Helium-Uranium Ratios for Pleistocene and Tertiary Fossil Aragonites

Abstract. *Uranium:helium ages are compared with* $Th^{230}:U^{234}$ *ages and stratigraphic ages for selected Pleistocene and Tertiary shells and corals. Agreement is good except for those fossils for which independent criteria (for example, aragonite:calcite,* $Ra^{226}:Th^{230}$*, or* $U^{234}:U^{238}$ *ratios) indicate a chemically open system. Certain of the Tertiary samples yield erroneously low ages which probably result from secondary addition of uranium. The helium geochronometer appears to yield reliable minimum ages and may be applicable to direct dating of aragonitic fossils—especially those of Pleistocene age—when used in conjunction with other isotopic and geologic information.*

Several proposed correlations of the absolute and paleontologic time scales have been reviewed by Kulp (*1*). During the last few years absolute ages assigned to most critical points in the paleontologic time scale have changed very little and are generally agreed upon. Hence the mere presence of a reasonably complete Paleozoic or Mesozoic faunal assemblage normally permits more precise absolute chronology of a site than the direct application of absolute dating methods of phases occurring at the site. However, in the late Tertiary and Pleistocene it is frequently impossible to derive the absolute age with satisfactory precision from the faunal assemblage alone owing to the short time-spans involved and the slowness of evolutionary change. Moreover, it is in just this time range that the dating of associated igneous rocks is frequently very difficult, primarily because the very short absolute time spans involved seldom include enough separate igneous events at a specified site to provide satisfactory time resolution. Thus, development of a geochronological method directly applicable to fossils would be valuable for problems of absolute Pleistocene geochronology, and would almost certainly yield further information concerning Pleistocene eustatic changes, glacial cycles, human chronology, and related problems.

From an analytical point of view, the helium method has advantages over the argon method: the production rate of helium in pure carbonate fossils greatly exceeds the argon-production rate, and the problem of atmospheric contamination is much less serious because helium abundance in the atmosphere is only 0.05 percent of argon abundance. In order that the helium method may be useful, however, certain additional conditions must be approximated.

If uranium was incorporated in a shell or coral during or shortly after the life of the animal and the fossil did not subsequently exchange uranium or radioactive daughters with its surroundings, then the helium-production rate at any time in the past can be calculated from knowledge of the present concentrations of uranium isotopes. If helium now present in the fossil resulted only from decay of uranium and its daughters and no helium was lost to the surroundings, then measurement of present concentrations of uranium and helium yields the age of the fossil. Certain other initial conditions, such as absence of initial Th^{230}, must also be known; these will be discussed in connection with the method of age calculation.

Studies of the helium method (*2*) have shown that low ages based on helium, obtained on common rock-forming minerals, do not necessarily reflect diffusive loss of helium from the lattices of those minerals; under ideal conditions, some mineral lattices even appear to retain helium quantitatively for longer than 10^8 years.

The distribution and history of alpha emitters in the sample may be far more critical parameters. It is known, for example, that living mollusk shells contain far less uranium on the average than do similar fossil shells, indicating that most of the uranium in the latter is probably secondary (*3*). However, fossil shells in the 10^4-year range of age have concentrations of uranium no less on the average than those of fossils in the 10^6-year range; it seems that the process of net uranium addition may cease a few thousand years after the death of the animal. However, the possibility of uranium exchange between the fossil and its surroundings is not eliminated by such data; in some instances exchange could be detected by measurement of $U^{234}:U^{238}$ ratios in the fossils (see *3*).

We have attempted to determine the effects of possible helium loss and uranium exchange on the helium ages of aragonitic fossils by performing helium-age determinations on various samples of fossil shells and coral for which several types of independent estimates of age are available. Specifically, we have made three types of comparison to test the above assumptions: (i) we compared the He:U ratios of several fossils known to be of the same age but having very different uranium contents; (ii) we compared helium ages with ionium ages; and (iii) we compared helium ages with well-defined stratigraphic ages.

