

# Rare earth element patterns of carbonado and yakutite: evidence for their crustal origin

KEN SHIBATA\*, HIKARI KAMIOKA

Geological Survey of Japan, Tsukuba 305, Japan

FELIX V. KAMINSKY, VASSILI. I. KOPTIL

Central Research Institute of Geological Prospecting for Base and Precious Metals, 113545, Moscow, Russia

AND

DARCY P. SVISERO

Institute of Geosciences, University of Sao Paulo, C. P. 20899, Sao Paulo, Brazil

## Abstract

Carbonado and yakutite are both porous aggregates of polycrystalline micrometre-size diamond, with very different characters from those of monocrystalline diamond. The genesis of carbonado is very controversial, whereas yakutite is thought to have been formed by meteorite impact. Neutron activation analyses of trace elements in carbonado and yakutite indicate that their rare earth element (*REE*) abundance patterns have common characteristics: heavy *REEs* are not much depleted and a negative Eu anomaly is observed. These patterns are quite different from those of kimberlite and monocrystalline diamond and are similar to those of crustal materials such as shale, supporting the hypothesis of a crustal origin for carbonado and yakutite.

**KEYWORDS:** carbonado, yakutite, diamond, florencite, rare earth element, crust.

## Introduction

CARBONADO is unique among diamond varieties, as it is not found in kimberlite, has light carbon isotopic ratios, and contains mineral inclusions typical of the crust. Central African carbonados contain inclusions of the *REE* mineral florencite (Trueb and de Wys, 1971), which may indicate the hydrothermal and/or weathering environments in which carbonados have been kept. Dubinchuk *et al.* (1976) and Kaminsky (1987) proposed a hypothesis that carbonado formed from organic carbon by irradiation of high-energy particles from uranium, and Ozima *et al.* (1991) presented noble gas data that suggest the crustal origin of carbonados from Central Africa and Brazil. Although these lines of evidence strongly suggest the crustal origin of carbonado, consideration of the chemistry of carbonado has been limited because of analytical difficulties.

\* Present address: Department of Earth and Planetary Sciences, Nagoya University, Nagoya 464-01, Japan.

Yakutite was first found in Northern Yakutia, Russia, in 1966, and is commonly thought to be a type of carbonado because of its similar appearance. However, the nature of yakutite is different from common carbonado, and yakutite is now believed to have been formed from graphite by meteorite impact (Kaminsky *et al.*, 1985).

No quantitative elemental analyses on carbonado and yakutite have been reported yet. Here the first comprehensive elemental abundance of carbonado and yakutite by the neutron activation method are presented, and their origin on the basis of *REE* patterns is discussed.

## Samples and experimental methods

One carbonado from Central Africa, two from Brazil, an one yakutite from Siberia were studied. The locality of the Central African carbonado is unknown except that it comes from sediments in the Ubangi district. The Brazilian carbonados were collected from gravels in the headwater area of the Santo Antonio River, District of Palmeiras, Bahia. Carbonados are obtained from concen-

trates whose mineral assemblage includes magnetite, rutile, amphibole, zircon, tourmaline, hematite, and monazite. Typical kimberlitic indicators such as Cr-pyrope, Mg-ilmenite and Cr-spinel are absent. Yakutite was found in alluvial deposits of the Ibeliakh River basin, Northern Yakutia, together with diamond monocrystal, Mg-ilmenite, pyrope, Cr-spinel and zircon (Kaminsky *et al.*, 1985). The analysed sample shows weak orange-red photoluminescence, and contains 35–40% lonsdaleite, which is diamond with a hexagonal structure, and small irregular graphite inclusions. X-ray diffraction of carbonado and yakutite shows three major lines at 2.06,

1.262 and 1.075Å. The carbonados show very sharp lines, whereas yakutite has broad lines.

