

## The nature and significance of occluded fluids in three Indian diamonds

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### Abstract

Fluids extracted from two Type I and one Type II diamonds from the Panna mine of India have been analyzed by mass spectrometry. Two extraction methods were used. In the first, each crystal was crushed at 200°C in the high vacuum inlet of a high-sensitivity mass spectrometer. In the second, gases were released by graphitizing selected crushed fragments with a rhenium heater operated at about 3000°C under high vacuum. Gas compositions varied between the three crystals and the two methods, but they are qualitatively consistent. The compositions are also qualitatively consistent with those reported earlier for diamonds from other global locations. The range in volume percent for major constituents released by crushing are H<sub>2</sub> (58.5–65.3), H<sub>2</sub>O (10.8–26), CO (tr–2.7), CO<sub>2</sub> (9.9–18.3), CH<sub>4</sub> (5.4–10), N<sub>2</sub> (tr–1.2), and by graphitization, H<sub>2</sub> (41.1–45.3), H<sub>2</sub>O (20.9–28.5), CO (5.5–6), CO<sub>2</sub> (12.1–16.4), CH<sub>4</sub> (4.4–12.7), N<sub>2</sub> (2.7–3.7). Average H, O, C, and N atomic percents from crushing and graphitization are, respectively, 73.6, 17.4, 8.4, 0.6; and 64.5, 17.5, 16.0, and 2.0. Hydrogen was the most abundant compound found by both methods of extraction, and it was more abundant in the Type II diamond than in the Type I diamonds. A positive qualitative correlation was found between N<sub>2</sub> and CO contents and anomalous birefringence. Variations in entrapped fluid composition with diamond crystal form and source locations are discussed in terms of diamond crystallization depth in the upper mantle, the redox state, and the age of diamond crystallization. The H<sub>2</sub>:H<sub>2</sub>O ratio found in the occluded fluid of Indian diamonds can be interpreted as supporting a molten iron–silicate equilibrium in the mantle at the time of the Earth's core formation.

### Introduction

The general nature of the Earth's crust is well documented because it can be studied directly. In contrast, most of our information about the mantle has been derived indirectly from astronomical and geophysical calculations, meteorite compositions, and laboratory studies on peridotitic material. Data from mantle samples are of considerable value because they relate directly to internal geologic processes.

One of the few direct channels from the upper mantle appears to be kimberlite pipes. Kimberlite is not a pristine rock; however, diamonds brought up by kimberlite are quite inert, impermeable, strong, reasonably consistent world-wide, and often contain

inclusions of at least some of the mantle constituents that were present when and where the diamond crystallized. Diamond is perhaps the ideal standard global container for direct sampling of the mantle.

Numerous publications exist on solid inclusions in diamond (*e.g.*, Mitchell and Giardini, 1977); over two dozen minerals have been identified. Knowledge about the mantle's solid phases is important, but so is knowledge of its fluid constituents. Parameters such as H<sub>2</sub>:H<sub>2</sub>O provide important information on redox conditions and melting temperatures.

Data on fluids occluded in diamonds from Africa, South and North America have been previously reported (Melton and Giardini, 1974, 1975); here coverage is extended to India. In addition, comparative data, obtained by two different fluid extraction meth-

ods on the same diamond, are given. The methods have been used separately in the past (Melton and Giardini, 1974, 1976), but questions existed as to the reliability of each. This study shows that data sets from the two methods are reasonably consistent, and are not drastically different from compositional variations found earlier from multiple crushings of a single diamond (Melton and Giardini, 1974).

### The diamond samples

Three representative diamonds were selected from about fifty industrial-quality crystals from the Panna mine, India. The smallest diamond, 0.33 carat, Type II (Berman, 1965), light pinkish-tan, had a smoothly rounded, slightly tabular shape. It contained six small tabular surface cavities, each aligned approximately perpendicular to the surface. At a magnification about 10 $\times$ , two small black inclusions were visible within the diamond. Strong anomalous birefringence was present throughout the crystal in the following patterns over different regions: undulating, interlocking irregular circles, parallel segmented rectangles, and tartan cross hatching; the latter is illustrated in Figure 1.

The second diamond, 0.51 carat, Type I (Berman, 1965), colorless to light tan, was of near-spherical shape. No solid inclusions were detected to 60 $\times$ . It exhibited strong anomalous birefringence only in its central region. The pattern of birefringence consisted of undulating, interlocking irregular circles superimposed on parallel lineations.

The third specimen, 0.875 carat, was smoothly rounded but near-tabular in shape. It was Type I, and ranged from colorless, to light yellow, to light orange. Three small, tabular, perpendicularly-oriented surface cavities were present on one side. A nearly square, planar, homogeneously birefringent region existed in the center, parallel to the tabular plane of the crystal. No solid included matter was detected.

