

Diamond Crystallization in Fluid and Carbonate–Fluid Systems under Mantle P – T Conditions: 1. Fluid Composition

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Abstract—Graphite and a fluid-generating substance (silver oxalate, oxalic acid, or anthracene) were sealed in a platinum or a gold capsule and run for a long time at elevated pressure (5.7 GPa) and temperature (1200 or 1420°C). Both the starting materials and gases released from the capsule after the experiment were analyzed by gas chromatography. The results of the thermodynamic modeling of C–O–H fluid at 5.7 GPa and 1200–1500°C and at 7 GPa and 1300–1900°C were evaluated. The composition of the fluid generated by the decomposition of real substances was calculated. The experimental and calculated data show that the composition of CO₂ and H₂O–CO₂ fluids changed considerably during the long-term diamond crystallization experiments in the C–O–H system. The compositions of water and methane–hydrogen fluids are more stable. The compositional changes of the H₂O–CO₂ and H₂O fluids with increasing temperature from 1200 to 1420°C indicate a decrease in hydrogen fugacity in the material of the high-pressure cell surrounding the experimental capsules.

INTRODUCTION

Fluid components of the C–O–H system are the most probable source of carbon for natural diamond formation [1, 2]. It is usually believed that this process can occur in the mantle, if there is carbon oversaturation in a growth medium and the P – T conditions correspond to the thermodynamic stability field of diamond. Until recently, comprehensive modeling of diamond genesis was hampered by the lack of experimental evidence on diamond crystallization under parameters and in media approaching real mantle conditions.

Diamond crystallization in fluid systems under mantle P – T conditions has been experimentally studied in the past decade. For example, spontaneous nucleation and growth on seed crystals were studied in the CO₂–C, H₂O–CO₂–C, H₂O–C, and CH₄–H₂O–C systems at 7.7 GPa and 1400–2100°C [3–7]. Diamond crystallization under the P – T conditions of the upper mantle (5.7 GPa and 1200–1420°C) was experimentally simulated in the CO₂–C, H₂O–CO₂–C, H₂O–C, and CH₄–H₂–C systems [8, 9] and in the petrologically significant carbonate–fluid systems K₂CO₃–H₂O–CO₂–C, Na₂CO₃–H₂O–CO₂–C, and CaMg(CO₃)₂–H₂O–CO₂–C [10–12]. An important problem of diamond formation in these systems is the effect of fluid composition on the intensity of crystallization. It was established that diamond nucleation and growth on seed crystals were more intense in CO₂–H₂O than in CH₄–H₂ fluids [8, 9]. No significant difference in the intensity of these processes was detected in the CO₂–C, CO₂–H₂O–C, and H₂O–C systems.

Up to 10 mol % H₂O and CO is synthesized from CO₂ or CO₂ + H₂O in a platinum capsule at 0.8 GPa and 800°C in a few tens of hours [13]. Long experiments with CO₂ resulted in fluid reduction and graphite crystallization [14–16]. In experiments with gold capsules, the fluid composition is much less variable. For example, only 2 mol % H₂O and CO were generated in CO₂ fluid in a 24-h run [13]. 20 mol % CH₄ and 1.5 mol % H₂ were produced in a gold capsules with water fluid in a 60-h run at 2.4 GPa and 1000°C [17]. The fluid derived by the decomposition of stearic acid undergoes oxidation and its H/O ratio decreases from 18 to 5 within 72 h. The effect of the high-pressure cell material surrounding the capsule on fluid composition was analyzed by Rosenbaum and Slagel [13]. They tested NaCl, talc–NaCl (talc/NaCl = 1/9), and hematite–NaCl (hematite/NaCl = 1) mixtures, and the most considerable changes in fluid composition were established when the capsule was surrounded by NaCl. The character of compositional changes was supposed to depend on hydrogen fugacity in the materials enclosing the capsule in the high-pressure cell, which had different sorption capacities with respect to H₂O, H₂, and other gases.

Thus, the experimental data presented in [13–17] showed that C–O–H fluid sealed in noble metal capsules changes its composition during long experiments at $P < 4$ GPa and $T < 1300$ °C. This change is explained by hydrogen diffusion through the capsule walls. The intensity and direction of this process depend on the composition of fluid, capsule material, hydrogen fugacity in the surrounding material, run duration, and, prob-

ably, experimental P - T conditions. During long experiments the compositional instability of the fluid can significantly influence the intensity of diamond crystallization. The goal of this study was to determine fluid composition and evolution in platinum and gold capsules under P - T - τ conditions similar to those employed in experiments on diamond crystallization from the fluid phase [8–12].