Before analysis, all samples were cleaned ultrasonically in distilled water. In order to obtain information about impurities which might exist on sample surfaces, in grain boundaries, or incorporated as inclusions, leaching treatment using HF-HNO<sub>3</sub> was carried out for 30 minutes on a hot plate. Samples and their leachates were analysed by instrumental neutron activation methods for 39 elements including the REE. They were irradiated at the Japan Atomic Energy Research Institute for 6 hours with the thermal neutron flux of  $5.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ . Measurements were

Table 1. Analytical results with sample descriptions

Sample	90718 carbonado	2 carbonado	3 carbonado	9 yakutite
Locality	Central Africa	Brazil	Brazil	Siberia
Color	brown	black	brown	black
Density(g·cm <sup>-3</sup> )	3.40	3.40	3.32	3.47
Weight (mg)*	76.85	53.89	63.04	44.65
Sc (ppm)	6.33 (0.1)	0.504 (0.3)	0.260 (0.3)	0.0943(0.6)
Cr (ppm)	57.2 (0.4)	38.4 (0.4)	2.737 (1.8)	2.72 (1.7)
Fe (%)	0.539 (0.3)	0.471 (0.3)	0.010 (2.7)	0.0486(1.0)
Co (ppm)	1.86 (0.6)	3.41 (0.5)	0.203 (1.9)	0.212 (2.2)
Ba (ppm)	97.9 (4.4)	71.0 (3.6)	7.0 (15.8)	-
La (ppm)	43.0 (0.3)	22.5 (0.3)	3.84 (1.1)	0.611 (3.3)
Ce (ppm)	79.0 (0.3)	33.7 (0.3)	3.15 (0.8)	0.845 (1.9)
Nd (ppm)	36.2 (7.2)	9.50 (8.2)	1.4 (17.2)	-
Sm (ppm)	8.76 (0.2)	1.57 (0.3)	0.241 (1.2)	0.106 (2.2)
Eu (ppm)	1.92 (0.8)	0.307 (1.2)	0.0459(2.6)	0.0108(7.6)
Tb (ppm)	3.01 (6.7)	0.240 (8.1)	0.038(15.5)	-
Yb (ppm)	12.0 (1.2)	0.858 (1.7)	0.449 (2.2)	0.0786(7.8)
Lu (ppm)	1.83 (1.9)	0.116 (2.4)	0.0731(2.5)	0.0121(7.4)
Hf (ppm)	1.66 (0.9)	0.197 (2.5)	0.189 (1.8)	0.0934(2.5)
Ta (ppm)	0.447 (2.5)	0.049(10.8)	1.42 (1.2)	0.022(11.1)
Au (ppb)	1.23 (5.3)	5.92 (3.6)	69.7 (0.8)	2.09 (9.8)
Th (ppm)	12.4 (0.3)	1.51 (0.6)	1.53 (0.5)	0.286 (1.2)
U (ppm)	4.39 (5.2)	0.725 (7.2)	0.28 (11.4)	-

$\gamma$ -ray counting errors ( $1\sigma$ ) are given in parentheses.

\* Sample weight after acid treatment.

- : not detected.

Following elements were also analyzed but were not detected (detection limits were 0.1~10 ppm for most of them) or had large analytical errors (>20% at  $1\sigma$ ); Na, K, Ni, Zn, Se, As, Br, Rb, Sr, Zr, Ru, Ag, Sb, Cs, Dy, Tm, W, Re, Os, Ir and Pt.

performed using a highly automated INAA system (Tanaka *et al.*, 1988) with a pure Ge detector.

### Results and discussion

Concentrations of more than half of measured elements are less than the detection limit, or their errors are large; thus analytical results of 18 elements are given in Table 1. A large difference in elemental abundance exists between the Central African carbonado and yakutite. However, the *REE* patterns are more or less similar to each other: the heavy *REEs* are not much depleted, showing nearly flat heavy *REE* patterns except for sample No. 3, and a negative Eu anomaly is observed (Fig. 1). Kimberlite and carbonatite are both characterised by high *REE* concentrations and large light *REE*/heavy *REE* ratios, without an Eu anomaly in most cases

(Cullers and Graph, 1984). Diamond has the same pattern although the abundance is lower by 3 orders of magnitude (Akagi and Masuda, 1988). Thus the *REE* patterns of carbonados and yakutite do not resemble those of kimberlite and carbonatite, but are similar to those of crustal materials such as the North American shale composite (NASC) (Gromet *et al.*, 1984). The crustal characteristics demonstrated by the *REE* patterns supports hypotheses of the crustal origin for carbonado proposed by Dubinchuk *et al.* (1976) and Kaminsky (1987).

