

A carbon isotope, oxygen isotope and nitrogen abundance SIMS study of diamonds from Guanaimo, Venezuela

D.J. Schulze*, B. Harte**, J.W. Valley*** & D.M.deR. Channer****

* Dept. Geology, University of Toronto, Erindale College, Mississauga, Ontario Canada L5L 1C6

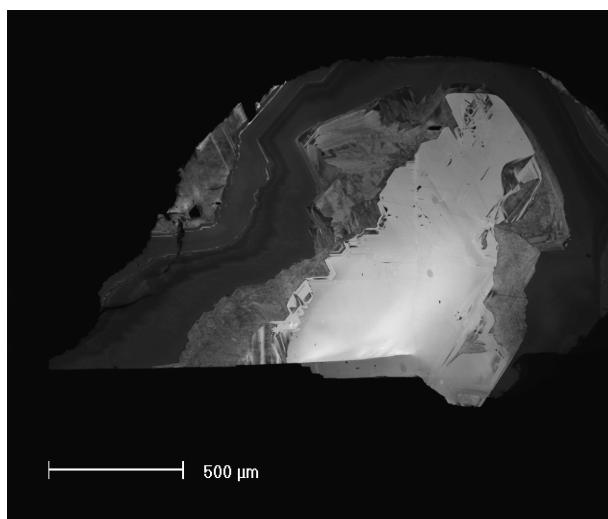
** School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JW

*** Dept. Geology and Geophysics, University of Wisconsin, Madison, Wisconsin, USA 53706

**** Guanaimo Mining Company, Caracas, Centro Gerencial Mohedano, 9D Urb. La Castellana, Venezuela

Introduction

As part of an ongoing study of diamonds and their mineral inclusions from the Guanaimo region of Venezuela, we have investigated the carbon isotope composition and nitrogen abundance of inclusion-bearing diamonds of eclogite-suite. Our initial emphasis has been on those stones for which we have previously used secondary ion mass spectrometry (SIMS) to determine the oxygen isotope composition of garnet and coesite inclusions (Schulze et al., 2003, 2004).



Cathodoluminescence (CL) imaging of polished sections of the diamonds revealed the common presence of complex growth zoning. Based on these images, locations for SIMS analyses in 22 stones with eclogitic inclusions were chosen with the objectives of evaluating possible variations in $\delta^{13}\text{C}$ and N_{ppm} in relation to growth zones and inclusion locations.

Results and Discussion

Within the suite as a whole, the carbon isotope compositions show a wide range, with $\delta^{13}\text{C}$ from -23 to -6‰_{PDB}, and nitrogen contents from <1 ppm to approximately 3100 ppm by weight (2660 atomic ppm). Within individual diamonds variations in both $\delta^{13}\text{C}$ and N_{ppm} are very complex and zoning trends from core to rim vary considerably from stone to stone.

All Guanaimo diamonds studied to date are significantly zoned in either $\delta^{13}\text{C}$ or N_{ppm} , or both. Almost the complete range in these values for the whole diamond suite may be found within individual diamonds. For example, in sample #10, N ranges from 62 to 2660 ppm (Fig. 1) and in sample #34, $\delta^{13}\text{C}$ is in the range -22.3 to -7.5‰.

Examples of core to rim zoning trends are shown in Figure 1. Large changes in N_{ppm} , either increases or decreases, seem to be possible at any stage of diamond growth, and may occur with little change in $\delta^{13}\text{C}$ (see also Harte et al., 1999). Large changes in $\delta^{13}\text{C}$ are usually increases and appear to be most common in the earlier stages of diamond growth. The complexity and variety of $\delta^{13}\text{C}$ and N_{ppm} zoning values are very difficult to harmonise with the “limit sector” values of Cartigny et al. (2001) which are associated with an igneous fractionation model.

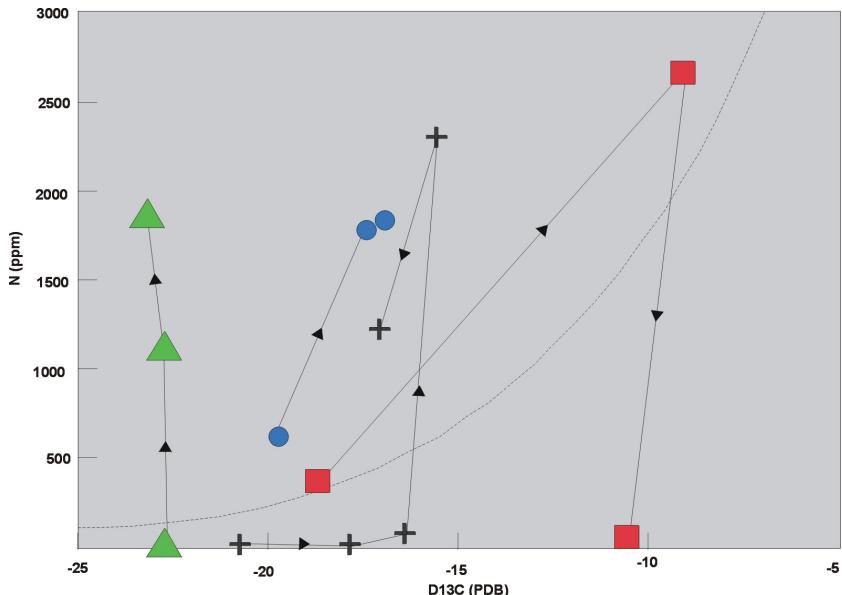


Figure 1: N abundance and C isotope data for some Guaniamo diamonds. Different symbols represent individual diamonds, with arrows indicating compositional changes from the interior to the edge of the diamonds. The curved line represents the “Limit Sector” of Cartigny et al. (2001).