EXPERIMENTAL PROCEDURE

The experiments were performed in a BARS multi-anvil high-pressure apparatus of the split sphere type [12]. The experimental conditions were $P = 5.7$ GPa and $T = 1200$ and 1420°C . The high-pressure cell had the form of a tetragonal prism ($19 \times 19 \times 22$ mm) (Fig. 1) and was made from refractory materials having no phase transitions in the range of experimental conditions. Pressure in the cell was determined at room temperature using calibration curves constructed on the basis of changes in the resistance of reference substances, Bi (2.55 GPa) and PbSe (4.0 and 6.8 GPa). Temperature was measured by a Pt6%Rh/Pt30%Rh thermocouple, whose juncture was situated in the graphite heater with a diameter of 9 mm and a height of 15.8 mm. The thermocouple emf was corrected on the basis of special experiments on Ag and Au melting. An additional correction was based on the results of diamond synthesis experiments in the Ni-C system [12].

Fluids were generated in the experiments from high-purity graphite (99.99%), distilled water (H_2O), silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$ stored in a desiccator at 90 – 100°C), and anthracene ($\text{C}_{14}\text{H}_{10}$). The fluid-generating substances and seed crystals of synthetic diamond (0.5 mm in size) were sealed in Pt or Au capsules by arc welding. The procedure of reagent

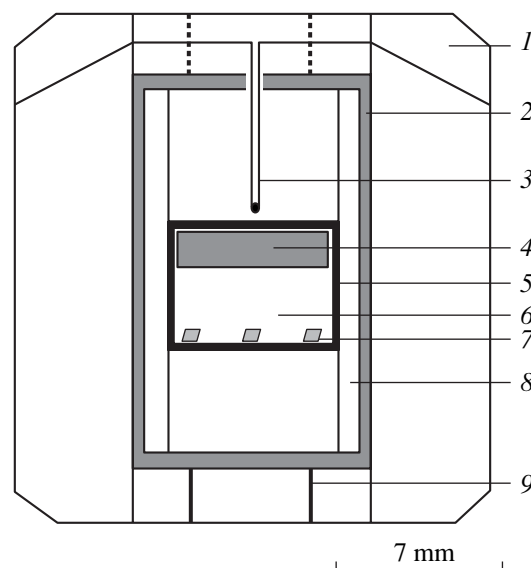


Fig. 1. High-pressure cell used in long experiments for the investigation of changes in fluid composition. (1) ZrO_2 container; (2) graphite heater; (3) thermocouple; (4) graphite; (5) platinum or gold capsule; (6) fluid-generating substance; (7) diamond seed crystals; (8) MgO sleeve; (9) molybdenum conductors.

preparation strongly affects the experimental fluid composition. In order to determine the real fluid composition, we analyzed the fluid-generating substances by gas chromatography (Table 1) or studied the composition of adsorbed gases by thermal extraction (Table 2).

The experiments were terminated by switching off the power supply, after which the temperature

Table 1. Composition of gases formed in the chromatograph during the decomposition of fluid-generating substances

Substance	Extraction temperature, $^\circ\text{C}$	Gas composition, mol %					
		CO_2	H_2O	CH_4	H_2	N_2	CO
$\text{Ag}_2\text{C}_2\text{O}_4$ (without drying)	200	97.2	2.1	0.8	n.d.	n.d.	n.d.
$\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$ (drying at 90 – 100°C)	200	58.6	37.1	2.81	1.47	n.d.	n.d.
$\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$ (without drying)*	200	26.8	69.2	3.60	0.35	n.d.	n.d.

* Not used in the experiments.

Table 2. Composition of gases adsorbed by graphite and anthracene (extraction temperature 600°C)

Substance	Gas composition, mg/kg										
	CO_2	H_2O	H_2	N_2	CO	CH_4	C_2H_2	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	C_3H_8	C_4H_{10}	C_5H_{12}
Graphite	70	n.d.	n.d.	n.d.	20	10	20	4	20	10	7
Anthracene (without drying)	10	210	n.d.	n.d.	4	0.4	1	n.d.	1	1	n.d.

decreased with a rate of 150°C/s [18]. Note that silver oxalate, which was used as a CO₂ fluid source in some experiments, is thermally decomposed under elevated *P*–*T* conditions to give metallic silver. During long experiments the silver penetrates to the walls of platinum capsules, which resulted in capsule failure [9]. Because of this phenomenon, we failed to study the composition of experimental CO₂ fluid.

