

The evolution of diamond morphology in the process of dissolution: Experimental data

ALEXANDER F. KHOKHRYAKOV AND YURI N. PAL'YANOV*

Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Koptyug Pr., 3, Novosibirsk, 630090, Russia

ABSTRACT

In this paper, we report results of experiments on the dissolution of octahedral, pseudo-dodecahedral, and cubic natural diamond crystals in water-containing carbonate and silicate systems at high-pressure and high-temperature conditions in the diamond stability field. The dissolution agents used include CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, $\text{CaMgSi}_2\text{O}_6$, and kimberlite from the Udachnaya pipe, Yakutia, with addition of distilled water. The obtained diamond dissolution forms were studied using scanning electron microscopy and double-beam interferometry. A quantitative analysis of rounded diamonds was carried out by the photogoniometry method. The experimental data show that diamonds change their morphology from octahedrons, dodecahedrons, and cubes to tetrahexahedroids when dissolved in water-containing systems. Octahedron transforms into tetrahexahedroid when the weight loss is 20–25%; cube, when the loss is >50%; and pseudo-dodecahedron passes into tetrahexahedroid when the weight loss is as low as 10%. Comparison of crystal morphology, surface features, and goniometric data of diamond dissolution forms produced in water-containing systems and of rounded natural diamonds showed their complete identity. It has been established that the morphological variations of rounded natural diamonds depend on the initial habit of the crystals and the degree of their dissolution. With the significant dissolution of the starting crystals the dissolution forms of initial octahedrons, pseudo-dodecahedron, and cubes are similar. The evolution of the diamond crystals morphology is terminated with the formation of tetrahexahedroid with curvature parameters $AB = 36^\circ 07'$, $CD = 13^\circ 15'$, and $DD = 13^\circ 15'$. The obtained quantitative data allowed us to construct a scheme for the morphological evolution of natural diamond crystals during their dissolution.

Keywords: Diamond, morphology, dissolution, HPHT experiment

INTRODUCTION

A characteristic feature of natural diamond morphology is the widespread occurrence of rounded crystals. Because they appear similar to flat-faced crystals, these are called rounded dodecahedrons or dodecahedroids (Fersman and Goldschmidt 1911; Kukharensko 1955; Orlov 1977; Sunagawa 1984). From a strictly crystallographic viewpoint, with regard to the presence of edges and corners, these diamonds are rounded tetrahexahedrons or tetrahexahedroids (Moore and Lang 1974; Robinson 1978). It was reported (Orlov 1977) that tetrahexahedroids differ from each other in the curvature of rounded surfaces and angles between adjacent surfaces.

The most common opinion is that the morphology of these crystals is a result of dissolution of diamond in kimberlitic and lamproitic magmas (Moore and Lang 1974; Orlov 1977; Robinson 1978; Sunagawa 1984; Gurney et al. 2004). Investigations into the morphology of natural diamonds suggest that, during dissolution, octahedra gradually transformed into transitional forms and, thereafter, into tetrahexahedroids (Sunagawa 1984; Robinson et al. 1989; Otter and Gurney 1989; McCallum et al. 1994). In experiments on diamond dissolution in different media at atmospheric pressure, it was not possible to produce rounded crystals morphologically similar to natural diamonds (Frank and Puttick 1958; Evans and Sauter 1961; Harris and Vanse 1974; Mendelssohn and Milledge 1995). Such rounded

diamond crystals were produced only at high pressures and temperatures (Khokhryakov and Pal'yanov 1990, 2004; Arima 1998; Khokhryakov et al. 2001; Kozai and Arima 2005). The experiments showed the important role of water (Kanda et al. 1977; Pal'yanov et al. 1995), CO_2 (Kozai and Arima 2005) and redox conditions (Yamaoka et al. 1980; Arima 1998; Khokhryakov et al. 2002; Kozai and Arima 2005) during the natural dissolution of diamond. However, the variation of diamond morphology upon dissolution has not been studied extensively. Kozai and Arima (Kozai and Arima 2005) studied the morphological evolution for only natural diamond octahedrons. The authors described the morphological characteristics based on a classification scheme where all tetrahexahedroids belong to the same class. However, as we already noted natural diamond tetrahexahedroids have different morphologies and curvature of their rounded surfaces (Kukharensko 1955; Orlov 1977).

In the present work, we report the results of experiments on dissolution of octahedral, pseudo-dodecahedral, and cubic crystals of natural diamonds in water-containing carbonate and silicate systems under the mantle P - T conditions and present data on the produced dissolution forms. A quantitative analysis of rounded diamonds was carried out by the photogoniometry method. The change of the morphology of initial octahedrons, pseudo-dodecahedrons, and cubes was traced to 85% initial weight loss. The morphology of produced dissolution forms was compared with that of rounded natural crystals. The data obtained allowed construction of a scheme for the morphological evolution of natural diamond crystals during their dissolution.

