

THE OBSERVATION OF NITROGEN, WATER, CARBON  
DIOXIDE, METHANE AND ARGON AS IMPURITIES  
IN NATURAL DIAMONDS

CHARLES E. MELTON, *Department of Chemistry*

AND

C. A. SALOTTI<sup>1</sup> AND A. A. GIARDINI, *Department of Geology,  
University of Georgia, Athens, Georgia 30601*

ABSTRACT

A unique method of destructive analysis has been developed for the study of gaseous impurities in diamonds and other minerals. Crystals are crushed at room temperature in a high vacuum sample inlet system of a research mass spectrometer. This is done by means of a suitably designed crusher which is incorporated in the inlet system of the spectrometer. Crusher elements are constructed from tungsten carbide. The spectrometer used for the analysis has a detection sensitivity of about  $10^{-20}$  cc at STP. In a preliminary study of diamonds, the gases  $N_2$ ,  $H_2O$ ,  $CO_2$ ,  $CH_4$ , and Ar have been identified. The most abundant is  $N_2$ .

INTRODUCTION

In order to establish a basis for understanding the origin of natural diamonds, a great deal must be known about both conventional chemical properties of carbon and the environment in which diamonds formed. Some information on the environment can be obtained by analyzing impurities trapped within crystals.

The fact that diamonds typically have numerous impurities has been known for years (Chesley, 1942; Mitchell and Giardini, 1953; Raal, 1957; Meyer and Boyd, 1967-68). Kaiser and Bond (1959) found evidence for the first time that nitrogen was a major impurity in Type I diamonds, with concentrations as high as  $4 \times 10^{20}$  atoms per  $cm^3$ . This was determined by mass spectrometric analyses of gases obtained from graphitization experiments at  $2000^\circ C$ . On the basis of precision lattice and density measurements of the crystals used, they concluded that the nitrogen was contained substitutionally for carbon in the diamond lattice. Other workers have used a variety of physical methods to generally verify the substitutional concept of Kaiser and Bond (1959). It is generally accepted today that better than 99 percent of the substitutional nitrogen impurity in Type I diamonds is dispersed in discrete planar arrays lying in  $\{100\}$  planes. The paramagnetic spin resonance studies of Smith, Sorokin, Gelles, and Lasher (1959) indicate

<sup>1</sup> Present address. Department of Geology, University of Wisconsin, Milwaukee, Wisconsin 53200.

that a small amount of nitrogen (up to  $10^{17}$  atoms per  $\text{cm}^3$ ) exists in isolated substitutional sites within the crystal structure of either Type I or II diamonds.

There are a few reports in the literature of possible gaseous inclusions in diamond. Bauer and Spencer (1904), and Eppler (1961) described liquid inclusions that are interpreted as  $\text{CO}_2$ . Chrenko, McDonald, and Darrow (1967), through infrared spectroscopy, investigated the impure opaque diamond coating that sometimes surrounds a clear diamond core in Congo stones, and found evidence from some type of carbonate and water of hydration as impurity phases, with some possibility of a nitrate also being present. Sharp absorption bands observed at 3,107 and  $1,405\text{ cm}^{-1}$  are interpreted as carbon-hydrogen vibrations in diamond. In a related sense, Roedder (1965) has found primary inclusions of highly compressed and generally liquified  $\text{CO}_2$  in phenocrysts of olivine taken from DuToitspan, Wesselton, and DeBeers kimberlites of South Africa.

We report here on the positive identification of gaseous nitrogen, water, carbon dioxide, methane, and argon released on crushing under high vacuum of externally clean, well-crystallized diamond crystals.

#### EXPERIMENTAL

Mass spectrometry is one of the most powerful tools for gas analysis. It offers the possibility of identifying, in most cases unambiguously, the composition of the gas phase quantitatively and of detecting gaseous components at very low relative concentrations. The research mass spectrometer is about  $10^6$  times more sensitive than any other spectroscopic method (Melton, 1970). Because of these considerations the mass spectrometer is the best possible tool for investigation of occluded gases in crystals.

The instrument used in this study is a 15.24 cm radius  $90^\circ$  sector type of magnetic scanning instrument designed and constructed at the University of Georgia. The analyzer tube is constructed of inconel and all other parts are of stainless steel. Oil diffusion pumps are used to evacuate the system. Base pressure is better than  $2 \times 10^{-8}$  torr with liquid nitrogen trapping. The instrument, experimental procedures and necessary calibration have been described elsewhere (Melton, 1970 and 1971). Only a brief recount will be given here.