Prior to insertion of the respective diamonds into the high vacuum fluid extraction chamber, they were cleaned as follows: (1) 10 minutes in concentrated HF + 10% HNO<sub>3</sub> in an ultrasonic bath followed by 24 hours in the acid; (2) ultrasonic washings in water; (3) one hour of boiling in aqua regia; (4) repeated ultrasonic washings in deionized distilled water. The crystals were then dried at 105°C in a vacuum furnace ( $P \sim 10^{-2}$  torr).

### Experimental

The apparatus, experimental techniques, and calibration procedures used in this work have been de-

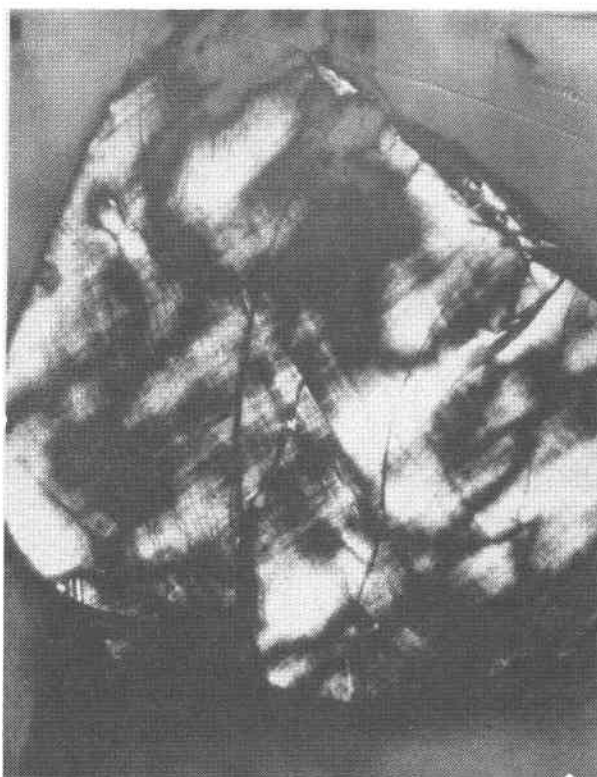


Fig. 1. Tartan pattern of anomalous birefringence present in one region of the 0.33 carat, Type II, Panna diamond seen in a crushed fragment using polarized light. The width of the field of view is about 0.8 mm. No significant change was noted in the pattern and volume of anomalous birefringence before and after crushing.

scribed (Melton and Giardini (1974, 1975, 1976, 1980). Briefly, the mass spectrometer is a single-focusing 90° instrument with a 15.24 cm radius of curvature operated in the pressure range of 10<sup>-10</sup> torr. The detector is a 14 stage electron multiplier placed immediately after the final defining slit.

For the first series of experiments, the three diamonds were individually crushed in the high-vacuum inlet system of the instrument. In each case, the crushing chamber was maintained at 200°C and 10<sup>-8</sup> torr approximately 12 hours prior to crushing. Each diamond crushed easily; their crushing strengths were comparable to diamonds of cube form from other locations.

For the graphitization experiments, the larger crushed fragments were used. Each sample was graphitized by wrapping it in an electrically-heated rhenium filament positioned in the center of a large Nonex glass vacuum chamber. The latter was attached to the inlet system of the spectrometer. Before graphitization, the diamond was maintained in the filament furnace at a temperature of 800°C and a

vacuum of  $10^{-8}$  torr for several hours to remove possible surface contaminants.

Background values for the apparatus were established with blank tests. Filament temperatures to 2500–3000°C were determined by power input and optical pyrometry. The pyrometer was calibrated by melting Au, Pt, and Re filaments in the Nonex chamber under high vacuum.

Significant amounts of fluid were released by the apparatus surfaces in the background calibration tests. Repeated, timed tests at a number of temperatures, to the selected graphitization temperature of about 3000°C, showed that the composition and quantity of fluid released was quite constant at a given temperature and time. Average values obtained from the 3000°C blank tests were subtracted from the values obtained when diamond was present. Compositional differences between "identical" experiments with diamond present and absent, respectively, were quite consistent.

In view of possible serious complications caused by chemical reactions within the fluid released by the graphitizing diamond, between the respective fluids released by the diamond and the apparatus, and between the released fluids and heated surfaces in the apparatus, the obtained compositional data on fluid released from diamond by graphitization in a rhenium filament at about 3000°C are presented as being at best only semiquantitative relative to the data obtained by crushing at 200°C.

