

NOBLE GASES IN DIAMONDS: OCCURRENCES OF SOLARLIKE HELIUM AND NEON

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Abstract. We have measured noble gases in 17 diamond samples, mostly inclusion free, from diverse, known locations. The ³He/⁴He ratios are characterized by a large spread (10⁴), ranging from values below atmospheric to close to the solar ratio. Highest ratios were seen for an Australian colorless diamond composite and an Arkansas diamond. These samples also have imprecise but intriguing neon isotopic ratios, which are close to the solar value. An origin for the solarlike He and Ne in the diamond samples is unlikely to be accounted for by the presence of nucleogenic or spallogenic components. For single diamond stones a positive correlation is found between ³He/⁴He and ¹³C/¹²C, possibly indicating that heavy carbon is accompanied by primordial helium. However, the He result for the Australian colorless diamond composite with low δ¹³C value requires another explanation, possibly sedimentary carbon contaminated with cosmic dust. The wide variation in ⁴He/⁴⁰Ar ratios observed from diamond samples suggests a complex history for the source regions and the diamond crystallization processes. Results for two Australian diamond composites (colorless and colored), which came from the same kimberlite pipe, are especially notable: the colorless stones contain no radiogenic components but solarlike He and Ne isotopic ratios, whereas the colored stones are enriched in radiogenic and fissiogenic components. Seemingly the Australian diamonds crystallized in a heterogeneous environment in the mantle source region. A pair of Arkansas diamonds, believed to be from a single pipe, exhibits similar anomalies.

Introduction

Because of their supposed mantle origin, chemical inertness, and high temperature/pressure stability, diamonds are suitable for studying noble gases in the mantle. Previous noble gas work on diamonds has shown interesting and puzzling results. Ozima et al. [1983] found high ³He/⁴He atomic ratios (maximum: 3.2 x 10⁻⁴), higher than the planetary (= 1.43 ± 0.20 x 10⁻⁴ [Reynolds et al., 1978]), but not the solar ratio

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(= 4.0 ± 0.4 x 10⁻⁴ [Geiss et al., 1972]) in industrial class diamonds, probably South African in origin. Such a high ³He/⁴He ratio had never before been observed in any terrestrial samples, except ones contaminated by cosmic dust. Calculations based on these data and assumed U and Th contents suggest that the material in the diamonds with high ³He/⁴He ratio has been isolated for times nearly as long as the age of the earth (>4 b.y.). There is another confusing noble gas result from diamonds. Melton and Giardini [1980] reported Ar isotopic ratios from crushing of a 6.3 carat sample of Arkansas (United States) diamond; their value of the ⁴⁰Ar/³⁶Ar ratio is extremely low (=189) versus the atmospheric value of 295.5. Such a low Ar ratio has never been found before in a terrestrial sample. If that result is valid, some diamonds originate in a region of the mantle from which we have never before sampled noble gases.

Enticed by those results, we have undertaken a study to reexamine noble gases in diamonds. Our approach is to study well-documented, inclusion-free (if possible) diamond samples from different locations and to measure all the noble gas elemental abundances and as many of the isotope abundances as possible. This paper updates preliminary results reported earlier [Honda et al., 1985a, b].

Analytical Procedures

Samples

Most of the diamond samples have been examined for texture and screened for inclusions by one of us (E.R.); exceptions are the industrial class and Zaire diamonds (hereafter IDn and ZAI, respectively). Samples ID1, 2, 3, and 4 were obtained commercially from a diamond dealer. ID1 is a composite of 12 small individual stones with few solid inclusions. ID2, 3, and 4 are single stones. They have significant inclusions, and their crystal form is very irregular. Five gem-quality South African individual stones were donated by De Beers Consolidated Mines, Ltd. A type I diamond was collected from the Premier pipe which is known to be of Precambrian age (1.25 b.y.) (PR1). Both type I and II diamonds were collected from the Finsch pipe (FI1 and 2) and from among the De Beers, Wesselton, Dutoitspan, and Bulfontein pipes (DE1 and 2). These last five pipes are known to be of Cretaceous age (J. B. Hawthorne, De Beers, private communication, 1985). All the samples

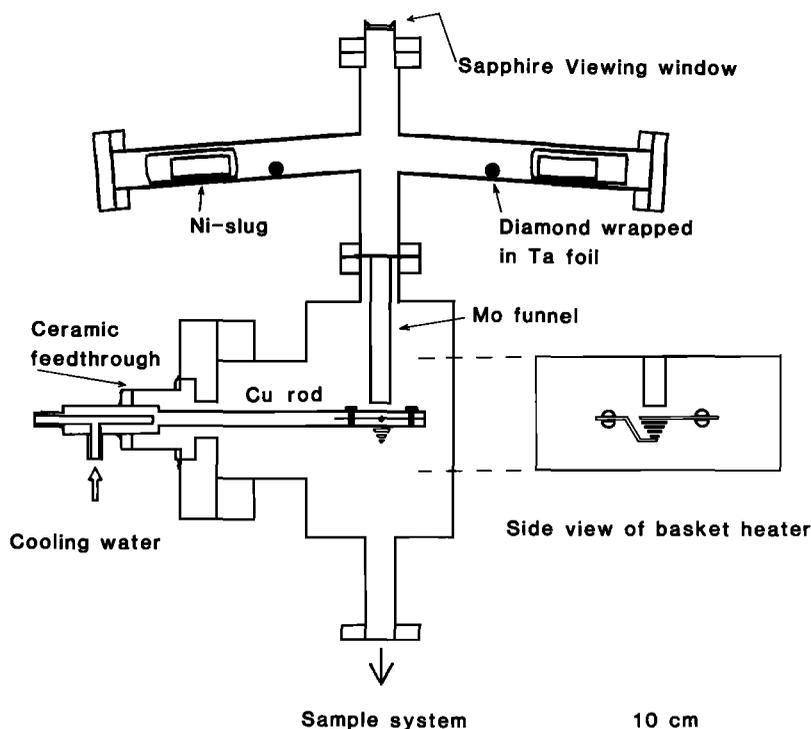


Fig. 1. Furnace for preheating and graphitization of diamond samples.

show very slight birefringence except along some cracks. Thirty-seven small individual stones (10 mg average weight) from the Argyle region, Western Australia, were donated by the CRA Exploration Pty., Ltd. The stones all come from the one pipe in the Argyle region (W. J. Atkinson, CRA Exploration, private communication, 1985). All are clear, inclusion-free stones, but some stones show overgrowth and/or deep pits. We have made two composite samples based on color of the stones; colorless (12 stones) and orange or pale-brown (25 stones) (ACL and ACO). Two gem-quality Arkansas diamonds (catalog numbers 125974 and 149577) were obtained from the U.S. National Museum (USNM). The sample 125974 (AR1) consists of the fragments remaining from previous crushing for Ar isotopic analysis by Melton and Giardini. They did not obtain a publishable value for the ratio $^{40}\text{Ar}/^{36}\text{Ar}$ from this sample but suspected it was anomalously low. A detailed description of AR1 appears in Roedder [1984]. Sample 149577 was donated to the USNM in 1922. Although there is no absolute certainty about its Arkansas origin (J. S. White, USNM, private communication, 1985), those familiar with the appearance of Arkansas diamonds vouched for its authenticity. The sample as received consisted of a slightly rounded dodecahedron that had been sawed in half through the middle parallel to the (100) plane. We crushed one-half into smaller fragments and separated them into two samples (AR2 and 3) in order to check for reproducibility of noble gas amounts and isotopic ratios. The other half was sent to the Department of Earth and Planetary Sciences, Washington University, St. Louis, for neutron activation analysis.

The small diamond stones from Diamantes

Garimpos Aragarças, Brazil, were obtained through U. Cordani of the University of São Paulo. The stones have rough surfaces, composed of many steplike facets of cubic, octahedral, dodecahedral, and/or tetrahedral forms. The stones were split into two composites based on the degree of inclusions; with inclusions (12 stones, BIN) and without inclusions (10 stones, BCL). A single stone (BCD) which is a milky white rounded cube with multiple surface facets was analyzed for noble gases with an expectation of an enrichment in noble gases. A half-cut Zaire cubic diamond (ZAI) was obtained through M. Ozima of the University of Tokyo, and noble gas analysis for the other half of the sample is in process there. We have many more descriptive data on these samples in our files than are presented here.

Prior to noble gas analysis, samples were cleaned in equal parts of 18% HF and 41% HNO_3 for 8 hours in an ultrasonic bath. They were then washed ultrasonically in, successively, distilled water, 50-50 acetone and methanol, and finally ethanol.

Gas Extraction

The noble gas content of pure diamonds is so low and the release temperature so high that the task is about as difficult as can be encountered in noble gas mass spectrometry. In our case it was necessary to completely redesign the furnace and extraction system for the spectrometer system. The furnace (Figure 1) is a tungsten coil configured as a "basket" and housed in an air-cooled stainless steel enclosure. Samples, wrapped in tantalum foil, were vacuum-dropped

into the basket through a guiding funnel from a stainless "Christmas tree." Temperatures can be measured with an optical pyrometer through a viewing window above the heater. A power of 600 W is applied to the heater. Under these conditions the samples were heated to an indicated temperature of 2000°C, where graphitization is rapid [Evans, 1979] (see below) while the tungsten coil has an indicated temperature of 2300°C, as estimated from blank runs.

