## EQUILIBRIUM MELTING RELATIONS OF THE ECLOGITIC SYSTEM GARNET - PYRRHOTITE AT 7 GPA

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The problem of diamond genesis at the Earth mantle conditions is one of the most important in the field of genetic mineralogy, petrology and geochemistry. The question of chemical and phase compositions of the parent diamond-formatting media is the most debatable.

In the present work the main attention is given to the genetic questions connected with existing of primary inclusions of sulphide minerals and melts in diamonds, which regard to number of the most widespread together with silicate inclusions. It points to participation of sulphide substance in the processes of diamond formation. However, there are contradictory notions as to a role of sulfides in the diamond-forming processes.

For example, a detection of inclusions of sulphide minerals in the nucleation centers of diamond [1,2] has given a base for the hypothesis of leading role of sulphide environment in diamond genesis.

For the first time, an efficiency of sulphide melts for diamond formation at the mantle conditions was proved in 2002 [3, 4].

A *carbonatitic* (*carbonate-silicate*) model of diamond genesis has received for a convincing substantiation basing on natural and experimental data last years. Experimental data demonstrate that silicate melts do not dissolve carbon and are not effective for the processes of diamond formation [5] in contrast to the melts with chemistry of natural parental media such as the carbonate-silicate-carbon [6,7] and sulfide - carbon [3, 8, 9, 10] ones.

The carbonatitic model is based on the composition of the primary fluid microinclusions which are represented by multicomponent carbonate-silicate melts with dissolved chloridic, phosphatic and other components [11, 12], and also on observations of carbonate and silicate inclusions in diamonds [13].

The version of carbonatitic nature of parent media responsible for spontaneous crystallization of diamond at *PT*-conditions of its thermodynamic stability, has received a convincing experimental substantiation due to realization of processes of diamond crystallization in melts of substances which are chemical analogues of natural parent medias as in simplified modeling [14, 15,16], and in real multi-component approximations [6, 7].

Some mineralogists have suggested that parent diamond-forming environment is represent by complex hybrid melts of carbonate, silicate and sulphide components [13, 17]. Development of such conceptions could be promoted by findings of silicates and sulfide inclusions coexisted in one diamond crystal in a central inclusion position [2].

Meanwhile, liquid immiscibility of sulphide, on the one hand, silicate and carbonate, on the other hand, is discovered in carbonatite samples from the upper mantle [18]. There are also preliminary qualitative experimental data of liquid immiscibility of sulphide and carbonate-silicate melts [19, 20].

Thus, the problem of phase relations, first of all, sulphide and silicate melts, at PT-parameters of diamond formation is actual and important for developing a modern conceptions about parent diamond-forming media.

In this connection, the main objectives of the experimental study are following:

Experimental research of phase relations of the mantle sulfide-silicate systems corresponding to diamond-bearing assemblages, using a model multicomponent eclogitic system garnet - pyrrhotite as an example at pressure 7 GPa and high temperatures corresponding to the area of diamond thermodynamic stability. Under this research, it was supposed to study an opportunity of sin genetic crystallization of diamond and silicates from sulphide melt;

Experimental study of the opportunity and main physical and chemical features of diamond crystallization in sulfide - carbon system (pyrrhotite – carbon) and silicate - sulfide - carbon system (garnet - pyrrhotite – carbon) for an estimation of diamond-forming ability of sulfide - silicate systems. The multicomponent silicate-sulfide system with boundary composition of natural pyrope-almandite-grossuraric garnet (Grt)<sup>1</sup> and natural pyrrhotite (Po) was investigated. The boundary minerals were taken from the eclogite of pipe Udachnaya (Yakutia).

<sup>&</sup>lt;sup>1</sup> **Symbols of phases**: Grt – garnet, Po – pyrrhotite, Prp – pyrope, Sulf – sulfide, Lsil – silicate melt, Lsulf – sulfide melt,  $\beta$  - basalt.

The composition of a garnet:  $SiO_2 - 39.16$ ,  $TiO_2 - 0.64$ ,  $Al_2O_3 - 21.05$ ,  $Cr_2O_3 - 0.03$ , FeO - 21.86, MnO - 0.44, MgO - 8.55, CaO - 8.50, Na<sub>2</sub>O - 0.09 (mac. %). The composition of pyrrhotite: S - 38.96, Fe - 60.74, Ni - 0.00, Cu - 0.00, Co - 0.06, As - 0.04 (mac. %).

The model silicate-sulfide system with boundary components of synthetic pyrope (Prp) and sulphade ( $Fe_{1-x}S$ ) was studied as well.