### Results and discussion

When diamonds are crushed in a high vacuum at 200°C, the fluid released has little opportunity to either react or absorb on the surfaces that are present. The composition of the gas, when monitored by a mass spectrometer, is essentially invariant over the time needed for analysis. Results from the crushing experiments with Panna diamonds are given in Table 1. Hydrogen accounts for almost 60% of the gas released from each of the three crystals. Although Type II diamonds are generally assumed to be rich in nitrogen (Kaiser and Bond, 1959), the abundance of released  $N_2$  from the Type II crystal was not significantly higher than that from the Type I crystals. Water was abundant in all of the crystals, but the amount of argon was very small. The Type II diamond did release a trace of  $O_2$ . This has been observed before only with diamonds of cubic form (Melton and Giardini, 1974).

Following the crushing experiments, approximately 0.015 gram samples of the larger fragments

Table 1. Composition and volume of gases released from Panna diamonds crushed at 200°C under a vacuum of  $10^{-8}$  torr

Diamond wt. (carat)	0.33	0.51	0.875
Type	II	I	I
Gas	Volume percent		
H <sub>2</sub>	65.3	59.9	58.5
CH <sub>4</sub>	10.0	5.4	5.5
H <sub>2</sub> O	10.8	14.0	26.0
CO	2.7	1.5	tr
Ar	tr	tr	tr
N <sub>2</sub>	1.2	0.9	tr
O <sub>2</sub>	0.1	—	—
CO <sub>2</sub>	9.9	18.3	10.0
STP gas vol. ( $10^{-5}$ cc)	9.6	29.0	18.5
Average atomic percent for the three diamonds			
H = 73.6			
O = 17.4			
C = 8.4			
N = 0.6			

from each of the diamonds were recleaned, respectively wrapped in a high purity rhenium filament, and heated at about 3000°C for 100 seconds to release entrapped gas by graphitizing the diamond. Results from these experiments are given in Table 2. Because of the hot filament, some reaction of the released gas is to be expected. Comparison of the atomic percents from crushing and graphitization shows H<sub>2</sub> is lower and C higher in the graphitization experiments. Although the general composition of the fluid released by the two methods is quite similar, the crushing data are apparently more accurate.

Two graphitization experiments were conducted on crushed fragments from the 0.51 carat Type I diamond. In one, fragments with strong anomalous birefringence were graphitized, and in the other, non-birefringent fragments. Sample weights (~0.015 g) were within 10% of each other. The only significant

Table 2. Composition of gas released by graphitizing 0.015 g samples of Panna diamond fragments at 3000°C and  $10^{-8}$  torr

Original diamond wt. (ct.)	0.33	0.51	0.875
Type	II	I	I
Gas	Volume percent		
H <sub>2</sub>	45.3	41.1	41.8
CH <sub>4</sub>	4.4	11.7	12.7
H <sub>2</sub> O	28.5	23.0	20.9
CO	6.0	5.6	5.5
Ar	tr	tr	tr
N <sub>2</sub>	3.7	2.9	2.7
CO <sub>2</sub>	12.1	15.7	16.4
Average atomic percents for the three diamonds			
H = 64.5			
O = 17.5			
C = 16.0			
N = 2.0			

difference observed in the released fluids was higher  $N_2$  and CO contents from the birefringent diamond.

A comparison of average results from crushed Indian, African, and North American diamonds, respectively, is given in Table 3. All diamonds have similar occluded fluids. Significant compositional differences do exist, however, both for a given source location (e.g., Table 1), and for different global locations (Table 3), the latter being generally greater.

One proposed explanation for differences in occluded fluid compositions is that they reflect diamond crystallization over a broad range of temperature related to mantle depth (Melton and Giardini, 1975). This infers a mantle composition that was globally-homogeneous and temperature-depth dependent during the time of diamond formation. This concept has both theoretical (Melton and Giardini, 1975), and experimental support. The high oxygen content of the occluded fluid in diamonds of cubic form, relative to other forms (Table 3), is consistent with the diamond synthesis work of Giardini and Tydings (1962). Their results strongly suggest that natural diamond cubes crystallized at shallow mantle depth whereas those of other habits crystallized deeper.

