American Mineralogist, Volume 60, pages 413–417, 1975

Experimental Results and a Theoretical Interpretation of Gaseous Inclusions found in Arkansas Natural Diamonds

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Abstract

A detailed analysis of the composition of gaseous inclusions in seven Arkansas diamonds ranging in size from 2.06 to 0.37 carats and containing other inclusions has been made by mass spectrometric techniques. The diamonds were crushed in the high vacuum inlet of a research mass spectrometer. The released gases were found to be of variable composition and similar to those reported earlier from diamonds of African origin. The gases are composed of C, H, O, N and Ar atoms; water is the most abundant compound, followed in decreasing abundance by hydrogen, nitrogen, carbon dioxide, methane, carbon monoxide, methyl and ethyl alcohols, and argon. Based on the tentative assumption that the gases are genetically related to the host diamond, a theoretical gas-solid diamond growth model is presented which can account for the observed compositional variations in the included gas.

Introduction

Two approaches have been used to obtain information about the environment in which natural diamonds form. The first involves detailed analyses of included solids. While uncertainties exist, evidence indicates scores of different solids were occluded when diamonds crystallized (Williams, 1932; Mitchell and Giardini, 1953; Harris, 1972; Meyer and Boyd, 1972; Giardini *et al,* 1974). Despite the wealth of information thus accumulated, simplified application of the results to a theoretical model is inadequate to specify accurately the conditions of diamond genesis. The second approach has been to analyze the gaseous material present in diamonds (Melton, Salotti, and Giardini, 1972; Melton and Giardini, 1974). However, the earlier results were from only a few diamonds, whereas data from a large number of samples from several localities are needed. This study adds data on diamonds from a different continent (North America), and results are presented here on the included gas from seven Arkansas diamonds of varying body color, size, and shape, and with varying contents and types of other included matter. We have also formulated, at least qualitatively, a generalized model for diamond-growth based on gas-solid interactions; it shows that the variations in included gas composition might reflect diamond growth over a wide range of temperature in the earth.

Experimental

The apparatus used in this study was the same as that described in an earlier publication on gases released from diamonds (Melton and Giardini, 1974). All experimental techniques and calibration procedures also were given therein. Briefly, the mass spectrometer is a single-focussing 90° instrument with a 6-inch radius of curvature. The detector system consists of a 14-stage electron multiplier placed immediately after the final defining slit. The diamond specimens, all of which contained visible inclusions, are crushed in the high vacuum inlet system of the instrument. The released gas is then analyzed mass spectrometrically. By suitable calibration, partial pressures of the various gaseous species may be measured.

The Arkansas diamonds were obtained from three different sources. Samples No. 1-3 were provided by Dr. Paul DeSautels of the Smithsonian Institution. Samples No. 4 and 7 were purchased from Mr. Dicke Hughes, a former owner of the Murfreesboro,

TABLE 1. Description of Arkansas Diamonds

Specimen No.	Weight (carats)	Description and Source
1	2.06	Pale yellow, with translucent internal regions, from the Smithsonian Institution *
2	1.53	Colorless, with white cloud-like translucent internal regions, from the Smithsonian Institution *
3	0.885	Colorless flat cleavage plate, with a thin 2 x 1 mm near-rectangular black inclusion, from the Smithsonian Institution *
4	0.759	Colorless, with three small black inclusions, from Mr. Dicke Hughes, Murfreesboro, Arkansas
5	0.542	Pale yellow, with several transparent inclusions, from Mr. Flay Garner, Murfreesboro, Arkansas
6	0.425	Colorless, with two small brownish inclusions, from Mr. Flay Gamer, Murfreesboro, Arkansas
7	0.365	Brown, with several transparent small inclusions, from Mr. Dicke Hughes, Murfreesboro, Arkansas

*From the Roebling Collection through the courtesy of Dr. Paul Desautels.

Arkansas, kimberlite property. Samples No. 5 and 6 were purchased from Mr. Flay Garner, a resident of Murfreesboro, and were certified to have been found in the Murfreesboro, Arkansas, kimberlite by Mrs. Sue McCarty, Facility Manager of the Arkansas Crater of Diamonds Park.

A description of the Arkansas diamonds used in this study is given in Table 1, and typical curves for the ultraviolet spectrum of these type I and type II diamonds are shown in Figure 1.

Results and Discussion

The range of compounds in the occluded gas from African diamonds that also contained solid inclusions has been shown to be fairly consistent, but the relative percentages varied markedly from diamond to diamond (Melton and Giardini, 1974). These differences were tentatively interpreted as reflecting variations in environment during diamond genesis.