Figure 2 below, illustrates the correlation between the carbon isotope composition of specific Guaniamo diamonds and the oxygen isotope composition of the garnet and coesite mineral inclusions (also determined by SIMS) in the same diamonds. Most of these silicates have elevated $\delta^{18}\text{O}$ values ($>6\text{\textperthousand}$ VSMOW), which cannot be attributed to high-temperature mantle processes (Clayton et al., 1975). In mantle rocks, such elevated oxygen isotope signatures are interpreted as representing subducted oceanic material that had been altered on the ocean floor at low temperatures by interaction with seawater. The $\delta^{18}\text{O}$ values of the diamond inclusion minerals in this study (as high as $+16.9\text{\textperthousand}$) are thus compelling evidence for the subducted nature of the protoliths of at least some diamonds in the Guaniamo suite (Schulze et al., 2003,2004).

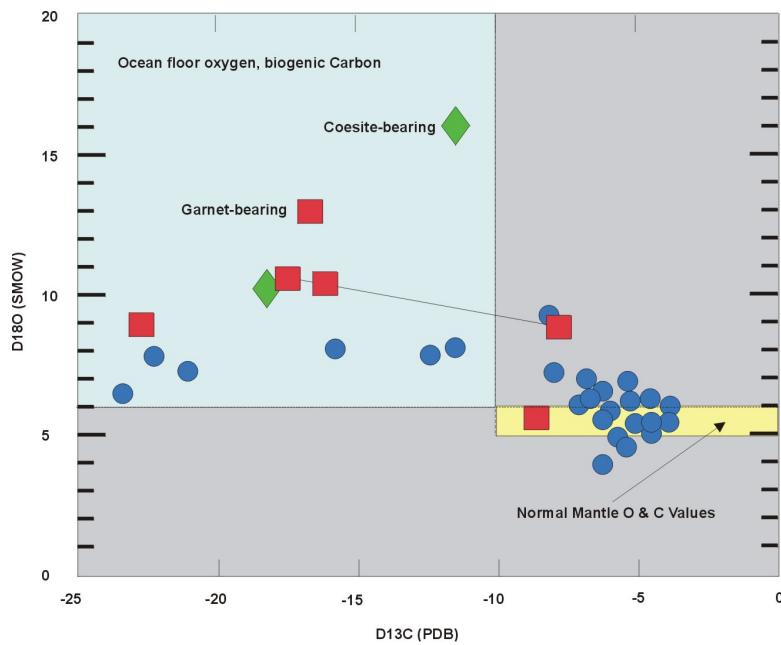


Figure 2: Correlation between C-isotope composition of eclogite-suite diamonds and O-isotope composition of coexisting silicate minerals. New SIMS data from this study on diamonds and their inclusions is shown as diamonds (coesite-bearing) and squares (garnet-bearing). Circles represent data from previous studies of eclogite xenoliths in which silicate minerals and diamonds occur as separate grains. The field marked ocean floor oxygen – biogenic carbon indicates the region in which both the isotope values suggest an original ocean floor origin. The solid box ($\delta^{18}\text{O}$ 5 to 6, $\delta^{13}\text{C}$ 0 to -10) represents the typical oxygen and carbon isotope values found for the mantle.

The explanation for very low (not typical mantle) carbon isotope values ($\delta^{13}\text{C} < -10\text{\textperthousand}$) found widely within diamonds has been controversial. Although many workers interpret such low values as indicating the presence of biogenic carbon subducted into the diamond stability field (e.g., Kirkley et al., 1991), others maintain that igneous fractionation processes within the upper mantle are responsible for such low $\delta^{13}\text{C}$ values (e.g., Cartigny et al., 2001). Our demonstration that such low carbon isotope values occur in the same parts of diamonds that also show silicates possessing extremely high $\delta^{18}\text{O}$ values offers strong support for the subducted biogenic carbon hypothesis. Thus in Figure 2 the Guaniamo diamonds (filled symbols) commonly occur in the upper left quadrant that represents the combined field of OFO (ocean floor oxygen) and BIC (biogenic carbon). On this basis we interpret the relatively large increase in $\delta^{13}\text{C}$ seen in going from the core outwards in many Guaniamo diamonds (Figure 1), as resulting from the mixing of mantle C-O-H fluids with subducted C-bearing material during the growth of the diamonds.

References

- Cartigny P., Harris J.W. & Javoy M. 2001. Diamond genesis, mantle fractionations and mantle nitrogen content: a study of $\delta^{13}\text{C-N}$ concentrations in diamonds. *Earth Planet. Sci. Lett.* 185, 85-98.
- Clayton R.N., Goldsmith J.R., Karel K.J., Mayeda T.K. & Newton R.P. 1975. Limits on the effect of pressure in isotopic fractionation. *Geochim. Cosmochim. Acta* 39, 1197-1201.
- Harte B., Fitzsimons I.C.W., Harris J.W. & Otter M.L. 1999. Carbon isotope ratios and nitrogen abundances in relation to cathodoluminescence characteristics for some diamonds from the Kaapvaal province, S. Africa. *Mineralogical Magazine* 63, 829-856.
- Kirkley M.B., Gurney J.J., Otter M.L., Hill S.J. & Daniels L.R. 1991. The application of C isotope measurements to the identification of the sources of C in diamonds. *Appl. Geochem.* 6, 477-494.
- Schulze D.J., Harte B., Valley J.W., Brenan J.M. & Channer D.M.DeR. 2003. Extreme crustal oxygen isotope signatures preserved in diamond. *Nature* 432, 68-70.
- Schulze D.J., Harte B., Valley J.W., & Channer D.M.DeR. (2004) Evidence of subduction and crust-mantle mixing from a single diamond. *Lithos*.