Similar differences and similarities exist in the na-

Table 4.  $H_2:H_2O$  and  $CO:CO_2$  STP volume percent ratios observed thus far from individual African, American, Brazilian, and Indian diamonds at 200°C and a  $10^{-8}$  torr vacuum

Diamond samples*	$H_2:H_2O$	Average	$CO:CO_2$	Average
Brazilian cube	0.02	0.03	0	0.12
African cube	0.02		0.46	
" "	0.03		0	
" "	0.04		0	
Arkansas #3	0.07	0.62	0.17	0.26
" #5	0.31		0.10	
" #6	0.41		0.19	
" #2	0.52		0.40	
" #1	0.69		0.32	
" #7	0.83		0.35	
" #4	1.52		0.26	
African hexoctahedron	0.89	2.01	0.94	0.83
" "	2.51		1.55	
African fragment	2.62		0	
Indian 0.875 ct.	2.25	4.19	0.01	0.12
" 0.51 ct.	4.28		0.08	
" 0.33 ct.	6.05		0.27	

\* Data taken from Melton and Giardini (1974, 1975), and this report. One sample composed of 39 small, flattened octahedra with inclusions, from consolidated African production, is not tabulated. Its  $H_2:H_2O$  and  $CO:CO_2$  values are 0.19 and 22.9, respectively.

ture of solids occluded in natural diamonds, and a similar explanation has been proposed (Mitchell and Giardini, 1977). Quartz as a diamond inclusion sets the minimum depth of diamond formation at less than 100 km. The presence of alpha olivine and absence of beta olivine sets the apparent maximum depth at about 400 km.

Occluded fluid data such as  $H_2:H_2O$  and  $CO:CO_2$  provide a quantitative measure of mantle redox conditions at the depth and time of diamond formation. A summary of the above ratios that have been obtained thus far from crushing single diamond crystals at 200°C and  $10^{-8}$  torr is given in Table 4. As the data show, one to two orders of magnitude difference exists in  $H_2:H_2O$  between diamonds of cube form relative to other forms; one Arkansas diamond that contained a high water content is an exception.  $CO:CO_2$  ratios are less consistent; the low ratio for Indian diamonds may reflect, in part, a CO shift to methane.

According to the interpretation discussed above, and the criterion set forth by Ringwood (1979), the high  $H_2:H_2O$  ratio given by Indian diamonds is consistent with crystallization in a mantle environment that had experienced molten iron-silicate equilibrium. If that is correct, these occluded fluid data support the Earth genesis model that calls for homogeneous accretion, subsequent fusion of iron, overturning, and core formation.

Some of the compositional differences in occluded matter could reflect regional inhomogeneities in

Table 3. Average volume percent and atomic percent compositions of gases released from natural diamonds crushed at 200°C under a  $10^{-8}$  torr vacuum

Diamond* source	Arkansas	Africa	African cubes	India
Average volume percent				
$H_2$	19.4	37.4	1.8	61.3
$CH_4$	3.7	6.5	4.1	7.0
$H_2O$	39.6	16.5	67.0	16.9
$C_2H_4$	-	1.1	0.1	-
$N_2$	15.9	0.3	2.1	0.7
CO	3.8	21.0	3.2	1.4
$CH_3OH$	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	12.7
Average atomic percent				
H	51.2 (56.1)**	56.3	47.5	73.6
O	27.8 (30.4)	20.9	39.9	17.4
C	9.2 (10.1)	15.4	11.2	8.4
N	11.7 ( 3.3)	7.2	1.3	0.6
Ar	0.1 ( 0.1)	0.2	0.1	tr

\*Except for Zaire cubes, the diamonds were of octahedral, hexoctahedral, or rounded indeterminate habit.

\*\*Recalculated, omitting one diamond of high (87%) nitrogen content.

mantle composition at diamond-forming depths. If so, such differences could be time dependent. Global emplacement ages for diamond-bearing kimberlites span more than 2000 m.y. (Dawson, 1967). Melton and Giardini (1980) obtained a crystallization age of about 3000 m.y. for an Arkansas, U.S.A., diamond, showing it to be far older than the well-documented Arkansas kimberlite emplacement age of 100 m.y. (Gogineni *et al.*, 1978). Welke *et al.* (1974) reported an average crystallization age of 1500 m.y. for a group of African diamonds from the Premier mine. This age falls within the 1100–1900 m.y. range that has been assigned to this kimberlite emplacement. Uncertainties exist in the accuracy of all such age determinations because of experimental difficulties. All are, however, Precambrian. The Panna mine, first described by Hamilton (1819), contains diamonds in Precambrian conglomerates; thus the age of Panna diamonds is in approximate agreement with those determined for African and North American diamonds.

Further work on the age of crystallization of well-characterized single diamond crystals from kimberlites is needed for further consideration of a time dependence of mantle composition. The present data seem to indicate that the fluid associated with the upper mantle was reasonably consistent world-wide over the range of time and depth that diamonds crystallized. The data further suggest that those diamonds that contain a high relative concentration of H<sub>2</sub> in their occluded fluid crystallized in a deeper, more highly reduced environment.

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