Methanol may be the diffusing species. Volume discontinuities perhaps correspond to pressures at which specific fractions of methanol (that is, methanol adsorbed into specific positions in the zeolite framework) are squeezed out. As methanol molecules are removed from the channels and cages the entire crystal becomes progressively more compressible. Gradual reabsorption of methanol into compressed channels and cavities could explain the sluggish reversal of the volume discontinuities. Other possible diffusing species are alkali cations or water molecules, for which rapid movement in zeolite channels might be impeded by the larger methanol molecules.

This novel transition and compression behavior is not restricted to zeolite 4A; preliminary experiments on the potassium-exchanged zeolite 3A reveal the same sequence of volume discontinuities in alcohols, though shifted approximately 3 kbar to higher pressure. It is anticipated that studies on other large-channel zeolites, as well as with other pressure-transmitting fluid media, will also reveal fluid-dependent compression and diffusion-controlled, high-pressure transformations.

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Primitive Helium in Diamonds

Abstract. *Thirteen diamond stones from various unspecified mines in South Africa were analyzed for the isotopic ratio of helium-3 to helium-4. Values of the ratio ranged from less than* 10^{-7} *to* $(3.2 \pm 0.25) \times 10^{-4}$. *The latter value is higher than the primordial helium-3/helium-4 ratio in meteorites and close to the ratio for solar-type helium. Such extremely high values may represent primitive helium that evolved very little (that is, showed very little increase in radiogenic helium-4) since the formation of the earth.*

Characterization of the state of noble gases in the mantle is important for constraining models of the evolution of the earth's atmosphere. A number of attempts have been made to do this by examining the noble gases in mantle-derived materials. Diamonds are unique among such materials because of their extremely high resistance to chemicals and high temperatures, which promises better preservation of the noble gases. In addition, diamonds are thought to originate in the deeper mantle, whose nature cannot be inferred from a study of volcanic rocks. Previous studies on batches of diamond stones (*1*), where 10 to 15 stones were analyzed at one time in order to obtain sufficient noble gases, showed that the diamonds had a higher ^{3}He/^{4}He ratio than atmospheric helium. We report here the results of measurements of the ^{3}He/^{4}He isotopic ratio in single diamond stones.

We studied 13 industrial-grade diamond stones (1 to 2 carats each) that were commercially available and thought to come from various unspecified mines in South Africa. The diamonds were kept in hot HNO_3 (80°C) overnight and then rinsed with acetone and distilled water. Noble gases were extracted by graphitization (*1*); the diamond stones were heated to 2050°C in a vacuum and completely converted to graphite. Helium isotopic measurements were made with a mass spectrometer equipped with a double collector and having a resolution of about 600. The mass spectrometer has never been used for extraterrestrial samples. Repeated analyses of atmospheric helium (^{4}He $\cong 5 \times 10^{-6}$ cm^{3}STP) gave a ^{3}He/^{4}He ratio of $(1.16 \pm 0.016) \times 10^{-6}$. The measured ^{3}He/^{4}He value (R) was represented as its ratio to the average value in air ($R_a = 1.16 \times 10^{-6}$), which eliminates the effect of instrumental mass discrimination in the final results. The results are shown in Table 1. The errors in R/R_a were calculated as the sum of all the possible errors in the ^{3}He and ^{4}He measurements and in the hot blanks—that is, 50 percent of the hot blanks—and must therefore be considerably overestimated. Hence we consider that the very high ^{3}He/^{4}He values observed in some samples cannot be attributed to experimental uncertainty but must represent the helium in the diamonds. Two diamond samples have values of the ^{3}He/^{4}He ratio that are higher than the primordial ratio in meteorites, He-A [^{3}He/^{4}He = $(1.42 \pm 0.2) \times 10^{-4}$] (*2*) and are close to the solar value (^{3}He/^{4}He $\sim 4 \times 10^{-4}$) (*3*).

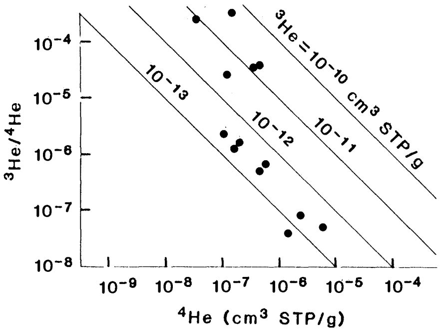

Fig. 1. Plot of ^{3}He/^{4}He versus ^{4}He for diamond samples.

