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Article *in* European Journal of Mineralogy · March 1999

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Diamond formation during reduction of oxide- and silicate-carbon systems at high P-T conditions

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Abstract: Although it is accepted that most natural diamonds crystallized from silicate melts, and P-T conditions of their formation are estimated to be 900–1500°C and 50–60 kbar, no diamonds have been synthesized at such "low" temperatures and pressures in silicate-carbon systems. We have synthesized diamonds in fayalite+graphite and magnetite+graphite mixtures by partial reduction of the samples with hydrogen and metallic titanium at 1300–1400°C and 55–55 kbar. Hydrogen provided local reduction of the samples with separation of metallic iron, which catalyzed the transformation of graphite into diamond. Iron reacted with other elements and was not found in free state in the products of the experiments. Such experiments can be regarded as a simplified model of the formation of some types of natural diamonds during the interaction of reduced fluids with carbon-bearing mantle rocks.

Key-words: diamond, hydrogen, reduction, silicate, oxide, high pressure.

Introduction

Natural diamonds occur in silicate rocks, and the majority of the inclusions in diamonds consist of silicates and sulphides (Sobolev, 1974; Meyer, 1987; Bulanova *et al.*, 1990), suggesting their formation in silicate-sulphide-carbon media. According to geothermobarometric data, most diamonds were formed at 900–1500°C and 50–60 kbar (Boyd *et al.*, 1985; Haggerty, 1986; Meyer, 1987; Harris, 1992). However, experimental synthesis of diamonds at these P-T conditions is only possible in the presence of transition metals (Fe, Ni, Co, *etc.*) melts, while diamond formation in other systems requires higher temperatures and pressures (Wentorf & Bovenkerk, 1961; Chepurov *et al.*, 1987). In silicate-carbon systems, diamonds were synthesized at 70–80 kbar and 1800–2200°C (Arima *et al.*, 1993), but did not occur at 50–60 kbar and 1400–1600°C (Wentorf, 1966; Chepurov & Sonin, 1987). Pressures about 70–100 kbar are

necessary for diamond formation in the presence of non-ferrous metals, oxides, carbonates, sulphates, or without catalyst-solvent (Table 1). In the (Fe, Ni)-S-C system, diamonds did not occur at 65 kbar, 1700–1750°C and at 55 kbar, 1400–1450°C, but they were formed at the same P-T conditions under the influence of hydrogen (Chepurov *et al.*, 1994).

The presence work was aimed at the study of possibilities of diamond synthesis at 50–55 kbar and 1300–1400°C in the presence of iron-containing silicate and oxide phases, which would be reduced by hyrogen in the course of the experiments.

Experimental procedures

The experiments were performed with multi-anvil high-pressure equipment of the "split sphere" type (Pal'yanov *et al.*, 1990) at 45–55 kbar and 1300–1400°C. The high-pressure unit consists of infu-

Table 1. Minimum P-T conditions for synthesis of diamond in the presence of various catalysts-solvents.

Catalysts-solvent	P kbar	T °C	References
without	110	1300	Onodera *et al.*, 1991
without	100	1800–1900	Hirano *et al.*, 1982 Onodera *et al.*, 1988
without	90	2200–2300	Hirano *et al.*, 1982
ferrous metals (Fe, Mn, Ni, Co)	50	1250–1300	Bundy *et al.*, 1961, 1973 Connon & Conlin, 1971
non-ferrous metals (Cu, Zn, Al)	65–80	1800–2000	Shulzhenko, 1990
silicates	70–77	1800–1900	Arima *et al.*, 1993
oxides	85–90	1830	Shalimov *et al.*, 1993
oxides	90	2000	Shulzhenko & Getman, 1971
hydroxides	77	2000–2150	Akaishi *et al.*, 1990a
carbonates	77	2150	Akaishi *et al.*, 1990b
carbonates	80–100	1550–1800	Jenes *et al.*, 1995 Litvin *et al.*, 1997
sulphates	77	2150	Akaishi *et al.*, 1990a

