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Interstellar Carbon in Meteorites

Abstract. *The Murchison and Allende chondrites contain up to 5 parts per million carbon that is enriched in carbon-13 by up to +1100 per mil (the ratio of carbon-12 to carbon-13 is approximately 42, compared to 88 to 93 for terrestrial carbon). This "heavy" carbon is associated with neon-22 and with anomalous krypton and xenon showing the signature of the* s-*process (neutron capture on a slow time scale). It apparently represents interstellar grains ejected from late-type stars. A second anomalous xenon component ("CCFXe") is associated with a distinctive, light carbon (depleted in carbon-13 by 38 per mil), which, however, falls within the terrestrial range and hence may be of either local or exotic origin.*

Primitive meteorites contain several noble gas components of anomalous isotopic composition, at least some of which seem to be of exotic, presolar origin (*1–6*). These noble gas components are trapped in solid, mainly carbonaceous, carrier phases constituting less than 1 percent of the meteorite, and differ from each other in isotopic ratio, release temperature on stepped heating, and grain size of the carrier phase (Table 1). Together with their noble gas components, these carriers contain a rich record of stellar nucleosynthesis and interstellar chemistry that is waiting to be deciphered.

Table 1. Anomalous noble gas components with carbonaceous carrier phases.

Property	Ne-E (L)*	*s*-Xe	CCFXe
Characteristic ratio	$\frac{^{20}Ne}{^{22}Ne}$	$\frac{^{130}Xe}{^{132}Xe}$	$\frac{^{136}Xe}{^{132}Xe}$
Component	*< 0.01*	*0.48*	*0.64*
Atmosphere	*9.8*	*0.15*	*0.32*
Release *T*, °C	600	1400	1000
Carrier	Cα	Cγ	Cδ
Grain size, μm	1–10	0.1–3	0.01–1

*There is a second type of Ne-E that is located in an inorganic carrier [spinel and/or apatite (*6*)] and has a much higher gas release temperature (1200°C). On the basis of release temperature, these two components are designated L (low) and H (high).

The $^{12}C/^{13}C$ ratio varies greatly in stars, as production and survival of carbon isotopes depend sensitively on stellar mass, temperature, and hydrogen abundance (*7, 8*). This ratio ranges from 4 to > 100 in late-type stars, and even the mean interstellar ratio, 60 ± 8 or 67 ± 10 (*9*), differs appreciably from the terrestrial ratio of 89. Thus exotic carbon in meteorites should be easily recognizable by its anomalous isotopic ratio.

Previous studies of meteoritic carbon revealed only modest isotopic variations, with $\delta^{13}C$ (*10*) ranging from +65 per mil for carbonates to −30 per mil for organic matter (*11*). This variation, though exceeding the normal terrestrial range of +10 to −45 per mil (*10*), is consistent with kinetic isotope fractionation in the hydrogenation of CO at 350 to 500 K (*12*) and hence does not require nuclear processes. Recently, however, Kerridge (*13*) found traces of distinctly heavier carbon (+110 per mil) in the 1050°C fraction from stepped combustion of organic matter from the Murray C2 chondrite and suggested that it reflected nucleosynthesis rather than mass fractionation. Comparable enrichments in ^{14}N have been found for nitrogen and have likewise been attributed to nuclear processes (*14*).

In a directed search for exotic carbon, we measured several carbonaceous meteorite samples enriched in anomalous noble gases. Samples were prepared from the Allende (C3V) and Murchison (C2) chondrites by a series of chemical treatments that removed silicates and "normal" carbonaceous matter with its associated normal noble gases, while leaving a residue—typically 0.1 to 0.5 percent of the meteorite—containing the carriers of anomalous gases (*3, 5*). These carriers have not been structurally characterized, as they constitute less than 10 percent of the total carbon in the meteorites and have not yet been isolated in pure form. An earlier characterization as carbyne (*15*) now seems in doubt (*16*), but the material does not exactly match known types of amorphous carbon (*17*). Accordingly, they have been given noncommittal names such as Cα or Cβ (*5*).