The only way to explain the extremely high ^{3}He/^{4}He ratio seems to be to attribute it either to indigenous mantle helium trapped in the diamonds or to a nuclear reaction ^{6}Li(n,α)^{3}H → ^{3}He in the diamonds. First we consider the latter possibility. Since some diamond mines in South Africa, such as the Premier Mine, are known to have originated as much as 1.2×10^{9} years ago (*4*), it is possible that some diamonds resided for more than 10^{9} years in the crust, where the thermal neutron flux could have been high enough to produce significant amounts of ^{3}He in the diamonds. Assuming $t = 1.2 \times 10^{9}$ years for the age of the diamonds and taking ϕ = eight neutrons per square centimeter per day for the neutron flux in the crust, which was estimated for average granitic rocks (*5*), we find that the amount of lithium needed to account for the observed amount of ^{3}He ($\sim 4 \times 10^{-11}$ cm^{3}STP/g) in sample 82401 is

$$n(\mathrm{Li}) = \frac{\mathrm{Li}}{^{6}\mathrm{Li}} \times \frac{n(^{3}\mathrm{He})}{\sigma\phi t} \simeq 44 \text{ ppm}$$

where σ is the cross section for the reaction ^{6}Li(n,α)^{3}H ($\sigma = 930 \times 10^{-24}$ cm^{2}). Although there are no reported data on the lithium content of diamonds, we consider such a high lithium content (~ 44 ppm) extremely unlikely for the following reason. The potassium content of diamonds seldom exceeds 10 ppm even for highly inclusion-rich samples (*4*, *6*). Since the K/Li ratio does not vary much in crustal rocks or volcanic rocks, being about 10^{3} (*7*), it is safe to assume that the lithium content of diamonds is much less than the potassium content, say less than 1 ppm.

Figure 1 shows the ^{3}He/^{4}He values plotted against the ^{4}He content of dia-

Table 1. Helium isotopic data. Data are for the 2050°C fractions of samples 1-A through 5. The 900°C fractions were negligibly small. Total fusion at 2050°C was used for samples 82401 through 82406. Errors in ^{3}He and ^{4}He for the diamond samples are sums of the standard deviations of the peak height measurements and 50 percent of the hot blank. Errors in ^{3}He/^{4}He are estimated as the sum of the errors in ^{3}He and ^{4}He. The ^{4}He peak height determination was reproducible within about 10 percent. Hot-blank corrections were applied to all abundances.

Sample		Hot blank (2050°C)		Diamond		
Number	Weight (g)	^{3}He (10^{-13} cm^3 STP/g)	^{4}He (10^{-7} cm^3 STP/g)	^{3}He (10^{-13} cm^3 STP/g)	^{4}He (10^{-7} cm^3 STP/g)	R/R_a
1-A	0.2115	0.2	0.11	1.9 ± 0.1	1.51 ± 0.07	0.91 ± 0.10
2-A	0.1473	0.2	0.15	2.2 ± 0.1	0.99 ± 0.08	1.57 ± 0.17
3-A	0.1828	2.4	0.12	87 ± 4.6	0.37 ± 0.06	168 ± 38
1	0.3299	1.0	0.08	3.0 ± 0.6	1.93 ± 0.05	1.1 ± 0.02
2	0.3124	6.2	0.11	< 1.8	21.2 ± 0.3	< 0.06
3	0.3324	1.3	0.14	2.5 ± 0.9	58.8 ± 0.7	0.03 ± 0.01
4	0.3466	0.8	0.15	0.6 ± 0.4	14.7 ± 6.2	0.03 ± 0.02
5	0.2976	0.8	0.18	2.4 ± 1.3	4.73 ± 0.12	0.36 ± 0.3
82401	0.1788	1.6	0.20	424 ± 4	1.34 ± 0.10	226 ± 18
82402	0.2671	1.4	0.13	121 ± 5	3.75 ± 0.05	23.1 ± 1.6
82403	0.1383	3.0	0.25	4.1 ± 2.1	5.85 ± 0.23	0.5 ± 0.3
82405	0.1170	2.8	0.30	150 ± 7.0	4.42 ± 0.16	24.2 ± 2.0
82406	0.1466	2.3	0.21	31.7 ± 3.2	1.23 ± 0.11	18.4 ± 4.0