Gas in the capsules was analyzed before and after experiments using a device assembled from LKhM-80 chromatographs. The detection limits of this device were experimentally determined as follows (ng): CO₂—0.06, H₂O—0.4, H₂—0.13, N₂—0.03, CO—0.5, CH₄—0.03, C₂H₂—0.05, C₂H₄ + C₂H₆—0.04, C₃H₈—0.05, C₄H₁₀—0.09, C₅H₁₂—0.08, and C₆H₁₄—0.1. After experiments the capsules were placed into a special extractor within the chromatograph for thermal and mechanical degassing [18].

THERMODYNAMIC MODELING

A number of studies have addressed the thermodynamic modeling of the C–O–H fluid under mantle *P*–*T* conditions [19–22]. Our calculations were aimed at estimating fluid composition under the *P*–*T* conditions of experiments on diamond crystallization using various fluid-generating substances.

The composition of fluid in equilibrium with diamond (graphite) and oxygen fugacity ($\log f_{\text{O}_2}$) were calculated for the systems studied at 5.7 GPa, 1200–1500°C and 7 GPa, 1300–1900°C. The calculations were carried out by the method of Gibbs free energy minimization using the Selektor software package [23]. The fluid was considered as an ideal mixture of real gases, including CO₂, CO, CH₄, H₂O, H₂, O₂, C₂H₂, C₂H₂O, C₂H₄, and C₂H₄O. The standard-state thermodynamic properties of gases were taken from the *g_reid* database (part of the Selektor program), and those of diamond and graphite, from [24]. The oxygen fugacity values for the forsterite–enstatite–magnesite–diamond and iron–wüstite buffers were calculated using the thermodynamic data from [24]. In all calculations carbon was taken in excess relative to the other elements. The H/(H + O) value corresponded to the molar ratio of these elements in the system, taking into account the difference between the real and ideal compositions of graphite and fluid-generating substances. Gas chromatographic data (Tables 1, 2) were recalculated to molar ratios and normalized to a total of 1.

Our previous papers [9, 18] presented thermodynamic calculations of the composition of C–O–H fluid derived from silver oxalate (Ag₂C₂O₄), oxalic acid (H₂C₂O₄ × 2H₂O), distilled water (H₂O), and anthracene (C₁₄H₁₀) under the experimental *P*–*T* conditions. Calculations were made for the ideal compositions of the reagents. The results suggested that CO₂, H₂O–CO₂, H₂O, and CH₄–H₂ supercritical fluids can be

generated by these substances (Table 3; Figs. 2a–2d). Silver oxalate produces a fluid consisting of CO₂ (99–93 mol %) and CO (1–7 mol %). Such an initial composition provides an oxygen fugacity corresponding to the CCO buffer and H/(H + O) = 0. Oxalic acid yields a fluid consisting of H₂O (~66 mol %), CO₂ (~32 mol %), and minor CO, H₂, and CH₄ (less than 2 mol % in total). Water–graphite interaction gives a water fluid with 5–8 mol % CO₂, H₂, CH₄, and CO (in descending order). Anthracene–graphite interaction produces a methane–hydrogen fluid (up to 93 mol % CH₄ + 7 mol % H₂) at 7 GPa and 1700°C. The concentrations of major components in fluids generated by a single substance in the temperature interval from 1200 to 1420°C vary by no more than a few percent. For the methane–hydrogen fluid, variations in CH₄ and H₂ concentrations may reach 5 mol %. The CO₂ fluid generated by silver oxalate decomposition is characterized by the lowest H/(H + O) and the highest $\log f_{\text{O}_2}$ (Fig. 2a). The $\log f_{\text{O}_2}$ value of H₂O–CO₂ fluid differs from that of the CCO buffer by about 0.5 and approaches the EMOD buffer with increasing temperature. The $\log f_{\text{O}_2}$ value of water fluid is between the EMOD and IW buffers. The methane–hydrogen fluid shows the highest H/(H + O), and its $\log f_{\text{O}_2}$ is significantly below the IW buffer. Note that CO₂, H₂O–CO₂, and H₂O fluids in equilibrium with diamond at 7.0 GPa and 1700°C (Fig. 2c) are stable at higher oxidation potential ($\log f_{\text{O}_2}$ from –2 to –4) than those equilibrated with diamond at 5.7 GPa and 1420°C ($\log f_{\text{O}_2}$ from –3.5 to –5.6). The results of gas chromatography revealed that the initial fluid-generating substances differed from the ideal compositions. Therefore, the thermodynamic calculations of fluid composition were made with the real compositions of the substances (Tables 1, 2). Table 3 shows that the CO₂ fluid derived from the real silver oxalate contains about 9 mol % H₂O. The thermal decomposition of real anthracene produces methane–hydrogen fluid containing up to 5–6 mol % H₂O. Oxygen fugacity values in fluids generated by the same real and ideal substances differ only slightly (by a few tenths of a logarithmic unit). According to the thermodynamic calculations, the abundances of other gases (C₂H₂, C₂H₂O, C₂H₄, and C₂H₄O) are negligible. Revised thermodynamic data for gases, diamond, and graphite [21, 22] can be used to refine the results of calculations and estimate the role of hydrocarbons in the fluid.