The first two components in Table 1 are generally attributed to stellar nucleosynthesis. The component *s*-Xe has an isotopic pattern (*4, 5*) that agrees strikingly well with the calculated pattern for the *s*-process in red giants [neutron capture on a slow time scale (*18*)]. Neon-E, being monoisotopic ^{22}Ne (*6*), apparently is derived from the β^+-emitter ^{22}Na (half-life $t_{1/2}$ = 2.6 years), and since the amounts are much too large for production in the early solar system, a stellar origin is assumed by default.

The third component, CCFXe (carbonaceous chondrite fission xenon), has remained controversial. Most authors favor an exotic origin—stellar nucleosynthesis in a supernova (*2, 19*)—but others attribute it to processes in the early solar system [fission of an extinct superheavy element (*20*) along with mass fractionation of nebular xenon during trapping (*21*)]. Carbon isotope measurements may help settle this question, as a grossly anomalous ratio in the pure carrier itself would conclusively prove an exotic origin.

The carbon from all samples in this study was released by stepped combustion (*22–24*).

Murchison. Most of the carbon in the bulk meteorite combusts between 200° and 550°C (Fig. 1) and is isotopically light: δ^{13}C = −10 to −15 per mil, in good agreement with previous analyses of organic carbon in this meteorite (*25*). This carbon apparently comes from the organic polymer, which contains only isotopically normal noble gases (*26*). The small amount of carbon persisting beyond 550°C is isotopically much heavier, reaching +53 per mil at 950°C (Fig. 1).

At least part of this heavy component might be (Ca,Mg,Fe)-carbonate, which occurs in C2 chondrites, decomposes between about 600° and 900°C, and has a δ^{13}C of +35 to +51 per mil (*11, 25*). To check this possibility, we removed the carbonate (along with some silicates) by treating the meteorite with 100 percent H_3PO_4 (48 hours at 25°C), which reduced the sample to 14.4 percent of its original weight while raising the carbon content to 4.56 percent. Stepped combustion of the residue (Fig. 1) indeed shows a much lower carbon release above 600°C (0.3 versus 4.5 percent), yet a small high-temperature (high-*T*) component remains that is even heavier than before (+149 versus +53 per mil at 950° to 1000°C).

Table 2. Heavy carbon and *s*-process xenon in Murchison.

Sample	Weight (%)	Carbon: Total (%)	Carbon: Heavy* (ppm)	$^{130}Xe_s$ (10^{-12} cm^3/g)
Bulk	≡ 100	1.56	≥ 4.1	≥ 0.18
H_3PO_4	14.4	4.56	15	
2C10m	0.048	3.46	1300	66
2C10f	0.078	65.0	4500	190

*Calculated on the assumption that the high-temperature fractions are mixtures of two kinds of carbon, with δ^{13}C = +1100 and −38 per mil (or −20 per mil for 2C10m). The temperature intervals used for the last three samples are shown in Figs. 1 and 2, and contain 0.5, 50, and 6.3 percent of the total carbon. The value for the bulk meteorite is a lower limit, based on 2C10m+f only.

This heavy carbon could well be one of the exotic components we seek. To determine whether it is associated with anomalous noble gases, we analyzed Murchison separates 2C10f and 2C10m, which had been treated with HCl, HF, HNO_3, and NaOCl and are greatly enriched in Ne-E and *s*-Xe (*5, 27*).

The most dramatic feature of these Murchison residues (Fig. 2) is the rapid rise of δ^{13}C above 600°C, to a maximum of +1100 per mil in 2C10f. The true value may be a little higher, as the blank correction was conservative and some ordinary carbon may have survived to high temperatures. The corresponding ^{12}C/^{13}C ratio is 42.