sible oxides, which do not experience phase transitions at the conditions of the experiments. For the heating of the reaction volume, a tubular graphite heater was used. Pressure during the experiments was determined from changes of the electric resistance of Bi and PbSe before the heating of the high-pressure unit, and temperature was measured with the help of PtRh thermocouples. The thermocouple and the pressure reading pickup were calibrated using graphite-diamond and quartz-coesite phase transitions, and with melting temperatures of metals in the high-pressure unit using the DTA method. At the end of the experiment, the samples were cooled at a rate of 100–150°C/s by the switching off the voltage, without pressure release.
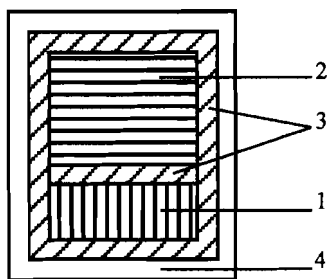
The starting materials were chemically pure graphite, hydrothermally synthesized fayalite (Fe_2SiO_4), magnetite (Fe_3O_4) prepared by the heating of pure synthetic hematite in a flow of aqueous hydrogen at 400°C, and natural ilmenite ($FeTiO_3$) from the Leningradskaya kimberlite pipe (Yakutia). Experiments were conducted with fayalite-graphite, magnetite-graphite and ilmenite-graphite compositions. In order to obtained reducing conditions in the experiments, titanium hydride and metallic titanium were used. Titanium hydride was obtained by heating metallic titanium in a hydrogen atmosphere at 700°C for 4 hours (Sokol & Fedorov, 1988).

The powder of the initial phases (fayalite, magnetite or ilmenite) and the reducing agent (ti-
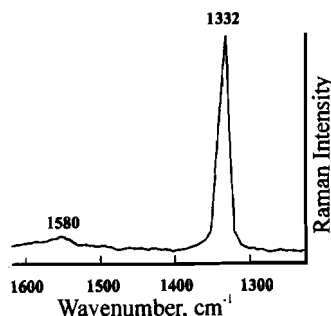

Fig. 1. Bild-up of the run capsules. 1 – material under study, 2 – metallic titanium or titanium hydride, 3 – graphite, 4 – platinum ampoule.

Fig. 2. Raman spectrum of synthesized diamond. 1332 cm^{-1} – diamond, 1580 cm^{-1} – graphite.

Table 2. Conditions and results of experiments of reducing of magnetite and fayalite (with graphite) at high P-T conditions.

Exp. number	P (±1) kbar	T (±20) °C	t h	Starting composition		Phase composition of the products of experiments	
				sample (+ graphite)	reducing agent	sample	reducing agent
8004	45	1350	0.5	Mgt	TiH$_2$	G, W, Il	TiH$_2$, Ti, Ti$_2$O, TiO
8008	55	1400	3.2	Mgt	TiH$_2$	D, G, Car	TiH$_2$, Ti, Ti$_2$O
8015	55	1300	6.0	Mgt	TiH$_2$	Mgt, G	TiH$_2$, Ti
8016	50	1300	1.0	Fa	TiH$_2$	D, Il, G, Fer, Sp, Car	TiH$_2$, Ti, Ti$_2$O
8017	55	1400	3.0	Fa	TiH$_2$	D, G, Il, Fer, Sp	TiH$_2$, Ti, Ti$_2$O
8018	55	1300	6.0	Fa	TiH$_2$	Sp, G, W (?)	TiH$_2$, Ti
8019	50	1300	3.0	Fa	Ti	D, Il, Fer, Co, Car	Ti, Ti$_2$O, TiO
8052	50	1300	3.0	Fa	no	Fa, G	not determined
8025	55	1400	3.0	G	Ti	G	Ti, Ti$_2$O, TiO
8020	50	1300	1.0	Il	TiH$_2$	Il, G	TiH$_2$, Ti, TiO$_2$

