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Mineral inclusions in four Arkansas diamonds: their nature and significance

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Abstract

Totally-enclosed inclusions recovered from four Arkansas diamonds by burning in air at 820° C are identified by XRD and EDAX analyses as: (1) enstatite, olivine, pyrrhotite + pentlandite, (2) eclogitic garnet, (3) enstatite + peridotitic garnet + chromite, olivine + pyrrhotite, pyrrhotite, pentlandite, pyrite + pyrrhotite, pentlandite + a nickel sulfide, (4) diamond, enstatite, magnetite. This is the first report of nickel sulfide in diamond. A review of inclusions found in Arkansas diamonds shows a similarity with those from world-wide localities, and indicates a global consistency in diamond-forming environments.

Introduction

Since diamonds are relatively inert, impermeable, and hard, inclusions therein are about as well preserved as they could possibly be. Their study provides enlightment about the environment wherein diamonds formed.

A considerable literature exists on diamond inclusions, but most of it deals with diamonds of African, Siberian, and South American origin (*e.g.*, Meyer and Tsai, 1976; Mitchell and Giardini, 1977; Orlov, 1977). In all, about thirty minerals have been identified. But for a few notable exceptions, *e.g.*, quartz in Brazilian diamonds, they can be classed as being derived from either eclogitic or ultramafic rock. There have been, however, relatively few studies on inclusions in North American diamonds. The purpose of this work was to investigate crystalline inclusions in four Arkansas diamonds. The diamonds of 0.43, 0.45, 0.50, and 0.62 carat weight were obtained from Mr. Dicke Hughes, a former operator of the Arkansas kimberlite property that is now known as the Crater of Diamonds State Park. The diatreme is located about 4 km SSE of Murfreesboro, Pike County, Arkansas (Gogineni *et al.*, 1978).

Description of the diamonds

The 0.43 ct. diamond was a pale yellow rounded, flattened, apparently twinned hexoctahedron. Both opaque and transparent totally-enclosed inclusions were apparent under binocular microscope examination. The 0.45 ct. stone was colorless and of elongated rounded shape with a highly polished surface. Four inclusions were detected. The 0.50 ct. crystal was a colorless rounded tetrahexahedron with a cleavage plane on one side and contained transparent and opaque inclusions. The 0.62 ct. diamond was also colorless and of rounded tetrahexahedral form. Several relatively large flat opaque inclusions ("carbon spots") were observed. All the diamonds were free of detectable surface cleavage cracks.

Experimental

The diamonds were cleaned and burned by the same procedures described by Newton *et al.* (1977). The furnace temperature was 820°C. After combustion, residual matter from each diamond was recovered from the bottom of its platinum boat with a sharply-pointed wood stick moistened with distilled water, transferred to a glass slide, examined by optical microscopy, then mounted on sharply-pointed wood sticks with mucilage for XRD analysis. Subsequent to X-ray diffraction analyses, samples were recovered and transferred to SEM/EDAX mounts for chemical analyses. The latter were conducted in conjunction with co-mounted reference standards previously analyzed with a MAC-400 electron beam probe.

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Analytical data

0.43 ct. diamond

Recovered inclusions are one enstatite crystal, three olivine crystals, and one composite crystal of pyrrhotite and pentlandite. The enstatite was colorless and tabular-prismatic in form. Unit-cell dimensions are given in Table 1. The crystal was lost in attempting transfer from XRD to EDAX mounts. Thus, chemical data are not available.

The three olivine crystals were all casts of octahedral form (Fig. 1). Although initially colorless, all became orange-red as a result of the diamond burning process. All had similar unit-cell dimensions (Table 1) and chemistry (Fo_{92}—Table 2).