The combustion pattern of 2C10m is complex (Fig. 2), suggesting the presence of several components differing in reactivity as well as isotopic composition. (The isotopic pattern from 600°C upward is not well determined, as the net carbon content was only 34 to 68 ng per step, comparable to the 20-ng blank.) For comparison, we calculated nominal concentrations of a uniform heavy carbon component of δ^{13}C = +1100 per mil (Table 2 and Figs. 1 and 2). Sample 2C10f, with ~ 4500 ppm heavy carbon, is about 10^3-fold enriched relative to the original meteorite. Sample 2C10m has a smaller absolute but higher relative enrichment: about 4 percent of its carbon is heavy. With so large a relative enrichment, the release pattern of heavy carbon in 2C10m can be traced down to 500°C. It seems to be bimodal or even trimodal (Fig. 2). The extreme width of the pattern also suggests that more than one type of heavy carbon is present. Only the high-*T* peak comes close to reaching δ^{13}C = +1100 per mil; the carbon in the low-*T* peak may well be less extreme, perhaps not even exceeding the highest observed values of +200 to +300 per mil.

Which of the three noble gas components belongs to the heavy carbon? Not CCFXe, as 2C10m is depleted 600-fold in CCFXe but only threefold in heavy carbon, relative to 2C10f (*5*). The other two components—*s*-Xe and Ne-E(L)—both seem to be linked to heavy carbon. They follow heavy carbon in wet oxidation, concentrating in the most resistant residue (*4, 5*). Their outgassing temperatures are far apart—1400°C for *s*-Xe and 600°C for Ne-E(L)—and so it seems plausible to assign these two components to the high-*T* and low-*T* peaks in the combustion pattern of 2C10m (Fig. 2). Though outgassing and combustion are quite different processes, both depend on grain size and structural stability; thus a phase that is more labile in one process ought to be more labile in the other.

The *s*-Xe component correlates closely with heavy carbon, both being about threefold enriched in 2C10f relative to 2C10m (Table 2). We cannot yet check for a similar correlation for Ne-E(L), as this component is masked in 2C10f (*5*). In terms of our previous nomenclature, "heavy carbon" thus is a mixture of Cβ

Table 3. Allende meteorite: chemical treatments.

Sample	Solvent	Weight (%)	Carbon (%)	^{132}Xe (%)	^{136}Xe	$^{136}Xe_{anom}$ (%)
Bulk*		≡ 100	≡ 100	≡ 100	0.338	≡ 100
BB†	HF/HCl	0.253	87	90	0.340	97
BG	HNO_3	0.234	69	14	0.464	75
B1B	$Cr_2O_7^{2-}$	0.039	8	6	0.644	70

*Absolute values for the bulk meteorite are C = 0.23 percent, ^{132}Xe and $^{136}Xe_{anom}$ = 17, and 0.48 × 10^{-10} cm^3/g at standard temperature and pressure. †Sample BB was a colloidal fraction of the HF,HCl-insoluble residue.

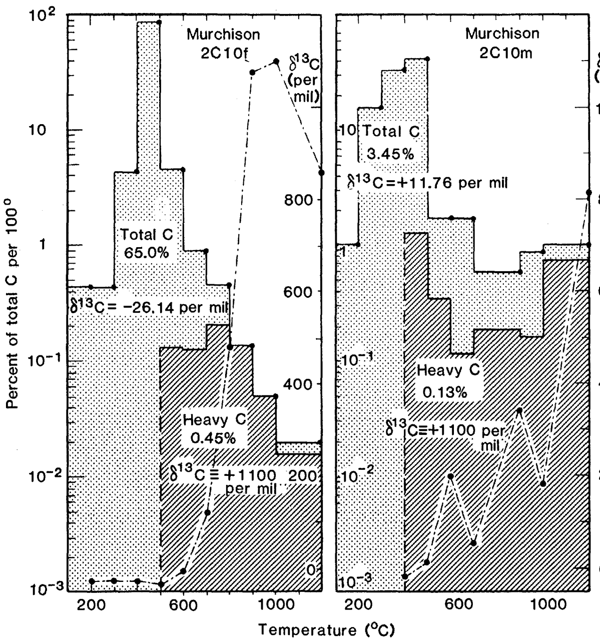
with other components, probably including Cα.