Results from the crushing of Arkansas diamonds under similar conditions—about 10^{-8} torr vacuum and 200°C (Table 2)—were consistent with those obtained from African diamonds. Similar compounds were present and, for example, the abundance of water varied from a minimum of 2.9 volume percent for the 1.53 carat type I diamond that contained internal white translucent regions, to a maximum of 76.9 percent for the 0.885 carat type II diamond that contained a large solid inclusion of black color. The abundance of nitrogen ranged from essentially 0 percent in the 0.425 carat type I diamond that contained two small brown-colored inclusions to 87.1 percent in the 1.53 carat type I diamond.

To compare the gases from the Arkansas diamonds with those previously reported from other locations (Melton and Giardini, 1974), data have been reduced to "average" compositions and percent atomic abundances (see Table 3). As can be seen, there are differences and they are much larger than the presumed inaccuracies in the experimental method (± 5%).

The abundance of water released from diamonds of cube form is much larger than that released from diamonds of other crystal forms. We tentatively conclude, therefore, that the cube form crystallized in an environment rich in oxygen compared to the other crystal forms of diamond. A corresponding difference should be detectable in the mineralogy and geochemistry of the kimberlites where these different crystal forms exist.

It was suggested earlier that the C-H-O gas system found entrapped in natural diamonds may be indicative of a gas phase–diamond growth mechanism under a variable environment (Melton and Giardini, 1974; Giardini *et al*, 1974). Such a mechanism is, of course, hypothetical since the gases released from diamonds have not been proven to be genetically related to the diamond. The gases may properly belong to mineral inclusions that also have been present in the diamonds that have been crushed. Diamonds with inclusions have been used because

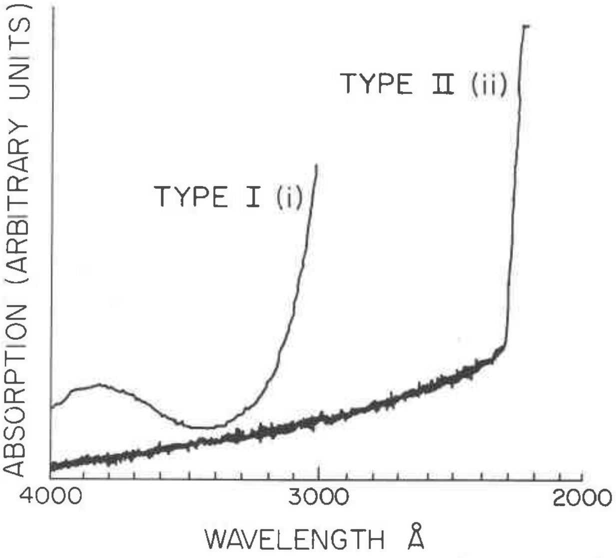

FIG. 1. (i) Absorption spectrum of a 2.06 carat Type I Arkansas diamond. (ii) Absorption spectrum of a 0.885 carat Type II Arkansas diamond.

they can be crushed "easily," and thereby with a minimum of gas contamination from the crushing apparatus.

The fairly common presence of nitrogen in the occluded gas may constitute a genetic link to diamond (Kaiser and Bond, 1959), since nitrogen is not otherwise known as a common constituent in plutonic minerals. Also, the works of Eversole (1962), Deryagin *et al* (1969), and others on diamond growth by gas reactions further suggest a genetic link between diamond and its included gas.

In pursuit of the concept of a gas phase–solid growth mechanism, a model has been developed and is given below. First, however, we shall briefly review the thermodynamic relations governing possible diamond crystallization. Consider the equilibrium reaction between diamond and graphite,

$$\mathrm{C\,(diamond)} \rightleftharpoons \mathrm{C\,(graphite)}$$

The difference between the heats of combustion for the two substances is found experimentally to be $\Delta H_{298} = -450$ cal/mole (Weast, 1971–72). The change in entropy, ΔS, for the reaction can be estimated from heat capacities to give $\Delta S_{298} = 0.80$ cal/degree mole. From these quantities and the well known relationship for free energy, ΔG,

$$\Delta G = \Delta H - t\Delta S, \tag{1}$$

where t is the temperature, ΔG is -685 cal/mole at 298 K and one atmosphere. Using the relationship,

$$\left(\frac{\Delta G}{\Delta P}\right)_t = -V, \tag{2}$$

(V = volume, P = pressure) combined with the densities of diamond and graphite, $\Delta G = 0$ at about 22, 000 atmospheres and room temperature.

