American Mineralogist, Volume 62, pages 583–586, 1977

Mineral inclusions in an Arkansas diamond

M. GARY NEWTON, CHARLES E. MELTON

Department of Chemistry, University of Georgia
Athens, Georgia 30602

AND A. A. GIARDINI

Department of Geology, University of Georgia
Athens, Georgia 30602

Abstract

Six isolated and totally enclosed inclusions were recovered from an Arkansas diamond by burning it in air at 850°C. They are identified as (a) three euhedral crystals of chromian diopside, (b) a euhedral bicrystal of chromian diopside + orthopyroxene with minor unidentified included matter, (c) anhedral olivine (Fo_{92}) + a small amount of attached unidentified vitreous-like silicate rich in Si and Al with minor Fe, Ti, Zn and K, (d) finely polycrystalline periclase + minor magnetite. X-ray diffraction, chemical, and morphological data are given. The periclase may have existed in the diamond as magnesite. If so, the observed inclusions bear resemblance to equilibrium phases recently reported for silicate + carbonate reactions under mantle-like conditions. Interpretation of *P–T* equilibrium conditions for the diamond-inclusion system based on the silicate–carbonate reaction and two-pyroxene geothermometer suggests 5×10^4 kbars and 1300°C, but the olivine + vitreous-like phase inclusion may indicate a pressure well below 5×10^4 kbars.

Introduction

The questions of kimberlite and diamond genesis are important for both scientific and economic reasons. Considerable attention has been given in recent years to foreign matter trapped within diamond. Because diamond is relatively inert, such matter provides an historical record of kimberlite evolution during and after diamond formation.

To date, most studies have been on African, Siberian, and South American diamonds (Harris, 1968; Sobolev *et al.*, 1970, 1972; Meyer and Boyd, 1969, 1970, 1972; Meyer and Svisero, 1975; Fesq *et al.*, 1975; Prinz *et al.*, 1975). Only a few studies exist on North American diamonds (Melton and Giardini, 1975; Giardini and Melton, 1975a, b). To further extend knowledge on North American diamond and kimberlite, we report on included solids recovered from a diamond from the Prairie Creek kimberlite near Murfreesboro, Arkansas.

Experimental method

The diamond was cleaned in the following ways: (1) 10 minutes in concentrated HF + 10 percent HNO_3 in an ultrasonic bath followed by a 24-hour soak in the acid, (2) ultrasonic washing in water followed by one hour of boiling in aqua regia, (3) repeated ultrasonic washings in deionized distilled water. The diamond was dried at 105°C, examined with a binocular microscope to 90×, and found free of surface cleavage cracks.

Inclusions were recovered by burning the diamond in air at about 850°C for 48 hours. It was contained in a clean platinum boat within a 2.5 cm diameter × 91 cm long quartz-glass tube capped at both ends with 400-mesh nylon screens. Heat was supplied by a Lindberg furnace with its controller set at 850°C.

After burning, residual included matter was recovered from the bottom of the platinum boat with sharply-pointed wood sticks moistened with distilled water. Inclusions were examined by optical microscopy, scanning electron microscopy, X-ray dispersive qualitative chemical analyses relative to reference standards, single-crystal X-ray diffraction analysis (Enraf-Nonius CAD-4 diffractometer, Cu*Kα* radiation), X-ray powder diffraction analysis (11.46 cm dia camera, Cu*Kα* radiation), and for one inclusion, a dipyroxene crystal, electron-probe chemical analysis.

Analytical study

The diamond showed no crystal form. It was rounded with a high surface gloss, oblong in shape, transparent, tan in color, and weighed 0.361 carats. Several totally enclosed and isolated crystal inclusions were observed. Short cleavages in the diamond extended from three of the inclusions, but all terminated well within the diamond. Recovered crystal inclusions ranged from about 50 to 150 μm in maximum dimensions.