Mgt – magnetite, Fa – fayalite, G – graphite, Il – ilmenite, W – wüstite, D – diamond, Car – iron carbide, Fer – ferrosilite, Sp – iron spinel, Co – coesite.

tanium hydrode or metallic titanium) were put into a graphite ampoule. The reducing agent had no direct contact with the sample, being separated from it by a graphite pellet. The graphite ampoule was inserted into a platinum ampoule, which was closed by arc-welding. The build-up of the run capsule is shown in Fig. 1. In the course of experiment, titanium hydride decomposed with gradual release of hydrogen. The rate of decomposition decreases abruptly with the increase of pressure (Sokol & Fedorov, 1988). The produced hydrogen and metallic titanium provided highly reducing conditions in the reaction chamber.

After the experiments, the Pt ampoule with the sample was heated to 150°C, then pierced, and the released gases were chromatographically analyzed, according to the technique decribed by Osorgin et al. (1995). The solid products of each run were examined by optical and scanning electron microscopy, X-ray diffraction and Raman spectroscopy.

Results and discussion

Experimental conditions and results of phase analyses of the samples are given in Tables 2 and 3. In the case of fayalite and magnetite reduction, diamond formed from graphite at common P-T conditions of diamond synthesis in metal-carbon systems. Diamond was identified by its hardness, the samples scratching tungsten carbide, by X-ray diffraction and by Raman scattering spectra (Fig. 2). Diamond was formed as imperfect octahedral single crystals or as parallel intergrowths, 0.2 mm
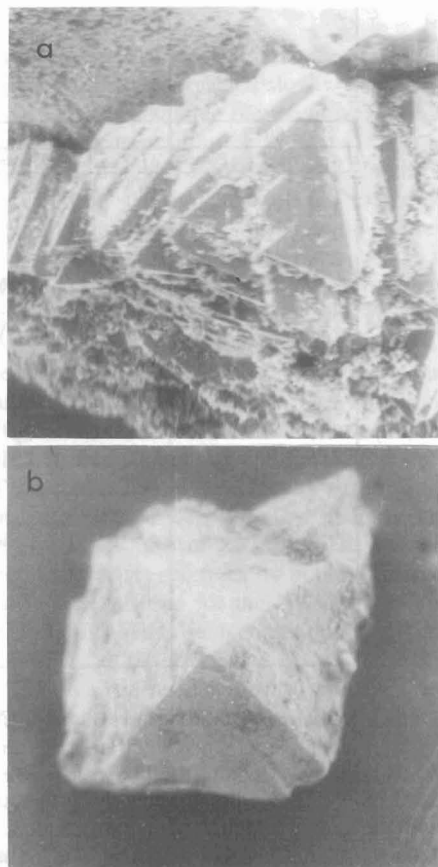
Fig. 3. Diamond crystals synthesized by the reduction of graphite mixtures with magnetite (a, ×120) and fayalite (b, ×75).

Table 3. Results of X-ray diffraction of experimental products.

8004			8008			8015			8016		
d (Å)	I	Phases	d (Å)	I	Phases	d (Å)	I	Phases	d (Å)	I	Phases
3.75	4	II	3.36	100	G, Car	3.36	10	G	6.42	5	Fer
3.36	100	G	2.11	1	G, Car	2.95	20	Mgt	3.35	45	G
2.71	4	II	2.07	2	D, Car	2.52	100	Mgt	3.21	20	Fer
2.57	3	II	2.03	2	Car	2.41	10	Mgt	2.90	100	Fer, Sp
2.49	7	W	2.02	3	Car, G	2.09	30	Mgt	2.74	50	II
2.26	8	II	1.87	1	Car	1.71	15	Mgt	2.58	35	Fer
2.15	10	W	1.68	9	G, Car	1.61	45	Mgt	2.54	25	II
2.12	3	G				1.48	50	Mgt	2.49	15	Sp
1.88	3	II							2.29	10	Fer
1.70	2	II							2.23	10	II
1.68	4	G							2.12	10	Fer, G
1.52	3	W							2.06	40	D, Sp
									2.01	15	G
									1.99	15	Fer, Car
									1.86	15	II
									1.72	25	II
									1.61	10	Fer
									1.53	40	Fer, G
									1.50	15	II
									1.47	20	II
									1.46	20	Sp
									1.26	25	D