The helium contents of these fossils were determined by use of the statically operated, gas mass spectrometer (*4*). Aragonite samples (< 1 g) were decrepitated *in vacuo* by means of radiofrequency induction heating. Evolved CO_2 was frozen on a cold trap at liquid-nitrogen temperatures; the trap was then isolated and the gas remaining in the rest of the system was gettered with hot Ti. Finally, other cold and charcoal traps were immersed in liquid nitrogen to remove any gases remaining after chemical clean-up. The total pressure of gas remaining after this operation, of which helium was a minor constituent, was usually in the neighborhood of 10^{-6} mm-Hg; when this pressure was achieved the helium was introduced into the tube. The spectrometer was repeatedly calibrated with a gas pipette that admitted a known amount of He^4 to the tube; sensitivity was constant within about 10 percent for months. The entire vacuum line, except the spectrometer tube, was constructed of 1720 Pyrex glass to minimize inward diffusion of atmospheric helium.

The most serious analytical limitation encountered was that modern samples, especially of coral, which should have contained virtually no helium, often yielded apparent helium contents [3 to 6 × 10^{-9} cm^3 total He at standard temperature and pressure (STP)] exceeding that of the normal "empty crucible" system blank (~ 1 to 3 × 10^9 cm^3 at STP). We have not yet made sufficient measurements to define the origin or constancy of this "nonradiogenic" helium; the possibility that it represents the decay of great initial excesses of relatively short-lived intermediate daughters (for example, Ra^{226}) can be discounted, since sufficiently great excesses of this type have not been observed in corals or shells of any age (*3*). This problem does not seriously affect interpretation of most ages presented in this paper, but if an effort were made to overlap the C^{14} range with the helium method, the origin and variability of this finite "sample blank" would have to be thoroughly understood. If it is related to the presence of very small amounts of detrital material in the sample, substitution of acid solution for the decrepitation procedure may eliminate the problem.

Routine fluorometric measurements of uranium contents at Lamont Geological Observatory (*3*) were checked, on selected samples, by isotope-dilution techniques (alpha spectrometry at Lamont and mass spectrometry at Brookhaven National Laboratory). The methods employed in the alpha spectrometric measurement of contents of U^{238}, U^{234}, and Th^{230} in shells and corals and the calculation of the corresponding ages are discussed by Kaufman and Broecker (*5*) and Thurber *et al.* (*6*).

Reproducibility of both uranium and helium measurements was normally within 10 percent. When isotope-dilution results and fluorometric results were compared on different portions of the same samples, they agreed within this error, as did helium replicates measured by the two spectrometers, in which sensitivities and amounts of He^4 admitted by the spike pipettes both differed by a factor exceeding 3. A 15-percent analytical error has therefore been assigned to the ages. In some instances the apparent "sample blank," already discussed, was a significant factor in increasing this uncertainty; a result was that in certain instances ages could not be assigned.

The first test of the assumptions of the method was to obtain U:He ratios for shells of identical age but of different uranium content. Each of several raised beaches in California provides various shells of identical age (*5*). One such suite studied was from terraces that correlate with the 70-foot marine terrace of the Palos Verdes hills; the other was from another Palos Verdes terrace 1230 feet (375 m) above the present sea level. Results on these samples appear in Fig. 1 and Table 1; the latter includes results on