The sample system is fabricated from stainless steel in a compact geometry which permits the entire assembly, including the furnace, to be baked as a unit. The total volume of the sample system is 800 cm³. After 72 hours or more of baking at 250°C, the sample system pressure is 3×10^{-10} torr or less. The basket heater is outgassed at an indicated temperature of 2400°C at least 8 hours preceding the taking of a procedural hot blank. If the hot blank is satisfactory, a sample is dropped, preheated to 1000°C for 30 min to pump off noble gases from air contamination of the sample and foil, and then graphitized at 2000°C for 10 min. Gases in the foil were measured by the same procedure as used for samples but gave zero amounts when blank corrected. No contaminating gases from the foil were observed as sometimes occurs with reprocessed tantalum (H. Craig, University of California, San Diego, private communication, 1986). A model AP-10 appendage pump (S.A.E.S. Getter, Milan, Italy) and a titanium flash getter were used for gas cleanup. Stainless steel sieve material (Nupro SS-8Fe-7) was used instead of charcoal for noble gas separation. The release temperatures used for He+Ne, Ar, Kr, and Xe are -196 (LN₂), -140, -100, and 100°C, respectively.

Noble Gas Mass Spectrometry

Noble gases were analyzed in a Reynolds [1956] type glass mass spectrometer, locally designated as BMS4. The procedures for data analysis were similar to those previously reported by Srinivasan [1973], Kyser and Rison [1982], and Poreda and Radicati [1984].

Our system is not the ultimate one for ³He/⁴He work because it involves a small glass mass spectrometer which cannot resolve the ³He⁺, HD⁺, and H₃⁺ peaks. There is also a small amount of ⁴He diffusion into the spectrometer during runs. Nevertheless, when equipped with the sample system just described, our system is reasonably competitive with the best systems used elsewhere for helium abundance mass spectrometry. The hydrogenic interference to ³He was corrected based on the H₂ peak. The "3/2" correction factor was determined from measurements of mass 3 and 2 in the background, as 7.27×10^{-4} . A conservative 100% error was assigned to this factor in all the calculations made in this paper. The residual hydrogenic contributions at mass 3 correspond in size to a ³He signal of 2×10^{-13} cm³ STP. The discrimination for measuring ³He/⁴He ratios has been determined by analyzing gas from a pipette filled with a helium sample from Yellowstone National Park (YS-5) which has been measured in our lab at Berkeley (using a large metal mass spectrometer with a nonmagnetic ion source, result 15.7 ± 0.2 times the air

value) and at the University of California at San Diego (result 16.2 ± 0.3 times the air value). Despite use of a steering magnet in our ion source, the correction factor for discrimination is reasonably close to unity (0.906 ± 0.039).

For Ne isotopic measurement it is necessary to correct for interference from ⁴⁰Ar⁺⁺ and H₂¹⁸O⁺ to ²⁰Ne, and CO₂⁺⁺ to ²²Ne. Those correction factors were as follows: (20/40) = 0.155 ± 0.039 , (20/18) = 0.00205 ± 0.00051 , and (22/44) = 0.0046 ± 0.0011 . A generous 25% uncertainty has been assigned to each of those correction factors; observed variations in the measured values are more nearly 5% on the average. The interferences typically contribute 20% and 30% to the blank levels of ²⁰Ne and ²²Ne, respectively. The average ²⁰Ne/²²Ne and ²¹Ne/²²Ne ratios for over 30 hot blanks, after interference and mass discrimination corrections, were 10.2 ± 0.4 and 0.029 ± 0.001 , respectively, which can be compared with the accepted atmospheric values of 9.8 and 0.029.

Elemental sensitivities were routinely monitored with two gas pipettes built into the system, one with an air fill and the other with a He-Ne fill from the Yellowstone gas. These pipettes were filled at known pressures and admit known fractions of the reservoir gas. In addition, independent sensitivity checks were made against weighed quantities of a glass containing noble gases which were assayed by isotopic dilution in another Berkeley system, BMS6 (G. Lux, Solubility and diffusivity of noble gases in silicate liquids: With applications to natural samples, submitted to *Geochimica Cosmochimica Acta*, 1986]. These cross checks plus measurements in BMS6 of the Bruderheim standard have standardized the sensitivities of various Berkeley systems satisfactorily within 10%.

As mentioned earlier, the ⁴He blanks are somewhat high due to helium diffusion through glass, namely, 3×10^{-9} cm³ STP. For ²²Ne, ⁴⁰Ar, ⁸⁴Kr, and ¹³²Xe, the typical blanks are 5×10^{-12} , 2×10^{-9} , 1×10^{-13} , and 1×10^{-14} cm³ STP, respectively.

Carbon Isotopic Analysis

After the noble gas analysis at Berkeley, the graphitized diamond in Ta foil was retrieved from the W basket heater and stored in a plastic vial for a few months before combustion and carbon isotopic analysis at Pasadena. Each carbon isotope run consumed about 3 mg of graphite, partly powder but partly small chunks which, for the composite samples, were probably often relics of small individual stones. A standard analytical technique was used for the combustion of the diamonds. Briefly, the graphite was sealed with an excess of CuO in a highly evacuated quartz tube and heated to 1000°C for about 16 hours. After cooling, during which the surplus oxygen combined with the cuprous oxide, the CO₂ was taken up for isotopic analysis. In a few of the runs it appeared as if small traces of ungraphitized diamond had been present and had failed to combust completely, but our tests on several diamonds show that no significant fractionation of carbon isotopes occurs due to

partial combustion. For example, an Arkansas diamond combusted to 65% completion produced CO₂ of a $\delta^{13}\text{C}$ value of -9.5‰ . The next 13% combustion produced CO₂ where $\delta^{13}\text{C}$ was also -9.5‰ .

Results and Discussion

Step Heating Experiment

There is an inconsistency in the literature about the rate of He volume diffusion in diamond. Luther and Moore [1964] studied the He diffusion coefficient in diamond using a synthetic crystal, doped with boron, irradiating the sample with neutrons, and creating ⁴He atoms by the ¹⁰B(n,α) reaction. They then measured the He released in a step heating experiment. Their measured diffusion coefficient is extremely high:

$$D_{\text{He}} = 7.0 \times 10^{-4} \text{ cm}^2/\text{s} \times \exp(-23.4 \pm 4.9 \text{ kcal}/RT)$$

for $1510 < T < 2470 \text{ K}$.

If their result applies to natural diamonds, He in them should be geologically mobile, even at moderate temperatures. Göbel et al. [1978], on the other hand, worked with helium-bearing diamonds from urelites and obtained a ³He diffusion constant of $D/a^2 = 10^{-6}/\text{s}$ at 1230°C, where a is the radius of the diamond crystals. Since their values of a were $< 1 \mu\text{m}$, their He diffusion coefficient is at least 7 orders of magnitude smaller than the value obtained by Luther and Moore [1964]. In preliminary runs, we investigated this question by a step heating experiment with an industrial-class diamond (ID2). Successively heated for 30 min at indicated temperatures of 1200, 1700, 2000, and 2050°C, the fractional releases of ⁴He were 0.007, 0.027, 0.964, and 0.002, respectively. This experiment shows almost all the helium to be released along with the 2000°C graphitization of the sample and has given us confidence in our measurements of temperature [Evans, 1979]. If the release is treated as volume diffusion from a 5-mm-diameter sphere (which approximates the size and shape of the sample), the relative amounts of helium released at 1700 and 2000°C give an activation energy of 270 kcal/mole and a pre-exponential factor (D_0) of $1.8 \times 10^{21} \text{ cm}^2/\text{s}$. The activation energy obtained, which does not depend upon our geometrical assumptions about the diffusion zone(s), is 10-fold higher than for helium diffusion in silicates and close to that for graphitization of diamond at zero pressure (253 kcal/mole [Evans, 1979]). Our results imply that helium is immobile in gem-sized diamonds even for times approaching the age of the earth and storage temperatures of about 1000°C. Because the heavier noble gases have even smaller diffusion coefficients, they too would be geologically immobile.

