

# HELIUM, ARGON AND CARBON ISOTOPE CONSTRAINTS ON THE FORMATION OF CUBIC AND POLYCRYSTALLINE DIAMOND

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**Introduction:** Diamonds show the largest variation in He isotopes of any terrestrial materials. The reported  $^3\text{He}/^4\text{He}$  isotope data span the range from crustal radiogenic He ( $^3\text{He}/^4\text{He} \approx 10^{-8}$ ) to values exceeding the planetary value ( $^3\text{He}/^4\text{He} \approx 10^{-4}$ ). Ideally, the primary He isotope composition will reflect the time-integrated  $^3\text{He}/(\text{Th}+\text{U})$  ratio of the diamond growth environment. However, interpretation of the diamond He data is made difficult by the effects of secondary processes that cause changes in  $^3\text{He}/^4\text{He}$  both within and between diamonds (Kurz et al., 1987). Secondary effects leading to a significant increase in  $^3\text{He}/^4\text{He}$  include cosmogenic  $^3\text{He}$  production in alluvial diamonds (Lal et al., 1987) and nucleogenic  $^3\text{He}$  production by  $^6\text{Li}(\text{n},\alpha)\text{T} \rightarrow ^3\text{He}$ , while those causing a decrease in  $^3\text{He}/^4\text{He}$  involve  $\alpha$ -implantation at the diamond surface ( $\leq 20\mu\text{m}$ ; McConville et al., 1991) and zonations of inherited  $^4\text{He}$ , Th and U in the diamond (Kurz et al., 1987).

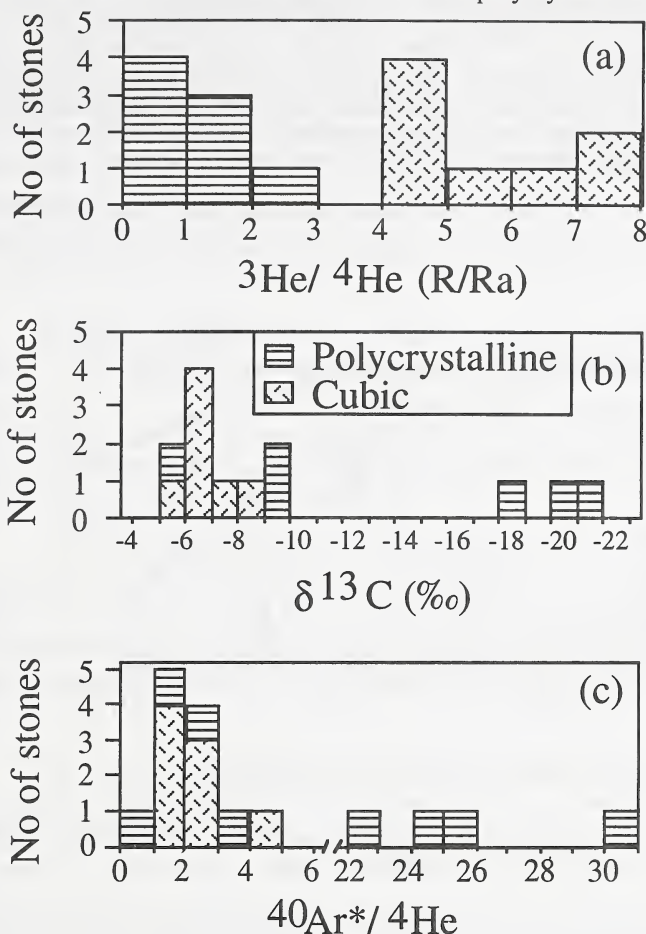
The problems outlined above have a strong influence on the He isotope compositions of gem quality diamond because they contain low total He concentration, however their effect on diamonds with high He contents will be much less important. Analysis of He in volatile-rich mantle fluids in microinclusions in diamond is preferred because the relatively high ambient He content of the mantle means that He isotopes in these fluids are least likely to have been affected by secondary processes and therefore will be most representative of the mantle source. Previously, significant amounts of trapped He were obtained during *in vacuo* crushing experiments on Orapa stones (Kurz et al., 1987), and high  $^4\text{He}$  and  $^{40}\text{Ar}$  contents in an inclusion-rich Sierra Leone diamond were reported by McConville and Reynolds (1989). The work reported here aims to show that He isotope measurements can give important new insights into the origin of diamond especially when used in conjunction with isotopic data from other volatile elements.