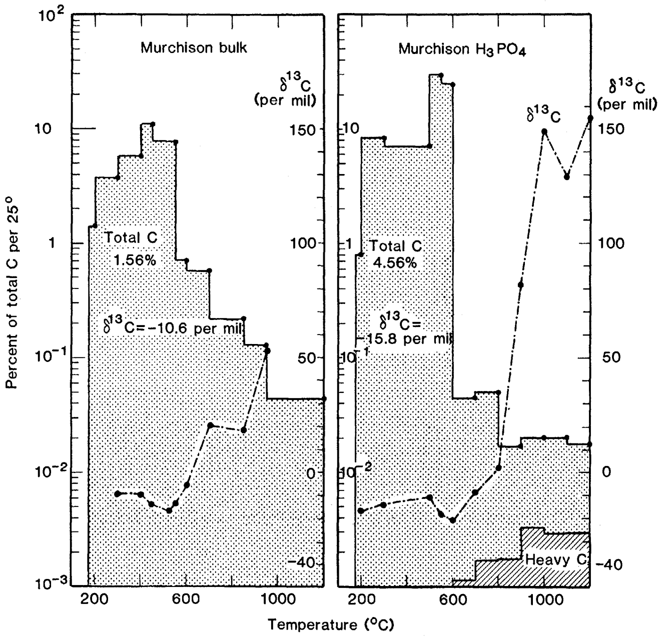
The association of *s*-Xe and Ne-E(L) with heavy carbon supports earlier suggestions that these components reside in grains ejected by red giants (*4*) or novae (*8*), respectively. A detailed discussion of the astrophysical implications will be given (*28*).

Allende. The principal anomalous component in this meteorite is CCFXe, which is located in colloidal material (*2*, *3*). We prepared three samples that were progressively enriched in this component (Table 3). Sample BB is dominated by normal planetary gases, as shown by the nearly atmospheric ^{136}Xe/^{132}Xe ratio. An etch with HNO_3 (sample BG) removes most of this (surface-sited) normal xenon, while leaving ~ 70 percent of the carbon and ~ 75 percent of the anomalous ^{136}Xe. Subsequent treatment with $Cr_2O_7^{2-}$ (sample B1B) destroys all but 8 percent of the original carbon, while leaving most of the anomalous ^{136}Xe. Evidently a minor, dichromate-resistant part of the carbon (Cδ) contains much of the CCFXe, whereas the major, dichromate-degradable part (Cγ) contains essentially no noble gases (*29*).

The stepped combustion data are shown in Fig. 3. Samples BB and BG show similar isotopic trends: a gradual rise from less than −25 to −15 per mil, followed by a jump to positive values for the last, minor fraction (*30*). Mean compositions ($\delta^{13}C$ = −18.9 and −17.3 per mil) are very close to those for the bulk meteorite, −17.3 per mil (*31*). Sample B1B, however, shows quite a different trend: $\delta^{13}C$ falls rather than rises (−19 to −32 per mil) and gives a mean of −30.4 per mil, well below that of the bulk meteorite. Apparently Cδ, the dichromate-resistant carrier of CCFXe, is isotopically light. The existence of such a light component was inferred from stepped combustion of the bulk meteorite (*23*, *31*).