The apparatus of high pressure and temperature "anvil-with-holl" was applied for realization of the goals.

Powdered mixtures of the minerals in the ratios of 0:100, 25:75, 50:50, 75:25 and 100:0 were placed in graphite ampoules-heaters, then the prepared samples were subjected to pressure of 7-8 GPa and temperatures of 1200 - 2030°C in the "anvil-with-holl" apparatus with the cell made from lithographic limestone [21]. At the choice of such parameters we were guided by conditions of diamond stability [23]. Some preliminary date is in [9, 10].

The formation of two-phase subsolidus assemblage of Po + Grt (fig. 1), partial melting assemblages of sulphide melt (Lsulf) + Grt (fig. 2), and also Lsulf + silicate melt (Lsil) + Grt\* (restitic Grt) (fig. 3), and in completely melted two-phase assemblage Lsulf + Lsil (fig. 4) was revealed for the eclogitic systems pyrrhotite- garnet. The phase diagram of the system under study is presented on the fig. 5. The model Prp – Fe<sub>1-x</sub>S system, phase diagram is shown on the fig. 6 and discussed later.



Thus, that substantially important effect of complete sulfide - silicate liquid immiscibility is experimentally established at parameters of diamond formation for the first time. By the careful microprobe analysis, the evidence of formation of sulfide - silicate solid and liquid solutions is not established for both investigated systems. Herewith, very clean contours of various phases and their chemical analyses on presence of extraneous "foreign" elements, - sulfur in silicate and magnesium and aluminum in sulfide, - (tab. 1) purports that mutual solubility of components in coexisted sulphide and silicate melts is absent, i.e. migration of components from one liquid phase in to another does not occur: garnet components are not dissolved in sulphide melt, sulphide components were not revealed in silicate melt. Thus, sulphide and silicate melts are in a state of the complete liquid immiscibility.

