

SHORT
COMMUNICATIONS

Experimental Study of the Effect of High Pressure and High Temperature on Silicate and Oxide Inclusions in Diamonds

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Received January 10, 2006

DOI: 10.1134/S0016702906100107

The investigation of primary inclusions in natural diamonds is the main source of information on the environment of diamond formation. It is usually assumed that inclusions trapped during diamond crystallization did not change during the postcrystallization period and, therefore, adequately reflect the composition of the crystallization medium. Most natural diamonds were formed in the Earth's mantle long before their transportation to the surface by kimberlite or lamproite melts, which implies that diamonds resided over a considerable time period (hundreds of millions and even billions of years) in the Earth's mantle after the termination of their crystallization [1–3]. Thus, investigations are needed to demonstrate the invariance of inclusions during the postcrystallization period or evaluate their possible changes, which must be accounted for during the reconstruction of the conditions of diamond genesis.

Our previous studies showed that under the influence of high P – T parameters, metal inclusions in diamond change their faces and shapes and move along the direction of temperature gradient through the recrystallization of diamond material, which results in expelling metal inclusions from diamonds [4]. Fedorov et al. [5] estimated the time necessary for the purification of diamonds from metal inclusions in the Earth's mantle. It was shown [6] that, in contrast to previously studied [4] small metal inclusions, large metal inclusions (~0.1 mm and greater in size) decrepitated during high- P and high- T (HPHT) treatment: a rosette of cracks appeared around the inclusions, and some of the cracks might reach the surface of crystals.

This paper reports experimental results on the influence of a HPHT impact on silicate and oxide inclusions, which are among the most widespread in natural diamonds. Natural and synthetic diamonds were used in the experiments. Natural diamond crystals (from

Yakutian kimberlite pipes) were from 1 to 4 mg in weight and contained individual inclusions of olivine, chromite, or garnet. Synthetic diamonds were grown in a BARS high-pressure apparatus from a $\text{Fe}_{0.36}\text{Ni}_{0.64}$ + basalt (5–10 wt %) + graphite mixture at temperatures of 1400–1500°C and pressures of 50–60 kbar using the method described in [7]. After the dissolution of the metal phase, the experimental products consisted of diamonds coexisting with fine-grained olivine, pyroxene, garnet, and spinel, which were identified by the methods of optical microscopy, X-ray diffraction, and microprobe analysis. The synthetic diamond crystals contained numerous metal inclusions, from 0.01 mm or smaller to 0.2 mm in size, as well as inclusions of olivine, pyroxene, spinel, garnet, and wüstite, which were no larger than a few hundredths of a millimeter. Synthetic diamond crystals weighing 5–20 mg were used in the experiments on HPHT annealing.

The experimental HPHT annealing of diamond crystals was carried out using the BARS apparatus in a high-pressure cell manufactured from refractory oxides (ZrO_2 , MgO , and CaO); the construction of the cell was reported elsewhere [4]. In order to explore, in more detail, possible structural changes of silicates during their interaction with diamonds at high P – T parameters, we conducted experiments on the HPHT annealing of mixtures of diamond and silicate powders. These experiments were performed using sealed Pt capsules, which were loaded into high-pressure cells similar to those used in experiments on the HPHT annealing of diamond crystals.

The diamond crystals were optically examined and photographed on an MBI-15 microscope. The X-ray investigation of diamond crystals was carried out using a Gondolfi URS-55 camera and Cu radiation. The X-ray diffraction patterns of silicate powders were recorded

Table 1. Conditions of experiments on high-pressure high-temperature annealing

Run no.	Starting sample	<i>T</i> (°C)	<i>P</i> (kbar)	<i>t</i> (h)	Changes of crystals observed under a microscope
1	SD*, crystal 1	1800	70	1	Appearance of cracks and surface frosting
2	SD, crystal 2	1800	70	2	Appearance of cracks and strong surface frosting
3	SD, crystal 3	2000	70	2	Strong fracturing and frosting, partial graphitization
4	ND**, crystal 1 with an olivine inclusion	1800	70	1.5	Weak surface frosting
5	ND, crystal 2 with an olivine inclusion	1800	70	2	Weak surface frosting
6	ND, crystal 3 with an olivine inclusion	2000	70	1	Strong surface frosting
7	ND crystal with a chromite inclusion	1800	70	2	Weak surface frosting
8	ND crystal with a garnet inclusion	1800	70	2	Surface frosting
9	Olivine + diamond mixture	1800	70	2	–
10	Orthopyroxene + diamond mixture	1800	70	2	–
11	Garnet + diamond mixture	1800	70	2	–

*SD, synthetic diamond.

