

CARBONADO: A COMPARISON BETWEEN BRAZILIAN AND UBANGUI SOURCES BASED ON CARBON AND NITROGEN ISOTOPES.

D. Shelkov¹, A.B. Verchovsky¹, H.J. Milledge² and C.T. Pillinger¹.

1. Dept. of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK,
2. Department of Geology, University College, Gower Street, London.

Introduction: Carbonado has been known as a polycrystalline form of a diamond since at least 1840's (Trueb and de Wys, 1971). It was first discovered and mined as a placer mineral in Sincoro county in Brazil. Subsequently it has been found as a placer in the States of Bahia, Parana and Minas Gerais (Trueb and de Wys, 1969; Kaminsky, 1991) and is known from other areas particularly in Venezuela (Gran Sabana region) and Ubangui region (Berberati, Carnot, Nola in the West Ubangui and Ouadda, N'Dele in the East Ubangui) of the Central African Republic, where the name "carbon" (Trueb and de Wys, 1971) is more common. On the basis of previous studies several hypotheses for the formation of carbonado have been put forward including: (i) impact origin (Smith and Dawson, 1985); (ii) formation under influence of radiation by transformation of carbon rich material (Kaminsky et al. 1987); (iii) growth in kimberlites with a long crustal history (Kagi et al. 1994). In respect of the impact origin, we recently suggested (Shelkov et al. 1994) that Brazilian and Ubangui carbonados might have a common provenance, the link being a giant crater, proposed to explain the magnetic anomaly spread over 700,000km² of Central Africa (Girdler et al. 1992). This feature is Precambrian in age; plate tectonic processes may have subsequently separated the diamonds generated. No one explanation is completely satisfied in terms of previous observations concerning carbonado e.g. REE patterns, $\delta^{13}\text{C}$ values and radiogenic noble gases (Ozima et. al. 1991, Kaminsky, 1991 and Kagi et al. 1994). The current work reports new data aimed at identifying links between the two populations of carbonados. For reference, we also report some results for other forms of polycrystalline diamond.

Samples and experimental technique: Herein we investigate nitrogen abundance and its isotopes with carbon isotopic composition for samples of carbonado from Ubangui and Brazil along with specimens of framesite from the Jwaneng and Orapa kimberlite pipes (Botswana) shock diamonds from the Popigai crater and a sample of Yakutite (a distinct form of carbonado from Siberia). Samples were prepared prior to analysis by either chemical (perchloric acid) treatment with further preheating (1150°C - 4 hours) or just preheating (1150°C - 4 hours) under vacuum. Extraction of C and N was accomplished by bulk combustion at 1150°C. N abundance and isotopic composition were measured by static mass spectrometer and C isotope ratio by dynamic mass spectrometer. Reproducibility of the measurements as indicated by investigation of an internal diamond standard (diamond powder 10-15 microns), $\delta^{13}\text{C} = -11 \pm 0.4\text{‰}$, $\delta^{15}\text{N} =$

$-4 \pm 0.5\text{‰}$, N abundance = $1050 \pm 50\text{ppm}$; the errors are 1σ calculated from 10 measurements. $\delta^{15}\text{N}$ values of standards and samples are blank corrected and adjusted for non-nitrogen contributions estimated from the ion $m/z = 30$.

Results: Our results are summarised in the Table. There is essentially no difference between our $\delta^{13}\text{C}$ for individual Brazilian carbonado and the results obtained by Galimov et al. (1985). Based on our data, carbonado from Ubangui are indistinguishable from those collected in Brazil in respect of $\delta^{13}\text{C}$, N abundance and $\delta^{15}\text{N}$. One sample from Ubangui was so different from all the others ($\delta^{13}\text{C} = -6\text{‰}$ (repeated measurements) $\delta^{15}\text{N} = 22\text{‰}$ as to be totally unrelated to the main dataset; the cause of this huge discrepancy is presently unknown.

Whereas Brazilian and Ubangui carbonados are similar they can easily be discerned from framesites which have a higher N abundance and are enriched in ^{13}C and ^{15}N isotopes. We were unable to distinguish framesites from different kimberlite sources. Both the Jwaneng and Orapa pipes contain normal single crystal diamond with isotopic compositions similar to the framesites studied here. We did not encounter any of the isotopically heavier framesites measured by others (Kirkley et al. 1991). The Popigai and Yakutite specimens are even more ^{13}C enriched; our Yakutite had a $\delta^{13}\text{C}$ similar to many specimens measured by Galimov (1978). Popigai samples were extremely low in nitrogen (two could not be measured, $< 5\text{ppm}$) but our Yakutite had about the same amount of nitrogen as Brazilian and Ubangui carbonados; previous workers, on the basis of infrared, have suggested the Yakutite might have very low N. More details of studies involving Popigai/Yakutite will be reported elsewhere.