The importance of adsorbed gases for diamond crystallization was demonstrated in carbonate–carbon systems at 7 GPa and 1700–1750°C [18]. It was found that diamond crystallized in the presence of H₂O–CO₂ fluid, which was generated mainly at the expense of gases adsorbed on the surface of initial reagents. After

Table 3. Thermodynamic calculations of the composition of fluid generated by the decomposition of initial substances under experimental P - T conditions

Initial composition (weight, mg)	H/(H + O)	P , GPa	T , °C	Fluid composition, mol %					
				CO ₂	CO	H ₂ O	CH ₄	H ₂	log f_{O_2}
Ag ₂ C ₂ O ₄ (140) + graphite (30)	0	7.0	1700	93.18	6.82	–	–	–	–2.03
	0	5.7	1420	96.71	3.29	–	–	–	–3.86
	0	5.7	1200	99.08	0.92	–	–	–	–5.14
Ag ₂ C ₂ O ₄ (140)* + graphite (30)*	0.09	7.0	1700	84.38	6.48	9.11	–	0.03	–2.07
	0.09	5.7	1420	87.56	3.14	9.28	–	0.02	–3.90
	0.09	5.7	1200	89.71	0.88	9.40	–	0.01	–5.19
H ₂ C ₂ O ₄ (70) + graphite (30)	0.333	7.0	1700	55.84	5.27	38.70	0.01	0.17	–2.26
	0.333	5.7	1420	58.00	2.55	39.34	0.01	0.10	–4.09
	0.333	5.7	1200	59.46	0.71	39.80	0.00	0.03	–5.37
H ₂ C ₂ O ₄ × 2H ₂ O* (70) (dried at 90–100°C) + graphite* (30)	0.389	7.0	1700	48.15	4.90	46.77	0.02	0.15	–2.31
	0.389	5.7	1420	50.01	2.37	47.48	0.01	0.12	–4.15
	0.389	5.7	1200	51.29	0.66	48.04	0.00	0.01	–5.43
H ₂ C ₂ O ₄ × 2H ₂ O (70) + graphite (30)	0.500	7.0	1700	30.91	3.92	64.73	0.04	0.39	–2.51
	0.500	5.7	1420	32.17	1.91	65.67	0.03	0.22	–4.34
	0.500	5.7	1200	33.01	0.53	65.64	0.01	0.06	–5.62
H ₂ C ₂ O ₄ × 2H ₂ O* (70) (without drying) + graphite* (30)	0.566	7.0	1700	19.45	3.11	76.76	0.10	0.58	–2.71
	0.566	5.7	1420	20.30	1.51	77.78	0.07	0.33	–4.54
	0.566	5.7	1200	20.81	0.42	78.66	0.02	0.10	–5.82
H ₂ O(70) + graphite (30)	0.667	7.0	1700	2.00	1.00	93.37	1.39	2.23	–3.69
	0.667	5.7	1420	1.77	0.45	95.11	1.31	1.37	–5.60
	0.667	5.7	1200	0.93	0.09	97.74	0.69	0.56	–7.17
H ₂ O(70) + graphite* (30)	0.667	7.0	1700	1.97	0.99	93.37	1.42	2.24	–3.70
	0.667	5.7	1420	1.73	0.44	95.11	1.33	1.39	–5.61
	0.667	5.7	1200	0.89	0.09	97.76	0.72	0.54	–7.19
C ₁₄ H ₁₀ (70) + graphite (30)	1	7.0	1700	–	–	–	82.83	17.17	–
	1	5.7	1420	–	–	–	88.69	11.31	–
	1	5.7	1200	–	–	–	93.51	6.49	–
C ₁₄ H ₁₀ * (70) + graphite* (30)	0.984	7.0	1700	–	0.01	5.71	77.65	16.63	–7.87
	0.984	5.7	1420	–	–	5.89	83.15	10.95	–9.82
	0.984	5.7	1200	–	–	6.04	87.67	6.29	–11.69
Graphite* (30)	0.74	7.0	1700	0.38	0.45	85.13	13.19	0.84	–4.83
	0.74	5.7	1420	0.28	0.18	84.84	14.14	0.55	–6.81
	0.74	5.7	1200	0.07	0.02	84.71	14.88	0.31	–8.70

Note: The initial compositions H₂C₂O₄ (70) + graphite (30) and H₂C₂O₄ × 2H₂O* (70) (without drying) + graphite (30) were not used in the experiments.