Perhaps the most essential part of the instrument is the ion source. It is in this region that neutral gas molecules are converted into an ion beam. Thus, high coefficients of conversion and focusing are essential for high transmission and sensitivity. To ensure high transmission, the exit slits for the present source are unusually large, measuring  $0.635 \times 1.27$  cm. With this ion source we measured an efficiency (ions produced vs. ions collected) of 88.3 percent. Large exit slits significantly decrease the resolution of the apparatus, but analysis of the occluded gases did not require high resolution. Our resolution is about 130 amu.

The second critical component of a research instrument is the ion detection circuit. Ions were detected by means of a 14 stage electron multiplier attached to a vibrating capacitor amplifier. The output from the amplifier is used to activate

a strip chart recorder. The circuit is calibrated for linearity by measuring the isotopic abundance of neon on three different scales and comparing the experimental results with the known value. Our linearity is better than 0.25 percent over all ranges.

A schematic diagram of our crystal crusher is shown in Figure 1. Before crushing a diamond, the crusher was baked out under high vacuum at 300°C for at least 24 hours. This removed adsorbed species from internal surfaces. After preliminary bake-out, the crusher was quickly dismantled to place the diamond charge in the crushing chamber. The crusher was then resealed and evacuation was continued for about an additional 24 hours. Diamond crystals were crushed by tapping the impacting head with a hammer.

A possible source of error in the investigation is the contamination of gases released from the diamond by gases released from the crusher elements. To evaluate this, a duplicate experiment was run without diamond and only tungsten carbide in the crushing chamber. The principal gas released from the carbide was hydrogen (about 99 percent), with the remaining 1 percent being CO and N<sub>2</sub>. Other tests showed that continuous baking of the crusher under vacuum for 10 hours at 250°C essentially removed this source of contamination.

Another possible source of error is that of selective adsorption of the released gases on the surfaces of the spectrometer. This source of error cannot be eliminated, but the amount of selective adsorption can be determined by calibration. This was not done in the present experiments.

Our main interest in this preliminary work was to test our system and to explore the possible existence of occluded gas within diamond. Most of our limited supply of diamonds contained crystalline inclusions. We therefore selected for crushing only crystals that possessed smooth and unbroken external faces, and were structurally sound except for completely enclosed inclusions.

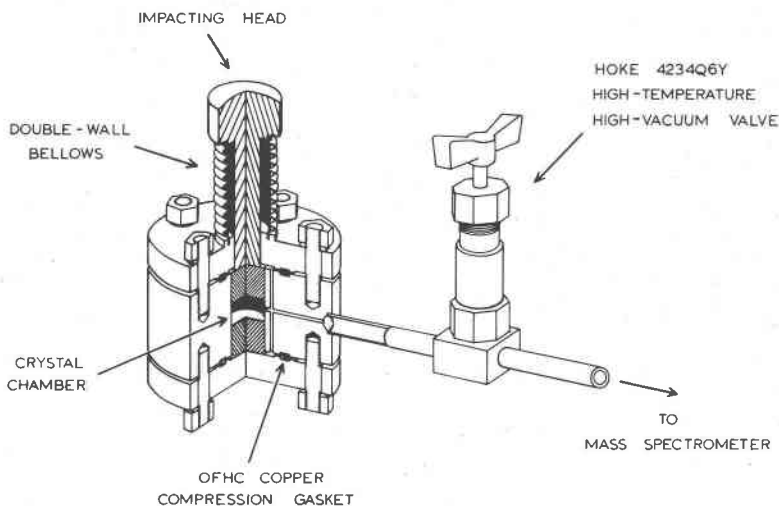


Fig. 1. Crystal crusher. All components made of 316 stainless steel except copper vacuum gaskets, and hydrogen-sintered carbide pistons above and below crystal chamber.

TABLE 1. PERCENT, BY VOLUME ( $\sim 10^{-8}$  CC) OF GASES TRAPPED IN A 1.13 CARAT (0.226 GRAM) DIAMOND

Gas	Percent
Water	17.0
Methane	0.5
Nitrogen	77.0
Argon	0.3
Carbon dioxide	5.0

Crushings were made on two samples. The first was a well-crystallized 1.13 carat slightly distorted octahedron that contained a myriad of minute colorless inclusions in the central region. The second consisted of about 200 small flattened octahedra, each about 1 mm on edge in triangular outline. Some were twinned. All contained one to two inclusions that ranged from colorless to reddish brown to black in color. The weight of this sample was 1.2 carats, but not all crystals became crushed during impaction.