**Samples:** Noble gases (Ar and He) and C isotopes were measured in sixteen diamonds containing mantle fluids in microinclusions. All diamonds were from southern African kimberlite sources (Orapa, Jwaneng and Zaire). Two types of diamond were analysed; green or grey cubic diamond (coated stones) and black polycrystalline stones (boart or framesite). He and Ar were extracted from microinclusions by *in vacuo* crushing and carbon isotopes were determined on the crushed residues.

**Results:** The He, Ar and C isotope results are shown as histograms in Fig 1; He isotopes are reported relative to the atmospheric  $^3\text{He}/^4\text{He}$  value of  $1.4 \times 10^{-6}$  (Ra). The total range in  $^3\text{He}/^4\text{He}$  values is between 0.08-7.01Ra (Fig. 1a) and cubic diamonds have distinctly higher  $^3\text{He}/^4\text{He}$  values (4-8Ra) than polycrystalline stones (0.08-3Ra). The lowest  $^3\text{He}/^4\text{He}$  values are close to radiogenic crustal He (0.01) whereas the highest He isotope ratios are close to the value for MORB glass of 8Ra which is considered representative of the degassed mantle.

The two groups of diamonds can also be resolved by C isotope compositions (Fig. 3b). With a single exception the polycrystalline diamonds are all more enriched in  $^{12}\text{C}$  than cubic diamonds, with  $\delta^{13}\text{C}$  extending down to -21.7‰. The cubic diamonds show a more restricted range in C isotopes (-5.9 to -8.2‰) and most are in fairly good agreement with the globally uniform  $\delta^{13}\text{C}$  values for coated stones of about -5‰ (Boyd et al., 1994 and references therein).

All diamonds have  $^{40}\text{Ar}/^{36}\text{Ar}$  greater than the atmospheric ratio (295.5), however there is no obvious difference in this ratio between cubic and polycrystalline diamonds.



**Figure 1.** Histograms of He, Ar and C isotope compositions of diamonds

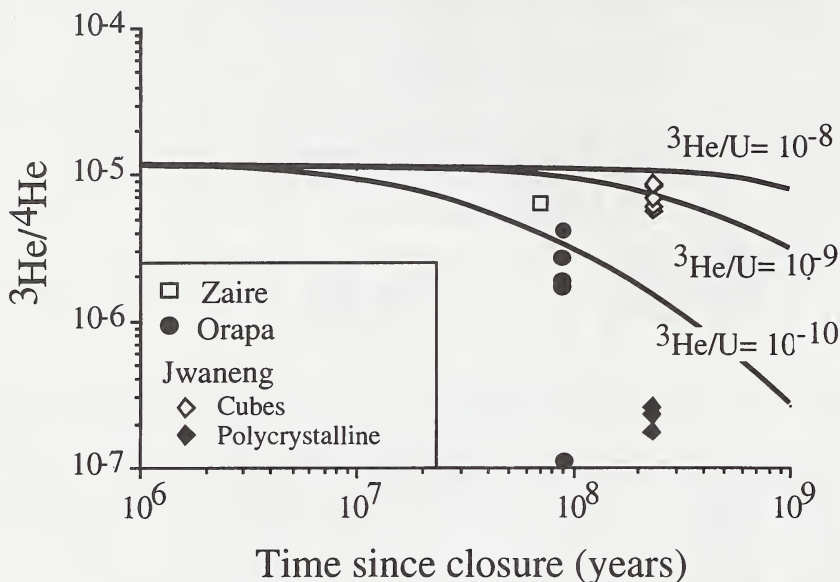
$^{40}\text{Ar}/^{36}\text{Ar}$  values are in the range 370-6000 and these are below the highest values obtained from MORB glass of  $>30,000$ , however this is probably explained by the presence of varying amounts of adsorbed atmospheric Ar on the diamond surfaces that is released during crushing.