**ND, natural diamond.

Table 2. Results of X-ray diffraction analysis of inclusions in synthetic diamonds before and after HPHT annealing

Crystal 1					Crystal 2				
before HPHT		run no. 1		phases	before HPHT		run no. 2		phases
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>		<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	
3.15	2	3.17	1	<i>Py</i>	–	–	3.37	2	<i>G</i>
2.92	<1	–	–	<i>Py</i>	2.77	<1	–	–	<i>Ol</i>
2.88	1	2.91	1	<i>Py</i>	2.62	1	2.60	1	<i>Gr</i>
2.54	<1	2.53	2	<i>Py</i> + <i>Ol</i> (?)	–	–	2.15	1	<i>W</i>
2.50	<1			<i>W</i> + <i>Ol</i> (?)	2.063	10	2.059	10	<i>D</i> + (Ni, Fe)
2.16	1	2.17	2	<i>W</i>	1.785	2	1.788	3	(Ni, Fe)
2.062	10	2.060	10	<i>D</i> + (Ni, Fe)	1.755	<1	1.760	1	<i>Ol</i>
1.784	2	1.788	2	(Ni, Fe)	1.554	<1	1.561	<1	<i>Gr</i> + <i>Sp</i> (?)
1.262	3	1.259	3	<i>D</i> + (Ni, Fe)	1.262	2	1.260	3	<i>D</i> + (Ni, Fe)
1.531	<1	1.536	<1	<i>W</i>	1.075	3	1.074	4	<i>D</i> + (Ni, Fe)
1.076	3	1.074	4	<i>D</i> + (Ni, Fe)	1.030	1	1.027	2	(Ni, Fe)
1.030	1	1.025	1	(Ni, Fe)	0.893	1	0.891	2	<i>D</i> + (Ni, Fe)
0.893	1	0.896	2	<i>D</i> + (Ni, Fe)					

Note: Phase abbreviations: *D*, diamond; (Ni, Fe), Ni–Fe alloy; *Gr*, garnet; *G*, graphite; *Ol*, olivine; *Py*, pyroxene; *Sp*, spinel; and *W*, wüstite.

on a DRON-3 diffractometer using CuK α radiation and metallic silicon as an internal standard.

Cracks emanating from large metallic inclusions appeared in the crystals of synthetic diamond after their HPHT treatment (Table 1). This resulted in that the crystals became opaque and the optical examination of inclusions in them became impossible. The HPHT treatment of natural diamonds at 1800°C pro-

duced only a slight frosting on their surface. The microscopic examination of these crystals did not reveal any changes in the morphology and relative position of inclusions after HPHT annealing (figure). After the HPHT treatment of natural diamonds at higher temperatures (Table 1), their microscopic investigation was complicated by the strong frosting of the crystal faces caused by their surface graphitization.