Due to the burning process, sulfide inclusions were converted to oxides. Sulfide identification is based on the texture, chemistry, and crystal structures of the residual oxides standardized against those derived from similar burnings of known reference sulfides. All sulfide residues were crustaceous in texture. The residual shape of the pyrrhotite + pentlandite residuum was near-spherical, indicating a globular shape for the original sulfide. XRD analysis gave patterns for magnetite and bunsenite. EDAX analysis showed a composition of 95–100% Fd, 5–0% Ni for pyrrhotite, and 25–50% Fe, 75–50% Ni for pentlandite.

0.45 ct. diamond

Identified inclusions consist of three rounded, elongated, orange-brown crystals of iron-rich garnet, one of which is shown in Figure 1. Their unit-cell dimensions (Table 1) and chemistry (Table 2) are similar. Their end-member composition is almandine 40, andradite 10, grossular 12, pyrope 38. They correspond to Group 3 garnet (common eclogite garnet) according to the classification method of Dawson and Stephens (1975). SEM examination revealed hillock-like irregularities on their rounded surfaces. The latter may reflect a partial solution prior to their inclusion in the diamond (Fig. 1).

A fourth crystal, tan to pale yellow, tabular and flexible, was lost during recovery from the platinum boat. In appearance it resembled a mica crystal.

0.50 ct. diamond

Six inclusions were recovered. The largest was a tricrystal composed of a colorless tabular-prismatic

Table 1. Single-crystal XRD data on mineral inclusions from Arkansas diamonds

Inclusion	Source diamond	Unit cell dimensions (A)
Fe-rich garnet	0.45 carat	a = 11.552(6)**
Cr-rich garnet	0.50 carat	a = 11.522(1)
Olivine	0.43 carat	a = 4.756(5) b = 10.195(8) c = 5.966(8)
Enstatite	0.43 carat	a = 18.230(5) b = 8.821(4) c = 5.187(2)
Enstatite	0.50 carat	a = 18.248(2) b = 8.807(8) c = 5.177(5)

* Enraf-Nonium CAD-4 computerized diffractometer, CuKα radiation.
**Bracketed numbers are the standard deviations.

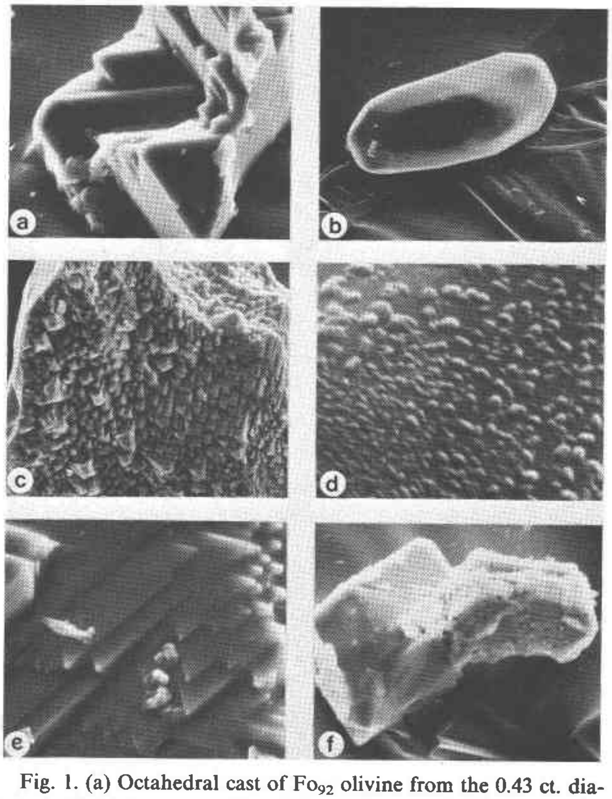

Fig. 1. (a) Octahedral cast of Fo_{92} olivine from the 0.43 ct. diamond. The inclusion is about 0.1 mm in length. (b) One of the three almandine-rich garnets from the 0.45 ct. diamond. Its length is about 0.06 mm. Their surfaces contained multitudes of hillock-like irregularities. A 10,000× view of the latter on the garnet shown is illustrated in (d). (c) 4000× view of the general octahedral topography of the outward-facing chromite layer on the chromium-rich garnet from the 0.5 ct. diamond trimineralic inclusion. (e) A restricted 20,000× view of the chromite. (f) The bimineralic inclusion composed of an octahedral cast of Fo_{92} olivine (left) and a crystal of pyrrhotite (attached homogeneous crustaceous residue of Fe and Ni oxides with a hexagonal shape on the right) from the 0.5 ct. diamond. The width of this inclusion is about 0.06 mm.