* E-mail: palyanov@uiggm.nsc.ru

EXPERIMENTAL METHODS

Experiments on diamond dissolution were carried out using a "split-sphere" type multi-anvil apparatus at $P = 5.7$ GPa, $T = 1400$ °C. A high-pressure cell in the form of a tetragonal prism was used. Details on the high-pressure cell design, and calibration of pressures and temperatures were presented in our previous works (Pal'yanov et al. 2002a). The temperature was measured in each run using a PtRh₃₀/PtRh₆ thermocouple. Powder starting materials, distilled water, and several diamond crystals were placed into sealed Pt capsules (6 mm in diameter, 5 mm long, and 0.2 mm thick walls). No buffer materials were added to the high-pressure cell. Previously

we showed that in this case oxygen fugacity in the Pt capsules under experimental conditions is 1–2 log units lower than the CCO buffer (Sokol et al. 2000, 2001). Diamond crystals were placed in the central and upper parts of the capsules. In our studies, we used natural diamond crystals 0.2–0.8 mm in diameter without dissolution features from the Udachnaya and Aikhal kimberlite pipes (Yakutia). The crystals were of octahedral, pseudo-dodecahedral, and cubic habits. The octahedrons had sharp edges and corners, with trigonal plates developed on the faces (Fig. 1a). Following D.N. Robinson (Robinson 1978), we use the term pseudo-dodecahedron to describe dodecahedra formed by octahedral terracing (Fig. 2a). The crystals of cubic habit had a step or blocky structure of the cube surfaces (Fig. 3a).

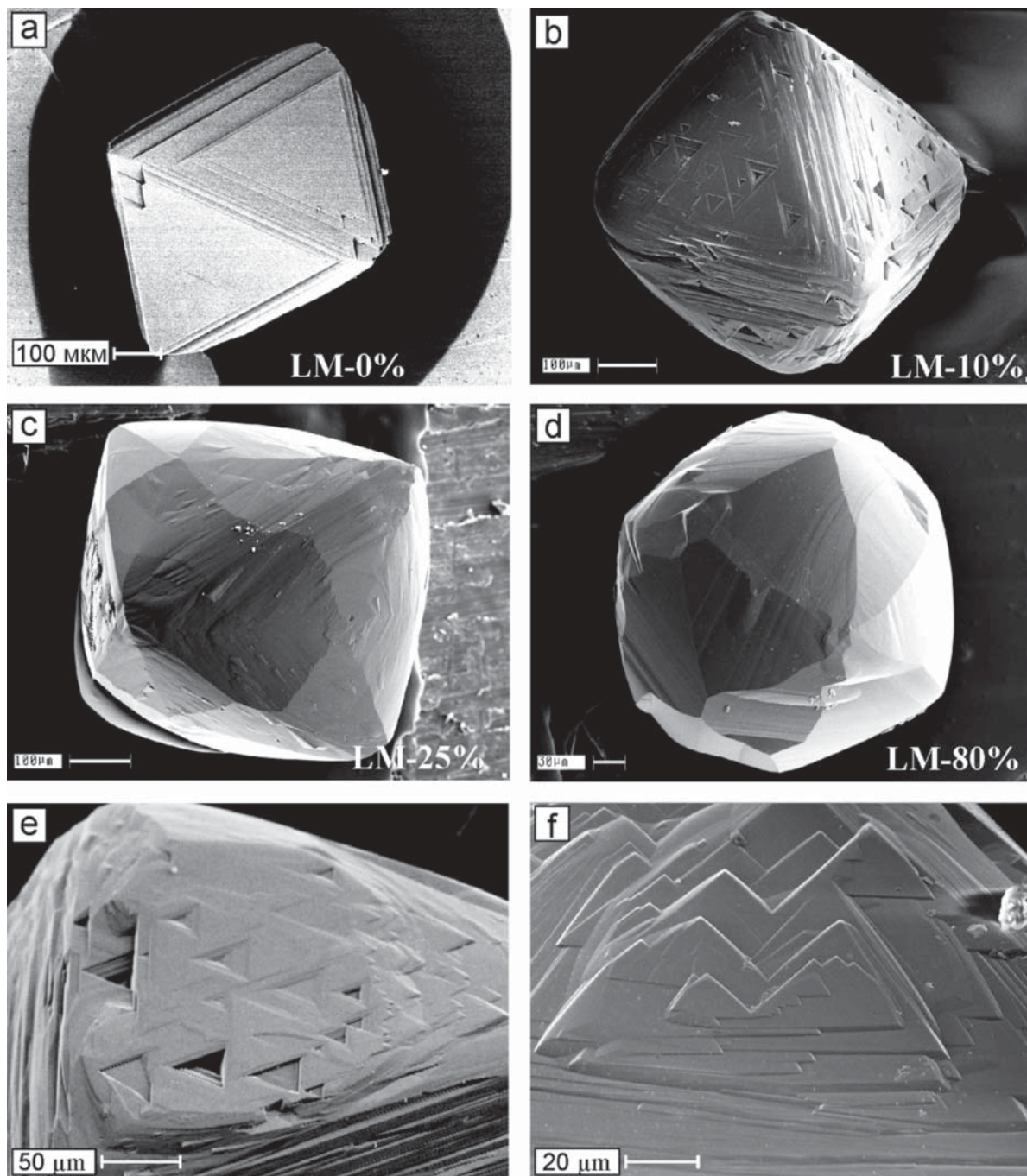


FIGURE 1. SEM images of diamond crystals partly dissolved in water-containing systems. (a) Initial octahedron form of the crystals. (b–d) Diamond crystals dissolved to different degrees (b = run UVS-1, c = run KW-4, d = run KW-6). (e) Negative trigons on the $\{111\}$ face; run KW-2. (f) Dissolution layers on the $\{111\}$ face; run DW-2. LM = mass loss of crystals.