* Taking into account the data of gas chromatography (Tables 1, 2).

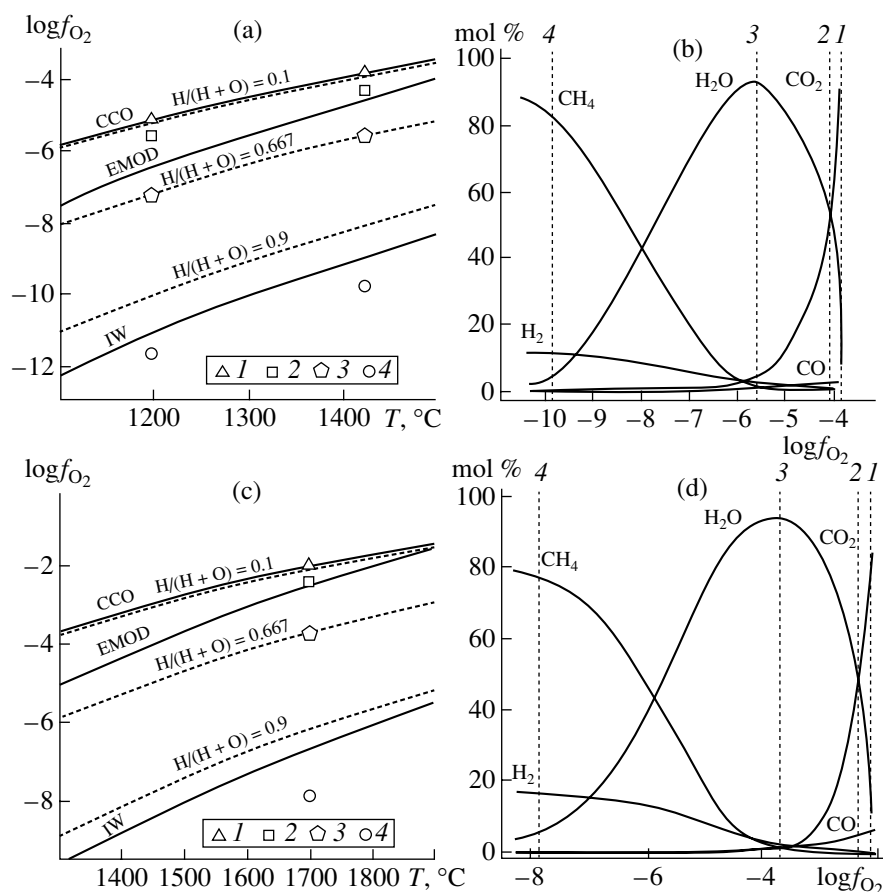


Fig. 2. Composition of fluid in equilibrium with diamond: (a) oxygen fugacity ($\log f_{\text{O}_2}$) as a function of temperature at 5.7 GPa for fluids derived by the decomposition of (1) $\text{Ag}_2\text{C}_2\text{O}_4$, (2) $\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$, (3) H_2O , and (4) $\text{C}_{14}\text{H}_{10}$; (b) fluid composition produced at 5.7 GPa and 1420°C as a function of oxygen fugacity; (c) oxygen fugacity at 7.0 GPa for fluids derived from (1) $\text{Ag}_2\text{C}_2\text{O}_4$, (2) $\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$, (3) H_2O , and (4) $\text{C}_{14}\text{H}_{10}$; and (d) fluid composition obtained at 7.0 GPa and 1700°C as a function of oxygen fugacity.

the experiments, some samples contained up to 0.5 wt % gas components.

COMPOSITION OF FLUID AFTER EXPERIMENTS

After the experiments the capsules were placed into the special extractor within the chromatograph, where they were punctured. All capsules contained abundant recrystallized metastable graphite forming small flakes and their aggregates up to 100–200 μm in size. Spontaneous diamond crystallization was detected in the $\text{CO}_2\text{--H}_2\text{O--C}$ and $\text{H}_2\text{O--C}$ systems at 1420°C and in the $\text{CO}_2\text{--H}_2\text{O--C}$ system at 1200°C. A comprehensive study of metastable graphite and diamond formation is beyond the scope of this paper. These process will be described in a companion paper, where the available data on diamond and graphite crystallization in fluid systems under conditions of diamond stability will be analyzed.