Source	$\delta^{13}\text{C}$	N (ppm)	$\delta^{15}\text{N}$	$\delta^{13}\text{C}^{***}$
Ubangui	-26.32 ± 1.08 (n=5)	67 ± 10 (n=4)*	3.4 ± 2.6 (n=4)*	-26.77 ± 2.54 (n=18)
Brazil	-27.93 ± 1.26 (n=6)	59 ± 18 (n=4)*	2.3 ± 2.8 (n=4)*	
Framesites	-21.20 ± 2.36 (n=9)	122 ± 18 (n=4)*	6.2 ± 4.0 (n=9)	
Popigai	-20.40 ± 1.1 (n=3)	27 ± 8 (n=5)†	6.1 ± 3.7 (n=6)	
Crater	-10.8 ± 1.5 (n=7)			
Yakutite	-13.3 (n=1)	65 (n=1)	1 (n=1)	-14.6 ± 2.68 (n=31)

* For the purposes of averaging, samples more than 3σ away from the mean are ignored.

** From Kaminsky, Oral Presentation 5th Kimberlite Conference.

† Some samples insufficient for nitrogen

Discussion: The current study is based on only a limited number of diamonds. However, the isotopic similarity between two populations of carbonado leads us to believe that formation of both the Brazilian and Ubangui stones took place in closely related, if not the same, event(s). The reservoir C and N isotopic composition of carbonado suggests some connection with a crustal reservoir of carbon because both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ are in the range for organic materials. According to recent data, (Mathez et. al. 1995), moissanite from kimberlites has a similar $\delta^{13}\text{C}$ range, but low values are quite rare for diamonds from kimberlites. There are differences in N and Ar content compared to impact diamonds from the Popigai crater and whilst this does not support the impact hypothesis, it does not deny it either. The mechanism for production of diamonds during catastrophic events is by no means clear (Hough et. al. 1995) and the contributions of carbon from the impactor vs the target are unresolved. So far N abundance and isotopes do not provide the means to divide groups of polycrystalline diamonds unambiguously; this may be due to measurement difficulties for low concentrations or poor sampling statistics. Given that eclogitic type of diamonds may have been produced from crustal carbon sources, it may be difficult to distinguish different processes where the crust is involved.

At the moment the best evidence that carbonados are of impact origin may be the morphological appearance of the specimens (Shelkov et. al. 1995) which have a surface layer explicable only in terms of highly unequilibrated processes. Impact is one of the few naturally known circumstances capable of producing the high P and T conditions required for formation or transformation of diamond.

References:

- Galimov E.M., Kaminsky F.V. and Ivanovskaya I.N. 1978. *Geokhimiya*, no. 3, 340-349.
 Galimov E.M., Kaminsky F.V. and Kodina L.A. 1985. *Geokhimiya*, no. 5, 723-726.
 Girdler R.W., Taylor P.T., Grawley J.J. 1992. *Tectonophysics* 212, 45-58.
 Hough R.M., Gilmour I., Wright I.P., Pillinger C.T. 1995. *Lunar Plant Sci XXVI*, 463-464.
 Kagi H., Takahashi K., Hidaka H., Masuda A. 1994. *Gchim Cosmochim Acta* 58, 2629-2638.
 Kaminsky F.V. 1987. *Dokl Akad Nauk, USSR* 291, 439-440.
 Kaminsky F.V. 1991. 5th International Kimberlite Conference, 136-143.
 Kirkley M., Gurney J., Rickard R., 1991. 5th International Kimberlite Conference, 127-135.
 Mathez E.A., Fogel R.A., Hutcheon I.D. and Marshintsev V.K. 1995. *GCA* 59/4, 781-792.
 Ozima M., Zashu S., Tomura K., Matsuhisa Y. 1991. *Nature* 351, 472-474.
 Shelkov D., Milledge H.J., Verchovsky A.B., Hutchison R., Collinson D.W., Pillinger C.T. 1994 *Meteoritics* 29, 532.
 Shelkov D., Verchovsky A.B., Pillinger C.T., Hutchinson R., Milledge H.J. 1995. *Lunar and Planetary Science XXVI*, 1281-1282.
 Smith V.J., Dawson J.B. 1985. *Geology* 13, 342-343.
 Trueb L.F., de Wys E.C. 1971. *Amer Mineral*, 56, 1252-1256.