A very similar carbon component shows up in Murchison 2C10f, the only





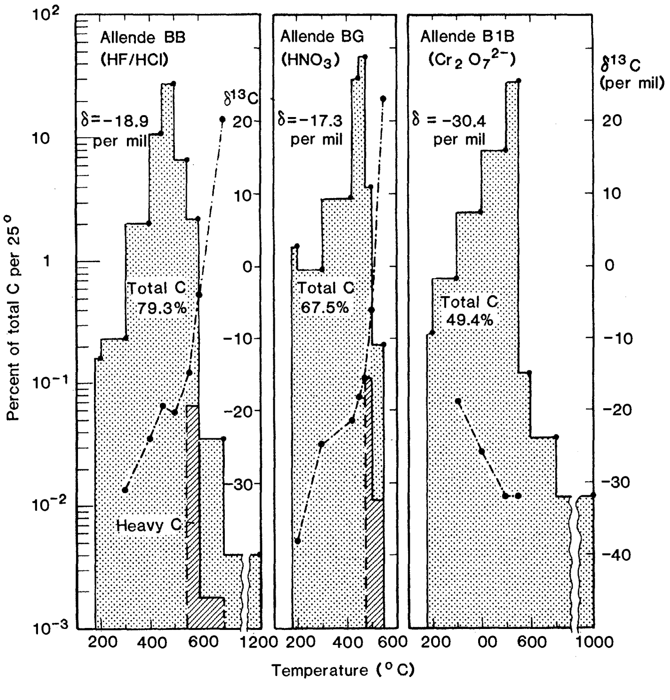


Fig. 1 (top left). Carbon released by stepped combustion of the Murchison meteorite before and after treatment with H_3PO_4. Dot-dashed line gives isotopic composition. In the bulk meteorite, the major part of the carbon, evolving to 550°C, is isotopically normal, but the last 6 percent is isotopically heavy. At least the portion between 600° and 850°C must be due mainly to carbonates, which are known to decompose in this interval and have $\delta^{13}C$ of +35 to +51 per mil. Treatment with H_3PO_4 removes 86 percent of the sample, including carbonates and water-soluble organic compounds, but still leaves a small (0.51 percent), very heavy carbon component that is released mainly between 1000° and 1200°C. For the H_3PO_4-treated sample, fractions from 700°C upward were blank corrected. Fig. 2 (top right). Two demineralized samples, from which most of the carbon was removed by NaOCl and H_2O_2, are about 10^3-fold enriched in heavy carbon and show $\delta^{13}C$ up to +1100 per mil (or up to +883 per mil before blank correction). The release curve of heavy carbon in 2C10m is very wide and bimodal, suggesting that at least two types of heavy carbon are present. They may be associated with Ne-E(L) and *s*-Xe. Sample 2C10f, which contains large amounts of CCFXe, also shows a characteristic light carbon component (−32 to −38 per mil) at 500°C. Fig. 3 (bottom right). Allende samples BB and BG show similar release patterns, with a dominant light component (about −20 per mil) followed by a small, heavy component (about +20 per mil). Sample B1B, which is about tenfold enriched in CCFXe, shows distinctly lighter carbon (−32 per mil), similar to the light carbon in *Murchison* 2C10f (Fig. 2). Apparently CCFXe is associated with (colloidal) carbon of $\delta^{13}C$ = −38 per mil—distinctive, but still falling within the terrestrial range.

sample of that meteorite enriched in colloidal material and hence also in CCFXe. The bulk carbon in this sample is markedly lighter ($\delta^{13}C = -26.14$ per mil) than that of the untreated meteorite (-10.3 per mil) or the H_3PO_4 residue (-15.8 per mil), let alone 2C10m ($+11.8$ per mil). The low $\delta^{13}C$ value reflects the presence of a major, light component combusting around 500°C, with $\delta^{13}C$ between -32 and -38 per mil. It was also seen in a second colloidal sample not reported here. No such component is evident in 2C10m, which has only $\sim 2 \times 10^{-3}$ the CCFXe content of 2C10f. (In calculating the nominal heavy carbon content of 2C10m, we therefore assumed a light component of -20 per mil, as seen in the 400°C fraction, rather than -38 per mil.)

In contrast to the heavy carbon carrier of *s*-Xe, the light carbon associated with CCFXe is not anomalous. Though falling at the low end of the meteoritic range (*11*), it is well within the range for terrestrial carbon or for chemical isotope fractionation (*12*). The most straightforward interpretation of this result is that CCFXe is of local rather than exotic origin. However, two possibilities for an exotic origin still remain:

1) The light carbon and CCFXe came from a single star that produced carbon of terrestrial isotopic composition, or from several stars that fortuitously gave the right mixture.

2) The actual carrier of CCFXe constitutes only a minute fraction of Allende B1B or Murchison 2C10f. Thus its isotopic composition, however anomalous, is swamped by the abundant ordinary carbon.

