
GEOCHEMISTRY

Nanodiamond Formation in Natural Processes from Fluid Systems at Low P – T Parameters

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Presented by Academician N.P. Yushkin March 11, 2010

Received June 3, 2010

Abstract—The paper presents a new physicochemical model of the formation of nanosized diamonds from an OHC fluid system under low temperature and pressure conditions corresponding to the graphite stability area. This model in general explains the specific features of the composition of gas mixtures for CVD and hydrothermal synthesis in terms of diamond growth and formation under metastable conditions. It also explains the origin of nanodiamonds and microdiamonds in metamorphic rocks of the Earth's crust and the genesis of nanodiamonds in outer space at low temperatures and pressures.

DOI: 10.1134/S1028334X11010326

Presently, there are a number of publications reporting the discoveries of microdiamonds in different rocks of the Earth's crust. Nanodiamonds were discovered in Hawaiian basalts, where they associate with an aqueous bicarbonate fluid [15]. This phenomenon has been continuously discussed by geologists since the 1970s. The majority of researchers automatically extrapolate the conditions of diamond synthesis at high temperatures and pressures to the natural conditions. However, some researchers believe that diamonds can form in the Earth's crust from reduced hydrocarbon fluids along with graphite at low P – T parameters [1, 3, 13]. Presently, diamonds and diamondlike films can be generated on the existing diamond substrate [5], and nanosized diamonds can be generated without a substrate under the conditions when they are thermodynamically unstable [4, 11].

The Kokchetav metamorphic rock complex (North Kazakhstan) is the largest of the diamond occurrences associated with rocks of the Earth's crust. The content of diamonds there in mineralized zones is an order of magnitude higher than that in kimberlites. Diamonds were discovered in rocks having very different compositions that underwent secondary alteration, a process that involved aqueous fluids; so diamondiferous rocks are rich in a fluid component [1, 13]. The authors of paper [13] assume that diamonds form due to deep “blow-off” of these zones with originally hydrocarbon fluids followed by deoxidization and the formation of free carbon (graphite and diamond) in metasomatic alteration processes at low temperatures

and pressures. Due to this, diamondiferous rocks are rich in the fluid component and have elevated contents of water, methane, hydrocarbons, and carbon dioxide [1], and the principal inclusions in the Kokchetav diamonds are graphite, water, and carbonates [8].

Nanosized diamond particles were initially discovered in space objects. Large quantities of nanodiamonds were encountered in meteorites that have fallen onto the Earth. The nanodiamond content in some meteorites can be 2–3 times higher than the content of graphite, carbides, and amorphous carbon [10]. Paper [14] notes an empirical relation of cosmic nanodiamonds to water, and paper [11], to organic compounds. Based on this, A. Kouchi et al. [10] assume that the original matrix from which nanodiamonds formed in outer space consisted of H_2O , CO , NH_3 , and CH_4 in the ratio 4 : 2 : 2 : 1. For the time being, the question where and how diamonds form in outer space is still open; however, microstructural analysis conducted for nanodiamonds retrieved from meteorites indicates that they formed as a result of condensation from a gas phase under low pressures [7].

Thus, it can be stated that nanodiamonds and microdiamonds are encountered in nature in the presence of an aqueous phase. This corresponds to the model of diamond formation in the rocks of the Earth's crust from a gas phase, where the stability of free carbon is governed by the oxidation–reduction potential of the environment [3]. The free carbon stability condition corresponds to the composition of the aqueous fluid. The principal sources of carbon during diamond formation were likely methane and hydrocarbon gases [3].

Paper [5] presents a theory of nucleation and growth of graphite and diamond from the gas phase. In

simultaneous synthesis of graphite (g) and diamond (d), the ratios of their critical radii are important factors. Paper [9] demonstrates that diamond particles up to 15 nm in size are more energetically stable than graphite particles of the same size. It follows from paper [5] that the ratio between the critical radii of graphite and diamond is determined by the following formula:

$$r_g/r_d = V_g \sigma_g \Delta \mu_d / V_d \sigma_d \Delta \mu_g, \quad (1)$$

where σ is the surface energy, V is the atomic volume of carbon, and $\Delta \mu$ is the chemical supersaturation potential.