Three inclusions were transparent, light green, euhedral crystals. Each showed a high surface gloss, rounding at some corners, and irregular morphologies. An example is shown in Figure 1. These inclusions were identified as diopside by single-crystal X-ray diffraction. Fifteen reflections were located and accurately centered by use of the diffractometer program SEARCH and indexed by program INDEX (Enraf-Nonius, CAD-4 System, Delft, Holland, 1972). Unit-cell parameters obtained for the monoclinic system are a = 9.685 A, b = 8.873 A, c = 5.258 A and β = 107.01°. These parameters are in agreement with published diopside cell dimensions. As further confirmation of the diopside structure, a full set of diffraction intensities was measured and the space group determined as $C2/c$ or Cc from systematic absences (hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$). Previous diopside structures have been reported to be space group $C2/c$.

The chemistry of the diopside inclusions was evaluated by S.E.M./X-ray dispersive analyses relative to diopside standards. All yielded consistent compositions of (in decreasing order of abundance) Si, Mg, Ca, Fe, Na, Al, Cr and Ti. They are chromian diopside.

Another inclusion showed separate green and yellow regions, and was initially interpreted as a twin (Fig. 2). Micron-size inclusions were observed in the yellow region adjacent to the sharp optical boundary of the bicrystal. The larger were transparent and square in outline. The smaller were reddish-brown and of indeterminate form.

Single-crystal X-ray analysis of the bicrystal produced several sets of 15 reflections from various regions of space. Upon indexing the various sets, it was found that the b and c dimensions were consistent among sets and practically identical to the diopside structure. The cell dimension a, however, was much longer than the diopside dimension and varied widely among data sets ($a = \sim 32$ to ~ 60A). Cell angles involving a were also variable but γ was consistently 90°. It was concluded that the green portion of the bicrystal was diopside, and that the variations in the cell dimensions were due to reflections arising from the yellow section. The data suggest that the b,c orientations are nearly aligned in the two sections of the bicrystal, thus accounting for the variation in the a dimension.

Subsequent to diffraction analysis, the bicrystal was mounted in epoxy glue, polished, and given an electron-probe chemical analysis. The green region was confirmed as a low-calcium chromian diopside. The yellow region showed a composition consistent with orthopyroxene (En_{87}). The minute inclusions within the orthopyroxene were not exposed at the polished surface and could not be analyzed. Chemical data are given in Table 1.

An elongated irregularly-shaped orange-brown

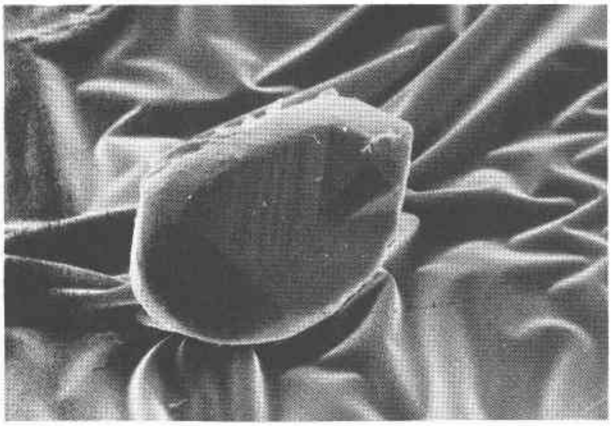

Fig. 1. A euhedral chromian diopside single-crystal inclusion. The unusual morphology, including some rounded surfaces, suggests an origin pregenetic to the diamond. The longest dimension of the inclusion is about 70 micrometers.