A Crushing Experiment: Noble Gas Heterogeneity in Diamonds

Nitrogen is the most abundant contaminant in most diamonds. Type I diamonds contain up to 0.34 wt. % of nitrogen. Some, but not all, of the nitrogen is trapped as a volatile in supposed fluid inclusions [Bibby, 1982], and small amounts

of nitrogen have been released on crushing of diamonds [Melton et al., 1972]. Since noble gases are also volatile and inert, it is possible that noble gases are trapped in those sites together with nitrogen. In order to test this hypothesis, one of the gem-class diamonds was cut in half along the (001) plane (FI1a), and one part crushed in air to a modal size of 100 μm (FI1b). The ⁴He amount of the crushed sample was $(3.1 \pm 0.2) \times 10^{-7} \text{ cm}^3 \text{ STP/g}$; by comparison with the result for the uncrushed sample given in Table 1, we infer that 40% of the He was lost during crushing, if He was uniformly distributed in the diamond stone. No significant differences were detected for the other noble gases between the crushed and uncrushed samples owing to the low noble gas concentrations. However, the apparent homogeneity cannot be generalized. The noble gas results for AR2 and 3, which were split from a single gem and moderately crushed, did not show consistency with respect to noble gas amounts and isotopic ratios. The ⁴He amount for the AR3 was only 34% higher than that of AR2; on the other hand, the ³He amounts for the two samples were very different ($237 \pm 57 \times 10^{-13} \text{ cm}^3 \text{ STP/g}$ for AR2 versus $< 24 \times 10^{-13} \text{ cm}^3 \text{ STP/g}$ for AR3). This indicates that noble gases other than ⁴He are trapped in diamonds heterogeneously. This observation may prove to have important implications with further development of the subject. It has previously been observed that nitrogen is inhomogeneously distributed in a diamond [Seal, 1965]. Bibby [1982] has inferred from that fact that type I diamonds can have a sufficiently slow growth rate that the extent of nitrogen uptake can vary as growth proceeds. As much as 4‰ variations in C isotopic composition have been observed in individual stones [Swart et al., 1983]. It is possible that the C isotopic variation was produced by the incorporation of carbon of a different isotopic composition during a multistage-formation process. Therefore the heterogeneous distribution of noble gases from the two samples, AR2 and 3, is a complication consistent with what has been seen earlier for nitrogen amounts and carbon isotopes. Instead of the ⁴He loss in crushing, it is quite possible that the difference in ⁴He abundance between the uncrushed and crushed FI1 samples reflects noble gas heterogeneity in the gem.

Helium Isotopes

Our helium results are shown in Figure 2a, where we have plotted the ³He/⁴He ratio versus the ³He concentration. The values are replotted without the analytical errors in Figure 2b so as to exhibit the trends better. Figure 2b also contains the values obtained at Tokyo by Ozima et al. [1983]. The lines with 45° slope are lines of constant ⁴He concentration. Berkeley data points with arrows indicate upper limits for the measured ³He content. The data are characterized by a large spread (4 orders of magnitude) in ³He/⁴He, ranging from values well below the atmospheric ratio to values well in excess of the planetary (but not the solar) ratio. We have thus confirmed that some diamonds have a higher ³He/⁴He ratio than any other terrestrial materials including midocean ridge basalts, or

TABLE 1. Noble Gas Elemental Abundance, He and Ar Isotopic Data

Sample [Mass (mg)]	Sample Character	³ He, ×10 ⁻¹²	⁴ He, ×10 ⁻⁶	³ He/ ⁴ He, ×10 ⁻⁶	²² Ne, ×10 ⁻¹²	³⁶ Ar, ×10 ⁻⁹	⁴⁰ Ar/ ³⁶ Ar	⁸⁴ Kr, ×10 ⁻¹²	¹³² Xe, ×10 ⁻¹²
ID1	C,U	2.90	0.549	5.70	*	*	*	*	*
[211.3]		±1.02	±0.047	±1.93					
ID2	S,U	1.15	4.75	0.24	*	*	*	*	*
[159.5]		±0.97	±0.24	±0.20					
ID3	S,U	49.0	22.3	2.20	<19	0.180	1240	16.1	13.6
[127.6]		±14.0	±1.2	±0.63	†	±0.033	±220	±6.5	±1.6
ID4	S,U	4.2	12.5	0.34	<6.0	0.0155	384	5.17	0.430
[143.6]		±2.9	±1.4	±0.24	†	±0.0045	±36	±0.46	±0.031
PR1	S,M	0.83	0.26	3.2	<4.9	0.093	295	1.84	0.443
[212.9]		±0.61	±0.11	±2.7	†	±0.018	±7	±0.82	±0.045
FI1a	S,M	0.23	0.524	0.44	20	0.015	267	0.68	0.194
[110.5]		±4.23	±0.028	±8.08	±22	±0.020	±37	±0.34	±0.031
FI1b	S,F	1.2	0.310	3.96	19	<0.020	-	<0.73	<0.17
[128.1]		±2.8	±0.015	±9.15	±20	†	†	†	†
FI2	S,M	0.55	0.164	3.0	<11	<0.081	-	0.87	0.220
[200.7]		±0.90	±0.010	±4.9	†	†		±0.47	±0.031
DE1	S,M	0.27	0.0236	12	4	0.027	263	1.39	0.457
[255.8]		±0.65	±0.0035	±28	±13	±0.017	±44	±0.37	±0.023
DE2	S,M	1.0	0.0249	42	7	0.020	381	2.63	0.207
[216.0]		±1.1	±0.00373	±46	±13	±0.011	±64	±0.66	±0.049
ACO	C,U	0.57	12.7	0.045	<20	0.0013	2800	0.05	0.008
[232.9]		±0.86	±0.6	±0.068	†	±0.0075	±16400	±0.15	±0.025
ACL	C,U	7.63	0.049	157	130	0.003	180	0.21	0.002
[114.3]		±1.73	±0.020	±75	±61	±0.028	±540	±0.32	±0.031
AR1	S,M	12.0	177.0	0.07	<320	0.14	670	2.6	0.29
[16.2]		±24.0	±5.0	±0.14	†	±0.04	±140	±2.5	±0.27
AR2	S,M	23.7	0.295	81	184	0.013	287	0.43	0.078
[123.2]		±5.7	±0.024	±18	±35	±0.005	±16	±0.18	±0.037
AR3	S,M	<2.4	0.395	<6.2	<59	<0.11	-	<0.13	<0.11
[91.0]		†	±0.020	†	†	†		†	†
BCD	S,U	3.5	2.07	1.7	490	0.52	5160	9.5	2.2
[16.5]		±25.7	±0.12	±12.4	±410	±0.12	±550	±2.5	±0.3
BCL	C,U	0.72	0.800	0.90	<9.9	0.187	39000	1.08	0.238
[130.1]		±3.10	±0.011	±3.88	†	±0.081	±17000	±0.31	±0.041
BIN	C,U	21.1	10.3	2.04	<41	0.0744	1490	0.14	0.117
[97.3]		±5.3	±0.5	±0.51	†	±0.0083	±140	±0.55	±0.042
ZAI	S,U	6.8	0.979	6.9	<52	0.087	14200	0.38	0.048
[72.5]		±2.3	±0.014	±2.3	†	±0.016	±2600	±1.13	±0.085

Sample origins: ID1, 2, 3, and 4 are industrial class diamonds of mixed locations; PR1 is Premier pipe, South Africa; FI1, 2 are Finsch pipe, South Africa; DE1, 2 are De Beers pool from three distinct pipes (see text), South Africa; ACO is Australian colored composite; ACL is Australian colorless composite; AR1, 2, and 3 are Arkansas diamonds; BCD is Brazilian milky white cloudy diamond; BCL is Brazilian clear composite; BIN is Brazilian composite with inclusions; and ZAI is Zaire cubic diamond.

Sample character: S, single stone; C, composite of small individual stones; U, uncrushed; M, moderately crushed (>2 mm in diameter); and F, finely crushed (~100 μm).

Data have been corrected for procedural hot blank and instrumental mass discrimination. Uncertainties of hot blank are assigned 25% for ⁴He, ²²Ne, ⁸⁴Kr, and ¹³²Xe, and 10% for ⁴⁰Ar. Noble gas amounts are in cm³ STP/g. Errors are one standard deviation. Additional errors for absolute gas amounts are 10% (see text).

†Sample amount less than blank. For these cases an upper limit on the sample amount has been arbitrarily set at 25% of the measured amount.

*These samples were run with an older extraction system in which blanks were high so that amounts of Ne, Ar, Kr, and Xe were not detectable.

MORB's [e.g., Craig and Lupton, 1976] and lavas from hot spots such as Hawaii [e.g., Rison and Craig, 1983]. There is no systematic correlation between the ³He/⁴He ratios and He concentrations. However, the samples which show a high ³He/⁴He tend to cluster around 10⁻¹¹ cm³ STP/g of ³He and 10⁻⁷ cm³ STP/g of ⁴He. The highest ³He/⁴He value (1.57 ± 0.75 × 10⁻⁴) was observed for ACL, while the lowest (<4.5 × 10⁻⁶) was for ACO which, interestingly, came from the same kimberlite

pipe. Two Arkansas samples (AR1 and 2), possibly from the same pipe, also gave wide variations in ³He/⁴He and He content. These variations may reflect heterogeneity of the source region where the diamond formed and will be discussed in greater detail in a later section. The Tokyo data points tend generally to lie along a slope-1 line of constant ⁴He, accompanied by variable amounts of ³He. Our values for the clear stones from South Africa tend to lie in this sequence.