It is hard to rule out the first alternative. Schramm and Olive (*33*) argued that solar-system carbon is a mixture of heavy, galactic carbon and light carbon from a massive B-star, so given the range of carbon isotope composition in stars, there are many ways of producing a mixture of $^{12}C/^{13}C \simeq 90$. In principle, correlated isotopic anomalies for other elements may narrow the range of possibilities. But although bulk Allende showed a small nitrogen anomaly on stepped pyrolysis or combustion [with $\delta^{15}N$ reaching -53 to -90 per mil in the fractions where CCFXe is released (*14*)], the resolution was not high enough to prove that this anomaly is linked to CCFXe or light carbon. Studies of demineralized carbon *residues* show nitrogen anomalies up to -115 per mil (*34*) or -274 per mil (*35*), apparently correlated with CCFXe. If this correlation is real, then CCFXe and its carrier are exotic.

The second alternative, a cryptic trace carrier, requires that the carrier be inseparable from the abundant "local" carbon by all treatments used thus far. This is quite conceivable and will have to be checked by more subtle chemical treatments.

Discussion. The isotopic anomaly for heavy carbon found here is very large, greatly exceeding the values for other elements except noble gases and deuterium [factor of < 5 (*36*)]. Apparently, macroscopic amounts of interstellar carbon have survived intact in some meteorites, without isotopic exchange with solar-system carbon. The greater resistance to oxidation, which allowed its selective enrichment and isotopic analysis, may reflect mainly its coarser grain size (Table 1) and hence slower reaction rate. However, this difference may well be enhanced by greater crystal perfection: whereas ordinary Allende carbon—apparently a low-*T* product—is highly disordered (*16, 37*), heavy carbon—if a high-*T* stellar condensate—ought to be well crystallized.

It is interesting that the $^{12}C/^{13}C$ ratio of heavy carbon is as low as 42—at the low end of the range for molecular clouds [mean values are 60 ± 8 or 67 ± 10 (*9*)]. The discrepancy is even greater when the age difference is considered: the meteoritic ratio was frozen in 4.5×10^9 years ago, while the galactic ratio has declined by some 20 to 30 percent since that time, owing to stellar production of ^{13}C.

Part of the discrepancy may reflect a difference in stellar source. Carbon grains generally condense only at $C/O > 0.9$ (*38*) and hence come mainly from carbon-rich stars (which in turn tend to be rich in ^{13}C), whereas CO—the dominant form of carbon in molecular clouds—readily forms at lower C/O ratios and hence will come from all types of stars. Thus one may expect isotopic differences between carbon grains and CO, which will persist if isotopic exchange is slow.

We stress, however, that the $^{12}C/^{13}C$ ratio of 42 reported here is not necessarily representative of interstellar grains. Nonrepresentative sampling by the meteorite is only a minor worry; since much of the carbon of low $^{12}C/^{13}C$ may come from low-mass stars with long evolutionary times (*7*), the sampling time and region must be correspondingly large. However, our experiment itself may have introduced certain biases. We were able to see only that part of the exotic carbon which combusted at high temperatures, after the bulk of the normal carbon was gone. Thus we may have missed exotic carbon components that—being finer-grained or otherwise more reactive—combusted in the same 400° to 500°C interval as normal carbon.

Interstellar grains have long been among the more elusive astronomical objects, which could be studied only by theoretical or indirect observational methods. It now appears that at least one class of interstellar grains is present in primitive meteorites, and can be studied by direct laboratory techniques.

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$$\delta^{13}C = 1000 \left(\frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{standard}}} - 1 \right)$$

The range of $\delta^{13}C$ values for most terrestrial samples is about -45 to $+10$ per mil. Isotopic compositions lighter than -45 per mil are observed, but the compound involved, methane, is produced by the rather specific and highly fractionating processes of biogenesis or catalytic cracking.
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24. In some temperature steps the quantities of carbon were too small for conventional isotopic measurement, but still above blank level. Such fractions were analyzed by isotope dilution, by first measuring the amount of CO_2 on a capacitance manometer and then mixing the sample with a metered amount of CO_2 of known isotopic composition. The reproducibility of this technique, as tested with CO_2 of known isotopic composition, is $< \pm 10$ per mil for a sample size of 100 ng.
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30. This jump—a hint of which was seen in earlier studies (*2, 3, 31*)—may be caused by a trace of heavy carbon associated with *s*-Xe (and Ne-E?). Though stepped heating failed to detect these noble gas components in Allende (*21, 32*), stepped combustion revealed minor amounts of both (*33*). Unfortunately, we took no isotopic data for B1B after the main peak at 550°C, and hence do not know whether the heavy carbon survived the dichromate treatment.
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Helium on Venus: Implications for Uranium and Thorium