TABLE 3. Average Volume Percent and Atomic Percent Compositions of Gases Released from Natural Diamonds Containing Crystalline Inclusions Crushed at 200°C under a Vacuum of about 10^{-8} Torr

	SOURCE OF DIAMONDS		
	Arkansas*	Africa*	African Cubes
Gas	Average Volume Percent		
H_2	19.4	37.4	1.8
CH_4	3.7	6.5	4.1
H_2O	39.6	16.5	67.0
C_2H_4	--	1.1	0.1
N_2	15.9	0.3	2.1
CO	3.8	21.0	3.2
CH_3OH	1.0	--	--
CH_3CH_2OH	1.0	0.5	1.4
O_2	--	--	0.8
C_3H_6	--	0.3	0.5
Ar	--	0.4	0.2
CO_2	15.5	7.5	19.0
	Average Atomic Percent		
H	51.2	56.3	47.5
O	27.8	20.9	39.9
C	9.2	15.4	11.2
N	11.7	7.2	1.3
Ar	0.1	0.2	0.1

*Crystals either of octahedral, hexoctahedral, or rounded indeterminant form.

TABLE 2. Percent Composition and Volume of Gases Released from Natural Arkansas Diamonds Crushed at 200°C under a Vacuum of 10^{-8} Torr

Sample No.	1	2	3	4	5	6	7	
Weight (cts)	2.06	1.53	0.885	0.759	0.542	0.425	0.365	
Type	I	I	II	I	I	I	II	
Gas	Volume Percent							Av.
H_2	19.3	1.5	5.4	38.9	14.0	24.6	32.3	19.4
CH_4	4.6	0.9	0.9	5.4	5.8	3.6	4.8	3.7
H_2O	28.0	2.9	76.9	25.6	45.0	59.9	39.1	39.6
CO	9.4	2.1	1.2	5.2	2.4	1.9	4.4	3.8
N_2	8.6	87.1	8.2	1.7	1.8	-	4.0	15.9
CH_3OH	-	-	-	-	5.2	-	1.6	1.0
CH_3CH_2OH	0.3	-	0.2	3.2	2.1	-	1.4	1.0
Ar	0.2	0.2	-	-	-	-	-	0.1
CO_2	29.6	5.3	7.2	20.0	23.7	10.0	12.5	15.5
STP Gas Volume (10^{-5} cc)	3.4	54	27	7.7	4.4	102	7.7	

According to the thermodynamics, therefore, diamond could be formed from graphite at room temperature and 22,000 atmospheres of pressure, but this has not yet been done. Rather, diamond is synthesized in the laboratory under a minimum pressure of about 50,000 atmospheres and a temperature of about 1500 K. Thus, the experimental results indicate that diamonds are not created in the laboratory under minimal thermodynamic conditions. Since we do find carbon gases in natural diamonds, such diamonds may have grown, at least in part, by a gas-solid mechanism. In fact, such a mechanism has already been proposed (Mitchell and Crocket, 1971).

To explore this possibility theoretically, we consider a model illustrated by Figure 2. A rigorous theoretical treatment of diamond growth by the gas-

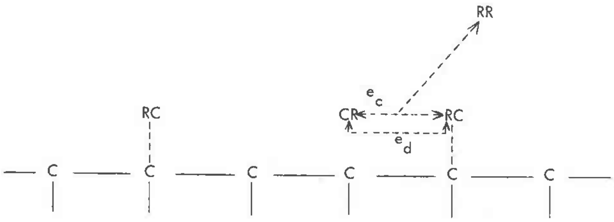

FIG. 2. Simplified one-dimensional model of the surface of a diamond crystal illustrating growth by a gas solid reaction. The letter e_c indicates interaction energy for RR, and e_d energy for CR.

solid reaction is not feasible. However, some insight into the mechanism can be gained by considering a crystal with interactions between near neighbors only. Assume a gas phase molecule of composition RC where C is carbon and R is a radical component composed of either atomic or molecular species. The gas molecule can attach to the crystal surface through either an RRC configuration or an RCC configuration. For diamond growth to occur, the RCC configuration is necessary (*i.e.*, the carbon must bond to the carbon).