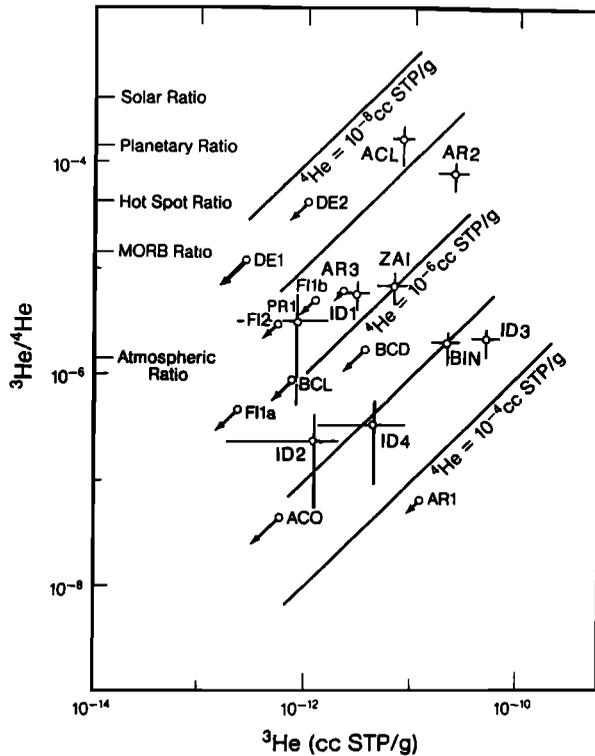


Fig. 2a. $^3\text{He}/^4\text{He}$ versus $[\text{}^3\text{He}]$ for diamond samples measured at Berkeley. For those samples with arrows, only an upper limit for $[\text{}^3\text{He}]$ was obtained.

Although the samples measured at Tokyo were not well characterized, most of them are considered to have come from locales in South Africa. Recently, Ozima et al. [1985] proposed a "calm" mantle evolution model based on their rough correlation between $^3\text{He}/^4\text{He}$ and ^3He content. They assumed that the mantle initially (4.5 b.y. ago) had the solar He ratio ($\approx 4 \times 10^{-4}$) and that since then the mantle has remained a closed and calm system with respect to ^3He and U,Th contents. From the helium isotopic evolution curves, by an addition of radiogenic ^4He to a variable amount of ^3He with the solar helium ratio, they estimated a relatively narrow range of U content (0.1-0.01 ppm) in the mantle where diamonds crystallized. A difficulty we have always seen in their model is that the range of ^3He values (3 orders of magnitude) is much greater than the range of U contents inferred from the data. Much more at odds with the simple model are our data for two of the industrial-class samples (ID3 and 4) and one of the Brazilian samples (BIN).

Neon Isotopes

Because neon concentrations in the diamonds are usually extremely low, we have successfully determined neon isotopic ratios only in few samples (Table 2). Since a large blank correction was applied, as well as interference corrections based upon masses 40, 44, and 18, we cannot eliminate the possibility of an experimental artifact being responsible for these Ne results. Nevertheless, it is interesting to note

that the samples, ACL and AR2, which gave high $^3\text{He}/^4\text{He}$ ratios in our data sets, seem to have a solarlike Ne isotopic ratio (Figure 3). The errors are such that we cannot as yet make a definitive statement, but there is an indication that the neon (as well as the helium) in some diamonds is of solar isotopic composition. The addition of other Ne components, such as spallogenic and/or nucleogenic, to the atmospheric component cannot elevate the tabulated Ne isotopic ratios from atmospheric to solar. For spallation on chondritic targets, $^{20}\text{Ne}/^{22}\text{Ne} = 0.90$ and $^{21}\text{Ne}/^{22}\text{Ne} = 0.91$ [Bogard and Cressy, 1973], so that adding 1%, for example, of spallation ^{22}Ne to the atmospheric component produces $^{20}\text{Ne}/^{22}\text{Ne} = 9.7$ and $^{21}\text{Ne}/^{22}\text{Ne} = 0.038$. The addition of a spallation component to the atmospheric component thus shifts a point almost horizontally from the atmospheric composition in Figure 3. In nucleogenic Ne produced by $^{17,18}\text{O}(\alpha,n)^{20,21}\text{Ne}$ and $^{24,25}\text{Mg}(n,\alpha)^{21,22}\text{Ne}$ reactions, ^{21}Ne is the predominant isotope [Kyser and Rison, 1982]. Therefore addition of a nucleogenic component also cannot elevate Ne isotopic ratios from the atmospheric ratios to the solar. Another possibility for producing the high Ne ratios from the atmospheric value is mass fractionation. To produce a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of 14.2 in the AR2 by mass fractionation of an initially atmospheric component (≈ 9.8), a 43% enrichment of ^{20}Ne relative to ^{22}Ne is needed. If we assume a (gaseous) diffusive process for mass fractionation, maximum $^{20}\text{Ne}/^{22}\text{Ne}$ enrichment in a single stage is 4.9%. At least eight stages

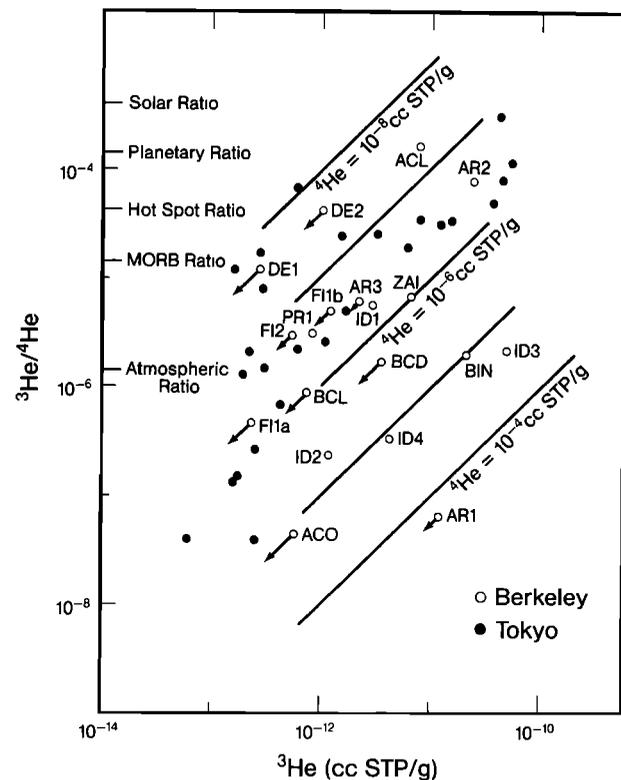


Fig. 2b. Same as Figure 2a but without error bars and combined with values measured at the University of Tokyo (Ozima et al. [1983]; solid circles).

TABLE 2. Ne Isotopic Results for Some Diamond Samples

Sample	^{22}Ne , $\times 10^{-12}$ cm ³ STP/g	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	f ¹
FI1	20 ±22	10.2 ±6.1	0.052 ±0.035	0.80
ACL	130 ±61	12.6 ±1.8	0.0304 ±0.0048	0.65
AR2	184 ±35	14.2 ±2.1	0.0329 ±0.0022	0.31
BCD	490 ±410	10.8 ±2.2	0.0338 ±0.0063	0.76
Hot blank ²	-	10.18 ±0.44	0.0290 ±0.0014	
Air ³	-	9.80	0.0290	
Solar wind ⁴	-	13.6 ±0.3	0.032 ±0.004	
Lunar soil ⁵	-	12.9 ±0.1	0.0313 ±0.0004	
Planetary ⁶	-	8.2 ±0.4	0.024 ±0.003	

Data have been corrected for interferences, instrumental mass discrimination, and hot blank. Errors are one standard deviation.

¹Blank fraction = (^{22}Ne blank)/(^{22}Ne total).

²Average Ne isotopic ratios for 30 blank runs.

³Eberhardt et al. [1965].

⁴Geiss et al. [1972].

⁵Eberhardt et al. [1972].

⁶Black and Pepin [1969].

of diffusive separation would be required to produce the 43% enrichment of $^{20}\text{Ne}/^{22}\text{Ne}$ seen. The larger amounts of ^3He and Ne in the most fractionated samples present another difficulty for mass fractionation since the fractionated output of a multistage diffusive process would most likely be attenuated in amount rather than amplified.

If the isotopic analyses are valid, the solar hypothesis is the most likely one.

We attempted to analyze fragments (AR3) from the same diamond stone as the sample AR2 to confirm the anomalous Ne isotopes. Unfortunately, noble gas amounts from the AR3 did not exceed the hot blank except for ^4He , so the presence of solarlike Ne still remains tentative.