A comparison of the chromatographic (Table 4) and thermodynamic (Table 3) data shows that the compositions of fluids from long experiments are significantly different from what is expected due to the chemistry of the initial fluid-generating substances. The greatest compositional difference was established for the $\text{H}_2\text{O--CO}_2$ fluid generated by oxalic acid. According to thermodynamic calculations, this fluid must consist of 50–51.3 mol % CO_2 and 47.5–48 mol % H_2O at the beginning of experiments at 1200–1420°C. However, after a 42-h run at 1420°C in a platinum capsule, its real composition was 16.9 mol % CO_2 and 82.5 mol % H_2O . Even more considerable compositional changes were detected in $\text{H}_2\text{O--CO}_2$ fluid after a 136-h run at 1200°C: CO_2 was almost completely reduced by hydrogen diffusing through the walls of the platinum capsule. Note less considerable changes in the composition of $\text{H}_2\text{O--CO}_2$ fluid sealed in a gold capsule and subjected to similar experimental conditions: after the experiment it contained about 9 mol % CO_2 and 91 mol % H_2O . At the beginning of experiments with initial distilled

Table 4. Composition of experimental gases extracted from capsules at 150°C

Initial composition (weight, mg)	Capsule	P, GPa	T, °C	τ, h	Diamond nucleation	Fluid composition, mol %					
						CO ₂	H ₂ O	CH ₄	H ₂	N ₂	CO
H ₂ C ₂ O ₄ × 2H ₂ O (20.3) + graphite (6.0)	Pt	5.7	1420	42	+	16.9	82.5	0.2	0.3	0.1	n.d.
H ₂ O (18.0) + graphite (6.1)	Pt	5.7	1420	42	+	9.7	89.5	0.7	0.1	n.d.	n.d.
C ₁₄ H ₁₀ (16.8) + H ₂ O (6.0) + graphite (6.1)	Pt	5.7	1420	42	n.d.	2.4	78.7	17.5	0.9	0.4	0.1
C ₁₄ H ₁₀ (16.8) + graphite (6.1)	Pt	5.7	1420	42	n.d.	n.d.	5.2	1.5	89.8	n.d.	3.51
H ₂ C ₂ O ₄ × 2H ₂ O (70) + graphite (15)	Au	5.7	1200	136	+	8.99	91.01	n.d.	n.d.	n.d.	n.d.
H ₂ C ₂ O ₄ × 2H ₂ O (90) + graphite (43)	Pt	5.7	1200	136	n.d.	0.52	99.47	0.01	n.d.	n.d.	n.d.
H ₂ O (48) + graphite (15)	Au	5.7	1200	135	n.d.	0.01	98.54	1.38	0.07	n.d.	n.d.
H ₂ O (55) + graphite (15)	Pt	5.7	1200	136	n.d.	n.d.	99.99	0.01	n.d.	n.d.	n.d.

water-graphite mixtures, the calculated fluid composition is 95.1–97.8 mol % H₂O and 1.7–0.9 mol % CO₂. After a 42-h run at 1420°C, the fluid released from the platinum capsule was much richer in CO₂ (9.7 mol %). After 135- and 136-h runs at 1200°C, the experimental fluids consisted of almost pure water, and their CO₂, CO, and H₂ concentrations were lower than the calculated values. Only in one of the runs, the methane concentration corresponded to the calculated value.

The composition of the gas phase after experiments with anthracene was dominated by hydrogen, which is inconsistent with thermodynamic calculations. The reason for this discrepancy is unclear. One probable explanation is that the temperature of gas extraction from the capsule was not sufficiently high. The point is that anthracene decomposition produces abundant soot, which subsequently transforms to fine graphite crystals. These forms of carbon can efficiently sorb some gases during thermal extraction. Note that the fluid obtained after anthracene decomposition retained its strongly reduced composition. The fluid produced by anthracene-water-graphite interaction is compositionally intermediate between water and methane-hydrogen fluids, with a strong prevalence of water over methane and hydrogen.