If each of N carbon atoms in a crystal is attached to the RC molecule, the two different resultant states can be designated as "a" and "b" where b state indicates possible diamond growth (RCC). The energy of these isolated states is either e_a or e_b. In the simple model the attached RC molecules interact with their nearest gas or solid phase neighbors. Let e_c be the interaction energy for a gas-solid phase RR pair—one species bonded to the crystal and the other in the gas phase (Fig. 2)—and let e_d be the interaction energy for a gas-solid phase CR pair.

When each of the N carbon atoms in the crystal has a CR molecule attached, the energy of the system is determined by the number and energy of possible bonding states n_b (RR) and by the number and energy of possible nonbonding states, n_d, (CR). Let e_c be the interaction energy for the possible bonding conditions and e_d be the interaction energy for the nonbonding condition (see Fig. 2). The energy of the system will be determined by e_c, e_d, e_a, e_b, N, n_b, and n_d. There are $(N - n_b)$ possible bonding states and $(N - 1 - n_d)$ nonbonding states.

From these assumptions and definitions, the energy is given as

$$E(n_b, n_d) = n_b(e_b - e_a) + n_d(e_c - e_d) + Ne_a + (N - 1)e_d \qquad (3)$$

Let $f(n_b,n_d)$ be the number of configurations with n_b elements in bonding states and n_d (RR) interactions. The canonical partition function (Q) for the system can be formulated as

$$Q = \sum_c f(n_b, n_d) \exp(-\beta n_b(e_b - e_a)) \cdot \exp(-\beta n_d(e_c - e_d)) \cdot \exp(-\beta N e_a) \exp(-\beta(N - 1)e_d) \qquad (4)$$

where β is 1/kt and $\sum_c$ is the sum over all designated configurations. The factors $\exp(-\beta N e_a)$ $(-\beta\ (N - 1)e_d)$ do not significantly affect the probability of different configurations and hence can be factored out of the sum. To simplify the discussion, we define

$$\Phi = \exp - \beta(e_b - e_a) \qquad (5)$$

$$\varphi = \exp - \beta(e_c - e_d). \qquad (6)$$

The quantity Φ is the ratio of the Boltzmann factors for bonding and nonbonding gas-phase RR states, and φ is the ratio of the Boltzmann factors for nonbonding and gas-phase CR interactions.

These simplifications lead to a partition function for the system of

$$Q = \sum_c f(n_b, n_d)\Phi^{nb}\varphi^{nd} \qquad (7)$$

The probability $p(n_b,n_d)$ of a group of configurations with parameters n_b and n_d is given by

$$p(n_b, n_d) = \frac{f(n_b, n_d)\Phi^{nb}\varphi^{nd}}{Q} \qquad (8)$$

The average values for n_b and n_d are

$$\langle n_b \rangle = \left[\frac{\partial \ln Q}{\partial \ln \Phi}\right]_\varphi = \sum_c n_b p(n_b, n_d) \qquad (9)$$

$$\langle n_d \rangle = \left[\frac{\partial \ln Q}{\partial \ln \varphi}\right]_\Phi \qquad (10)$$

To evaluate Q, matrix algebra must be used. The formalism gives a value of

$$Q(\varphi, \Phi) = \sum \mathbf{r}_{v1} A_{v1,v2} A_{v2,v3} \cdots A_{vN-1,vN} \mathbf{C}_{vN}. \qquad (11)$$

$$v1 = a,b$$

$$v2 = a,b$$

$$vN = a,b$$

where $\mathbf{r}_{v1}$ is the row vector $[1, \Phi]$, A is the matrix, and $\mathbf{C}_v$ is the column vector. Equation (11) can be simplified to give a partition function of

$$Q(\varphi, \Phi) = \mathbf{r} A^{N-1} \mathbf{C} \qquad (12)$$

where $\mathbf{r}$ is the row vector and A is the matrix and $\mathbf{C}$ is the column vector. To evaluate Q of Equation (12), let T be the matrix of the similarity transformation which diagonalizes A, and multiply by $T^{-1}T$ to obtain

$$T^{-1}AT = \begin{bmatrix} \lambda_0 & 0 \\ 0 & \lambda_1 \end{bmatrix} \qquad (13)$$

where λ_0 and λ_1 are the two roots of the secular equation. The partition function can now be written in terms of A as

$$Q = [1,\Phi]AA \cdots A\ 1,1 \qquad (14)$$

Since TT^{-1} is a unit matrix, the factor can be inserted in front of and behind every matrix A in the product to give

$$Q(\varphi,\Phi) = [1,\Phi]\ [TT^{-1}\ ATT^{-1}]^{N-1}\ 1,1. \qquad (15)$$

Consider a gas-diamond system as having equal probability for bonding and nonbonding states ($\Phi = 1$). The matrix A then becomes