Radiogenic and Fissionogenic Gases

The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios from the diamond samples range upward from the atmospheric value, within uncertainties, to 40,000, so that some diamonds contain radiogenic ^{40}Ar (produced by decay of ^{40}K). The most interesting Ar isotope result is the one for AR1, which was crushed and analyzed for Ar isotopes by Melton and Giardini. We found a $^{40}\text{Ar}/^{36}\text{Ar}$ value of 670 ± 140 and $^{40}\text{Ar} = 9.4 \pm 2.4 \times 10^{-8}$ cm³ STP/g from this sample; the ratio is definitively higher than the atmospheric value. Melton and Giardini [1980] reported that 2.7×10^{-6} cm³ STP/g of Ar with $^{40}\text{Ar}/^{36}\text{Ar}$ of 189 was released during crushing 6.3 carats of another Arkansas diamond. Considering the size of the AR1 fragments (~2 mm in diameter), and based on our crushing experiment with samples FI1a and FI1b, a substantial fraction of the noble gases would still remain in the sample and retain their original isotopic composition, if

the noble gases were located uniformly in the diamond. Thus we expected to be able to confirm the Arkansas $^{40}\text{Ar}/^{36}\text{Ar}$ ratio reported by Melton and Giardini [1980] but we did not. So far no other terrestrial samples contain a verified

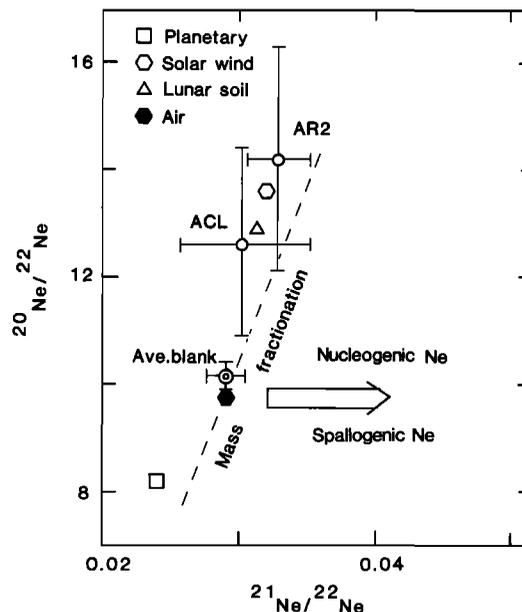


Fig. 3. Isotopic composition of neon from AR2 and ACL which gave high $^3\text{He}/^4\text{He}$ ratios in our data set. Neither the addition of a nucleogenic component nor a spallogenic component to an atmospheric composition can produce the observed neon isotopic ratios (see text).

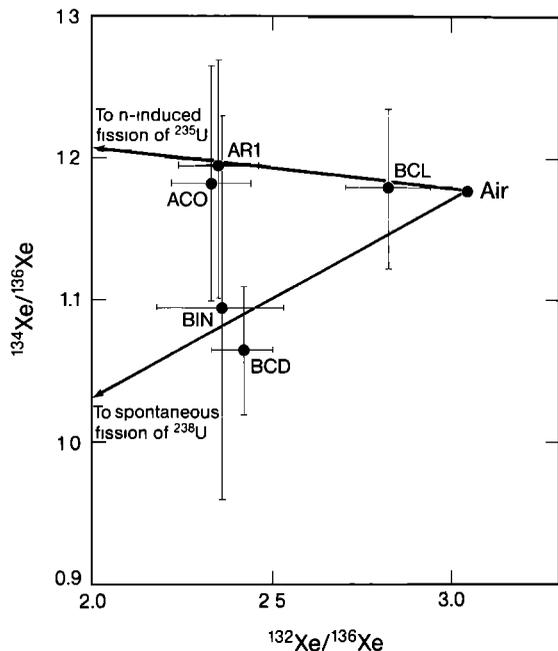


Fig. 4. Three-isotope plot for xenon of fission-like composition seen in the diamond samples. Mixing lines are plotted.

lower ${}^4\text{Ar}/{}^36\text{Ar}$ ratio than the atmospheric value that we cannot attribute to mass fractionation [e.g., Krummenacher, 1970].

The samples with a large ${}^4\text{He}$ content and small amounts of trapped xenon all display fissionlike Xe. Figure 4 plots ${}^{134}\text{Xe}/{}^{136}\text{Xe}$ versus ${}^{132}\text{Xe}/{}^{136}\text{Xe}$ for five samples which gave anomalous Xe spectra. For those samples, hot blank corrections were not attempted, since the blank Xe isotopes are essentially atmospheric (Table 3). Blank subtraction would therefore accomplish little except to compound the errors. Unfortunately, Xe isotopic ratios are not sufficiently

well determined here to distinguish definitively between spontaneous fission of ${}^{238}\text{U}$ and neutron-induced fission of ${}^{235}\text{U}$, which are the dominant possibilities. Fissionlike ${}^{136}\text{Xe}$ was estimated based on the positions of ${}^{132}\text{Xe}/{}^{136}\text{Xe}$ isotopic ratios between the atmospheric value (= 3.04) and either the spontaneous fission spectrum (= 0.595) or the neutron-induced spectrum (= 0.677). Fissionlike ${}^{136}\text{Xe}$ amounts in Table 4 were obtained choosing the spontaneous fission alternative; the ratios of fissionlike ${}^{136}\text{Xe}$ to ${}^4\text{He}$, assumed to be radiogenic, are also set out in Table 4. The ratios, except for two samples (BCD and BCL), are close to both the current production ratio (= 2.2×10^{-9}) and the accumulation production ratio over 4.5 b.y. (= 2.5×10^{-9}), assuming $\text{Th}/\text{U} = 3.7$. Hence three of the five samples support the hypothesis that ${}^4\text{He}$ and fissionlike ${}^{136}\text{Xe}$ were produced by decay of U and Th and have been stored nonselectively for times that may be long.

The ratio of ${}^4\text{He}$ to ${}^{40}\text{Ar}$ of the diamond samples varies from 0.8 to 9,000, where typical values for mantle-derived materials are 1-20 [e.g., Ozima and Podosek, 1983]. The following three possibilities are invoked to explain ${}^4\text{He}$ enrichment relative to ${}^{40}\text{Ar}$ in the diamonds. (1) U and Th were enriched in the source region relative to K, compared with K/U in the ordinary mantle, usually assumed to be 10^4 by weight. (2) The diamonds trapped He preferably to Ar during their crystallization from source regions with the normal ${}^4\text{He}/{}^{40}\text{Ar}$ ratio. In these two cases ${}^4\text{He}$ and ${}^{40}\text{Ar}$ are trapped gases, i.e., not produced in situ. (3) The diamonds trapped U preferentially to K and the daughters, ${}^4\text{He}$ and ${}^{40}\text{Ar}$, were produced in situ. In order to appraise these alternatives, maximum and minimum U contents were calculated based on ${}^4\text{He}$ content and limiting ages for the sample AR1. The estimated U content ranges between 7.3 ppm (using 106 m.y., the emplacement age of the Arkansas kimberlite [Gogineni et al., 1978]) and 0.18 ppm (using 4.5 b.y.), assuming in both cases $\text{Th}/\text{U} =$

TABLE 3. Xe Isotopic Results for Some Diamonds

Sample	[${}^{132}\text{Xe}$], $\text{cm}^3 \text{ STP}$ $\times 10^{-15}$	${}^{128}\text{Xe}$	${}^{129}\text{Xe}$	${}^{130}\text{Xe}$ (${}^{132}\text{Xe} = 1.0$)	${}^{131}\text{Xe}$	${}^{134}\text{Xe}$	${}^{136}\text{Xe}$
ACL	15.0 ± 1.5	0.0755 ± 76	0.834 ± 92	0.119 ± 29	0.673 ± 66	0.508 ± 24	0.429 ± 21
AR1	21.4 ± 1.4	0.0716 ± 61	0.828 ± 55	0.115 ± 17	0.627 ± 49	0.508 ± 20	0.425 ± 21
BCD	48.0 ± 4.8	0.087 ± 11	1.125 ± 88	0.164 ± 10	0.667 ± 18	0.464 ± 46	0.424 ± 31
BCL	51.1 ± 2.6	0.0830 ± 56	1.022 ± 26	0.158 ± 5	0.766 ± 12	0.418 ± 11	0.355 ± 14
BIN	27.2 ± 1.6	0.0767 ± 66	0.986 ± 22	0.159 ± 10	0.768 ± 17	0.440 ± 10	0.413 ± 14
Blank*		0.0736 ± 16	0.992 ± 6	0.15 ± 3	0.785 ± 5	0.380 ± 4	0.317 ± 3
Air†		0.0714	0.983	0.151	0.789	0.388	0.329

Only the analyses which show fissionlike Xe spectra are tabulated. Data have been only corrected for instrumental mass discrimination. Tabulated ${}^{132}\text{Xe}$ amounts are without blank corrections. Errors are one standard deviation.

*Average Xe isotopic ratios for 30 blank runs.

†Nier [1950].

TABLE 4. Radiogenic and Fissionogenic Gases

Sample	${}^4\text{He}$, $\times 10^{-6}$	${}^{40}\text{Ar}$, $\times 10^{-9}$	${}^{136}\text{Xe}$ fission', $\times 10^{-15}$	${}^4\text{He}/{}^{40}\text{Ar}$	${}^{136}\text{Xe}$ fission/ ${}^4\text{He}$, $\times 10^{-9}$
ID3	22.3 ± 1.2	170 ± 15	-	132 ± 14	-
ID4	12.5 ± 1.4	1.4 ± 2.2	-	9000 ± 14000	-
DE2	0.0249 ± 0.0073	1.8 ± 5.2	-	14 ± 41	-
ACO	12.7 ± 0.6	3.2 ± 3.1	8.4 ± 1.6	3900 ± 3800	0.66 ± 0.13
AR1	177.0 ± 5.0	57 ± 27	158 ± 49	3400 ± 1700	0.89 ± 0.28
BCD	2.07 ± 0.12	2550 ± 610	340 ± 110	0.81 ± 0.20	165 ± 55
BCL	0.800 ± 0.011	680 ± 150	11.9 ± 6.3	1.18 ± 0.27	14.9 ± 7.9
BIN	10.3 ± 0.5	89.0 ± 7.4	29.0 ± 4.4	116 ± 11	2.82 ± 0.45
ZAI	0.979 ± 0.014	1200 ± 70	-	0.82 ± 0.05	-

Gas amounts are cm^3 STP/g. Errors are one standard deviation. ${}^4\text{He}$ values are total amounts after blank corrections. ${}^{40}\text{Ar}$ values are amounts after blank corrections and subtracts of 295.5 times ${}^{36}\text{Ar}$. ${}^{136}\text{Xe}$ fission is calculated from ${}^{132}\text{Xe}/{}^{136}\text{Xe}$ assumed to be a mixture of atmospheric Xe (=3.04) and Xe for spontaneous fission of ${}^{238}\text{U}$ (=0.595).