monds; iso-^{3}He lines are drawn corresponding to the same ^{3}He content. Addition of radiogenic ^{4}He would move the isotopic ratio downward along an iso-^{3}He line. Since ^{3}He production in the mantle (*8*) and the diamonds is probably insignificant, we consider the large spread in ^{3}He/^{4}He values in Fig. 1 to be primarily due to addition of radiogenic ^{4}He, either in the diamonds or in the mantle source region where the diamonds trapped the helium. It is interesting that most of the diamonds with small ^{3}He/^{4}He values ($\lesssim 5 \times 10^{-6}$) lie approximately on a single iso-^{3}He line, suggesting that they evolved from a single component of helium with similar ^{3}He/^{4}He values. Diamonds with higher ^{3}He/^{4}He values ($> 10^{-4}$) may represent very primitive helium that evolved little since the formation of the earth. Preservation of such primitive helium throughout a geological age would be possible only in an environment where uranium and thorium were highly depleted or the U/He ratio was extremely small. Possible candidates for such an environment would be a deeper part of the mantle which has remained decoupled from the outer part of the earth, or diamonds whose uranium and thorium contents are generally extremely small ($\lesssim$ 0.1 ppb) (*4*). We prefer the latter interpretation, because we know of no geological evidence supporting the existence of such a primitive mantle.

We propose that the very high ^{3}He/^{4}He values found in some diamonds represent helium trapped by the diamonds soon after the formation of the earth. The lower ^{3}He/^{4}He values found in other samples then reflect either relatively high uranium and thorium contents or a relatively younger age of the diamonds, which trapped highly radiogenic "aged helium" in the mantle. Of further interest is the fact that the diamonds with smaller ^{3}He/^{4}He values have a much lower ^{3}He content than diamonds with higher ^{3}He/^{4}He values. This may indicate that the diamonds with smaller values formed in the mantle after it had degassed and had less ^{3}He, while the diamonds with primitive helium crystallized before the mantle degassed. The existence of nearly solar-type helium in the earth implies that the accretion of the earth may be different from that of meteorite parent bodies with respect to the time or the process involved. For example, this may indicate that the dust grains from which the earth accreted were subjected to intense solar wind radiation after the deuterium burning stage in the sun, while those from which the meteorite parent bodies accreted may have trapped only the planetary helium (He-A) in the surrounding solar nebula.

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Carbon-13 and Carbon-14 Abundances in Alaskan Aquatic Organisms: Delayed Production from Peat in Arctic Food Webs

Abstract. *Inputs of terrestrial peat carbon to the nearshore Alaskan Beaufort Sea from erosion and fluvial transport are of the same magnitude as in situ primary production within 10 kilometers of shore. Nevertheless, carbon-13/carbon-12 ratios and carbon-14 abundances in marine organisms show that only small amounts of the terrestrial carbon are transferred beyond the microbial level. Freshwater organisms, however, are heavily dependent on peat, as shown by pronounced seasonal radiocarbon depressions in resident fish and ducks. Tundra ponds and lakes are areas where accumulated terrestrial peat carbon is apparently transferred to aquatic insect larvae and passed on to higher organisms. The lack of functionally analogous abundant marine prey organisms may explain why peat carbon is not efficiently transferred to apical food web species in the marine environment.*

The intricacies of nearshore and estuarine marine food webs present formidable obstacles to assigning significance to various energy source materials supporting resident fauna. Primary production from phytoplankton, benthic microalgae, macrophytes, and allochthonous (originating outside the system) terrigenous vegetation can all contribute, and quantification of inputs is often difficult or impossible. Recent studies have sought to identify the carbon source and the consumer of interest by using natural ^{13}C/^{12}C isotope ratios (*1–4*). The marked difference in δ^{13}C resulting from C-3 and C-4 photosynthetic pathways yields a natural signal easily traced in herbivores that graze on these plants (*5*). As long as