crystal of enstatite (En_{91}) attached on one corner to a larger central pink rounded chromian pyrope garnet, which in turn was capped on a flat side opposite the enstatite by a thin black layer of chromite (Fig. 1). The rounded garnet surface also showed an etch-like hillock texture (Fig. 1). After initial single-crystal XRD analysis, the enstatite and garnet were broken apart and re-analyzed separately. Unit-cell dimensions for the enstatite and garnet are given in Table 1. Chemical analyses are given in Table 2. The garnet end-member composition is pyrope 32, knorringite 30, uvarovite 5, khoharite 2, almandine 31. It corresponds to a Group 10 garnet of Dawson and Stephens (1975). Surfaces of the chromite layer showed mainly an octehedral topography (Fig. 1), but dodecahedral and cubic topographies were also observed. EDAX analyses showed a 1:2 Fe:Cr cationic composition.

An olivine + pyrrhotite bicrystal was about half silicate and half sulfide (Fig. 1). The olivine (Fo_{92}, with a trace of Ni) has octahedral form. The hexagonal shape of the oxide residue of the sulfide suggests an initial crystal form. The cationic chemistry of the sulfide is 98% Fe, 2% Ni.

Table 2. Energy-dispersive X-ray analyses of some mineral inclusions from Arkansas diamonds

Mineral	Garnet	Garnet	Olivine	Olivine	Enstatite
Source diamond	0.45 ct	0.50 ct	0.50 ct	0.43 ct	0.50 ct
SiO_2	38.5%	42.1%	40.1%	40.3%	58.4%
Al_2O_3	21.9	18.3	-	-	-
Cr_2O_3	-	7.8	-	-	-
FeO **	21.0	6.8	8.3	7.8	6.1
MgO	10.3	22.4	51.1	51.3	35.5
NiO	-	-	tr	tr	-
CaO	8.4	2.5	-	-	-
Total	100.1	99.9	99.5	99.4	100.0
Fe_2O_3 ***	1.9	0.4			
FeO	19.3	6.4			
Number of cations for "n" oxygens in structural formula					
n =	12	12	4	4	6
Si	2.93	3.02	0.98	0.98	2.00
Al (IV)	0.07	-	-	-	-
Al (VI)	1.89	1.54	-	-	-
Cr	-	0.44	-	-	-
Fe (+3)	0.12	0.02	-	-	-
Fe (+2)	1.23	0.38	0.17	0.16	0.18
Mg	1.18	2.41	1.87	1.88	1.83
Ca	0.69	0.19	-	-	-
$\frac{Mg \times 100}{Mg + Fe}$	-	-	91.7	92.2	91.3

* EDAX analyses calibrated against co-mounted reference samples pre-analyzed with a Mac-400 electron beam probe with standard corrections applied.

** Total iron expressed as FeO.

*** Ferric and ferrous iron calculated based upon the garnet structural formula.

Four sulfide inclusions (pyrrhotite, pyrrhotite + pyrite, pentlandite, a nickel sulfide + pentlandite) were similarly identified on the basis of residual oxides relative to similarly-derived reference standards. The rectangular form of the oxide residuum of the pentlandite inclusion indicated an initial crystal form. The others showed rounded shapes, suggesting initial globular forms. XRD analysis of the residual oxide from the nickel sulfide + pentlandite inclusion gave only a bunsenite pattern. EDAX analysis showed that the inclusion consisted of about 90% nickel sulfide (95–100% Ni, 5–0% Fe) and 10% pentlandite (25% Fe, 75% Ni). There is not sufficient evidence to make a mineral identification of the nickel sulfide. The pyrite showed a nickel content ranging from 5 to 15%.