DISCUSSION

Diamond crystallization in fluid was experimentally modeled using molybdenum (graphite-lined) [3], platinum [4–9], and gold [9, 12] capsules. According to our data, the composition of fluid in platinum capsules is not constant. Owing to hydrogen penetration into the capsules, the concentration of water in H₂O–CO₂ fluid increases up to an almost pure water composition in experiments with a duration of more than 100 h. It is

evident that carbon dioxide reduction by hydrogen produces water and carbon. Although gold capsules are less permeable to hydrogen, they cannot prevent the reduction of CO₂-containing fluid. Hydrogen escaped in experiments with water at 1420°C, and the fluid became considerably enriched in CO₂ (up to 10 mol %). Fluid composition remained constants in the experiments at 1200°C. These data suggest that hydrogen fugacity decreased in the material surrounding the capsules, as temperature increased from 1200 to 1420°C. Hydrogen fugacity in high-pressure cells is probably

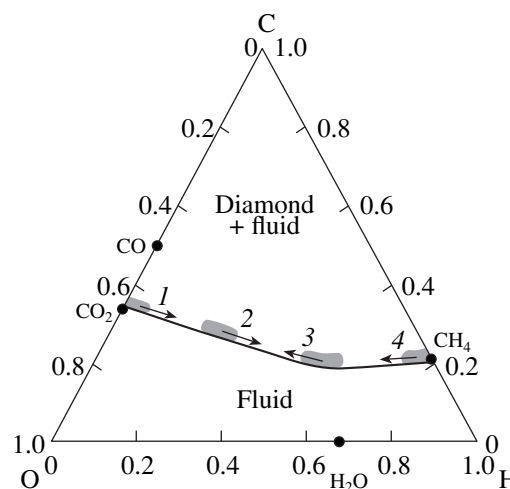


Fig. 3. Changes in the composition of C–O–H fluid during long experiments in platinum capsules: fluid produced by the decomposition of (1) Ag₂C₂O₄, (2) H₂C₂O₄ × 2H₂O, (3) H₂O, and (4) C₁₄H₁₀. The height of the compositional fields above the diamond stability boundary is shown arbitrarily, because the degree of fluid supersaturation in carbon during diamond crystallization is not known.

even lower at higher temperatures, and, hence, H₂O–CO₂ fluids generated in long experiments at $P = 5.7$ GPa and $T > 1420^\circ\text{C}$ must be richer in CO₂. Similar temperature-related changes in equilibrium fluid composition must occur at pressures of 7.0–7.7 GPa. A number of experimental studies on diamond crystallization in the C–O–H system were performed within this pressure interval.

Thus, the experimental data show that the compositions of H₂O–CO₂ and H₂O fluids converge during long experiments on diamond crystallization in the C–O–H system under elevated P – T conditions (Fig. 3). Changes in the composition of reduced fluids are caused by decreasing hydrogen fugacity in the capsules. The water–methane fluid is enriched in water during experiments, and the methane–hydrogen fluid loses hydrogen. Experimental problems prevented the investigation of changes in CO₂ fluid. Since the hydrogen potential in the high-pressure cell material must be very different from that within the capsules, the composition of fluid must be extremely variable. The rate of changes in fluid composition depends on the capsule material, sample composition, and the type of the high pressure cell. The obtained trends suggest that the similar intensities of diamond formation in CO₂, CO₂–H₂O, and H₂O fluids [8, 9] are caused by the convergence of fluid compositions during the experiments. Changes in fluid composition were probably less extensive in gold capsules.

This conclusion is consistent with the data obtained by a quadrupole mass spectrometer. As was shown for high-pressure cells used in the Advanced Materials Laboratory [3–7], experimental fluid generated from oxalic acid at 7.7 GPa and 1500°C in a platinum capsule was enriched in H₂O relative to the calculated composition [6]. On the contrary, Yamaoka *et al.* [5] concluded that water fluid gained 10–20 mol % CO₂ after a 24-h run at 7.7 GPa and 1500°C on the basis of changes in capsule mass during the experiments and the semi-quantitative mass spectrometric analyses of the experimental gases. Graphite–fluid equilibrium was rapidly reached in experiments with isotopically pure (¹³C) graphite [4]. The equilibrium ¹³C/¹²C ratio in fluid of the CO₂–H₂O–C system is reached within 6 h at 7.7 GPa and 1600°C.

The quenching rate in high-pressure experiments also exerts some influence on fluid composition. A decrease in quenching rate from 150 to 30°C/s results in a CO depletion in the fluid by several mole percent [15]. A comparison of thermodynamic and chromatographic data suggested that the composition of strongly reduced experimental fluids (C₂H₆, H₂, and CH₄) remains unchanged only at a quenching rate of 120°C/s [17]. A quenching rate of 0.3°C/s results in a decrease in hydrogen concentration by 2–4 mol %. Matveev *et al.* [17] argued that reactions occurring with decreasing temperature and that prevent fluid quenching cease only at $T < 800^\circ\text{C}$.