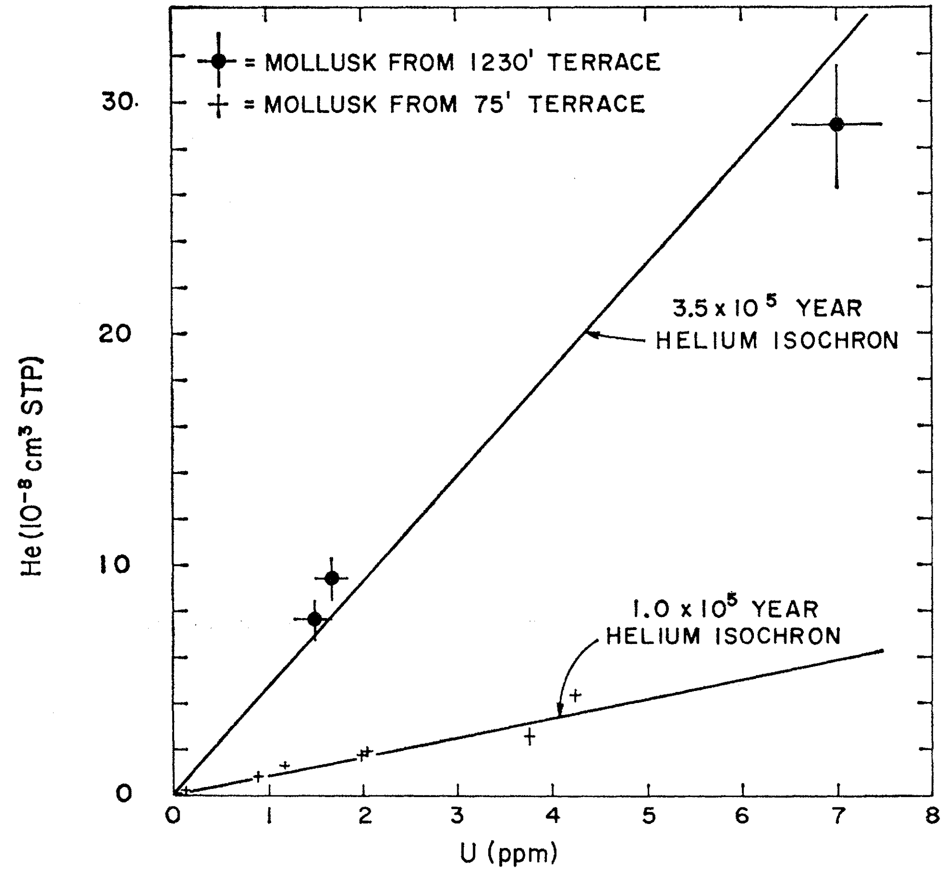

Fig. 1. Helium content of selected mollusk shells as a function of uranium content. Note that within each suite the He:U ratio is essentially constant despite great variations in uranium content. Note in particular the point almost coincident with the origin. The two suites fall on isochrons having quite different slopes as expected on the basis of the Th^{230}:U^{234} data (Table 1) and on geologic grounds.

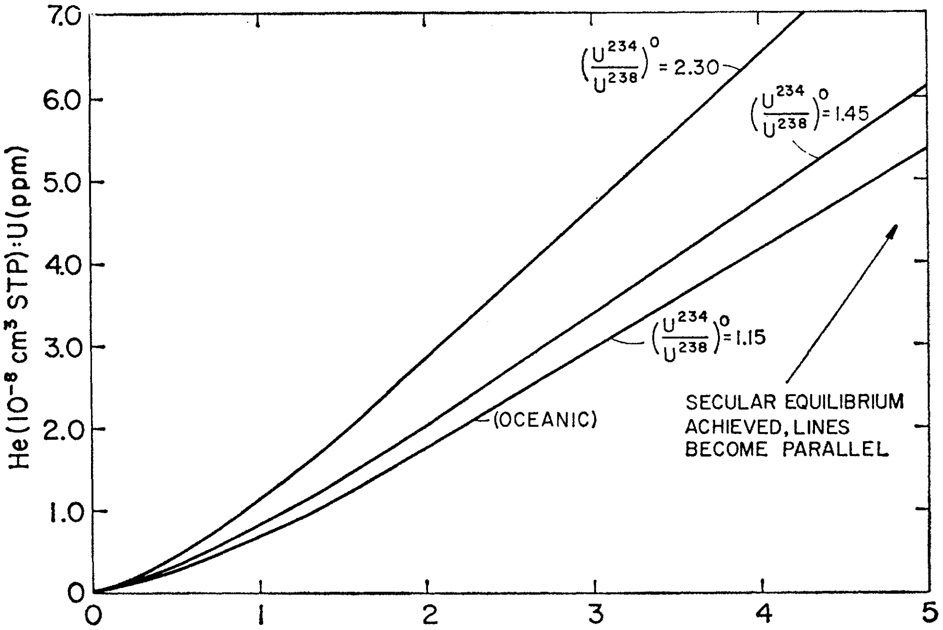

Fig. 2. Helium:uranium ratio versus time for closed systems having different initial U^{234}:U^{238} ratios. Note how the lines flex upward as Th^{230} and its daughters (assumed to be initially absent) build into transient equilibrium with the U^{234}. Note also that (to the right of the area shown) the lines must become parallel as secular equilibrium is approached, that is, as unsupported U^{234} disappears.