Abstract. *Helium is removed at an average rate of 10^6 atoms per square centimeter per second from Venus's atmosphere by the solar wind following ionization above the plasmapause. The surface source of helium-4 on Venus is similar to that on Earth, suggesting comparable abundances of crustal uranium and thorium.*

Studies of helium in Earth's atmosphere have a long and checkered history (*1–4*), providing valuable information on escape, on the composition of the solid body, and on physical processes regulating release of volatiles from the interior. The atmosphere contains 5.3×10^{-6} by volume of ^4He, formed by decay of uranium and thorium in crustal rocks, and 6.6×10^{-12} by volume of ^3He, for the most part primordial, emanating from tectonically active regions of the sea floor (*3*).

Helium escapes from the atmosphere predominately by nonthermal mechanisms, mainly as He^+ along magnetic field lines open to the interplanetary medium at high latitudes—the polar wind (*4*). Escape is efficient and must balance production on time scales of the order of 10^6 years. The rate of production of ^3He, 4 atoms per square centimeter per second, may be derived from measurements of the gas dissolved in the ocean, with independent information on the oceanic mixing time (*5*) and allowing for a small additional source from cosmic rays. The rate of escape, or equivalently production, of ^4He may be obtained by scaling results for ^3He, using the observed ratio of the gases in the atmosphere and correcting for minor enrichment of ^3He above the turbopause (*4, 6*). The source derived in this fashion, 2×10^6 cm^{-2} sec^{-1}, is in good agreement with limits established by MacDonald (*2*) from considerations of the planetary heat flux and available data for uranium, thorium, and potassium.

Helium was first observed as a component of Venus's atmosphere by Mariner 10 (*7*), and more extensive measurements were made by Pioneer. The abundance of ^4He in the upper atmosphere is known quite accurately (±20 percent) from mass spectrometric measurements on the Pioneer orbiter (*8*) and bus (*9*). Combined data from the orbiter, bus, and probe (*10*) indicate a mixing ratio for the gas in the bulk atmosphere of 1.2×10^{-5} with an uncertainty of about a factor of 2.

Helium ionized above the plasmapause on Venus is swept off by the solar wind, as discussed by Dessler (*11*). The ionization rate may be calculated as described by McElroy *et al.* (*12*) for oxygen. Using ionization rates for helium of 3.4×10^{-7} sec^{-1} for photoionization (*13*) and 6.4×10^{-7} sec^{-1} for electron impact (*14*), and measured concentrations of ^4He, we estimate a loss rate of 10^6 cm^{-2} sec^{-1}. We assume that loss of helium from the nightside is trivial and use data from Brace *et al.* (*15*) to define an empirical model for the height of the plasmapause. Collisions between hot oxygen atoms and helium were shown by Knudsen (*16*) to be important for escape of helium from Mars. They are not directly important for escape of helium from Venus but contribute an additional 20 percent to the abundance of helium above the dayside plasmapause. The loss rate for helium may be defined to about the same precision as that for oxygen; in both cases the uncertainty is related primarily to definition of the mean position of the plasmapause. McElroy *et al.* (*12*) argued that the momentum flux of solar wind is balanced mainly by addition of mass as O^+, allowing an independent estimate for escape of oxygen. These considerations suggest that escape rates for oxygen, and by extension for ^4He, are determined to an accuracy of about ±30 percent.

The rate for escape of ^4He derived here (10^6 cm^{-2} sec^{-1}), combined with the abundance inferred from Pioneer (1.8×10^{22} cm^{-2}), indicates a lifetime for ^4He in Venus's atmosphere of