U, Th and Ba concentrations of carbonados and yakutite are correlated roughly with the *REE* concentrations. Th/U ratios range from 2.1 to 5.5 and are comparable with the crustal abundance ratio. U concentrations of carbonados are similar to the values reported by Ozima *et al.* (1991), and are not high enough to explain the amount of *in situ* production of fissionogenic Xe and Kr.

Monocrystalline diamonds contain various

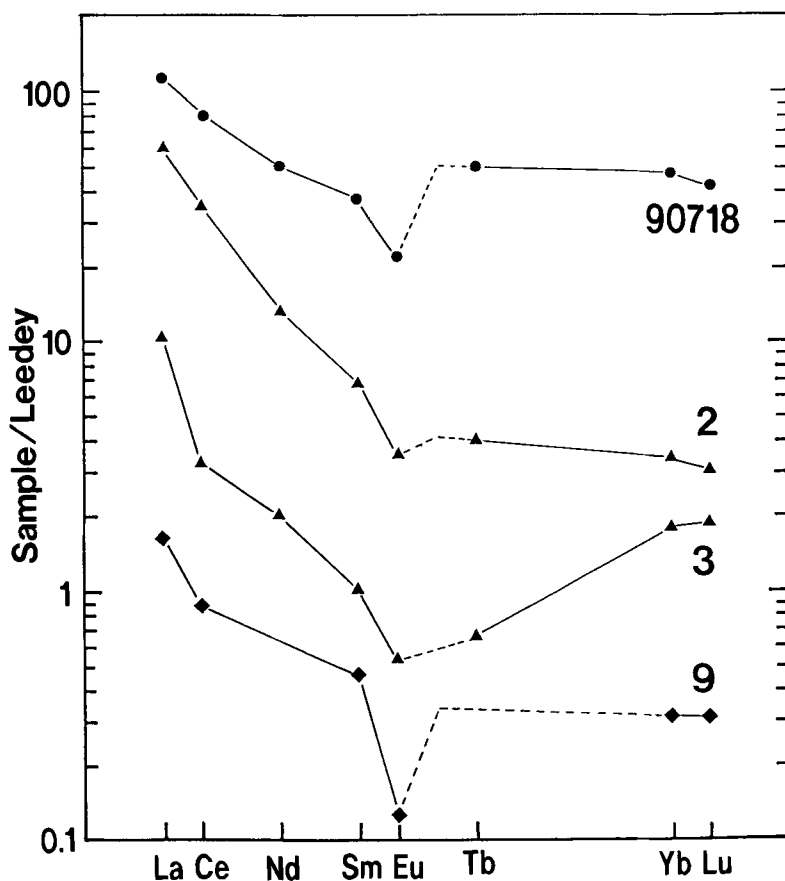


FIG. 1. Chondrite-normalized *REE* patterns of carbonados and yakutite. *REE* abundances in the Leedeey chondrite (Masuda *et al.*, 1973; Masuda, 1975) are used for the normalisation.

amounts of trace elements including *REE*, which are included for the most part in microscopic or sub-microscopic inclusions, either silicates, sulphides or fluid (Fesq *et al.*, 1975; Akagi and Masuda, 1988). Trace elements in carbonado are also believed to be contained mostly in inclusions that consist mainly of silicates and other minerals. In both cases, chemical compositions of inclusion provide important information on the environment during diamond formation.