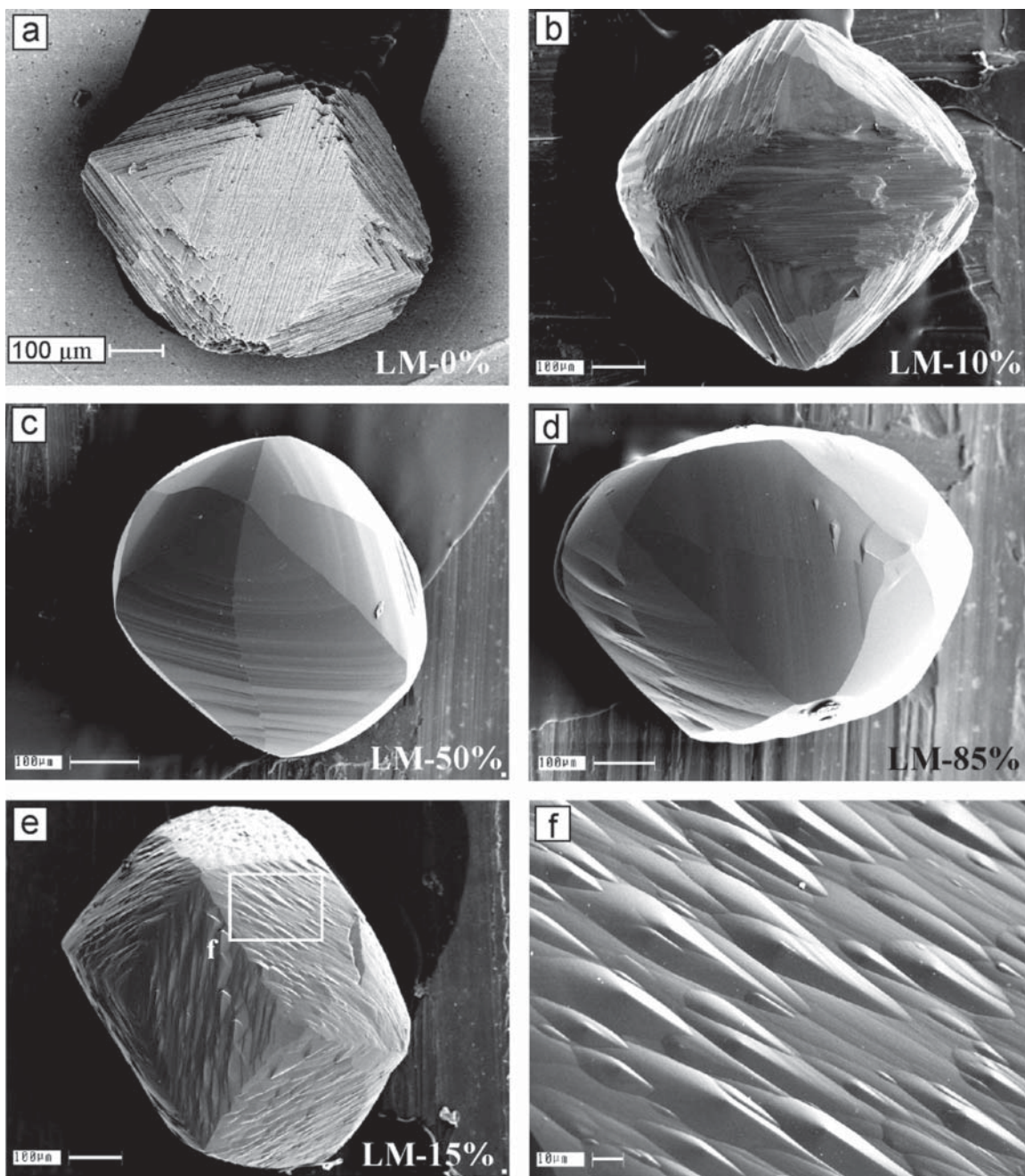


FIGURE 2. SEM images of diamond crystals partly dissolved in water-containing. (a) Initial dodecahedron form of the crystals. (b–d) Diamond crystals dissolved to different degrees (b = run UVS-3, c = run MW-1, d = run MW-2). (e) Dissolution form with hillocks on rounded surfaces; run DW-2. (f) Fragment of a rounded surface of the crystal shown on Figure 3e. LM = mass loss of crystals.

Model systems were chosen based on the concept that kimberlitic and lamproitic magmas are fluidized carbonate-silicate melts, and the main components of the fluids were, most likely, H_2O and CO_2 (Haggerty 1986; Wyllie 1995; Girmis et al. 1995; Navon 1999; Ryabchikov and Girmis 2005). Starting materials were natural magnesite (Chelyabinsk Region, Russia; impurity content ~0.5 wt%) as well as 99.9% pure $CaMgSi_2O_6$ and $CaCO_3$. The content of volatiles in the starting materials was no more than 0.2 wt%. We also used a basaltic kimberlite from the Udachnaya pipe (Yakutia), with the following composition (in wt%): 23.46 SiO_2 , 1.35 TiO_2 , 2.92 Al_2O_3 , 3.09 Fe_2O_3 , 5.03 FeO , 0.15 MnO , 27.62 MgO , 13.29 CaO , 2.25 Na_2O , 1.84 K_2O , 0.41 P_2O_5 , 4.45 H_2O , 9.41 CO_2 , 0.33 S, 0.14 F; total 100.04. The starting materials and experimental products were analyzed by X-ray

diffraction using a DRON-3 diffractometer.