a gastropod sample from the Lomita marl which is thought, on geological grounds, to be intermediate in age between the two terraces. The field relationships of all these samples are discussed by Kaufman and Broecker (*5*). The data in Table 1 are not corrected for possible "nonradiogenic" or "initial" helium; as we show later, this component of total helium must be negligible for these suites. Despite the wide range of uranium contents in the results, consistency of the He:U ratio within each suite is within the limits of experimental error. This may indicate that the uranium was added during the early history of the shells; if it was added during times comparable with the age of the shells, then different shells having different propensities to accumulate uranium (and having, therefore, different uranium contents) would not necessarily be expected to have identical He:U ratios. On the basis of such data alone, the possibility that addition of uranium was episodic some time significantly later than the death of the animal cannot be completely eliminated. However, such data, together with the general agreement between C^{14} and Th^{230}:U^{234} ages on shells and the evidence from concentrations of uranium discussed earlier, tends to indicate that later episodic or continuous addition of uranium is not the general rule. The Palos Verdes suites were selected for Th^{230}:U^{234} dating by Broecker and Kaufman largely on the basis of their aragonite : calcite and Th^{230}:Ra^{226} ratios (*5*).

A conclusion to be drawn from Fig. 1 is that, at least in these shells, the helium observed was produced solely by radioactive decay of uranium and its daughters in the shells. The fact that the helium correlates quantitatively with the uranium within each suite indicates that (i) no significant amounts of helium were initially present in these shells, and (ii) that no significant amount of the total yield of He from the purified samples can be attributed to extremely small amounts of extremely old detritus that may still be associated with them. This type of "isochron" check is strictly valid only for the particular suites of samples studied, but the general validity of the assumed, quantitative, cause-effect relation between alpha decay in Pleistocene shells and their helium content is also confirmed by the very small amounts of helium observed in modern and C^{14}-range shells (see Table 1), and by the fact that helium ages did not significantly exceed independent estimates of age for any of the fossils studied (Tables 1 and 2). These observations indicate that helium ages provide reliable minimum estimates of age for this type of sample.

We shall now consider the second test of the assumptions: comparison between helium ages and independent Th^{230}:U^{234} estimates of age, for which the helium ages were calculated in the following manner.

The helium age of a fossil, a few million years old, can be accurately calculated from its He:U ratio if one assumes that the helium production rate was constant and equal to the alpha-flux resulting from the uranium content of the fossil, together with all alpha-emitting daughters in secular equilibrium. However if the age is less than about 10^6 years it is necessary to take into account the initial radioactive disequilibrium conditions in the shell and the rate at which secular equilibrium is achieved. For the ages given here, we have assumed that both Th^{230} and Th^{232} concentrations were initially zero in these samples (*5, 6*) and that the present U^{234} : U^{238} ratio represents the initial ratio modified only by decay of unsupported U^{234} during the history of the sample. The age can be calculated by summing the integrated helium production rates, from t_0 to t, of what are considered, for convenience, to be three separate helium sources: (i) the excess U^{234} that decays from its initial value to the supported concentration, (ii) the contribution from Th^{230} and its daughters as they augment into transient equilibrium with the U^{234}, and (iii) the contribution from the (constant) concentration of U^{238}. The contribution by U^{235} and its alpha-emitting daughters adds a minor increment to the total results.

The total accumulated production of helium for any given uranium content is plotted as a function of time and of the initial U^{234}:U^{238} ratio in Fig. 2; it can be seen that the rate of production of helium increases slowly

Table 1. Comparison of He : U ages with Th^{230} : U^{234} ages (*14*) [< million years (my)] and stratigraphic ages (> 1 my) for various mollusk shells, and the shell contents of helium and uranium. (P), pelecypod; (G), gastropod; (STP), standard temperature and pressure.