8017			8018			8019			8020		
d (Å)	I	Phases	d (Å)	I	Phases	d (Å)	I	Phases	d (Å)	I	Phases
3.36	60	G	4.75	15	Sp	3.74	4	II	3.72	35	II
3.21	15	Fer	3.36	5	G	3.20	4	Fer	3.37	70	G
2.90	20	Fer	2.91	15	Sp	3.10	5	Co	2.23	100	II
2.74	20	II, Fer	2.48	100	Sp, W (?)	3.02	5	Fer	2.53	65	II
2.58	5	Fer	2.37	10	Sp	2.90	3	Fer	2.23	30	II
2.54	5	II	2.17	10	W (?)	2.75	10	II	1.86	50	II
2.51	5	Fer	2.05	60	Sp	2.54	5	II	1.72	75	II
2.47	5	Sp	1.89	10	Sp	2.39	2	Car	1.51	50	II
2.23	5	II	1.67	5	Sp	2.26	1	Car	1.46	20	II
2.13	5	Fer	1.58	25	Sp	2.24	2	II	1.33	10	II
2.06	100	D	1.45	50	Sp	2.11	3	Car			
1.72	5	II	1.39	5	Sp	2.06	100	D			
1.50	5	II				2.04	3	Car			
1.26	25	D				2.02	4	Car			
						1.98	2	Car			
						1.87	3	II			
						1.75	5	II			
						1.47	3	II			
						1.26	20	D			

X-ray powder diffractometer DRON-3, Cu_{K_α} -radiation

in size (Fig. 3). They were located along the contacts of the graphite pellet with the products of fayalite and magnetite decomposition. The highest degree of graphite transformation into diamond (about 1/3 of the graphite pellet) and of fayalite reduction was achieved when using metallic titanium as reducing agent (exp. 8019, Tables 1 and 2).

In experiments with titanium hydride, diamonds were only formed with TiH_2 decomposition. In experiments 8015 and 8018, during which only a minute part of TiH_2 decomposed (metallic titanium present only in the form of a thin film at the hydride surface), fayalite and magnetite were not reduced, and diamonds did not occur. There

Table 4. Results of chromatographic analyses of the gas phase in the reaction chamber after the experiments, and calculated equilibrium composition of the fluid for P-T conditions (Table 2) of the experiments.

Run No	Results of analyses *)						$\frac{H}{H+O}$	Equilibrium fluid composition**)						lgf_{O_2}
	content of gases (Mkg/mol.%)							content of components (mol.%)						
	CO_2	H_2O	H_2	CH_4	C_2H_m	N_2		CO	CO_2	H_2O	H_2	CH_4	C_2H_m	
8004	-	4.2/30	0.67/42	3.4/27	0.16/1	0.31	0.90	0.09	0.08	35	6.9	5,,5	1.4	-8.4
8008	-	1.5/65	-	0.64/31	0.12/1	0.28	0.80	0.1	0.3	64	4.8	30	0.6	-6.9
8015	2/1	70/91	0.5/6	1.1/2	0.1/0.1	7.0	0.68	0.2	2.1	92	1.3	4.4	0.03	-6.7
8016	-	33/75	0.33/7	6.2/16	1.5/2	0.56	0.76	0.1	0.5	75	3.2	2.1	0.3	-7.6
8017	-	8.8/24	1.2/29	14/42	3.1/5	1.0	0.92	0.05	0.03	29	7.0	62	1.8	-8.0
8018	3.9/3	38/67	1.7/27	1.7/3	-	4.8	0.73	0.1	0.6	83	2.4	14	0.2	-7.2
8052	24/1.2	798/98.3	-	3.3/0.5	-	1.9	0.66	0.5	4.0	92	1.3	2.2	0.01	-6.7
8025	-	13/10	7.6/53	39/34	4.8/3	3.8	0.96	0.02	6E-3	15	7.6	75	2.3	-8.6
8020	-	44/58	3.0/35	3.9/6	0.9/1	3.6	0.79	0.1	0.3	67	3.8	28	0.6	-7.8