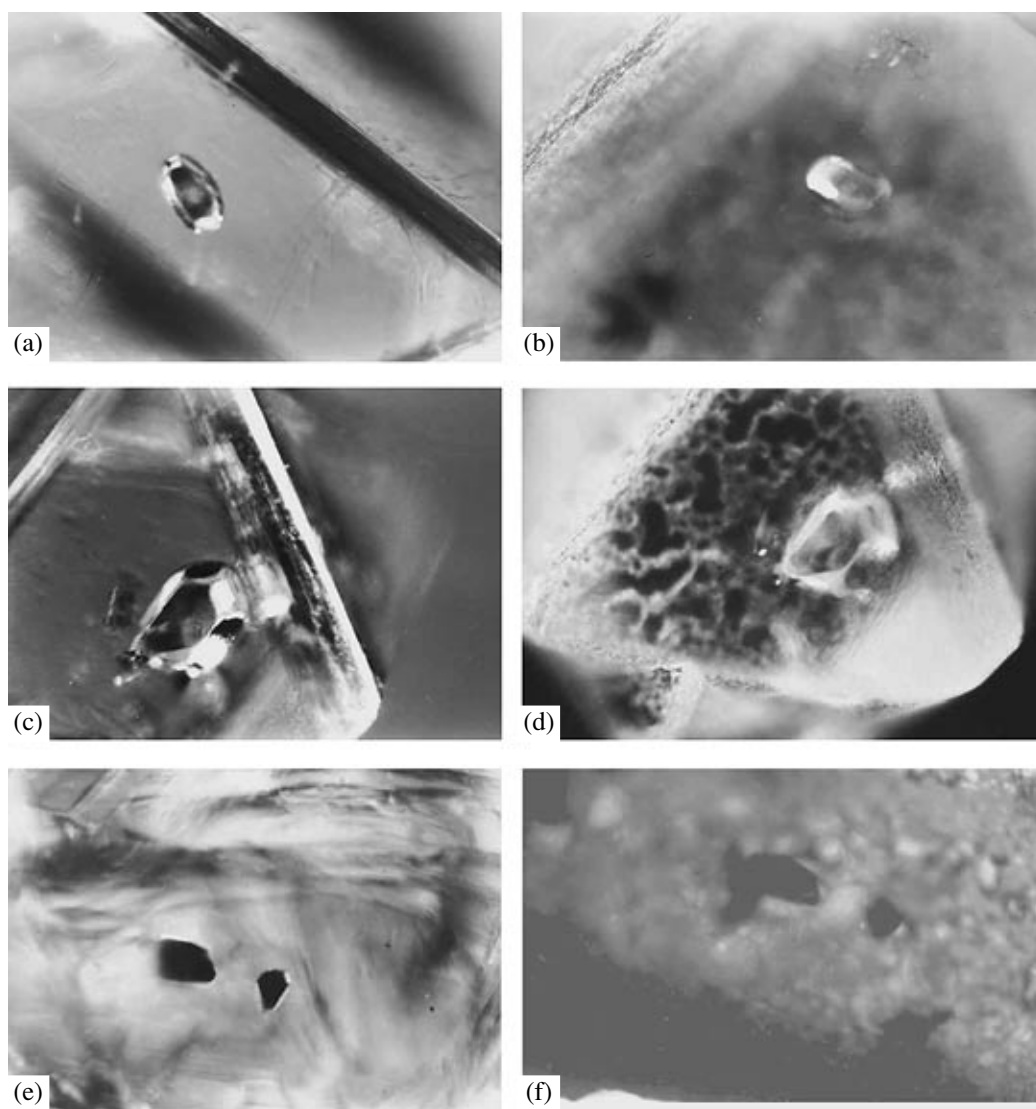


Fig. 1. Inclusions of (a–d) olivine and (e, f) chromite before (a, b, e) and after HPHT treatment ((b) run no. 4, (d) run no. 5, and (f) run no. 7).

The X-ray diffraction investigation showed no changes in the phase composition of inclusions in synthetic diamond crystals after their HPHT treatment, except for the appearance of a weak graphite line and a slight increase in the intensity of wüstite lines (Table 2). The latter is probably due to the partial oxidation of iron in metallic inclusions.

The accurate X-ray diffraction investigation of olivine, orthopyroxene, and garnet before and after their HPHT treatment together with diamond showed that the lattice parameters of olivine and orthopyroxene did not change, whereas the lattice parameter of garnet decreased slightly (Table 3). The latter effect could be related to the dissolution of carbon in the garnet structure at high P – T parameters.