Sample	U (ppm)	He, STP (10^{-8} cm^3/g)	Age, U:He	Independent estimate of age
		1200-foot terrace, Palos Verdes hills, California		
(G) 807E	1.5	7.7	390,000 ± 60,000	5 samples, > 300,000 1 sample, 325,000 ± 60,000
(P) 807A	1.7	9.2	420,000 ± 60,000	
(G) 807D	7.0	29.	330,000 ± 50,000	
		70-foot terrace, Palos Verdes hills		
(P) 853A	0.1	< 0.2	< 200,000	Range 120,000 to 140,000 (> 20 samples)
(P) YC-1	.9	.74	105,000 ± 30,000	
(P) 853C	1.2	1.3	130,000 ± 20,000	
(P) SS-1	2.0	1.9	115,000 ± 20,000	
(P) RS-1	2.1	2.0	115,000 ± 20,000	
(G) GS-1	3.8	2.7	95,000 ± 15,000	
(P) 855D	4.2	4.7	130,000 ± 20,000	
		Lomita marl		
829 DF	2.4	3.4	155,000 ± 30,000	185,000 ± 20,000 (3 samples)
		Israel		
(G) MIS-1		0.36		Collected alive
(G) IS-20	1.8	.76		20,000 ± 2,000
(G) IS-1	3.1	15.3	290,000 ± 50,000	360,000 ± 60,000
		Lake Lahonton, Nevada		
(P) 62-41		0.33		Modern
(G) 62-3		.79		1,200 (C^{14})
(G) 62-21	2.4	17.	440,000 ± 60,000	$400,000 \; {}^{+\,200,000}_{-\,100,000}$
(G) 62-22	3.2	25.	500,000 ± 60,000	Same bed as 62-21
		Plum Point, Maryland		
(P) MCL-1	0.88	240	23 ± 4 my	Upper Oligocene to Lower Miocene, 25 to 30 my
(P) MIF-1P	.58	250	36 ± 6 my	
		Paris Basin, France		
(G) EA-1	13	340	2.4 my	Eocene, 50 my
(G) EA-2 (acid leached)	17	390	2.3 my	

with Th^{230} build-in from t_0 (death of the animal), when production of helium results entirely from uranium-isotope decay, until $t > 10^5$ years, when most helium is produced by decay of Th^{230} and its daughters. Note that for young samples the age corresponding to any given helium:uranium ratio can be a significant function of the initial activity ratio of U^{234}:U^{238}. The line corresponding to the present ocean-water value (1.15) is indicated, and most freshwater bodies studied now show values < 2.0 (*7*). Eventually, as *t* exceeds 10^6 years (not shown in Fig. 2), and the excess U^{234} disappears, the lines become parallel, and the separation between them (which remains constant) becomes insignificant relative to the increasing value of the He:U ratio. Thus the age becomes, for Tertiary samples, a function purely of the observed helium-uranium ratio. For all calculations of age reported by us, the effect of the present U^{234}:U^{238} ratio (as measured on these samples by Broecker *et al.*) was taken into account.

Table 2. He ages compared with Th^{230} : U^{234} ages for samples of coral, together with their uranium and helium contents. Since recent corals repeatedly yield helium equivalent to ~40,000 years of helium production, it should be borne in mind that helium ages of the older samples may be similarly affected by this violation of the initial conditions assumed in the method; my, million years; STP, standard temperature and pressure.