The weight of diamond crystals before and after the experiments was measured with the accuracy of ± 0.01 mg. To estimate diamond dissolution rates, we calculated the surface area of the initial crystals and dissolution forms considering them as idealized polyhedra. Rounded crystals were considered as having a spherical form. From the measured masses and determined surface areas of the crystals before and after dissolution, the rates of dissolution were calculated in units of $mg/mm^2 \cdot h$ (specific weight rate). The crystals were analyzed with optical and scanning electron microscopes. Etch pits were examined using a double-reflecting interference microscope. Rounded crystals were studied using the photogoniometric method (Heimann 1975). The studies were performed on a photogoniometer with a cylindrical photo

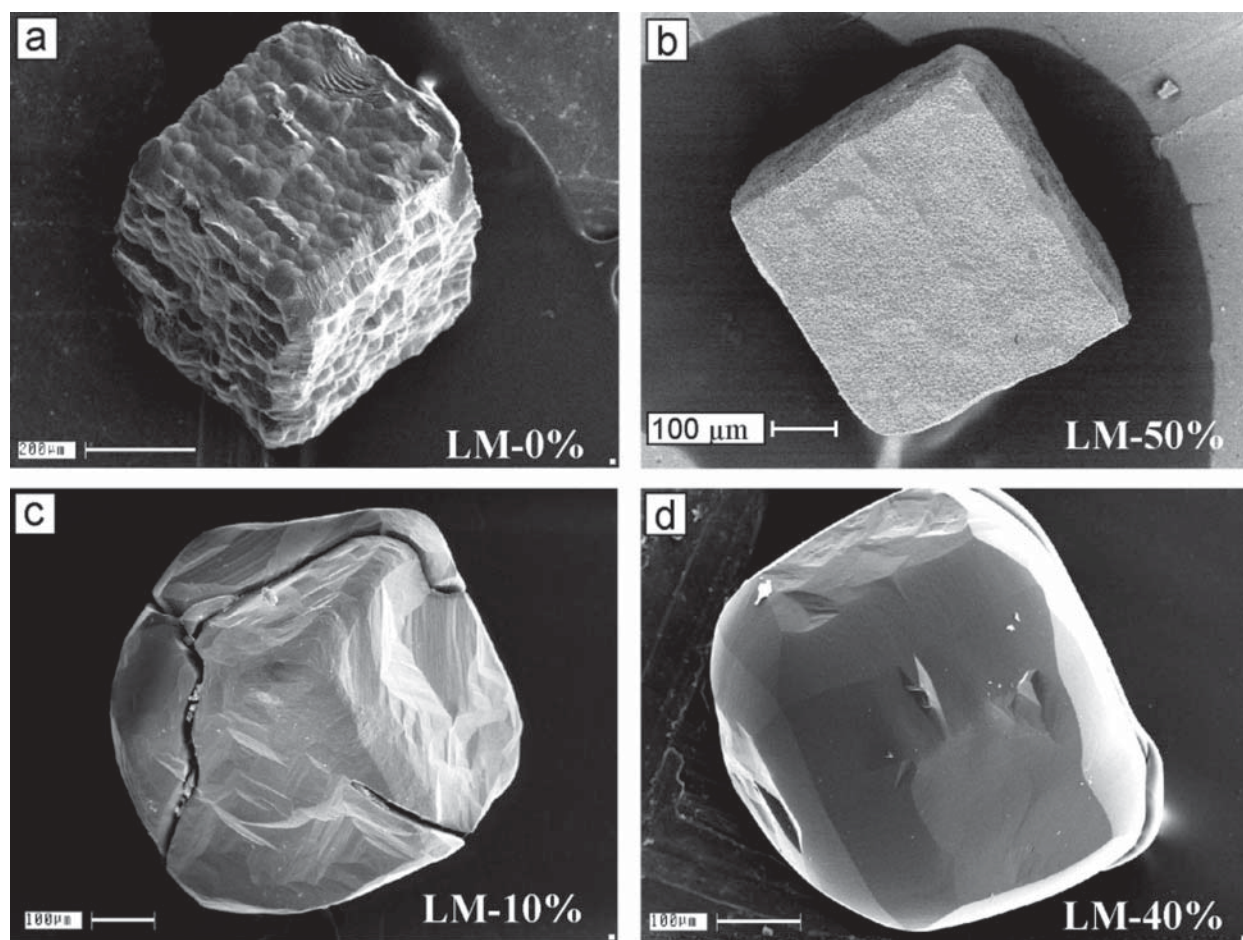


FIGURE 3. SEM images of diamond crystals, partly dissolved in water-containing systems. (a) Initial cube form of crystals. (b–d) Diamond crystals dissolved to different degrees (b = run DW-4, c = run UVS-1, d = run MW-1). LM = mass loss of crystals.

TABLE 1. Curvature characteristics of the principal types of rounded natural diamond

Types of rounded natural diamond	Curvatures averaged characteristic				Reference
	AB	CD	DD'	CC'	
Octahedroid	62°43'	21°25'	6°39'	47°29'	Kukharensky 1955
Dodecahedroid	36°	13°	14°	40°	Shafranovsky 1948
Dodecahedroid	36°07'	13°15'	13°15'	39°37'	Kukharensky 1955
Transitional forms (cube-tetrahexahedroid)	26°06'	14°03'	19°10'	47°16'	Kvasnitsa 1985
Tetrahexahedroid (cuboid)	46°	20°	7°	–	Bartoshinsky and Kvasnitsa 1991

camera with its axis parallel to the monochromatic light beam. A quantitative analysis of rounded diamonds was carried out by the method developed by I.I. Shafranovsky (Shafranovsky 1948; Orlov 1977). Shafranovsky established that the reflections from the rounded surfaces of diamond tetrahexahedroid are triangular in shape. Specific points of the reflection pattern were denoted by the letters A, B, C, and D (Fig. 4). The curvature of the rounded surfaces was calculated from the spherical coordinates of the vertices A, B, and C. The angular values AB and CD of the light reflections characterize the curvature of the rounded surfaces in two perpendicular directions. The values DD' correspond to the angles between the adjacent tetrahexahedroid surfaces. Using this method, the most frequently occurring types of natural diamond tetrahexahedroid were recognized previously (Table 1) (Orlov 1977).