*) mol.% are given without regard of N_2; $C_2H_m = C_2H_2 + C_2H_4 + C_2H_6$; CO is absent in the samples; analyses were performed on heat conduction detectors, He carrier gas.
**) System C-O-H in equilibrium with diamond; the calculations were performed by minimization of free enthalpy (G) according to the model of ideal mixture of real gases (Fedorov et al., 1992).

was, however, no fayalite in the products of the experiments, because it transformed into spinel at the given P-T conditions. Diamond was not formed in the check run with fayalite without reducing agent (exp. 8052), and in the case no iron-containing compounds were used as initial materials (exp. 8025). It is not surprising that no diamond formation was observed in the Ti-C system, even at 70 kbar and 1600–1700°C (Kushtalova et al., 1989).

Ilmenite reduction and diamond formation did not take place even with decomposition of TiH_2 (exp. 8020). This can be explained by the fact that ilmenite requires more reducing conditions (lower f_{O_2} values) in comparison with fayalite and magnetite (Fig. 4).
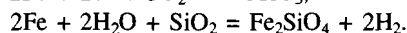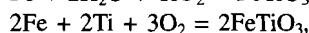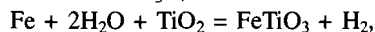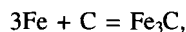
Apparently, diamond synthesis in experiments 8008, 8016 and 8019 is promoted by the catalytic effect of metallic iron, thus decreasing the P-T conditions for transformation of carbonaceous compounds into diamond. Transition metals (Fe, Ni, Co, etc.) serve as catalyzers of the graphite-diamond transformation: diamonds can only form at pressures of 50 – 60 kbar in the presence of metal-catalyzers (Table 1).

Metallic iron is formed by reduction of the samples by hydrogen, released during the decomposition of TiH_2, or through the action of metallic titanium by binding the oxidizing components (H_2O, O_2, CO, CO_2) in the medium. The higher degree of sample reduction in the runs with metallic titanium, in comparison with those with titanium hydride, is probably due to the higher oxida-

tion resistance of the latter. Titanium hydride did not react directly (or reacted slowly) with oxygen and water, hence sample reduction occurred only during its decomposition.

X-ray diffraction studies did not identify metallic iron in the products of the experiments (Table 3). Small quantities of Fe could be present in some samples, but its reflections 2.03 Å (I = 100), 1.433 Å (20) and 1.170 Å (30) are overlapped by reflections of other phases. In Table 4 the molecular composition of fluid is given, as determined chromatographically in the reaction chamber after the experiments. On the basis of H/(O+H) atomic ratio values, the equilibrium molecular composition of the fluid and f_{O_2} at the P-T conditions of the experiments were estimated using the method described by Fedorov et al. (1992) and Osorgin et al. (1995). It was established that the oxygen fugacity in the experiments was higher than that for the IW and IQF buffer equilibria (Fig. 4). In such conditions metallic iron is unstable and has to oxidize.