The difference in *REE* abundances and patterns of carbonado is related to the kind and amount of inclusions. Thus the high *REE* concentrations of the Central African carbonado may be attributed to florencite, which is a *REE*-concentrating mineral and the predominant inclusion in the carbonado (Trueb and de Wys, 1971). Florencite is characterised by enrichment of light *REE*, particularly Ce and La (Lefebvre and Gasparrini, 1980). It has not been identified in the Brazilian carbonado and yakutite. However, judging from the *REE* abundance and pattern, the Brazilian carbonados probably contain florencite. Another interesting occurrence of florencite is in diamond-bearing placers of Diamantina, Brazil, (Hussak and Prior, 1990) and Ubangi, Central Africa (Trueb and de Wys, 1971). The

association of florencite with carbonado in placers where carbonado is found may be an important factor in interpreting the origin of carbonado. Florencite is considered to be a hydrothermal mineral (Lefebvre and Gasparrini, 1980). It also occurs in weathering zones (Bain, 1970). This means that carbonado has been kept in hydrothermal and/or weathering environments. The association of florencite with carbonado might have been facilitated by their similar densities; florencite has a density of  $3.5 \pm 0.2 \text{ g/cm}^3$  (Lefebvre and Gasparrini, 1980).

The leaching experiment shows that the leached fractions are quite variable among samples and elements (Table 2). *REEs* in carbonados are leached much less than other elements. This suggests that *REE*-concentrating minerals such as florencite are scarcely leached out from carbonados. In this connection, florencite is known to be very resistant chemically. Similarities in the *REE* abundances and patterns of the Central African carbonado and its leachate (Table 2) confirm the previous observation (Trueb and de Wys, 1971) that the internal and external inclusions are similar to each other. Compared to carbonado, a substantial fraction of elements including *REEs* are leached out from yakutite,

Table 2. Percentages of elements leached by acid treatment

Sample	90718	2	3	9
Weight loss (%)	2.5	0.11	0.30	0.65
by leaching				
Sc	16.8	4.6	69.1	73.7
Cr	17.8	11.3	-	67.4
Fe	23.7	2.4	86.6	75.8
Co	21.3	4.0	65.7	79.8
La	3.5	0.2	1.9	24.4
Ce	5.3	1.2	-	47.1
Sm	4.6	2.5	-	38.0
Eu	5.0	-	-	55.0
Tb	3.4	-	-	-
Yb	5.4	1.3	-	-
Lu	5.9	-	-	-
Hf	22.9	11.9	-	64.0
Ta	15.7	90.5	98.6	95.3
Au	65.4	51.5	13.8	72.6
Th	10.1	-	30.5	38.0
U	18.7	29.0	-	-

The treatment was made with the mixture of 40 % HF and 65 % HNO<sub>3</sub> for 30 minutes at 80 °C.

suggesting that inclusions in yakutite are different from those in carbonado, and that yakutite is more porous than carbonado.

One might argue for an epigenetic origin for inclusions in carbonado. However, a considerable number of the pores are not connected to the surface (Trueb and Buttermann, 1969), and inclusions could not be introduced into such closed pores once carbonado was formed. Mineral inclusions were probably incorporated into carbonado during its formation in the upper crust. One possible mechanism of carbonado formation is the irradiation of organic carbon by high-energy particles in a uranium-rich environment (Dubinchuk *et al.*, 1976; Kaminsky, 1987). This mechanism is somewhat similar to diamond synthesis by chemical vapour deposition, in which diamond is formed as a metastable phase from a mixture of methane and hydrogen under plasma conditions. However, there is a big difference in the formation of chemical vapour deposition diamond under gaseous conditions and solid-state formation of carbonado. In the case of carbonado, high-energy particles from uranium may play the role of plasma. In fact, diamonds up to 1  $\mu\text{m}$  in size were found in uranium-bearing carbonaceous matter (Dubinchuk *et al.*, 1976), and diamond-like clusters were observed in coalified wood containing uranium (Ergun *et al.*, 1960). Further investigation on such materials is needed to substantiate the crustal origin of carbonado.

Yakutite is different from carbonado in many respects (Kaminsky *et al.*, 1985). It is generally smaller than carbonado, it contains lonsdaleite, and its carbon isotopic ratio is heavier. Diamond crystallites of yakutite are oriented and smaller: 0.1–1.0  $\mu\text{m}$  compared to 0.5–80  $\mu\text{m}$  of carbonado. Yakutite contains a much smaller number of inclusions than carbonado, confirmed by the lower abundance of trace elements including REE. Yakutite is believed to have been formed from graphite by shock metamorphism caused by meteorite impact (Kaminsky *et al.*, 1985). The crustal origin of yakutite is clearly demonstrated by the similarity of its REE pattern to that of crustal material.