RESULTS

The experimental results on the dissolution of diamond crystals in water-containing carbonate and silicate systems are given in Table 2. In all the experiments, the diamond dissolution agent

was a water-containing melt. The most reliable evidence for the existence of the melts during the experiments is the established sinking of diamond crystals down to the bottom of the Pt capsules. In experiments that utilized a water-containing carbonate and silicate solvents, a fine-grained aggregate of quench phases was found as the run product. An X-ray analysis showed that the aggregate consisted of diopside, coesite, and dolomite for the $\text{CaMgSi}_2\text{O}_4 + \text{H}_2\text{O}$ system, brucite and magnesite for the $\text{MgCO}_3 + \text{H}_2\text{O}$ system, and aragonite for the $\text{CaCO}_3 + \text{H}_2\text{O}$ system. In experiments with the use of kimberlite in the run products, we found quenched forsterite, diopside, dolomite (solid-solution), and garnet as well as individual crystals of forsterite up to 300 μm in size. The presence of liquidus forsterite in a kimberlite melt at the conditions of experiments performed in this study agrees with data of Edgar and

TABLE 2. Experimental results on diamond dissolution in water-containing carbonate and silicate systems at $P = 5.7$ GPa and $T = 1400$ °C

Run number	Time (h)	Reagent mg	H ₂ O content (wt%)	Diamond					
				Initial form of crystals*	Quantity of crystals	Initial weight mg	Final weight mg	Weight loss %	Dissolution rate, $\times 10^{-2}$ mg/mm ² ·h
CaMgSi₂O₆ + H₂O									
DW-1	0.17	145	13.8	O	8	4.75	4.56	4	1
DW-2	1.0	151	16.6	O	10	3.82	3.13	18	0.5
DW-3	1.5	147	15.6	O,C,D	10	4.64	3.16	32	0.7
DW-4	2.5	150	16.7	O,C,D	10	4.12	2.14	48	0.6
CaCO₃ + H₂O									
KW-1	0.5	146	16.4	O,C,D	9	4.56	4.47	2	0.11
KW-2	3.0	145	17.2	O,C,D	9	4.28	4.02	6	0.07
KW-3	6.0	149	16.8	O,C,D	10	4.64	4.06	12.5	0.07
KW-4	15	148	15.5	O,C,D	9	3.43	2.64	23	0.05
KW-5	30	145	17.2	O,C,D	11	5.51	2.50	55	0.06
KW-6	37	148	15.5	O, D	8	4.39	1.05	76	0.07
MgCO₃ + H₂O									
MW-1	15	150	16.7	O,C	5	4.19	2.31	45	0.16
MW-2	30	147	16.3	O,C,D	10	3.77	0.57	85	0.08
Kimberlite \pm H₂O									
UVS-1	3	139	15.0	O,C,D	8	3.23	2.90	10.2	0.10
UVS-2	10	130	4.5	O,C,D	8	3.58	3.26	9.0	0.03
UVS-3	10	134	9.0	O,C,D	8	3.39	3.05	10.0	0.03

* O = octahedron, C = cube, D = pseudo-dodecahedron.

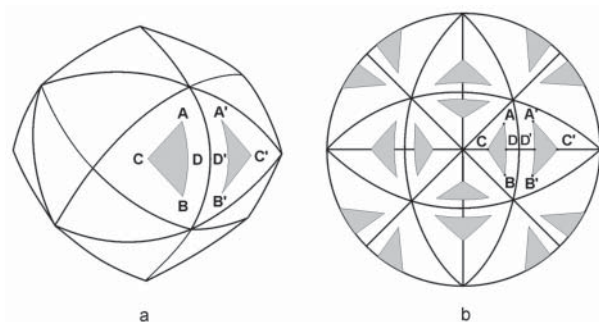


FIGURE 4. Schematic drawing and stereographic projection of tetrahexahedroid. (a) Schematic drawing of tetrahexahedroid showing orientation of the light triangular reflections (ABC) relative to the rounded surfaces of crystal. (b) Stereographic projection of tetrahexahedroid.

Charbonneau (1993) on the melting of group 1b kimberlites.

Analyses of 133 crystals used in the experiments on diamond dissolution showed that morphological changes of the diamond crystals in all studied water-containing systems follow the same regularities. Principal differences were established for crystals of different habits; therefore, we give generalized information on the dissolution behavior of octahedrons, pseudo-dodecahedrons, and cubes.