3.7. A measurement of the U content for the sample AR1 was attempted using an ion microprobe, but no detectable signals were found. The detection limit of U measurement is estimated to be 30 ppb with an uncertainty of a factor of 2 [S. P. Smith, Charles Evans & Associates, Redwood City, California, private communication, 1986], which may be an optimistic error estimate because the instrument has been calibrated for silicon samples and not diamonds. This indicates that ${}^4\text{He}$ is not formed in situ but is trapped and U was enriched relative to K in the source region and/or He was elementally fractionated relative to Ar during crystallization of the diamond. The latter possibility seems rather unlikely because the ratio of fissionogenic ${}^{136}\text{Xe}$ to ${}^4\text{He}$ of the diamond (and these gases appear to be trapped) agrees well with the calculated production value, indicating elemental fractionation did not occur between ${}^4\text{He}$ and ${}^{136}\text{Xe}$. Hence it seems most likely that the Arkansas diamond crystallized in a source region where U was enriched relative to K, and it trapped excess He and Ar which had already formed by decay from parent nuclides in the source region.

Th and U contents for the other half of the Arkansas diamond which furnished AR2 and 3 were determined by neutron activation analysis as 0.070 ± 0.010 and <0.05 ppb, respectively [R. Korotev, Washington University, St. Louis, private communication, 1986]. The maximum radiogenic ${}^4\text{He}$ estimation, based on Th content and assuming $\text{Th}/\text{U} = 3.7$ and $T = 4.5$ b.y., is then 3.3×10^{-8} cm^3 STP/g. Compared with the measured ${}^4\text{He}$ amounts in AR2 and 3, 2.95 and 3.95×10^{-7} cm^3 STP/g, we can safely say that the contribution of in situ decayed radiogenic ${}^4\text{He}$ is less than 10% and that almost all the measured ${}^4\text{He}$ amounts are trapped. If we assume that AR2 initially had helium of solar composition, 80% of the measured ${}^4\text{He}$ corresponds to trapped excess ${}^4\text{He}$.

In this context it is interesting to note that in the Arkansas kimberlite pipe the U content correlates directly with the ratio of carbonatite to kimberlite in the specimens. In other words, the carbonatitic materials control the U budget of the kimberlite-carbonatite mix [Brookins et al., 1977]. A large enrichment of ${}^4\text{He}$ relative to ${}^{40}\text{Ar}$ was found in a carbonatite (Premier mine, South Africa), while no enrichment of ${}^4\text{He}$ was observed in a kimberlite sill in South Africa [Kaneoka et al., 1978]. If diamonds crystallized from kimberlitic magmas and if carbonatitic fluids are the carrier of excess ${}^4\text{He}$ (but not comparable excesses of ${}^{40}\text{Ar}$), then the carbonatitic fluids must be mixed with the kimberlitic magmas prior to diamond formation. This mechanism would lead to a positive correlation between excess ${}^4\text{He}$, ${}^4\text{He}/{}^{40}\text{Ar}$, and degree of primary carbonization. We are distinguishing here between primary carbonizing by a carbonatitic fluid and possible secondary carbonizing from contact with carbonate-rich, sedimentary host rocks intruded by the kimberlite diatreme.

The sample available to us from western Australia was a composite of small stones for which one of us (E.R.) recorded enough descriptive data to permit a multifold separation into subclasses. Unfortunately, there was only enough material for two runs. For simplicity, more than anything else, the sample was divided according to the presence or absence of a yellowish brown coloration of the stones. Interestingly, this basis for sample separation was successful in generating samples with different noble gas signatures. The correlation between noble gas results and color is being explored further in additional samples we have obtained from western Australia and from South Africa.

In the case of the Brazilian samples (BCD, BCL, and BIN) the noble gas systematics are more complicated. Among the three Brazilian samples,

BCD has the lowest ${}^4\text{He}/{}^{40}\text{Ar}$ and highest ${}^{136}\text{Xe}/{}^3\text{He}$. The latter value is almost 2 orders of magnitude higher than the production value. On the other hand, BIN has the highest ${}^4\text{He}/{}^{40}\text{Ar}$ and lowest fissiogenic ${}^{136}\text{Xe}/{}^3\text{He}$, which is close to the production value. There is no additional information for the Brazilian diamond stones such as whether or not all stones came from the same location, specification of mineral inclusions, and K, U, and Th contents. Hence we are limited in our interpretation of the noble gas results. However, the Brazilian results may be explained by elemental fractionation. If we assume that all Brazilian diamond stones crystallized from a source region with a constant U/K and Th/U ratios, the result for the inclusion-bearing sample, BIN, could be considered the most representative one, since the fissiogenic ${}^{136}\text{Xe}/{}^3\text{He}$ ratio is close to the production value. In such a case, the results for the inclusion-free sample (and for BCD) suggest that helium was preferentially lost before or during diamond crystallization. Again we would say that almost all the noble gases we measure were trapped during crystallization, now with fractionation, and that the radiogenic and fissiogenic components were not produced in situ.

With respect to the radiogenic and fissiogenic components in diamonds, our results suggest a complex history of the diamond source regions and diamond crystallization processes. In this respect the results for two Australian diamond samples are especially indicative, since they came from the same kimberlite pipe and one (ACL) contains no radiogenic components with anomalous He and possibly Ne isotopic ratios, while the other (ACO) contains highly enriched radiogenic and fissiogenic components. This requires that diamonds crystallized in heterogeneous environments in the mantle source region even though brought to the surface in the same kimberlite pipe. The results we have obtained from Arkansas samples are less definitive, but they suggest the same thing.

The Origin of High ${}^3\text{He}/{}^4\text{He}$ Ratios

Nucleogenic. The range in diamond of α particles produced by radioactive decay from U and Th is about 10^{-3} cm. Hence the α particles from U/Th in adjacent minerals do not penetrate deep into diamonds. On the other hand, the neutron flux produced by the (α, n) reactions and fission is characterized by a comparatively long range (≈ 10 cm) and penetrates more deeply [Mamyrin and Tolstikhin, 1984]. From the neutron flux in the earth's interior, ${}^3\text{He}$ could be produced from the reactions, ${}^6\text{Li}(n, \alpha){}^3\text{H} \rightarrow {}^3\text{He}$ and ${}^{10}\text{B}(n, \alpha){}^7\text{Li} \rightarrow {}^3\text{He}$ if the required target elements are present in diamonds. The nuclide ${}^6\text{Li}$ has a high cross section of 940 barns. Mamyrin and Tolstikhin [1984] state that "in crystals free from trapped helium, an extremely high ratio of ${}^3\text{He}/{}^4\text{He}$ may occur (up to 10^{-3} and higher)" because of the Li reaction. Based on a neutron fluence and a Li content in diamonds, we can estimate the production of ${}^3\text{He}$ in diamonds. The neutron flux in the crust is estimated to be 8 neutrons/cm² · day [Mamyrin and Tolstikhin, 1984]. By assuming that Li content in diamonds is 1 ppm, which is probably the maximum allowable

estimate [Sellschop, 1979], ${}^3\text{He}$ is estimated to be produced at the rate of 7.7×10^{-13} cm³ STP/g per b.y. This is too low to account for the ${}^3\text{He}$ seen in many of the diamonds. However, we cannot exclude the possibility that some diamonds contain high Li amounts capable of producing the observed ${}^3\text{He}$. To explain the observed ${}^3\text{He}$ amount in AR2 (= 2.4×10^{-11} cm³ STP/g), for example, by the Li reaction with the neutron flux over 1 b.y., as stated above, 31 ppm of Li content would be required in the diamond.

Working with an ion-microprobe at the Lawrence Livermore Laboratory, D. Phinney (private communication, 1986) has ascertained that lithium is detectable in a fragment of the Arkansas gemstone we have analyzed as samples AR2 and AR3. Because of lack of calibration data, this observation cannot presently be expressed in terms of a lithium concentration, but the matter is being pursued.