№sam.	Compos., W.%	T,C	Exposition, min	Phases	Phase's compositions, weight% $\pm 2\sigma$					
1/875	$Grt_{25}(Fe_{1-X}S)_{75}$	1446	S	Grt+Po		Grt(875-1)	Grt(875-2)	Grt(875-3)	Po(875-4)	Po(875-5)
					Mg	4.70±0.23	$4.44 \pm 0.18$	4.76±0.24	<2σ	<2σ
					Al	10.71±0.28	10.45±0.25	10.48±0.31	<2σ	<2σ
					Si	19.09±0.50	19.23±0.42	19.35±0.47	<2σ	<2σ
					S	<2σ	$<2\sigma$	$<2\sigma$	41.72±0.58	41.55±0.59
					Ca	6.27±0.21	6.20±0.29	$6.00 \pm 0.30$	<2σ	<2σ
					Ti	0.51±0.20	0.41±0.20	$0.43 \pm 0.20$	<2σ	<2σ
					Mn	0.38±0.15	0.24±0.12	$0.29 \pm 0.12$	$<2\sigma$	<2σ
					Fe	16.31±0.50	17.01±0.48	16.55±0.53	57.88±1.00	58.07±0.89
					0	42.02±0.62	41.94±0.57	42.09±0.61	-	-
1/868	Grt <sub>50</sub> ( <sub>Fe1-X</sub> S) <sub>50</sub>	1607	15	Grt+Lsulf		(868-22)	Grt rim(868-26)	Lsulf(868-24)	Lsulf(868-25)	Lsulf incl.(868-27)
					Na	<2σ	<2σ	<2σ	<2	σ
					Mg	$4.62 \pm 0.30$	4.74±0.30	$<2\sigma$	<2	σ
					Al	10.40±0.35	10.28±0.35	<2σ	<2	σ
					Si	19.27±0.46	19.20±0.46	$<2\sigma$	<2	σ
					Р	<2σ	$<2\sigma$	<2σ	<2	σ
					S	<2σ	$<2\sigma$	41.51±0.63	41.08=	⊧0.64
					K	<2σ	$<2\sigma$	<2σ	<2σ	
					Ca	6.20±0.28	6.10±0.26	$<2\sigma$	<2σ	
					Ti	0.35±0.17	$0.33 \pm 0.17$	<2σ	<2σ	
					Cr	<2σ	0.17±0.15	$<2\sigma$	<2σ	
					Mn	$0.43 \pm 0.20$	$0.35 \pm 0.20$	<2σ	<2 <del>0</del>	
					Fe	16.46/6.76	$16.32 \pm 0.61$	57.03±1.04	58.01±1.05	
					Со	<2σ	$<2\sigma$	$<2\sigma$	<2σ	
					Ni	<2σ	$<2\sigma$	$<2\sigma$	<2σ	
					Cu	<2σ	<2σ	<2σ	<2	σ
					Zn	<2σ	<2σ	<2σ	<2	σ
					As	<2σ	<2σ	<2σ	<2	σ
					0	$41.99\pm0.81$	42.03±0.95	-	- L -:1/1/000 5)	C-++(1/000 C)
1/988	$Grt_{25}(Fe_{1-X}S)_{75}$	1657	10	Lsulf+Grt*+Lsil	0	1 25+0.52	Grt(1/988-3)	LSII(1/988-4)	LSII(1/988-5)	Grt(1/988-6)
					V Na	1.55±0.55	41.78±0.77	$45.84\pm0.78$ 1.75±0.21	44.95±0.77	41.90±0.75
					Ma	<20 <2σ	20 4 00±0 30	$1.73\pm0.31$ 0.43±0.18	$1.2/\pm0.29$ 0.65±0.15	<20 5 26±0 31
					11 41	<20 <2σ	$4.99\pm0.30$ 11 33+0 38	$0.43\pm0.18$ $4.75\pm0.27$	$6.29\pm0.13$	$5.20\pm0.31$
					Si	<20 <20	$18.24 \pm 0.33$	$4.73\pm0.27$ 30.23 $\pm0.51$	$27.56\pm0.50$	$18.24\pm0.30$
					S	37 29+0 57	<20 <20	<25 <25	0.24+0.13	<20
					K	n</td <td>&lt;20 &lt;2σ</td> <td>1 52+0 18</td> <td><math>1.00\pm0.15</math></td> <td>&lt;20 &lt;2σ</td>	<20 <2σ	1 52+0 18	$1.00\pm0.15$	<20 <2σ
					Ca	<2σ <2σ	$6.01\pm0.26$	$6.95\pm0.29$	$7.16\pm0.29$	$5.85\pm0.25$
					Ti	<2σ	0.24±0.16	$1.84 \pm 0.22$	1.39±0.21	0.28±0.15
					Cr	<2σ	<2σ	<2σ	<2σ	<2σ
					Mn	<2σ	0.32±0.20	<2σ	<2σ	0.42±0.19
					Fe	61.08±0.98	16.89±0.57	6.60±0.45	9.45±0.48	16.33±0.56
<u>1/874</u>		1768	5	Lsill+Lsulf		Lsilrim (874–5)	Lsilcenter (874 6)	Lsilrim (874-8)	Lsulflcenter	Lsulfrim
	75				Mg	4 51+0 18	$427\pm017$	$417\pm015$	<20	<20
	Grt <sub>25</sub> (Fe <sub>1-X</sub> S)				Al	$10.99 \pm 0.27$	$10.76\pm0.22$	$10.85 \pm 0.27$	<2σ	-20 <2σ
					Si	$19.43 \pm 0.62$	$19.39 \pm 0.57$	$19.37 \pm 0.58$	<2σ	<2σ
					S	<2σ	0.13±0.10	<2σ	41.67±0.64	41.62±0.62
					Ca	12.14±0.21	11.70±0.27	11.83±0.31	<2σ	<2σ
					Fe	10.27±0.45	11.20±0.67	11.33±0.65	58.09±0.98	58.13±1.00
					0	42.66±0.69	42.54±0.54	42.44±0.64	-	-

Table 1. Experimental conditions and phase's compositions of system eclogitic garnet Grt - pyrrhotite Po(P = 7 GPa)

Thus, for the first time phase equilibria in system garnet Grt - pyrrhotite Po are experimentally investigated. The resulting phase diagram of mantle sulfide - silicate system (fig. 5) concerns to the type

Fig. 5. State diagram of the Fig. 6. State diagram of the experimental system Grt-Po experimental system Prp-Fe<sub>1-X</sub>S T,C 7 GPa 7 GPa T, C 2000 2000 1/941 1900 1900 Lsil+Lsulf Lsil+Lsulf 1800 1800 1/874 Lsulf+Lsulf 170 1700 /988 /877 1/897 1/915 /959 1600 1600 100 ()1/99 /904  $\bigcirc$ 1/878 Grt+Lsulf Prp+Lsulf 1500 1500 1/910 /912 1/916 1/875 1/911 1400 1400 1300 1300 Prp+Fe<sub>1-X</sub>S Grt+Po 1200 1200 1100 1100 1000 1000 900 900 800 800 50 75 0 25 50 75 100 0 25 100 Prp weight.% Fe<sub>1-x</sub>S Grt weight % Ро

of phase diagrams of systems «with components, which crystallizes from their own melts» by definition of Zaharov [22].