All of the diamonds were free of finely laminar or mosaic surface texture, showed a distinct irregular anisotropy between crossed polarizers, and were free of visually noticeable color. On the basis of surface-texture and optical-strain information given by Robertson, Fox, and Martin (1934), we concluded that all were probably Type I. We did not run ultraviolet or infrared tests. The origin of these diamonds is not known but we think they are probably South African.

### RESULTS

In spite of the difficulties arising from the fact that small quantities of gases are hard to analyze, we have succeeded in obtaining some preliminary results for gases contained within diamond. The results are shown in Tables 1 and 2. The amount of gas released was not sufficient to distinguish quantitatively between CO and N<sub>2</sub>. This means that the N<sub>2</sub> abundance may be in error due to a possible 5 to 10 percent contribution from CO. The amount of possible CO was estimated from

TABLE 2. PERCENT, BY VOLUME ( $\sim 10^{-4}$  CC) OF GASES TRAPPED IN A GROUP OF SMALL DIAMONDS HAVING A TOTAL WEIGHT OF APPROXIMATELY 1.2 CARAT

Gas	Percent
Water	14.0
Methane	0.6
Nitrogen	80.0
Argon	0.3
Carbon dioxide	5.0

the known  $C^+/CO^+$  ratio from CO. Although  $CH_4^+$  has the same mass as atomic oxygen, atomic oxygen is much less abundant than  $O_2^+$  from  $O_2$ . Thus the known  $O^+/O_2^+$  ratio from  $O_2$  could be used to determine the contribution of  $O^+$  to mass 16.

No attempt was made in this uncalibrated preliminary work to obtain an isotopic abundance for the gases. We plan to attempt this in future quantitative studies.

#### DISCUSSION

We think the significance of the present data is twofold. First, five gaseous impurities have been released from within diamond at standard temperature, and quantitatively identified. Second, these gaseous impurities constitute an uncontaminated sample of gaseous components present during the growth of natural diamond. We do not know at this time whether these gases originate from within the diamond itself, or the inclusions that were present in our samples, their interfaces, or perhaps from all of these. We intend to look into this matter in the future.

The relative abundance of nitrogen in our analyses, when compared to the results of Kaiser and Bond (1959), does suggest that the nitrogen probably comes from the diamond. If this assumption is correct, then the density studies of Kaiser and Bond (1959), the electron microscope work of Evans and Phaal (1962) demonstrating the existence of platelet defects on {100} planes, and the magnetic resonance analyses of Smith *et al.* (1959) would further suggest that the planar arrays of substitutional nitrogen are not stable under the stresses of crushing, or outside of the diamond crystal structure.

Roedder (1965) has revealed the ubiquitous presence of essentially pure, primary  $CO_2$  in olivines (also, its presence in pyroxenes, garnet, and possibly spinel), and olivine is a common crystalline inclusion in diamond (Mitchell and Giardini, 1953; Meyer and Boyd, 1967). The  $CO_2$  that we find may have come from the inclusions in our samples.

We were somewhat surprised at the consistency of the relative abundances of the several gases in our two samples. However, Roedder (1965) also observes a consistency of essentially pure  $CO_2$  in olivines from a variety of different rock types from a multitude of world-wide localities.

Whether or not the gases we find represent a sample of mantle gas depends on whose opinion one wishes to accept relative to where in the earth natural diamonds were created. Kennedy and Nordlie (1968) conclude that diamonds could not have formed at a depth less than about 200 km. If their evaluation is correct, our gas composition

should be indicative of that existing in the mantle where diamond growth occurred. Lonsdale and Milledge (1965), however, feel that diamonds could not have formed at depths in excess of 30 km, and may even have formed *in situ* after injection of kimberlite masses. This range of possibilities had been considered by Giardini and Tydings (1962). The finding of Roedder (1965) that the maximum depth at which unbroken CO<sub>2</sub> inclusions in olivines could be filled is 16 km may have a bearing on the depth of diamond formation, but it is not yet known whether his observations are applicable to olivines within diamond. Additional work is needed to resolve the question of the genesis of natural diamonds.

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