Dissolution of octahedrons

The initial dissolution stage is marked by the development of ditrigonal and shield-shaped dissolution plates (Fig. 1f) and negative triangles (Figs. 1b and 1e) on the {111} faces. The triangles vary in size and are pyramidal or flat-bottomed. Their sides are thin-stepped and are formed by the {443}, {553}, {221}, and {833} faces. Non-stepped, flat-bottomed etch pits are composed of {111} faces. Shallow triangles are formed by vicinal surfaces lying at an angle of 1–2° to the {111} face. The crystal edges are truncated by the rounded surfaces of tetrahexahedroid with serrate laminae and hillocks. When a crystal is dissolved by 20–25%, the rounded surfaces completely replace the {111} faces (Fig. 1c). By the position of edges and corners, the dissolution form is tetrahexahedroid with

curvature parameters $AB = 56\text{--}66^\circ$, $CD = 18\text{--}22^\circ$, and $DD' = 5\text{--}10^\circ$. Upon further dissolution to >20–25%, the tetrahexahedroid becomes more rounded (Fig. 2d). In most cases, the tetrahexahedroids have smooth glossy surfaces. As the loss of crystal weight increases, the curvature parameters of the diamond surfaces gradually change and reach their final values of $AB = 36\text{--}42^\circ$, $CD = 7\text{--}16^\circ$, and $DD' = 15\text{--}19^\circ$ at 85% weight loss.

Dissolution of pseudo-dodecahedrons

At the initial dissolution stage, the edges and formation striation of the crystals become rounded. At a weight loss of 10–15%, the pseudo-dodecahedron transforms into a tetrahexahedroid with parameters $AB = 51\text{--}56^\circ$, $CD = 18\text{--}22^\circ$, and $DD' = 9\text{--}13.5^\circ$ (Fig. 2b). Crystal surfaces typically exhibit a rounded stepped sculpture that is determined by the primary structure of the faces. Some crystals show numerous dissolution hillocks (Figs. 2e and 2f). When the loss of the initial weight is more than 45–50%, the dissolution form is similar to the tetrahexahedroids obtained on the deep dissolution of octahedrons (Figs. 2c and 2d). In this case, the surface is smooth or thin-layered with single hillocks commonly occurring near the edges.

Dissolution of crystals of cubic habit

In most cases, crystals of this type become smaller while preserving their cubic habit, i.e., dissolution results mainly in rectangular etch pits (Fig. 3b). The etch pits are very small (<5 μm in size) and completely cover the {100} faces. On other crystals, intense dissolution occurs at the borders of blocks with the formation of deep etch channels, up to a complete separation of fragments (Fig. 3c). The formation of rounded surfaces with a tetrahexahedroid form with preservation of the sample's integrity, was observed for only three crystals (Fig. 3d). In these cases, the cube faces are almost totally replaced by the tetrahexahedroid surfaces with the curvature parameters $AB = 28\text{--}32^\circ$, $CD = 16\text{--}28^\circ$, and $DD' = 12\text{--}20^\circ$ on >50% dissolution. The rounded faces are normally frosted and weakly wavy, whereas the relic {100} faces exhibit a few stepped, flat-bottomed, and pyramidal etch pits of rectangular shape. It appears that dissolution of most diamond crystals with a cubic

habit, without formation of rounded surfaces, is related to the features of their internal structure. It is known that the majority of cubic natural diamonds have high concentrations of defects caused by their fibrous and mosaic structure (Moore and Lang 1972; Nakazawa et al. 1985).

DISCUSSION

Evolution of diamond morphology during dissolution

The results of this study have shown that the forms of diamond dissolution in water-containing carbonate and silicate systems have the same microrelief features as tetrahexahedroids of natural diamond, namely: negative trigons, ditrigonal or shield-like laminae on the {111} faces, serrate striation, and hillocks. Photogoniometric analysis of the produced dissolution forms also showed their similarity to rounded natural diamonds. Figure 5 shows literature data (Shafranovsky 1948; Kucharenko 1955; Kvasnitsa 1985; Bartoshinskii and Kvasnitsa 1991) and our results on the curvature parameters of natural diamond tetrahexahedroids. Also our experimental data on diamond crystals dissolved to different degrees. As seen from Figure 5, all curvature values of diamond dissolution forms produced in the experiments are within the variations of natural diamond curvature. The dissolution forms of original pseudo-dodecahedrons are in the upper part of the field of natural tetrahexahedroids of the octahedron-dodecahedroid series, whereas the dissolution forms of original octahedrons are in the lower part of this field. In the region of small values of AB and CD, corresponding to a significant degree of dissolution of starting crystals, the dissolution forms of the initial octahedron, pseudo-dodecahedron, and cube have similar values of curvature. This finding suggests that diamond crystals of different initial habits yield the same dissolution forms when the degree of their dissolution is high. The identity of the surface curvatures of natural and experimentally produced tetrahexahedroids may indicate that the experimental conditions are close to the natural conditions of diamond dissolution.

Quantitative data obtained in this study allow us to consider how the evolution of diamond form depends on the degree of crystal dissolution (Fig. 6). In the first stage, transitional forms with etch pits develop on the relic {111} and {100} faces. The edges of these crystals are truncated by tetrahexahedroid surfaces. Transformation of octahedron into tetrahexahedroid ceases when the weight loss reaches 20–25%, whereas the cube transformation is terminated when the weight loss is more than 50%. On dissolution of pseudo-dodecahedrons, no transitional forms are produced, and stepped {110} faces gradually transform into the surfaces of tetrahexahedroid. The reason for this is that the corners and most edges of dodecahedron and tetrahexahedroid coincide. The second stage begins with the disappearance of original faces. Depending on the initial crystal habit, tetrahexahedroids with surfaces of different curvature are formed. On further dissolution, the curvature of rounded surfaces gradually changes up to the formation of tetrahexahedroid with average curvature parameters of $AB = 36^{\circ}07'$, $CD = 13^{\circ}15'$, and $DD = 13^{\circ}15'$. As it follows from Figure 6, the transition from the first to the second stage, and the formation of the final dissolution form occurs at different dissolution degrees for crystals of different initial habits. This difference seems to be related to the degree of deviation of the initial crystal shape from