$$A = \begin{bmatrix} 1 & \varphi \\ \varphi & 1 \end{bmatrix}. \qquad (16)$$

A solution of this symmetrical matrix (T and T^{-1} are transposes of each other) gives for n_d

$$\langle n_d \rangle = \frac{\varphi}{1+\varphi}. \qquad (17)$$

A more detailed solution to some aspects of this theory can be obtained from Fowler and Guggenheim (1939), and from Margenau and Murphy (1956). This result shows that if the energy difference is negative (gas-gas RR more stable than CR) then φ (Eq. 6) varies from ∞ to 1 as the temperature (t) goes from 0 to ∞. The fractional number of bonding pairs varies from one ($t = 0$, $\varphi = \infty$) to ½ in the random state ($t = \infty$, $\varphi = 1$).

Thus, according to this analysis, diamond growth by an assumed gas-solid reaction can occur over a broad range of temperature. This type of growth would give a wide range of composition for occluded gas. The range and similarity in the composition of gas observed from African and from Arkansas diamonds (this study) are consistent with growth by a gas-solid reaction mechanism.

Acknowledgments

The authors would like to express their appreciation to Dr. Paul DeSautels of the Smithsonian Institution for providing three Arkansas diamonds, and to Mr. Danny Rankin, former Superintendent; Mr. Jim Cannon, current Superintendent; Mrs. Sue McCarty, Facility Manager; Mr. Grady McCarty, Maintenance Supervisor; and Mr. Robert Cross, all of the Crater of Diamonds State Park, Murfreesboro, Arkansas, for assistance with field work and in locating what we believe are authentic Arkansas diamonds. This work was supported by the National Science Foundation under Grant GA-33557.

References

DERYAGIN, B. V., L. L. BAILOV, V. M. ZUBKOV, A. A. KOCHERGINA, AND D. V. FEDOSEV (1969) Filamentary diamond crystals. *Sov. Phys. Crystallogr.* (Eng. transl.) **14,** 449–450.

EVERSOLE, W. G. (1962) Diamond synthesis. *U. S. Patents,* Nos. 3,030,187 and 3,030,188.

FOWLER, R. H., AND E. A. GUGGENHEIM (1939) *Statistical Thermodynamics.* Cambridge.

GIARDINI, A. A., V. J. HURST, C. E. MELTON, AND JOHN C. STORMER, JR. (1974) Biotite as a primary inclusion in diamond: Its nature and significance. *Am. Mineral.* **59,** 783–789.

HARRIS, J. W. (1972) Black material on mineral inclusions and internal fracture planes in diamond. *Contrib. Mineral. Petrol.* **35,** 22–33.

KAISER, W., AND W. L. BOND (1959) Nitrogen as a major impurity in common type I diamond. *Phys. Rev.* **115,** 857.

MARGENAU, H., AND G. M. MURPHY (1956) *The Mathematics of Physics and Chemistry,* 2nd. ed. Van Nostrand, Princeton, New Jersey, p. 305–307.

MELTON, C. E., C. A. SALOTTI, AND A. A. GIARDINI (1972) The observation of nitrogen, water, carbon dioxide, methane, and argon as impurities in natural diamonds. *Am. Mineral.* **57,** 1518–1523.

———, AND A. A. GIARDINI (1974) The composition and significance of gaseous inclusions in natural diamonds from Africa and Brazil. *Am. Mineral.* **59,** 775–782.

MEYER, H. O. A., AND F. R. BOYD (1972) Composition and origin of crystalline inclusions in natural diamonds. *Geochim. Cosmochim. Acta,* **36,** 1255–1273.

MITCHELL, R. H., AND J. H. CROCKET (1971) Diamond genesis—A synthesis of opposing views. *Mineral. Deposita* (Berlin), **6,** 392–403.

MITCHELL, R. S., AND A. A. GIARDINI (1953) Oriented inclusions of olivine in diamond. *Am. Mineral.* **38,** 136–138.

WEAST, R. C. (1971–72) Editor, *Handbook of Chemistry and Physics,* 52nd ed., The Chemical Rubber Co., Cleveland, Ohio, p. D-61.

WILLIAMS, A. F. (1932) *The Genesis of Diamonds,* Vol. 2. Ernest Benn Limited, London, p. 354.

Manuscript received, September 3, 1974; accepted for publication, December 18, 1974.