#### Acknowledgment

We thank M. Ozima for providing the Central African carbonado.

#### References

Akagi, T. and Masuda, M. (1988) Isotopic and element evidence for a relationship between kimberlite and Zaire diamonds. *Nature*, **336**, 665–7.

- Bain, D. C. (1970) Plumbogummite-group minerals from Mull and Morvern. *Mineral. Mag.*, **37**, 934–8.
- Cullers, L. C. and Graf, J. L. (1984) Rare earth elements in igneous rocks of the continental crust: predominantly basic and ultrabasic rocks. In *Rare earth element geochemistry* (P. Henderson, ed.), Elsevier, Amsterdam, 237–74.
- Dubinchuk, V. T., Kochenov, A. V., Penkov, V. F., Sidorenko, G. A., and Uspensky, V. A. (1976) New formation in organic matter of sedimentary rocks under radioactive radiation. *Dokl. Akad. Nauk SSSR*, **231**, 973–6.
- Ergun, S., Donaldson, W. F., and Breger, I. A. (1960) Some physical and chemical properties of vitrines associated with uranium. *Fuel*, **39**, 71–7.
- Fesq, H. W., Bibby, D. M., Erasmus, C. S., Kable, E. J. D., and Sellschop, J. P. F. (1975) A comparative trace element study of diamonds from Premier, Finsch and Jagersfontein Mines, South Africa. In *Physics and Chemistry of the Earth* (L. H. Ahrens, J. B. Dawson, A. R. Duncan, and A. J. Erlank, eds.) **9**, Pergamon, Oxford, 817–36.
- Gromet, L. P., Dymek, R. F., Haskin, L. A. and Korotev, R. L. (1984) The 'North American shale composite': Its composition, major and trace element characteristics. *Geochim. Cosmochim. Acta*, **48**, 2469–82.
- Hussak, E. and Prior, G. (1990) On florencite, a new hydrated phosphate of aluminium and cerium earths, from Brazil. *Mineral. Mag.*, **12**, 244–8.
- Kaminsky, F. V. (1987) Genesis of carbonado-polycrystalline aggregate of diamond. *Dokl. Akad. Nauk SSSR*, **294**, 439–40.
- Blinova, G. K., Galimov, E. M., Gurkina, G. A., Klyuev, Yu. A., Kodina, L. A., Koptil, V. I., Krivonos, V. F., Frolova, L. N., and Khrenov, A. Ya. (1985) Polycrystalline aggregates of diamonds with lonsdaleite from placers of Yakutia. *Mineral. Zhurn.*, **7**, (part 1) 27–36.
- Lefebvre, J.-J. and Gasparrini, C. (1980) Florencite, an occurrence in the Zairian copperbelt. *Can. Mineral.*, **18**, 301–11.
- Masuda, A. (1975) Abundance of monoisotopic REE, consistent with the Leedey chondrite values. *Geochem. J.*, **9**, 193–4.
- Nakamura, N., and Tanaka, T. (1973) Fine structures of mutually normalised rare-earth patterns of chondrites. *Geochim. Cosmochim. Acta*, **37**, 239–48.
- Ozima, M., Zashu, S., Tomura, K., and Matsuhisa, Y. (1991) Constraints from noble-gas contents on the origin of carbonado diamonds. *Nature*, **351**, 472–4.
- Tanaka, T., Kamioka, H. and Yamanaka, K. (1988) A fully automated  $\gamma$ -ray counting and data processing system for INAA and analysis of rock reference samples. *Bull. Geol. Surv. Japan*, **39**, 537–57.
- Trueb, L. F. and Buttermann, W. C. (1969) Carbonado: a micro-structural study. *Am. Mineral.*, **54**, 412–25.
- and de Wys, E. C. (1971) Carbon from Ubangi—a micro-structural study. *Ibid.*, **56**, 1252–68.

[Manuscript received 25 September 1992;  
revised 4 January 1993]