probably, the reactions (1) and (2)

discussed above take place in this case. In case of ternary system, Fe was also found in carbonate-silicate melt probably in the form of sulphide.

Thus, the system $\text{CaCO}_3 - \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{FeS}$ at high T-P is presented by the following phases: a Mg-Ca-carbonate $(\text{Mg,Ca})\text{CO}_3$, pyrope-grossular garnet $(\text{Mg,Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and pyrrhotite FeS. Actually there are two immiscible, carbonate-silicate and sulphide liquids with additional components indicated above.

Our high pressure experiments show that the model carbonate CaCO_3 -silicate $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -sulphide system represents two immiscible melts, carbonate-silicate and sulphide melts at diamond formation PT-conditions. It testifies that sulphide melts, being capable to diamond formation, are not effective for syngenesis of diamonds and their silicate and carbonate inclusions, in contrast to the silicate-carbonate melts. It means that sulphide melts cannot be dominating parent media for the bulk of natural diamonds which characterize by syngenetic inclusions of silicates and carbonates. At the same time, we can assume the limited role of sulphide-carbon melts at natural diamond formation. Sulphide melts can be included in the form of immiscible drops in carbonate-silicate parental media. Thus, if sulphide melts contains oversaturated dissolved carbon, spontaneous nucleation and growth of diamonds occur in them with typomorphic characteristics for sulphide parental media. Diamonds formed in sulphide melts can contain primary inclusions of sulphide material only. Diamonds can contain inclusions of silicate, carbonate, and sulphide material at the formation in carbonate-silicate (carbonatite) melts with the dissolved carbon.

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