Thus, the results of our experiments showed that the inclusions of olivine, pyroxene, garnet, spinel, and

chromite in diamonds are not changed by the heating of the crystals to 1800°C at a pressure of 70 kbar. The P – T parameters of our experiments are much higher than the pressures and temperatures supposed for the postcrystallization period of diamond occurrence in the Earth's mantle (800–1200°C and 40–50 kbar). The rate of possible changes of inclusions in diamonds under experimental P – T parameters must be several orders of magnitude higher than in the mantle. Consequently, although the duration of the experiments was not comparable with the duration of the postcrystallization mantle period in the genesis of diamond, it can probably be concluded that, in contrast to metallic inclusions, silicate and oxide inclusions inert with respect to diamond (such as chromite, spinel, etc.) have not changed during the postcrystallization period in the Earth's

Table 3. Results of X-ray diffraction analysis of olivine, orthopyroxene, and garnet before and after HPHT treatment with diamond

Olivine (run no. 9, Table 1)				Orthopyroxene (run no. 10)				Garnet (run no. 11)						
<i>hkl</i>	initial		after experiment		<i>hkl</i>	initial		after experiment		<i>hkl</i>	initial		after experiment	
	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>		<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>		<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
020	5.11	70	5.10	60	020	4.42	10	4.42	10	400	2.892	55	2.884	55
021	3.89	90	3.88	90	211	3.89	3	3.89	4	420	2.583	100	2.578	100
101	3.73	20	3.73	20	121	3.313	5	3.309	4	332	2.464	20	2.459	25
111	3.50	} 20	3.50	} 20	420; 221	3.177	100	3.175	90	422	2.359	20	2.354	20
120	3.49		3.49		321	2.946	15	2.945	20	510	2.266	20	2.262	25
121	3.011	} 25	3.008	} 20	610	2.879	80	2.878	100	521	2.110	15	2.106	15
002	3.000		2.997		511	2.831	10	2.831	10	611	1.874	20	1.871	20
130	2.771	100	2.771	95	421	2.709	10	2.709	15	620	1.827	5	1.823	5
131	2.516	95	2.515	90	131	2.539	15	2.539	20	444	1.668	15	1.664	15
112	2.462	100	2.461	100	202	2.499	5	2.498	10	640	1.602	30	1.598	30
041	2.352	25	2.351	20	521; 430	2.471	15	2.476	15	642	1.544	55	1.541	50
210	2.319	10	2.320	10	402; 621	2.254	3	2.252	5	800	1.444	15	1.441	10
122	2.272	40	2.270	35	630; 502	2.117	10	2.116	10	840	1.292	15	1.289	15
140	2.253	50	2.250	40	531; 322	2.098	10	2.097	15	842	1.261	20	1.258	15
211	2.162	15	2.163	15	721; 512	2.062	4	2.060	5	<i>a</i> ₀	11.554 (0.001)		11.530 (0.001)	
132	2.033	5	2.033	5	440; 241	1.987	10	1.986	10					
150	1.878	10	1.878	10	631	1.960	10	1.959	15					
113	1.812	5	1.812	4	821	1.888	3	1.888	4					
151	1.792	5	1.791	5	10.1.0; 640	1.789	5	1.789	5					
222	1.751	55	1.750	50	250; 621	1.735	5	1.734	10					
240	1.741	10	1.741	10	023	1.604	} 10	1.590	} 15					
241	1.672	15	1.672	15	10.2.1; 902	1.587		1.587						
133	1.619	20	1.619	20	650	1.530	} 15	1.258	} 15					
043	1.573	15	1.573	10	12.0.2	1.522		1.522						
004	1.497	40	1.497	30	10.3.1	1.487	15	1.487	15					
062	1.480	60	1.480	50	060	1.472	20	1.472	20					
170	1.395	30	1.395	25	11.0.2; 12.1.2	1.308	10	1.308	10					
322	1.352	15	1.352	15	<i>a</i> ₀	18.270 (0.004)		18.262 (0.006)						
<i>a</i> ₀	4.760 (0.001)*		4.759 (0.001)		<i>b</i> ₀	8.842 (0.003)		8.840 (0.005)						
<i>b</i> ₀	10.218 (0.002)		10.216 (0.001)		<i>c</i> ₀	5.192 (0.003)		5.195 (0.005)						
<i>c</i> ₀	5.988 (0.001)		5.989 (0.001)											

* Numbers in parentheses show standard deviations.

mantle and adequately reflect the environment of natural diamond crystallization.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research, project no. 05-05-65042.

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