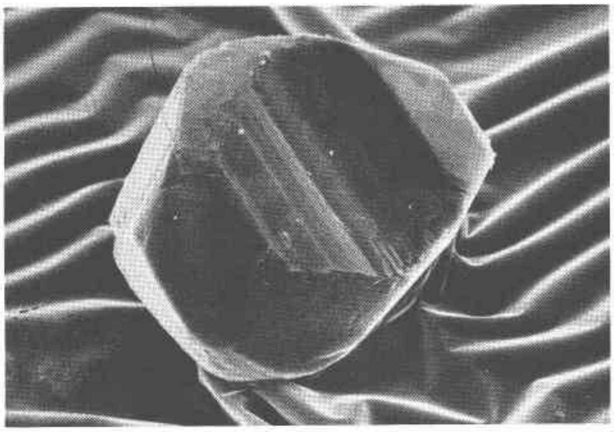

Fig. 2. The chrome diopside + orthopyroxene bicrystal inclusion. The striated forward section of the bicrystal is chromian diopside. The upraised flat rear section is orthopyroxene. The longest dimension of the bicrystal is about 100 micrometers.

grain was identified as olivine. It was friable and displayed an easy mica-like apparent cleavage. Micron-size protrusions were observed on parts of the outer surface (Fig. 3). A small quantity of glass-like grayish-white material was attached to one end of the olivine. Dispersive analysis of the olivine showed major Si and Mg, and minor Fe. No relative difference was detected on surfaces with and without minute crystal-like protrusions. The attached vitreous-like phase showed Si and Al as major constituents, with minor Ti, Fe, Zn, and K.

Powder diffraction analysis of the fragmented inclusion gave a good olivine pattern, plus a few broad and very weak reflections (d, I/I_0: 4.36, 5; 3.32, 3; 3.18, 8; 2.89, 10; 2.10, 3; 1.94, 3). The latter could be from either or both the olivine surface protrusions or the attached aluminosilicate. The averaged d_{130} spacing from two olivine films was 2.771 A, indicating approximately a 92 ± 1 percent forsteritic content (Yoder and Sahama, 1957). The unusual orange-red color of the olivine may be due to iron oxidation during the combustion process (Roedder, 1965).

Two small loose concentrations of finely polycrystalline, light tan "ash" were also recovered from the platinum boat. Dispersive analysis showed major Mg, minor Fe, and a trace of Ca. Powder X-ray diffraction gave a good periclase pattern plus three weak reflections corresponding to the strongest of magnetite. We conclude that the ash consists of major periclase and minor magnetite.

Table 1. Electron-probe analyses of a chrome diopside + orthopyroxene bicrystal inclusion from an Arkansas diamond

	green colored chrome diopside		yellow colored orthopyroxene	
	wt. %	cations	wt. %	cations
SiO_2	55.90	2.013	57.49	2.011
MgO	17.21	0.923	31.70	1.652
CaO	13.79	0.532	0.97	0.036
FeO	5.12	0.154	7.95	0.253
MnO	0.10	0.003	0.11	0.003
NiO	0.12	0.003	0.23	0.006
Na_2O	2.85	0.199	0.42	0.028
K_2O	0.15	0.007	0.05	0.002
Al_2O_3	2.95	0.125	0.52	0.021
Cr_2O_3	1.16	0.033	0.19	0.005
TiO_2	0.31	0.008	0.05	0.001
	99.66	4.000	99.68	4.018

Valence states cannot be distinguished in probe analyses. Total iron is given as FeO.

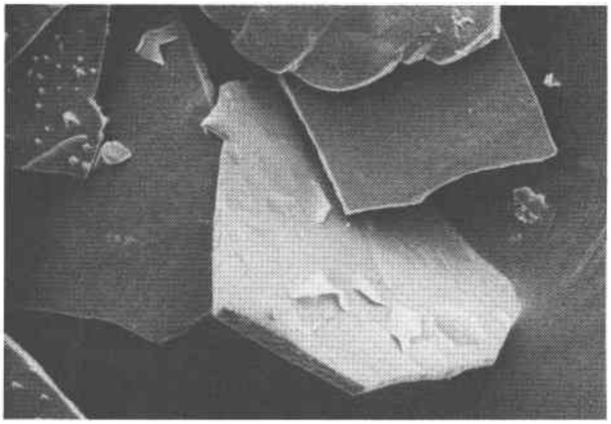

Fig. 3. Olivine: note the micron-size crystal protrusions observed on some parts of the outer surface of the anhedral shard-like inclusion, and cleavage-like fracturing. The largest dimension of the bright center fragment is about 25 micrometers.