The obtained results allow to presume formation of metallic iron and diamond in a dynamic regime in sample zones with local reduction. Thereupon, metallic iron takes part in such chemical reactions, as, for example,

$$3Fe + C = Fe_3C,$$
$$Fe + 2H_2O + TiO_2 = FeTiO_3 + H_2,$$
$$2Fe + 2Ti + 3O_2 = 2FeTiO_3,$$
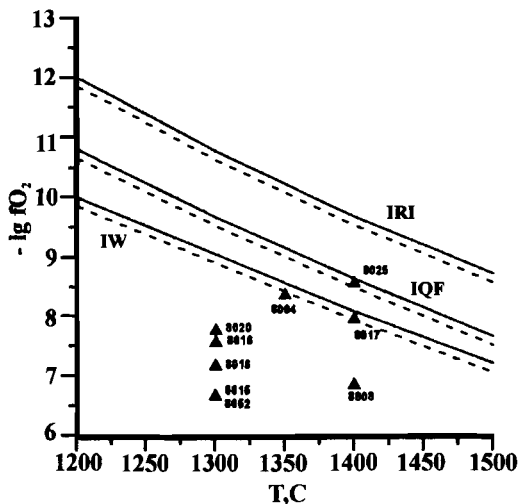$$2Fe + 2H_2O + SiO_2 = Fe_2SiO_4 + 2H_2.$$

Fig. 4. Values of $\lg f_{O_2}$ calculated from H/(O+H) ratios (Table 4) in experiments and lines of buffer equilibria at 50 kbar (solid lines) and 55 kbar (dashed lines). Buffers IW (iron-wüstite) end IQF (iron-quartz-fayalite) are calculated from expressions for $\lg f_{O_2}$, reported in Kadik & Lukanin (1986); buffer IRI (iron-rutile-ilmenite) is calculated from the equation of the chemical reaction $2Fe + 2TiO_2 + O_2 = 2FeTiO_3$.

The bulk metallic iron being bound in the compounds, the diamond synthesis stops.

Implications

Today may scientists are convinced of the participation of fluids in the processes of diamond formation. An opinion exists that diamonds have formed in conditions close to the stability limits of carbonates during reduction of CO and CO_2 (Ryabchikov *et al.*, 1981). On the other hand, some authors suggest strictly reducing conditions for diamond formation, corresponding to a fluid of hydrogen-methane composition (Marakushev, 1981; Nikolsky, 1981). However, most authors allow a wide range of redox conditions (Mitchell, 1973; Haggerty, 1986; Kadik, 1988; Simakov, 1988): from the conditions of moissanite formation up to the field of magnesite stability (Simakov, 1988), or a more narrow range corresponding to f_{O_2} values, from close to IW up to WM buffers (Mitchell, 1973; Haggerty, 1986). There is no doubt that diamonds with inclusions of native iron (Bulanova *et al.*, 1979, 1990; Sobolev *et al.*, 1981; Meyer, 1987; Garanin & Kudrayvtseva, 1990;

Gorshkov *et al.*, 1995, 1997) were formed in highly reducing conditions; this is also true for moissanite inclusions (Marshintsev, 1990); Leung *et al.*, 1996). Nevertheless, diamonds with such inclusions are rare, and for most natural diamonds it is impossible to determine the redox conditions of their formation from their mineralogical characteristics.

The experiments presented in this work, and previous results for sulphide-carbon systems (Chepurov *et al.*, 1994) might be treated as a simplified model for diamond formation in nature through the influence of a reducing atmosphere on carbonaceous silicate and sulphide rocks at high static or dynamic P-T conditions. This model probably reflects the process of formation of some natural diamonds of the first generation, *i.e.*, the stage of transformation of non-diamond carbon into diamond. Later on, as a rule, these diamonds were subjected to recrystallization and pressure-thermal annealing, and they were partially dissolved and oxidized with the formation of crystals of various habits, properties and sizes.