A research of phase relations of natural sulphide and silicate systems is supposed to be continued. In this connection, the great interest is represented by the boundary sections of such systems. The important boundary system in a considered case is the elementary system pyrope  $Mg_3Al_2Si_3O_{12}$  - Fe<sub>1-x</sub>S. The preliminary phase diagram of the system (fig. 6) is characterized by subsolidus assemblage Prp + Fe<sub>1-x</sub>S, two-phase assemblage of partial melting Lsulf + Prp, and also two-phase association of complete melting Lsulf + Lsil. The absence of a field of partial melting of a garnet is connected with the fact that pyrope is the congruently melted phase and its melting is characterized by an invariant point.

An interesting feature of behavior of pyrope gel mixes at hardening is found out at work with system pyrope - pyrrhotite. Pyrope melts (as well as melts of multicomponent natural garnet) form characteristic dendritic structure at quenching. However, pyrope amorphous gels form similar dendritic structures at temperatures even lower of pyrope melting point within the two-phase area Lsulf + Prp. That does not allow correcting estimate temperature of pyrope melting in the experiments. For this reason, the liquidus line is designated by a dashed line on the preliminary diagram of the system (in view of temperature for the natural garnet, experimentally determined.

Some complexities were found out with an establishment of temperature of sulfide melting also. It is practically impossible to establish a melting point by both textural peculiarities, and comparison of chemical analyses. That's why the technology of addition of fusible silicate rock basalt to sulfide was applied in experiment. It has allowed to draw a truly solidus line of the system. The case is that basalt melt, being immiscibilitive with sulphide one, forms in drop-like forms (fig. 7). When basalt melt co-exists with a solid sulphide mineral, which melts at more high temperatures, it flows round rough corners of the solid mineral (fig. 8).



By the experimental evidence, silicate minerals cannot crystallize from sulfide melts (as diamond can). This argues for an impossibility of a syngenesis of diamond and silicate minerals in sulfide melts.

Pyrrhotite -carbon and the investigated garnet - pyrrhotite systems, with graphite as a source of carbon for diamond are successfully used for diamond synthesis for the first time. The conditions of experiment were 7,5 - 9,6 GPa and 1800 - 2200°C. The choice of similar parameters was determined by known estimations of temperatures and pressure for graphite – diamond equilibrium curve [23].

Diamond crystallization was proceeded in sulfide - carbon melts with dissolved carbon in the state of labile over saturation in respect to diamond. Growth of diamonds on a seed is registrated also that testifies to existence of the conditions of metastable over saturation of carbon in respect to diamond.



Thus, for the first time "sulphide" synthesis of diamond are carried out with using of pyrrhotite - carbon melts in the mantle systems pyrrhotite - carbon (fig. 9) and eclogitic garnet - pyrrhotite - carbon (fig.10) at high pressure and temperatures. There are two immiscible melts silicate and sulfide coexisting with diamonds on fig. 10.

It is possible to draw the following conclusions on the basis of experimental results:

For the first time melting relations of the natural system garnet - pyrrhotite and model system pyrope -  $Fe_{1-X}S$  are studied. A results of this research are the phase diagrams concerning to the type of diagrams with components crystallizing from their own melts. The diagrams, based on microprobe studying of experimental samples testifies effect of immiscibility of silicate and sulphide melts at pressure 7.0  $\Gamma\Pi a$  and temperature 1800 - 2200°C. Due to last conclusion, formation of central mineral inclusions in diamonds consisting of coexisted sulfide and silicate is explained. Apparently, widespread

occurrence of sulphide mineral inclusions in natural diamonds is the result of "swimming" of growing crystal from carbonate-silicate parent media in sulphide one. Sulfides as admixed components of diamond-forming media form local congestions - drops, which are immiscible with carbonatite parent melts.

Efficiency of natural sulphide environments for diamond formation is experimentally proved. Synthesis of diamond is successfully carried out in systems pyrrhotite - carbon and a garnet - pyrrhotite - carbon at pressures 7,5 - 9,6 GPa and temperatures 1800 - 2200°C; the parameters correspond to the diamond stability conditions.

*Financial support*: 04-05-64979 (head A.V.Bobrov), joint grant of RFBR and the Ministriy of Economics and Science of the Moscow region <sup>1</sup> 04-05-97220 (head Ju.A.Litvin), the grant of leading scientific schools 1301.2003.5 (head Academician A.A.Marakushev)

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22) 2004 Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004 URL: http://www.scgis.ru/russian/cp1251/h\_dgggms/1-2004/informbul-1\_2004/term-10e.pdf Published on July, 1, 2004