It follows from the σ_g/σ_d ratios quoted in [9, 12] that $V_g \sigma_g / V_d \sigma_d$ for nanosized particles ≈ 1 . Then, on the one hand, r_g/r_d ratio can be expressed as

$$r_g/r_d = \Delta \mu_d / \Delta \mu_g. \quad (2)$$

On the other hand, the chemical supersaturation potential for graphite and diamond can be expressed as

$$\Delta \mu_g = RT \ln(P_i/P_{i,g}) \quad (3)$$

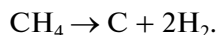
and

$$\Delta \mu_d = RT \ln(P_i/P_{i,d}), \quad (4)$$

where P_i and $P_{i,g,d}$ are the true pressure and the equilibrium pressure of the carbon bearing gas, from which free carbon forms.

It follows from (2)–(4) that the r_g/r_d ratio depends on the ratio between the pressure in the system and the equilibrium pressures of the carbon-bearing gas over graphite and diamond. The conditions of the formation of graphite particles correspond to $P_{i,g} < P_{i,d}$, while the conditions of the formation of diamond particles correspond to $P_{i,g} > P_{i,d}$. The difference between $\Delta \mu_g$ and $\Delta \mu_d$ depends on the difference between the $P_i/P_{i,g}$ and $P_i/P_{i,d}$ ratios; it tends to zero when the values of $P_{i,g,d}$ are low. This corresponds to optimal conditions of diamond formation from a gas mixture when graphite is thermodynamically stable.

For the case when the gas system consists only of methane, its equilibrium pressure over graphite or diamond is calculated from the CH_4 decomposition reaction:



If the effect of oxygen is taken into account, the situation becomes more complicated, since the equilibrium of free carbon with a mixture of gases (CO , CO_2 , H_2 , H_2O , CH_4 , and O_2) should be considered in the OHC system. The composition of this mixture that is in equilibrium with carbon will depend on the oxygen fugacities. Diamond formation is affected by the composition of the gas mixture, from which it forms. Paper [6] demonstrates that diamond synthesis conducted using the CVD methods originates from mixtures having a certain composition that form a sort of “corridor” on an OHC diagram, which widens as one moves from the H vertex to the CO composition. Paper [2]

justifies the possibility of nanodiamond formation from gas at low temperatures and pressures without a substrate due to adding oxygen to an HC system (and thereby converting it into an OHC system). In this system, oxygen pressures can be selected under which the diamond nucleus would be more stable than the graphite nucleus ($P_{i,g} > P_{i,d}$). These conditions are possible within a range of oxygen fugacities that is close to the upper limit of the stability of carbon in this system in terms of oxygen; this upper limit is the CCO buffer, where the equilibrium pressure of methane abruptly decreases (Fig. 1).

Calculations made for an OHC system at the P – T parameters corresponding to the CVD methods indicate that the oxygen pressures corresponding to the formation of diamond at such parameters correspond to the hydrogen and carbon dioxide compositions of gas mixtures (Fig. 1A). This model in general explains the specific features of the “diamond compositions” of gas mixtures mentioned in paper [6]. At the P – T parameters corresponding to the formation of Hawaiian basalts (1000°C and 20 kbar), the oxygen pressures under which diamond forms correspond to an aqueous bicarbonate composition of the fluid (Fig. 1B), which also explains the compositions of the fluid associated with nanodiamonds in basalts [15]. For the metasomatism conditions of the Kokchetav deposit (500°C and 1 kbar), an optimal area of diamond formation and growth from methane in the OHC system is a fluid having an aqueous bicarbonate composition (Fig. 1C). This explains the composition of the fluid inside diamonds [8] and the processes of silicate hydrate formation in the zone of diamondiferous rocks occurring with noticeable quantities of water involved [1]. This was experimentally confirmed in paper [4], which details how nanosized crystals and polytypes of these were generated from aqueous solutions of organic substances in the absence of a diamond substrate at the given P – T parameters. When nitrogen was added to the system, some of the diamonds could be up to 1 μm in size. The diamond stability area for the conditions of cold molecular clouds (250°C and 10^{-3} bar) also corresponds to a fluid having aqueous and bicarbonate compositions (Fig. 1D), which explains the relation of nanodiamonds in outer space to the aqueous component [14].

It can be concluded that this model in general explains the specific features of the composition of gas mixtures for CVD and hydrothermal synthesis in terms of diamond growth and formation under metastable conditions. It also explains the origin of nanodiamonds and microdiamonds in metamorphic rocks of the Earth’s crust and the genesis of nanodiamonds in outer space at low temperatures and pressures. It follows from the model that there is no need to involve ultrahigh temperatures and pressures to explain the presence of nanodiamonds and microdiamonds in the rocks of the Earth’s crust. Diamonds can form there at the P – T parameters corresponding to the formation of