$^{40}\text{Ar}^*/^4\text{He}$  are in the range 0.3-30 although most diamonds, regardless of type, have ratios of between 1 and 4. Four polycrystalline stones from Orapa have distinctly higher  $^{40}\text{Ar}^*/^4\text{He}$  values of between 22-30. Diamond  $^{40}\text{Ar}^*/^4\text{He}$  are all above the current mantle production ratio of about 0.18 and, with a single exception, are higher than the "popping rock" value of 0.47, which is considered to represent the least degassed sample of MORB (Sarda and Graham, 1990).

**Discussion:** Polycrystalline and cubic diamonds have different He and C isotope signatures indicating that these two populations of diamonds formed in separate mantle environments.

Cubic diamonds have  $\delta^{13}\text{C} \approx -6\text{‰}$  consistent with primitive mantle carbon, but  $^3\text{He}/^4\text{He}$  are slightly below the MORB value. Therefore, the data suggests that cubic diamonds formed in a region of the subcontinental mantle with isotopic characteristics similar to the present day MORB source. Lowering of  $^3\text{He}/^4\text{He}$  in cubic diamonds can be explained by radiogenic production of  $^4\text{He}$  from *in situ* U and Th decay in the inclusions. Fig. 2 shows closed system He

isotopic evolution for three different  $^3\text{He}/\text{U}$  values assuming that the diamonds initially trapped He with an upper mantle  $^3\text{He}/^4\text{He}$  of 8Ra. Boyd et al. (1994) have argued that cubic diamond growth occurred just prior to host kimberlite emplacement and for Jwaneng kimberlite an age of 245 Ma has been reported (Burgess et al., 1992). Thus, using the most reasonable estimate for the bulk earth  $^3\text{He}/\text{U}$  of  $\approx 10^{-9} \text{ cm}^3\text{STP g}^{-1}/\text{ppm}$  gives  $^3\text{He}/^4\text{He}$  of  $7 \times 10^{-6}$  (5Ra) after 245 Ma closed system evolution which is in good agreement with the observed He isotopic compositions in most Jwaneng cubic diamonds. With only a single measurement available for Zaire it is not possible to assess whether this model applies to cubic diamonds from this source.



**Figure 2.** Closed system He isotope evolution.  $^3\text{He}/\text{U}$  are in units of  $\text{cm}^3\text{STP g}^{-1}/\text{ppm}$ . The bulk earth  $^3\text{He}/\text{U}$  is estimated at  $10^{-9} \text{ cm}^3\text{STP g}^{-1}/\text{ppm}$ .

The diamond  $^{40}\text{Ar}^*/^4\text{He}$  of around 1-30 are higher than typical MORB ratios ( $\approx 0.067$ , Sarda and Graham, 1990). Reduction of the MORB value to below the current mantle production ratio (0.18) has been explained by He/Ar fractionation during degassing due to the higher solubility of He compared to Ar in basalt melts. Therefore, the higher Ar/He ratios of cubic and polycrystalline diamonds can be explained if their noble gases were derived from volatiles expelled during degassing of the mantle source.

Polycrystalline diamonds have anomalous  $\delta^{13}\text{C}$  ( $< -9\%$ ), radiogenic  $^3\text{He}/^4\text{He}$  values and high  $^{40}\text{Ar}^*/^4\text{He}$  compositions (Orapa) that points to growth in a very K-Th-U rich environment. This is shown in Fig. 2 where the low  $^3\text{He}/^4\text{He}$  measured in polycrystalline stones can not be explained by closed system evolution of He unless the region of the mantle in which these diamonds formed has anomalous  $^3\text{He}/\text{U}$  ( $\leq 10^{-10} \text{ cm}^3\text{STP g}^{-1}/\text{ppm}$ ). The C and He isotope data implies that polycrystalline diamonds may have formed in or from subducted crustal material.

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