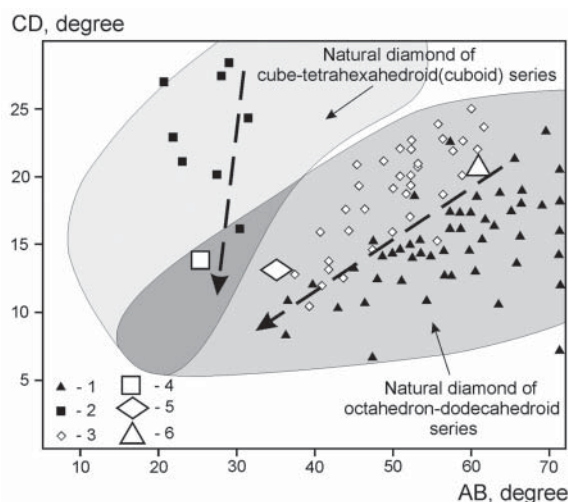


FIGURE 5. Curvatures parameter (AB, CD) of the experimentally obtained dissolution forms (initial forms: 1 = octahedron, 2 = cube, 3 = dodecahedron) and rounded crystal of natural diamond. Curvature characteristics of rounded natural diamond: 4 = tetrahexahedroid, 5 = dodecahedroid, 6 = octahedroid. Data on the curvatures of rounded natural diamond are from Shafranovsky 1948; Kucharenko 1955; Kvasnitsa 1985; and Bartoshinskii and Kvasnitsa 1991.

the final dissolution form of diamond in the studied systems. We calculated the volumes of dodecahedron, octahedron, cube, and the final tetrahexahedroids inscribed in these polyhedra. To determine the difference in the volumes of the initial crystals and final forms following diamond dissolution, we made following estimations. From the available collection of natural diamond tetrahexahedroids from the Ural (Russia) deposits, we selected crystals with curvature parameters similar to those of the dissolution forms produced after substantial dissolution of initial octahedrons and dodecahedrons. The volume of one highly symmetrical natural tetrahexahedroid was calculated from its weight and density (3.52 g/cm^3 for diamond). Then we calculated volumes of the idealized octahedron, dodecahedron, and cube circumscribed around this tetrahexahedroid. Geometrical analysis showed that the volume of the circumscribed octahedron, dodecahedron, and cube exceeds the volume of the tetrahexahedroid by 10%, 40%, and 65%, respectively. The degree of dissolution required for the crystals to attain tetrahexahedroid form follows the same sequence (Fig. 6).

The possible scheme of the evolution of natural octahedral diamond crystals during dissolution has been broadly discussed (Sunagawa 1984; Otter and Gurney 1989; McCallum et al. 1994). D. Robinson suggested a scheme for the transformation of an initial octahedron into a tetrahexahedroid, which includes five types of natural diamond crystals according to their degree of preservation (Robinson et al. 1989; Otter and Gurney 1989). According to this scheme, an octahedron completely transforms into a tetrahexahedroid when the loss of initial weight is 45% (Otter and Gurney 1989; McCallum et al. 1994). For a smaller loss of initial weight, the crystals have relic {111} faces. The scheme proposed by D. Robinson has been appealing for estimating the degree of diamond preservation in deposits (Otter and Gurney 1989; McCallum et al. 1994; Win et al. 2001; Karfunkel et al.

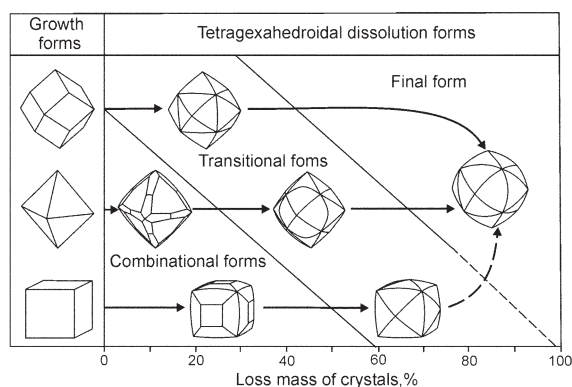


FIGURE 6. Evolution scheme for the crystal morphology of natural diamond during dissolution.

2001). However, our experimental data show that the transformation of octahedron into tetrahexahedroid ends when the loss of initial weight reaches 25%. The inconsistency between the experimentally determined value and the data of Robinson might be related to the fact that the calculated estimates did not take into account the change in the curvature of tetrahexahedroid during its dissolution. In addition, when evaluating the degree of natural diamond preservation only on the basis of visual observations, it is necessary to take into consideration the experimental data on the dissolution of dodecahedrons obtained in this study. Thus, a tetrahexahedroid can be an initial dodecahedron dissolved by 10–15% or an octahedron dissolved by 40–50%. Nevertheless, the experimentally established dependence of the morphology of diamond crystals on the degree of their dissolution might be of interest for solving practical tasks related to the development of criteria for diamond preservation.