0.62 ct. diamond

This diamond was not completely burned. It was possible to eject from the remaining diamond two small tabular colorless inclusions that XRD analyses showed to be diamond. A third small finely polycrystalline inclusion, fluffy in appearance, was subjected to powder X-ray diffraction analysis and found to contain enstatite and magnetite. "Carbon spots" observed in the diamond were apparently consumed in the burning process and presumably were carbon.

Discussion

Energy dispersive analyses (EDAX) are less sensitive and precise than electron beam probe analyses. Those presented here have been derived by means of comparative analyses conducted on co-mounted reference specimens that were previously analyzed with a MAC-400 electron beam probe, with standard corrections applied (Bence and Albee, 1968; Albee and Ray, 1970). Tabulated analytical data for the principal elements are believed to be correct to ±3% of the amounts present.

Inclusions in Arkansas diamonds reported here, and those previously identified (Newton *et al.*, 1977; Giardini and Melton, 1975; Melton and Giardini, 1975), are summarized in Table 3. With the possible exceptions of periclase (magnesite?) + magnetite and a nickel sulfide, the minerals and gases found thus far in Arkansas diamonds are essentially identical, with respect to both species and varieties, to those found in diamonds from other global localities, particularly South Africa.

The apparent abundance of sulfides in Arkansas diamonds is consistent with the observation of

Table 3. Summary of inclusions identified in Arkansas diamonds

1.	Chrome diopside	(a)
2.	Chromite	(b)
3.	Enstatite (En_{91} Fs_9)	(b)
4.	Enstatite (En_{87} Fs_{13})	(a)
5.	Chromium-rich garnet	(b)
6.	Iron-rich garnet	(b)
7.	Olivine (Fo_{92})	(a,b)
8.	Periclase (magnesite?) + magnetite	(a)
9.	Magnetite	(b)
10.	An unknown Fe, Ti, Zn, K-bearing aluminosilicate	(a)
11.	Pyrite	(b,c)
12.	Pyrrhotite	(b,c)
13.	Pentlandite	(b)
14.	Nickel sulfide	(b)
15.	Diamond	(b)
16.	Negative diamond crystals	(d)
17.	Amorphous carbonaceous matter plus Fe, Ni, S	(c)
18.	C - H - O - N - Ar gas mixtures	(e)

(a) Newton, Melton and Giardini (1977)
(b) This report
(c) Giardini and Melton (1975)
(d) Giardini and Melton (1975)
(e) Melton and Giardini (1975)

Sharpe (1966) on South African diamonds. Octahedral casts of forsteritic olivine are similar to those described by Sobolev *et al.* (1972) from Siberia and Prinz *et al.* (1975) from Africa. The same parallel applies to iron-rich eclogitic garnet and chromium-rich peridotitic garnet.

It appears, therefore, that diamond inclusions are the same world-wide (Phukan, 1971; Prinz *et al.*, 1975; Meyer and Svisero, 1975; Meyer and Tsai, 1976; Mitchell and Giardini, 1977; Orlov, 1977; this report). Some, like olivine, are by composition very specific, and others, such as enstatite, garnet, and sulfides, show a range of composition. The world-wide similarity of inclusions indicates a world-wide consistency in the nature of the upper mantle within the depth range of diamond formation.

Dawson and Stephens (1975), from their analysis of the chemistry of garnets found in kimberlites, associated xenoliths, and diamonds, have suggested that the type of rock in which diamonds are found may be unrelated to the diamond-forming process. From current data, the only type of occluded matter that seems to be consistently present in all diamonds, world-wide, is gaseous compounds of the elements C, H, O, and N (Melton and Giardini, 1974, 1975).

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