The composition of the fluid phase in the carbonate–fluid–carbon system was investigated only by Sokol *et al.* [18]. According to their results, irrespective of the cation composition of carbonate, the quenched fluids from experiments at 7 GPa and 1700–1750°C had H₂O–CO₂ compositions with no more than 12 mol % CO₂, which is in agreement with the trends described in this paper. However, the real composition of fluids under the experimental P – T conditions probably depended on the solubility of carbonate phases in C–O–H fluid. Unfortunately, there are no data on their solubility, and only rough estimates can be given. The diamond-forming H₂O–CO₂ or H₂O fluid (20 wt % of the system) probably completely dissolved K and Na carbonates in the K₂CO₃–H₂O–CO₂–C and Na₂CO₃–H₂O–CO₂–C systems at 5.7 GPa and 1150–1420°C [10, 12]. It can be supposed, therefore, that diamond crystallized from a fluid compositionally corresponding to the system. A more complex situation probably existed in experiments on diamond crystallization in dolomite–fluid systems. Sokol *et al.* [11] argued on the basis of arrangement and form of quench phases and the fall of seed crystals to the capsule bottom that the dolomite–H₂O–CO₂–C system underwent melting at 5.7 GPa and 1300–1420°C. It remains unknown whether the melt was in equilibrium with the fluid phase, or the system occurred above the P – T parameters of the second critical point. According to Wyllie and Ryabchikov [25], CO₂ solubility is relatively high in the melt of such a system, and the carbonate melt must be in equilibrium with water fluid. Although the fluid composition was more complex, the equalization of hydrogen fugacity within and outside the capsule influenced diamond crystallization in carbonate–fluid systems.

The ability of hydrogen to diffuse through the walls of platinum capsules can be used for special studies. For example, Pal'yanov *et al.* [26] used titanium hydride as an external hydrogen source in experiments on diamond formation accompanying the magnesite–coesite–enstatite interaction at 6–7 GPa and 1350–1800°C. The high hydrogen fugacity provided hydrogen ingress into the capsule and displaced mineral and fluid equilibria. As a consequence, the magnesite + enstatite + diamond + fluid \pm coesite or magnesite + forsterite + diamond + fluid \pm enstatite assemblages were formed.

Molybdenum capsules were used in a number of experiments on diamond crystallization in the C–O–H system. According to the data of Akaishi and Yamaoka [3], experimental products in the CO₂–H₂O–C system contained MoO₂. The Mo–MoO₂ buffer at 7.7 GPa and 1400°C provides $\log f_{\text{O}_2} = -6.7$. Our calculations show that fluid in equilibrium with diamond under such P , T , and $\log f_{\text{O}_2}$ values consists of H₂O (~70 mol %), CH₄ (~20 mol %), and H₂ (~10 mol %). The real fluid composition in the experiments with Mo capsules probably depended on the initial composition of the system, tem-

perature, duration, and other factors. The compositional changes of CO₂ and CO₂-H₂O fluids sealed in molybdenum capsules were probably no smaller than those in similar experiments with platinum capsules.

The above considerations suggest that oxygen buffering techniques must be used. However, the two-capsule method of fluid buffering is not practicable in high-temperature and long-duration experiments on diamond crystallization in the C-O-H system. Another problem is the absence of buffers controlling the composition of the CO₂-H₂O-C system at 5.7–7.7 GPa and $T > 1300^{\circ}\text{C}$. This is related to the fact that the composition of diamond-equilibrated fluid changes from CO₂ to H₂O within a narrow $\log f_{\text{O}_2}$ interval (less than two units at experimental P - T parameters). For example, this fluid transformation occurs at 5.7 GPa and 1420°C within the $\log f_{\text{O}_2}$ interval from -3.9 to -5.6. Buffering fluid composition is an important experimental problem, especially for diamond crystallization in CO₂ fluid.

CONCLUSIONS

(1) The H₂O-CO₂ fluid sealed in a platinum capsule together with graphite (diamond) showed an increase in water content from 47.5 to 82.5 mol % in a 42-h run at 5.7 GPa and 1420°C and up to 99.5 mol % in a 136-h run at 1200°C. The composition of H₂O-CO₂ fluid is better maintained in experiments with gold capsules, but their use is limited to low temperatures.

(2) The interaction of water with graphite at 5.7 GPa and 1200°C produced a water-dominated fluid, whose composition practically did not change during a 136-h experiment. Hydrogen diffusion out of platinum capsules and related carbon oxidation, resulted in the formation of about 10 mol % CO₂ during a 42-h experiment at 1420°C.

(3) The methane-hydrogen fluid produced by anthracene decomposition remained strongly reduced in a 42-h run at 5.7 GPa and 1420°C.

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