References

Akaishi, M., Kanda, H., Yamaoka, S. (1990a): High pressure synthesis of diamond in the systems of graphite-sulphate and graphite-hydroxide. *Japan J. Appl. Phys.*, **29**, 1172-1174.
––––(1990b): Synthesis of diamond from graphite-carbonate systems under very high temperature and pressure. *J. Cryst. Growth*, **104**, 578-581.
Arima, N., Nakayama, K., Akaishi, M., Yamaoka, S., Kanda, H. (1993): Crystallization of diamond from a silicate melt of kimberlite composition in high-pressure and high-temperature experiments. *Geology*, **21**, 968-970.
Boyd, F.R., Gurney, J.J., Richardson, S.H. (1985): Evidence for a 150–200-km thick Archaean lithosphere from diamond inclusion thermobarometry. *Nature*, **315**, 387-389.
Bulanova, G.P., Spetsius, Z.V., Leskova, N.V. (1990): Sulphides in diamonds and xenoliths from Yakutian kimberlite pipes. Nauka, Novosibirsk, 120 p. [in Russian].
Bulanova, G.P., Warshavsky, A.V., Leskova, N.V., Nikishova, L.V. (1979): Upon the question of "central inclusions" in natural diamonds. *Dokl. AN SSSR*, **244**, 704-706 [in Russian].

Bundy, F.P., Bovenkerk, H.P., Strong, H.M., Wentorf, R.H. (1961): Diamond-graphite equilibrium from growth and graphitization of diamond. *J. Chem. Phys.*, **35**, 383-391.

Bundy, F.P., Strong, H.M., Wentorf, R.H. (1973): Methods and mechanisms of synthetic diamond growth. *Chem. Phys. Carbon*, **10**, 213-272.

Chepurov, A.I., Fedorov, I.I., Sonin, V.M., Sobolev, N.V. (1994): Diamond formation in the system (Fe, Ni)-S-C-H at high PT parameters. *Dokl. AN SSSR*, **336**, 282-240 [in Russian].

Chepurov, A.I., Pal'yanov, Yu.N., Fedorov, I.I. (1987): Experimental investigation of diamond crystallization. *in* "Mineral formation in endogenic processes", N.V. Sobolev, ed. Nauka, Novosibirsk, 26-40 [in Russian].

Chepurov, A.I. & Sonin, V.M. (1987): On the crystallization of carbon in silicate and metal-silicate systems under high pressure. *Geologiya i Geofizika*, **1987**(10), 78-81.

Connon, P. & Conlin, E.T. (1971): Formation of diamond. IV. The behavior of the diamond-forming reaction with respect to catalyst composition. *J. Phys. Chem.*, **75**, 2158-2163.

Fedorov, I.I., Chepurov, A.I., Osorgin, N.Yu., Sokol, A.G., Petrushin, E.I. (1992): Modeling of component composition of C-O-H fluid in equilibrium with graphite and diamond at high temperatures and pressures. *Geologiya i Geofizika (Russian Geology and Geophysics)*, **1992** (4), 72-79.

Garanin, V.K. & Kudryavtseva, G.P. (1990): Morphology, physical properties and paragenesis of inclusion-bearing diamonds from Yakutian kimberites. *Lithos*, **25**, 211-217.

Gorshkov, A.I., Yan Nan Bao, Bershow, L.V., Ryabchikov, I.D., Sivtsov, A.V., Lapina, M.I. (1997): Native metals and other mineral inclusions in the diamonds from kimberlite pipe No 50, Lyaonin province (China). *Geokhimiya*, **1997**(8), 794-804 [in Russian].

Gorshkov, A.V., Titkov, S.V., Sivtsov, A.V., Bershov, L.V., Marfunin, A.S. (1995): First finds of native Cr, Ni, and α-Fe in carbonado from Yakutia. *Geokhimiya*, **1995** (4), 588-591 [in Russian].

Haggerty, S.E. (1986): Diamond genesis in multiply-constrained model. *Nature*, **320**, 34-38.

Harris, J.W. (1992): Diamond geology. *in* "The properties of natural and synthetic diamond", J.E. Field, ed. Academic press, London, 345-393.