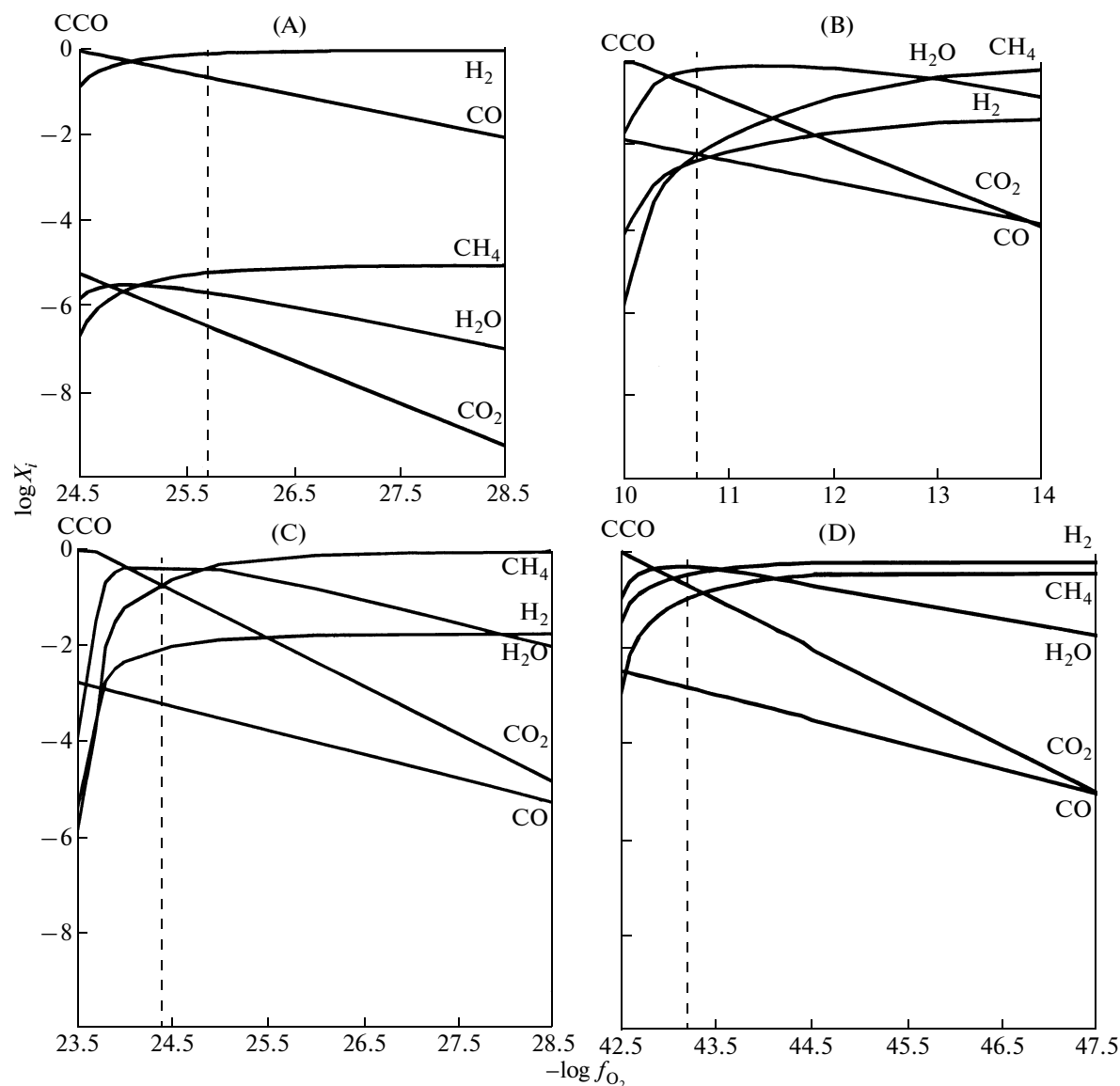


Fig. 1. The compositions of fluids of an OHC system that are in equilibrium with carbon: (A) at 1000°C and 10^{-3} bar, (B) at 1000°C and 20 kbar, (C) at 500°C and 1 kbar, (D) at 250°C and 10^{-3} bar (the CCO buffer is the upper limit of the stability of carbon in the system in terms of oxygen; the dashed line shows the boundary of the stability of diamond nuclei in terms of oxygen). X_i is the mole fraction of the component contained in the fluid system; f_{O_2} is the oxygen fugacities.

major mineral of rocks due to fluids involved in these processes. For rocks of the Earth's crust (and the upper portion of the upper mantle), such fluids can be originally hydrocarbon fluids deoxidized in the course of evolution of the system to aqueous and bicarbonate compositions.

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