Chemical Data on a Colorless Arkansas Diamond and its Black Amorphous C-Fe-Ni-S Inclusion

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Abstract

A 27-element emission spectrographic analysis of "inclusion-free" fragments of an 0.885 carat type II colorless Arkansas diamond, previously crushed for a mass spectrographic analysis of occluded gas, showed detectable traces of Na, Ca, Al and Si. XRD and chemical analyses of a thin (<2μm), lustrous, black, opaque, totally-enclosed inclusion lying on (111) of the same diamond showed it to be amorphous and, in decreasing order of abundance, heterogeneously composed mainly of C, Fe, S, and Ni. It is speculated that the black material represents epigenetic carbonization of diamond on (111) by included gas and decomposition products of iron sulfide and iron nickel sulfide inclusions.

Introduction

Previous analyses of trace impurities in African diamonds have been given by Chesley (1942), Raal (1957), Bunting and Van Valkenburg (1958), and others. The literature shows no such data for Arkansas, U. S. A., diamond. For geochemical comparison, a 27 element semi-quantitative emission spectrographic analysis has been made on 0.02 g of colorless and inclusion-free diamond (at a magnification of 90) obtained from a crushed 0.885 carat Arkansas specimen.

The specimen was colorless, type II, and in the form of a cleavage plate approximately 0.6 × 0.6 × 0.14 cm. It contained a centrally located and totally-enclosed single, thin (<2μm), near-rectangular (0.1 × 0.2 cm), lustrous, black, opaque inclusion lying parallel to (111). The diamond came from the Smithsonian Institution Roebling Collection. It has been crushed earlier by Melton and Giardini (1975) for analysis of occluded gas by mass spectrometry. The STP volume of the gas released at 200°C and 10^{-11} atm was 2.7 × 10^{-4} cc, and consisted of 76.9 vol H₂O, 8.2 N₂, 7.2 CO₂, 5.4 H₂S, 1.2 CO, 0.9 CH₄, 0.2 CH₃CH₂OH. Only a gentle impact was needed to crush the diamond. Essentially all of the black inclusion adhered to and was exposed on the cleavage surfaces of 7 diamond fragments.

Previous descriptions and analyses of black inclusions in African diamonds have been given by Sutton (1921), Sharpe (1966), Harris (1968, 1972), and Harris and Vance (1972). Identified minerals are pyrrhotite, pyrite, pentlandite, cohenite, magnetite, hematite, ilmenite, and graphite. The first data for black included matter in Arkansas diamond are reported here.

Trace Element Analysis

A 0.02 g sample of colorless and inclusion-free fragments of the diamond was selected at 90x under a binocular microscope equipped with polarizers. The fragments were digested at room temperature in concentrated HF and H₂SO₄, rinsed, boiled in aqua regia, repeatedly rinsed with deionized distilled water, briefly ignited at 800°C in a clean platinum crucible, mixed with 0.1 g of spectrographic-grade graphite, dried at 400°C, mixed in a clean plastic vial, transferred to preformed electrodes, and analyzed with a 21 foot Wadsworth-mount Jarrell-Ash spectrograph. Twenty-seven elements were sought. Detection limits are given in Table 1. Significant quantities of Na (70 ppm), Al (70 ppm), Ca (140 ppm), and Si (175 ppm) were detected. Accuracy is estimated at ±30 percent.
The presence of Fe and S at all sites, and absence of Ni at most sites, suggests a possible preexistence of two iron-sulfur compounds; probably pyrrhotite and pentlandite (Harris, 1972). If so, the low sulfur content could be due to (a) sulfur volatilization during the 200°C high-vacuum exposure when the diamond was crushed in the earlier gas analysis, and (b) electron-beam-induced volatilization (blistering).

The observed maximum of about 30 percent as the combined total for Fe, Ni and S, the opaque nature of the inclusion, and the graphite trace after 40 hours of X-ray exposure, suggested carbon as a fourth constituent. Subsequent to probe analysis, the inclusion (~10^-6 cc) was scraped from its diamond substrate with a clean stainless steel blade into a clean quartz tube. Binocular microscope examination at 90x showed no presence of admixed diamond. The tube was evacuated to 10^-10 atm, partially backfilled with pure O_2, heated to 700°C, and the resultant gas analyzed with a mass spectrometer (10^-13 atm background pressure). The combustion gas was mainly CO_2 (net CO_2: SO_2 ratio = 2500:1). Carbon is confirmed, therefore, as a principal constituent of the black inclusion.

Discussion

Chesley (1942) analyzed 33 diamonds from various sources by emission spectrometry and found Ca, Al, and Si to be persistent impurities. Raal (1957) performed similar analyses on 25 African diamonds and found Ca, Al, Si, Mg, Fe, and Cu as principal impurities. Bunting and Van Valkenburg (1958) analyzed 3 type I and 3 type II diamonds, and found Na, Ca, Si, and Cu as principal impurities in
the former and Na, Ca, Si, Mg, Fe, and Cu in the latter.

The diamonds referred to above were not screened for possible included matter, and some were colored. Nevertheless, with the possible exception of Mg, Fe, and Cu (see sensitivity limits, Table 1), the principal impurities in the Arkansas diamond are similar to those in diamonds from the above sources.

Harris (1968, 1972) and Harris and Vance (1972) have made detailed studies on black included matter in diamond. Their study of several hundred African diamonds identified black material as graphite, pyrrhotite and pentlandite, separately or together. Furthermore, Harris and Vance (1972) have shown experimentally that graphite often can be formed on mineral inclusions and internal fracture surfaces in diamonds by heating to a temperature of about 900°C. On the basis of the work described by Evans (1965) on nonequilibrium carbonization of diamond in CO₂, and Roedder (1965) on CO₂ in olivine, Harris and Vance (1972) interpreted graphite inclusions as being epigenetic to diamond, and as having formed at temperatures above 900°C after pressure release arising from volcanic breakthrough of the kimberlite.

The chemistry of the black material found in the present Arkansas diamond appears to be consistent in principle with the findings of Harris (1968) and Harris and Vance (1972). Their model for epigenetic carbonization appears consistent with that proposed by Green and Gueguen (1974) for kimberlite emplacement.

Melton and Giardini (1974, 1975) found that gas occluded in diamonds at 200°C is not principally CO₂, but usually a mixture mainly of H₂O, H₂, CO₂, N₂, CH₄, and CO. The H : O ratio has been found consistently to be about 2 : 1, and water often is the principal constituent. However, according to the equilibrium reaction,

$$2\text{H}_2\text{O} + \text{C} = \text{CO}_2 + 2\text{H}_2,$$

occluded gas in the diamond could transpose at elevated temperature primarily to CO₂ and H₂.

The reported occurrence of pyrrhotite, pentlandite, and graphite as black inclusions in diamond (Harris, 1968) invites speculation that the carbon and Fe, Ni, and S found in the Arkansas inclusion may be decomposition products from preexisting gas and syngenetic iron sulfide inclusions. If correct, the amorphous state may indicate an epigenetic reaction-temperature somewhat below the experimental temperatures employed by Harris and Vance (1972).

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References


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