Concentrations of finely polycrystalline matter were not noted during examination of the diamond. The two post-combustion ash-like concentrations may be residue from calcinable magnesium-bearing crystals such as magnesite.

Discussion

The suite of inclusions recovered from the Arkansas diamond is ultramafic. The high forsteritic content of the olivine (∼92%) is typical of olivines included in diamond (Meyer and Boyd, 1972). But its irregular shardlike form and attached unidentified glass-like aluminosilicate phase are unusual. Olivine inclusions are often euhedral orthorhombic crystals. Sometimes they show orientational influence by the host diamond (Mitchell and Giardini, 1953). They also have been found as internal molds in the host diamond (Sobolev *et al.*, 1972; Prinz *et al.*, 1975).

The outwardly monocyrstalline but sharply partitioned orthoclinopyroxene bicrystal is unusual, although such have been previously recognized (Sobolev *et al.*, 1970, Prinz *et al.*, 1975). According to the two-pyroxene geothermometer of Davis and Boyd (1966), the 0.37 Ca:(Ca + Mg) ratio of the diopside indicates an equilibration temperature of roughly 1300°C.

Neither periclase nor periclase + magnetite have been previously reported as included matter in diamond. In view of its ash-like state and the absence of observable ash in the diamond prior to combustion, it is possible that the periclase (+ magnetite) existed in the diamond as crystals of impure magnesite.

If this assumption is true, the inclusion suite consisting of chrome diopside + orthopyroxene, chrome diopside, and magnesite is reasonably consistent with the high pressure and temperature reaction,

$$\text{dolomite} + \text{enstatite} + \text{diopside} \leftrightharpoons \text{diopside} + \text{magnesite},$$

explored by Kushiro *et al.* (1975). They found the P–T equilibrium boundary for this reaction to be very close to that for graphite and diamond. Kushiro *et al.* predicted a possible presence of magnesite in the upper mantle. Our finding of periclase appears to support their prediction.

It has been shown by Wilshire and Jackson (1975) that the two-pyroxene geothermometer is subject to serious error. But if it is assumed that the 1300°C equilibrium temperature for the bipyroxene inclusion is reasonably correct, then, from the above work of Kushiro *et al.*, the pressure can be set at about 5×10^4 kbars. Since individual inclusions were isolated and apparently randomly distributed in the host diamond, the conditions, 5×10^4 kbars and 1300°C, can be interpreted as those under which the diamond formed. They do fall in the range of diamond synthesis with catalytic-solvent systems (Giardini and Tydings, 1962).

But the inclusion of olivine + attached vitreous-like phase may conflict with the above. The glassy phase seems to have had its origin as a liquid. This inclusion, therefore, resembles a product of incongruent melting. Two minerals found in diamond which do melt incongruently to yield olivine plus a liquid are phlogopite and enstatite. Phlogopite melts at pressures below 4×10^4 kbars (Giardini *et al.*, 1974) and enstatite below 3×10^4 kbars (Davis and Boyd, 1966).

Since the inclusion possessed a very irregular shape, it seems unlikely that it melted from a parent mineral while occluded in the diamond. Alternatives are that it existed at the time of inclusion, or that it formed during the diamond-burning process. The former seems more probable since both enstatite and phlogopite are stable at the recovery temperature.

If the above argument is valid, it can be inferred that at least part of the enclosing diamond formed at a pressure below 4×10^4 kbars. Natural diamond formation at such a low pressure would be a significant departure from published speculations ($P > 5 \times 10^4$ kbars).

Acknowledgments

Thanks are given to Dr. Larry Taylor for the electron-probe analyses, to Dr. G. Subbarayudu for assistance in other analyses, and to Dr. Dicke Hughes, a former owner of the Prairie Creek diamond-bearing kimberlite, for providing the diamond used in this study.