Formation conditions of natural diamond tetrahexahedroids

The results of this work together with previously published experimental data (Khokhryakov and Pal'yanov 1990; Pal'yanov et al. 1995; Arima 1998; Khokhryakov et al. 2001; Kozai and Arima 2005) show that natural diamond tetrahexahedroids can form at 1100–1450 °C and 1.0–5.7 GPa from the dissolution of octahedron and dodecahedron form. Thus, natural diamond dissolution resulting the formation of tetrahexahedroids might have occurred both during the diamond residence in the mantle and at the stage of kimberlite ascent.

According to experimental data (Kanda et al. 1977; Pal'yanov et al. 1995; Khokhryakov et al. 2001; Kozai and Arima 2005), tetrahexahedroids form in carbonate and silicate systems only in the presence of H₂O. Previously, we have established that diamond dissolves in dry alkali-basalt melt (H₂O = 0.10 wt%) at 2.5 GPa and 1350–1450 °C through the formation of triangular plates along the {111} faces (Pal'yanov et al. 1995), resulting in a trigon-trioctahedron form with striations along [110]. The dissolution forms of diamond in dry carbonate melts at 7 GPa and 1700–1750 °C are trigon-trioctahedroids with positive trigons on relic {111} faces (Khokhryakov and Pal'yanov 2000).

The obtained experimental data also allow estimating the rates of diamond dissolution. The most intense dissolution of diamond

occurred in the system “diopside + H₂O” at the rates of 0.5×10^{-2} to 1×10^{-2} mg/mm²·h (Runs DW-1 – DW-4). The dissolution rates in water-containing carbonate systems were by an order of magnitude lower (0.16×10^{-2} – 0.05×10^{-2} mg/mm²·h). In previous studies (Arima 1998; Kozai and Arima 2005), a conclusion was drawn that the rate of diamond dissolution decreases as the CO₂ content increases in kimberlite and lamproite. In addition, it was shown that the H₂O content of the system also exerts a great effect on the diamond dissolution rate (Kanda et al. 1977; Pal'yanov et al. 1995). The maximum rates of diamond dissolution in the “diopside + H₂O” system can be explained by partial consumption of carbon from the dissolved diamond leading to the formation of carbonates. This conclusion agrees fairly well with the data on phase composition of samples after experiments.

According to modern concepts, dissolution of diamond takes place mainly at the stage of ejection of crystals from the mantle as a result of reaction with kimberlite or lamproite magmas. At the same time, existing data on the internal structure of natural diamonds (Bulanova 1995; Anand et al. 2004) suggest that partial dissolution of diamond could have occurred in the mantle under *P-T* conditions of diamond crystallization. In this case, to reconstruct the conditions of the environment, it is necessary to take into account data on the composition of inclusions in natural diamonds, as well as results of studies on diamond crystallization in different systems. Studies of the mineral inclusions in diamonds provides evidence that silicates, oxides, sulfides, and carbonates were present in the diamond-forming media (Harris 1992; Sobolev et al. 1997; Navon 1999; Loest et al. 2003). Undoubtedly, an important component of the media is a fluid, whose composition in most cases is assessed to be H₂O-CO₂ (Navon 1999; Izraeli et al. 2001; Klein-BenDavid et al. 2004). Experimental investigations on diamond crystallization in non-metallic systems showed that carbonate (Akaishi et al. 1990; Sato et al. 1999; Pal'yanov et al. 2002a) and carbonate-silicate (Arima et al. 1993; Borzdov et al. 1999; Litvin and Zarikov 2000; Shatsky et al. 2002) melts are promising for modeling natural diamond formation. Sulfide melts are less efficient diamond-forming media as compared to carbonate and carbonate-silicate systems (Pal'yanov et al. 2006). Dry silicate melts do not provide nucleation and growth of diamond at all for *P-T* parameters up to 7 GPa and 1750 °C (Borzdoev et al. 1999). Of particular interest are the results of studies of diamond crystallization processes in the C-O-H systems (Yamaoka et al. 1992; Akaishi et al. 2000; Shaji Kumar et al. 2000; Pal'yanov et al. 2000; Sokol et al. 2001). It was found that the most favorable medium for diamond crystallization is the H₂O-CO₂ fluid (Sokol et al. 2004). The addition of an H₂O-CO₂ fluid to the crystallization system considerably decreases the *P-T* conditions of diamond formation in carbonate systems (Pal'yanov et al. 1999, 2002a) and provides conditions for diamond crystallization in water-containing silicate melts and silicate-containing H₂O fluids (Pal'yanov et al. 2005a). Possible examples of carbonate-silicate systems with fluids were demonstrated in experiments in which diamond crystallizes from the carbon of carbonates due to carbonate-silicate interaction (Pal'yanov et al. 2002b, 2005b). Thus, mineralogical and experimental data, taken as a whole, suggest that carbonate and carbonate-silicate systems containing a H₂O-CO₂ fluid are the most likely media for growth and dissolution of diamond under

the mantle conditions. We suggest that growth and dissolution of diamond might have alternated in the same systems depending on carbon saturation and redox conditions.

ACKNOWLEDGMENTS

The authors are grateful to N.V. Sobolev for fruitful discussions and Yu. Borzdov, A. Sokol, and I. Kupriyanov for their assistance throughout the study. The authors thank Makoto Arima and an anonymous reviewer for their thoughtful and detailed reviewer and comments.

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MANUSCRIPT RECEIVED JUNE 8, 2006

MANUSCRIPT ACCEPTED JANUARY 9, 2007

MANUSCRIPT HANDLED BY PAUL ASIMOW