The other possibility for producing ${}^3\text{He}$ is the B reaction. Since B is often the third most abundant contaminating element (next to O and N) given in published analyses, especially in type II diamonds (0.01-10 ppm [Sellschop, 1979]), it might be possible to produce ${}^3\text{He}$ by the ${}^{10}\text{B}(n, \alpha){}^7\text{Li} \rightarrow {}^3\text{He}$ reaction. We can estimate a ${}^3\text{He}$ production rate using a cross section of 3 barns obtained recently by Lal and Craig [1986] and a maximum B content of 10 ppm. The estimated ${}^3\text{He}$ production rate by the B reaction is 1.4×10^{-13} cm³ STP/g b.y. Therefore this reaction does not appear to be a likely explanation for the high ${}^3\text{He}/{}^4\text{He}$ ratio in diamonds. D. Phinney (private communication, 1986) did not see a boron signal in the mass spectrum just alluded to which had a detectable Li signal from the Arkansas stone.

Spallogenic. One may argue that the high ${}^3\text{He}/{}^4\text{He}$ ratio in the diamonds is due to the addition of spallogenic He, induced by cosmic rays, since the spallogenic ${}^3\text{He}/{}^4\text{He}$ ratio is ~ 0.1 [Bogard and Cressy, 1973], depending upon the target elements. In this case two possibilities can be considered for a spallation origin for diamond noble gases: external and internal.

First we will consider the internal origin. In this case, diamonds would be exposed to cosmic rays on the earth's surface and ${}^3\text{He}$ and ${}^3\text{H}$, which decays to ${}^3\text{He}$ ($T_{1/2} = 12.6$ yr), would be produced by reactions ${}^{12}\text{C}(n, \alpha){}^{10}\text{Be}$ and ${}^{12}\text{C}(n, \alpha){}^{10}\text{B}$, respectively. The thresholds for these reactions are 19.5 and 18.9 MeV, respectively. Although cross sections for these reactions are not available, we can estimate the ${}^3\text{He}$ production rate by spallation from ${}^{12}\text{C}$ using cross sections for other appropriate target elements. Neutron cross sections for production of ${}^3\text{He}$ and ${}^3\text{H}$ from Mg, Al, and Si with energy of 30 MeV or higher will be similar to that of protons where for all three elements the cross section rises to a constant value of 10 mb above 30 MeV proton energy [Walton et al., 1976]. We will guess that to within factors of 2 or 3, carbon cross sections are similar. The neutron flux with energies greater than 30 MeV at sea level is estimated to be 1.3×10^{-3} neutron cm⁻² s⁻¹ [Lingenfelter et al., 1972]. Combining the neutron flux with the cross section, the ${}^3\text{He}$ production rate from the C reactions stated above is estimated to be 1.6×10^{-12} cm³ STP/g m.y. at sea level, so that for sample ID3 a sea level

TABLE 5. Carbon Isotope Results for Graphitized Diamond Samples

Sample	$\delta^{13}\text{C}_{\text{PDB}}$
ID1*	-5.6
	-7.5
	-8.2
ID3	-6.8
ID4	-7.5
PR1	-4.6
FI1a	-6.2
FI1b	-6.1
FI2	-4.5
DE1	-4.4
DE2	-5.7
ACO*	-6.3
	-9.8
	-10.1
ACL*	-8.2
	-8.6
	-10.5
AR1	-11.0
AR2	-3.3
AR3	-3.3
BIN*	-4.1
	-9.2
	-13.7
	-15.0

Average sample amount per run is 3 mg. For the single stones the average values from the two or three measurements made are presented. Uncertainty for these results is $\pm 0.1\text{‰}$, except for AR1 ($\pm 0.8\text{‰}$).

*For composite samples, results of all runs are presented.

exposure of 31 m.y. would be required. But the production rate decreases by a factor e every 74 cm, assuming a density of 2.7 g/cm^3 . Reasonable burial histories for mined diamonds, which most of our samples are, are hardly consistent with this process for ^3He production.

In the external origin, spallogenic noble gases would have been produced before the crystallization of diamonds by cosmic rays in space (meteorites) and at high altitudes above sea level (observed in the summit lavas on Maui by Kurz [1986] and by Craig and Poreda [1986]) and then subducted into the earth's interior, where the diamonds crystallize. If we assume all the ^3He content in the ACL and AR2 samples is produced by spallation, we can estimate the spallogenic Ne content based on production ratios of ^3He to ^{21}Ne from the relative data on chondrites ($^3\text{He}/^{21}\text{Ne} = 5.5$ [Bogard and Cressy, 1973]). The estimated spallogenic ^{21}Ne contents for ACL and AR2 are 1.4×10^{-12} and $4.3 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$, respectively. By assuming that measured ^{22}Ne amounts for those samples are a mixture of atmospheric Ne and the spallogenic Ne ($^{22}\text{Ne}/^{21}\text{Ne} = 1.11$), the expected measured $^{21}\text{Ne}/^{22}\text{Ne}$ values are 0.039 and 0.052. These values are far above the real measured ones (see Figure 3). Hence considering the Ne isotopic ratios, an external spallation origin to explain high $^3\text{He}/^4\text{He}$ ratios in the diamonds is unlikely.

Is there a solar component in diamonds? None of the possibilities discussed so far can account for the high He and Ne isotopic ratios observed

from two of our diamond samples. The remaining possibility is existence of a solar component. If we assume that the ^3He contents in the ACL and AR2 are solar in origin and that the noble gas elemental abundance is the same as the abundance observed in lunar soils [Eberhardt et al., 1972], the expected amounts of heavier noble gases (Ar, Kr, and Xe) with the solar component would be below blank levels and could not be seen in diamonds.

There are two possible origins for the solarlike gas in the diamonds: primordial and sedimentary. As to the first possibility, Ozima et al. [1983] suggested that the dust which later accreted to form the earth might have been subjected to intense solar wind radiation after the deuterium burning stage in the sun. Their model was discussed above and leads to estimates of the time of isolation of the helium-uranium system involved which are approximately equal to the age of the earth. There has been an unconfirmed report [Zashu et al., 1985] of excess ^{129}Xe in a Zaire diamond. If confirmed, this observation would lend considerable support to this primordial origin. Why atmospheric neon and xenon differ isotopically from those elements in the solar wind is, of course, a related and unsolved problem.

Alternatively, there are arguments based on the mineralogy of inclusions and on carbon isotopes for diamonds having been formed from sedimentary carbon. Ringwood [1977] argues that high chromium contents, high Mg/Fe ratios, and low calcium contents, which are characteristic of a major clan of garnet inclusions in diamonds, represent an oceanic crust signature. The precursors to these garnets are believed to have formed in magma chambers within the oceanic crust or uppermost suboceanic mantle and to have interacted with sources of carbon in the overlying sediments, so that there is some evidence for possible sedimentary components associated with diamonds. A compilation [Deines, 1980] of all diamond $\delta^{13}\text{C}$ analyses does not simply show a compact, Gaussian distribution centered at -5‰ , which is assumed to be an average value of mantle carbon, and cutting off sharply at -1‰ (relative to PDB) on the high side, but shows in addition a 10% tail on the low side, extending all the way to a value of -30‰ and thereby encompassing the full range of negative δ values seen in terrestrial samples. Deines [1980] and Milledge et al. [1983] speculated that the irregular distribution of $\delta^{13}\text{C}$ values in diamonds reflects the distinctive isotopic signatures of various subducted sedimentary components, such as marine carbonate for heavier carbon and continental sedimentary organic carbon for lighter carbon.

If these speculations are valid, we might be able to see sedimentary noble gas signatures in some diamonds. Merrihue [1964] observed high $^3\text{He}/^4\text{He}$ ($>10^{-4}$) from sea sediments. His results have recently been confirmed by Ozima et al. [1984]. Solar wind-saturated cosmic dust with a diameter less than $10 \mu\text{m}$ contains $0.1 \text{ cm}^3 \text{ STP/g}$ of He [Rajan et al., 1977] presumed to have the solar He ratio because elemental patterns of the noble gases in dust particles measured by Hudson et al. [1981] are solar. Hence only a 1 ppm contamination by cosmic dust in sediments can

produce a measured $^3\text{He}/^4\text{He}$ ratio higher than 1×10^{-4} , which presumably would be accompanied by solar Ne. Thus solar He and Ne in diamonds may originate in cosmic dust that was trapped in sediments and subducted into the earth's interior where diamonds crystallized.