References

Davis, B. T. C. and F. R. Boyd (1966) The join $Mg_2Si_2O_6$–$CaMgSi_2O_6$ at 30 Kb pressure and its application to pyroxenes from kimberlite. *J. Geophys. Res.*, *71*, 3567–3576.

Fesq, H. W., D. M. Bibby, C. S. Erasmus, E. J. D. Kable and J. P. F. Sellschop (1975). A comparative trace element study of diamonds. *Phys. Chem. Earth*, *9*, 817–836.

Giardini, A. A. and C. E. Melton (1975a) Chemical data on a colorless Arkansas diamond and its amorphous C–Fe–Ni–S inclusion. *Am. Mineral.*, *60*, 934–936.

——— and ——— (1975b) The nature of cloud-like inclusions in two Arkansas diamonds. *Am. Mineral.*, *60*, 931–933.

——— and J. E. Tydings (1962) Diamond synthesis: observations on the mechanism of formation. *Am. Mineral.*, *47*, 1393–1421.

Harris, J. W. (1968) The recognition of diamond inclusions. Pt. 1: Syngenetic mineral inclusions. Pt. 2: Epigenetic mineral inclusions. *Ind. Diamond. Rev.*, *28*, 402–410 and 458–461.

Kushiro, I., H. Satake and S. Akimoto (1975) Carbonate-silicate reactions at high pressure and possible presence of dolomite and magnesite in the upper mantle. *Earth Planet. Sci. Lett.*, *28*, 116–120.

Melton, C. E. and A. A. Giardini (1975) Experimental results and a theoretical interpretation of gaseous inclusions found in Arkansas natural diamonds. *Am. Mineral.*, *60*, 413–417.

Meyer, H. O. A. and F. R. Boyd (1969) Mineral inclusions in diamond. *Carnegie Inst. Wash. Year Book*, *67*, 130–135.

——— and ——— (1970) Inclusions in diamond. *Carnegie Inst. Wash. Year Book*, *68*, 315–322.

——— and ——— (1972) Composition and origin of crystalline inclusions in natural diamonds. *Geochim. Cosmochim. Acta.*, *36*, 1255–1273.

——— and D. P. Svisero (1975) Mineral inclusions in Brazilian diamonds. *Phys. Chem. Earth*, *9*, 785–795.

Mitchell, R. S. and A. A. Giardini (1953) Oriented olivine inclusions in diamond. *Am. Mineral.*, *38*, 136–138.

Prinz, N., D. V. Manson, P. F. Hlava and K. Keil (1975) Inclusions in diamonds: garnet iherzolite and eclogite assemblages. *Phys. Chem. Earth*, *9*, 797–815.

Roedder, E. (1965) Liquid CO_2 inclusions in olivine-bearing nodules and phenocrysts from basalts. *Am. Mineral.*, *50*, 1746–1782.

Sobolev, N. V., Z. V. Bartoshinskiy, E. S. Yefimova, Yu. G. Lavrent'yev and L. N. Pospelova (1970) Olivine–garnet–chrome diopside assemblage from Yakutian diamond. *Dokl. Akad. Nauk. SSSR*, *192*, 1349–1352.

———, A. I. Botkunov, I. T. Bokumento and V. S. Sobolev (1972) Crystalline inclusions with octahedral faces in diamonds. *Dokl. Akad. Nauk. SSSR*, *204*, 117–120.

Wilshire, H. G. and E. D. Jackson (1975) Problems in determining mantle geotherms from pyroxene compositions of ultramafic rocks. *J. Geol.*, *83*, 313–329.

Yoder, H. S. and T. G. Sahama (1957) Olivine x-ray determinative curve. *Am. Mineral.*, *42*, 475–491.

Manuscript received, July 23, 1976; accepted for publication, December 30, 1976.