Hirano, S.L., Shimoto, K., Naka, S. (1982): Diamond formation from glassy carbon under high pressure and temperature conditions. *J. Mater. Sci.*, **17**, 1856-1862.

Jones, A.P., Taniquchi, T., Dobson, D., Rabe, R., Milledge, H.J., Taylor, W.R. (1995): Experimental nucleation and growth of diamond from carbonate-graphite systems. Sixth International Kimberlite Conference, Extended Abstracts, UIGGM SB RAN, Novosibirsk, 269-270.

Kadik, A.A. (1988): Influence of melting upon the evolution of fluid and redox regimes of the earth upper mantle. *Geokhimiya*, **1988** (2), 235-245 [in Russian].

Kadik, A.A. & Lukanin, O.A. (1986): Degassing of the upper mantle on melting. Nauka, Moscow, 96 p. [in Russian].

Kushtalova, I.P., Stasyuk, L.F., Radic, S.M., Ristic, M.M. (1989): The influence of high pressures on titaniuim-carbon reactino. *in* "High pressure science and technology", Proc. XI AIRAPT Int. Conf., Naukova Dumka, Kiev, **2**, 166-169.

Leung, I.S., Taylor, L.A., Tsao, C.S., Han, Z. (1996): SiC in diamond and kimberlites: implications for nucleation and growth of diamond. *Intern. Geol. Rev.*, **38**, 595-606.

Litvin, Yu.A., Tchudinovskih, L.T., Zharikov, V.A. (1997): Crystallization of diamond and graphite in the mantle alkali carbonaceous melts in experiment at 7-11 GPa. *Dokl. AN*, **335**, 669-672 [in Russian].

Marakushev, A.A. (1981): Upon the problem of fluid regime of diamond-bearing rocks formation. *Geol. Rudn. Mestor.*, **204**, 3-17 [in Russian].

Marshintsev, V.K. (1990): Natural silicon carbide in kimberlites of Yakutia. *Mineral. Zhurn.*, **12**, 17-26 [in Russian].

Meyer, H.O.A. (1987): Inclusions in diamond. *in* "Mantle Xenoliths", P.H. Nixon, ed. John Wiley and Sons Ltd., New York, 501-522.

Mitchell, R.H. (1973): Composition of olivine, silica activity and oxygen fugacity in kimberlite. *Lithos*, **6**, 65-81.

Nikolsky, N.S. (1981): The role of fluids in graphite, diamond and cohenite formation. *in* "Vsesojusn. Sovesh. Geokhim. Uglerod.", GEOHI AN USSR, Moskow, 190-193 [in Russian].

Onodera, A., Higashi, K., Irie, I. (1988): Crystallization of amorphous carbon at high static pressure and temperature. *J. Mater. Sci.*, **23**, 422-428.

Onodera, A., Irie, Y., Higashi, K., Umemura, J., Takenaka, T. (1991): Graphitization of amorphous carbon at high pressure to 15 Gpa. *J. Appl. Phys.*, **69**, 2611-2617.

Osorgin, N.Yu., Fedorov, I.I., Sonin, V.M., Bagryantsev, D.G. (1995): Study of chemical and molecular composition of fluid for C-O-H system in the experiments under P-T parameters of diamond synthesis. *in* "Mater. Genetich. Exper. Miner.", N.V. Sobolev, ed. UIGGM SB RAN, Novosibirsk, 74-80 [in Russian].

Pal'yanov, Yu.N., Malinovskii, Y.Yu., Borzdov, Yu.M., Khokhryakov, A.F., Chepurov, A.I., Godovikov, A.A., Sobolev, N.V. (1990): Growth of large diamond crystals on without-press apparatus of "split sphere" type. *Dokl. AN SSSR*, **316**, 1221-1224 [in Russian].

Ryabchihov, I.D., Green, D.H., Wall, V.J., Brey, G.P. (1981): The oxidation state of carbon in the environment of the low velocity zone. *Geokhimiya*, **1981** (2), 221-232 [in Russian].