We have measured the $\delta^{13}\text{C}$ values for 15 of our samples, and the results are set out in Table 5. The "replicate" values for the composite samples ID1, ACO, ACL, and BIN tend to scatter, most likely due to sampling various stones preferentially. Carbon isotope ratios in diamond seem to vary according to provenance. The results of six South African diamonds are well clustered (-4.4 to -6.2‰) close to the average carbon value in diamonds. On the other hand, we observed low $\delta^{13}\text{C}$ values from the Australian composite samples ACL and ACO (-6.3 to -10.5‰). The results for AR1 and the single stone furnishing AR2 and AR3, supposedly both from Arkansas, cover the range of $\delta^{13}\text{C}$ values in our data set (-3.3 ; -11.0‰). Figure 5 shows the He isotopic ratio plotted against $\delta^{13}\text{C}$ data. Considering the data for single stones in Figure 5 (open circles), there seems to be a positive correlation between He ratio and $\delta^{13}\text{C}$ value. The points for ACL depart most from the correlation. The plot of He content versus $\delta^{13}\text{C}$ (Figure 6) shows a weaker, but nevertheless convincing, correlation, and again the points for ACL are the most discordant. Our preliminary and intuitive interpretation is that the heavy and primitive carbon is accompanied by primordial helium, with the solar value as a potential end-member. If the fluids which form the diamonds also contain sedimentary carbon

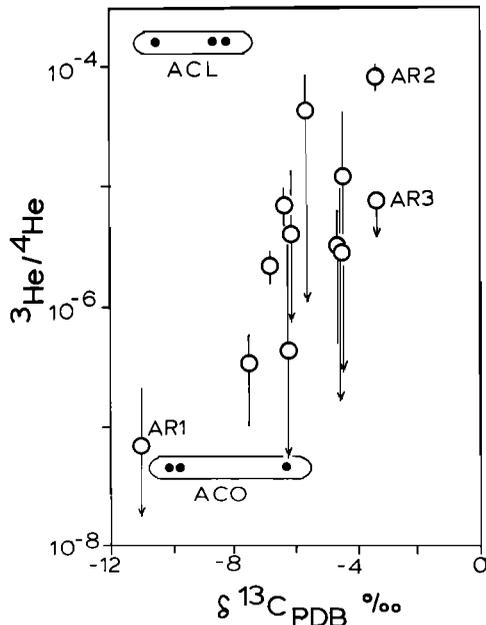


Fig. 5. $^3\text{He}/^4\text{He}$ versus $\delta^{13}\text{C}$ for single diamond stone samples and composite samples from Australia. For the Australian composites, ACL and ACO (solid circles), replicate $\delta^{13}\text{C}$ measurements are plotted. Variability in the $\delta^{13}\text{C}$ values for the composites is ascribed to the "replicates" containing relicts of individual stones.

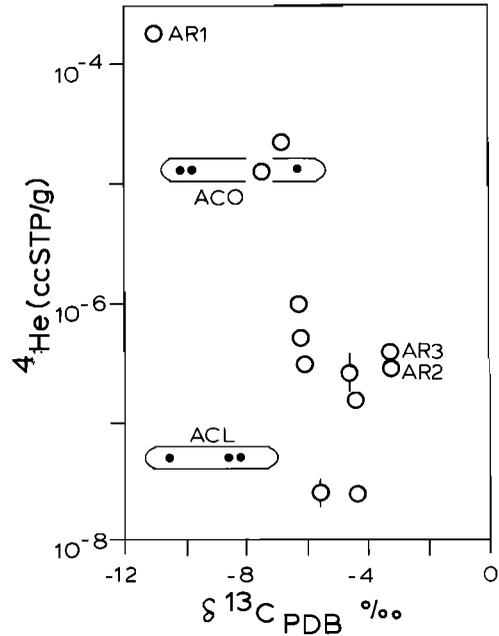


Fig. 6. $[\text{He}]$ versus $\delta^{13}\text{C}$ for diamond samples (see Figure 5).

from the crust, then they are likely to be diluted with crustal helium with lower $^3\text{He}/^4\text{He}$ ratios. In this context, it is interesting to note that postulated mantle sources for hotspot and MORB magmas may differ in $\delta^{13}\text{C}$ [Gerlach and Thomas, 1986; Exley et al., 1986]. Exley et al. [1986] suggested that the Loihi samples, possibly originating from an undepleted (hotspot) source region, contain high $\delta^{13}\text{C}$ accompanied by high $^3\text{He}/^4\text{He}$ compared with the MORB average.

This model seems not to be entirely applicable to the Australian diamond results. The majority of the Argyle, Australia, diamond stones with eclogitic inclusions, which are dominant, have significantly lighter $\delta^{13}\text{C}$ values lying mostly in the range -0 to -12‰ [Jaques et al., 1986], and most of our carbon isotopic results for ACL and ACO are within this range. Because only 10% of ACL was consumed for carbon analysis, one might suppose that the remaining 90% of ACL had heavier $\delta^{13}\text{C}$ accompanied by the solar noble gases and that individual stones fit the correlations. This seems not to be the case, however, simply because the diamond stones with lighter $\delta^{13}\text{C}$ value, accompanied presumably by a high amount of radiogenic helium (Figure 6), would dilute the helium isotopic signature completely; and the high $^3\text{He}/^4\text{He}$ would not be observed, as it was, from the whole of sample ACL. Hence the He results for ACL do not fit the simple model stated above; and another source, possibly sedimentary carbon contaminated with cosmic dust, is required for the solarlike noble gases in the Australian diamond sample.

At present we cannot say with any certainty whether the solarlike noble gases in the diamonds, if indeed solar, are primordial or sedimentary in origin. In either case, however, it needs to be explained how the solar noble gas can be transported without contamination by atmospheric and radiogenic components into the

diamond stable regions; >45 kbar, >1000°C [Bundy, 1980; Gurney et al., 1979].

A related question is why the solarlike noble gas has not been found so far in any other mantle-derived materials. Because this may be due to incomplete sampling, a more complete survey is needed. This discrepancy may be explained on the basis of noble gas diffusion, especially for He. As we stated earlier, He in diamonds is essentially outgassed by the graphitization process, not by the diffusion process. On the other hand, even at moderate temperatures (~1200°C), He can diffuse out from a 1-cm olivine crystal in 50 years [Hart, 1984], and the noble gas diffusion in melt phases is certainly more rapid than in crystals. Although we cannot apply the diffusion result directly to the mantle, especially because we do not know the effect of pressure on the diffusion process, we can at least say that He is probably significantly more mobile geologically in silicates than in diamonds. Therefore noble gas isotopic signatures in silicates would be expected to be better mixed and possibly derived from a broad region of the mantle.

Addendum

We need not lack for more imaginative suggestions as to how diamond sources can exhibit spatial heterogeneity on a short-distance scale. For example, Allègre and Turcotte [1986] have discussed a "marble cake" model for the mantle in which two distinctly different regions are convectively stirred into it and deformed by elongation (thinning) so as to produce global mixing but striking local inhomogeneities, the older layers being all the thinner. The marbling is comprised of oceanic crust, partially depleted by subduction zone volcanism, and a complementary, highly depleted upper mantle. The first of these components would contain radiogenic gases while the second could carry a residuum of primitive and possible solarlike gases. Diamonds originating in these locally disparate regions of ancient marbled mantle could rise in the same pipe but display different isotopic patterns for the dissolved noble gases. Allègre and Turcotte see evidence for their model in pieces of the mantle transported to the surface and displaying a marble cake structure, namely, the high-temperature peridotites, also called orogenic lherzolite massifs, of Spain, Morocco, the Alps, the Pyrenees, and Venezuela.

Another imaginative scenario was provided free of charge, and with license to quote it, by Craig of the Scripps Institution of Oceanography at the University of California, San Diego, who furnished a helpful and thoughtful review of this paper and concluded his remarks thusly:

"Diamonds probably formed in the earth the way they are formed in the laboratory (in general): by precipitation from solution in molten iron. This means that at least the original diamond "cores" date back to earth-core formation, and part of the heterogeneity is due to the range of time (and space) covered by core formation. Blobs of iron were melting throughout the early mantle, and picking up carbon and other junk (including "solar" rare gases in some cases, depending on the surroundings) as they sank

through the mantle. When the iron was saturated with carbon, there was usually a surface which became supersaturated, and the diamonds formed at this surface, trapping (in some cases) solar He and Ne, and probably mixtures with planetary gases in others.

"The stability region of diamonds in the earth has both upper and lower limits, with the lower limit still in the upper mantle. Thus when the sinking iron reached the lower stability limit of diamonds, they could no longer precipitate, and the lower mantle material became homogenized. Only diamonds within the stability zone were preserved: these must have been extremely heterogeneous in carbon isotope ratio, rare gases, inclusions, etc. The hotspot plumes probably come from well below the diamond stability zone, and have quite different rare gas contents which look more like planetary gases.

"The reason that isotopic patterns in the light rare gases in diamonds can differ from atmospheric patterns, as seen in this paper, is the following: the regions where diamonds formed were regions of metallic iron blobs with material containing trapped solar gases (which became trapped in the diamonds when they formed). But the gases in these areas made up only a small part of the rare-gas inventory of the mantle. Most of that inventory consisted of planetary gases which by outgassing produced the atmosphere we now have. This atmosphere is a little bit enriched in ^{20}Ne relative to the plume material now coming up from the mantle, reflecting the early input of a small solar component. It is also a little depleted in ^{20}Ne relative to MORB, because MORB has affinities with the zone in which diamonds formed, and so MORB retained a little of that solar Ne and is enriched in $^{20}\text{Ne}/^{22}\text{Ne}$ vs. the atmospheric neon.

"Diamonds must have been formed over the entire stability zone in which they are stable, ranging in time back to the formation of the earth, which must account for their incredible heterogeneity."

Providing, in turn, a review of Craig's text, just quoted, we think its plausible spontaneity makes up for the lack of polishing, removal of repetitions, and insertion of weakening qualifications to which it would inevitably be subjected if published in the usual way. We are pleased to have it, fresh and unadorned with computations and citations, riding piggyback on and having the last word in our text.

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