Sample depth (feet)	U (ppm)	He, STP (10^{-8} cm^3)	Age, U:He	Age, Th^{230} : U^{234}
		Eniwetok		
< 25	3 (Av. of 3)	1.3 ± 0.3 (Av. of 3)	40,000 ± 10,000 (Av., equivalent)	< 5,000 yr
50	3.0	3.8	155,000 ± 30,000	115,000 ± 5,000
85	2.6	5.4	220,000 ± 50,000	240,000 ± 60,000
100 A	2.3	9.0	380,000 ± 60,000	$300,000 \begin{smallmatrix} +100,000 \\ -40,000 \end{smallmatrix}$
100 B	2.3	9.1	380,000 ± 60,000	225,000 ± 40,000*
140	4.5	18.6	400,000 ± 60,000	235,000 ± 30,000*
170-190	3.1	12.6	400,000 ± 60,000	280,000 ± 60,000
700	1.51	138	8.5 ± 1.5 my	Near Miocene-Pliocene boundary, ~ 11 my
2000	0.70	217	26 ± 4 my	Lower Miocene, ~23 my
		Bikini		
900	2.5	147	5.9 ± 1.0 my	Mid-Miocene, ~17 my

* "Initial" U^{234} : $U^{238} \neq 1.15 \pm 0.04$ (*6*).

In Table 1 Th^{230}:U^{234} ages obtained on selected mollusk shells by Broecker *et al.* are compared with the estimates of age based on helium; the shells selected show good agreement between the two estimates in most instances. Note that in the case of the samples from Lake Lahonton and Israel the C^{14}-range and modern samples yielded less than 5 percent of the helium yielded by samples from the same sites for which the age comparisons are made, indicating that the possible significance of initial helium in the latter can be discounted. Very young samples from the Los Angeles County sites were not run, but, as stated earlier, the same conclusion in these instances derives from the fact that the points in Fig. 1 fall close to helium isochrons drawn to pass through the origin; ages based on helium are compared with the range of Th^{230}:U^{234} ages found for several other shells from the same terraces.

We have made a similar comparison of age for some aragonitic coral samples. A number of cores up to 4000-feet long and extending well into the Tertiary exist for certain coral reefs in the Pacific; their upper parts have been dated by the ionium method (*8, 6*) and certain of them are well correlated with the paleontological time scale in the Mid- and Lower-Miocene (*9*). Helium and uranium contents along with ages based on helium of several samples from these cores are listed in Table 2. The independent estimates of age are based on the Th^{230}:U^{234} ratios or stratigraphic positions of the cores. Of particular importance is the initial U^{234}:U^{238} ratio, which is calculated from the present ratio and the ionium age of the sample.

The present U^{234}:U^{238} ratio in the oceans is about 1.15, and there is considerable evidence that this has not changed drastically during the last few hundred thousand years; for this reason Thurber and Broecker (*6*) consider that, if initial U^{234}:U^{238} ratios in coral samples are not 1.15 ± 0.03, the Th^{230}:U^{234} ages of the samples are suspect. Note that in Table 2 the three samples showing the greatest discrepancy between ages based on helium and Th^{230}:U^{234} ratio are those whose initial U^{234}:U^{238} ratios do not fall within Broecker's acceptable range, while those for which the two age estimates are essentially in agreement exhibit ratios that overlap this range within the limits of experimental error. Note also that in the anomalous instances the ionium ages show a reversal with depth, which is not expected on any stratigraphic basis; in no case does the age based on helium exhibit such a reversal. On the other hand, any exchange of uranium isotopes is probably accompanied by an effect on the helium age.

It can be concluded on these bases that, as with the shells, there is no evidence of significant loss of helium by Pleistocene coral samples. In the discordant instances either method or both may be in error owing to uranium-isotope exchange. One may predict that the ionium ages would be strongly affected in such instances since, for samples older than 200,000 years, the Th^{230}:U^{234} and U^{234}:U^{238} ratios are such insensitive functions of time. However, the general consistency of the two methods in the remaining instances, together with the continual increase in apparent age with depth, increases the validity of the results by both methods on these samples.

We have also measured the helium ages of some Tertiary corals from the same cores; the samples are known to be Upper, Middle, and Lower Miocene in age, and are unusual for such old coral in that they have not been extensively recrystallized to calcite. Again the agreement in age between the helium results and the estimates based on stratigraphic position is satisfactory for the Eniwetok samples. One of these samples appears to have retained helium quantitatively for up to 30 times longer than the history of the oldest Pleistocene sample; on the other hand it is disturbing that the Bikini coral sample, which exhibits a typical uranium content for unaltered coral (~ 3 parts per million), yields the anomalous age, while samples having low contents of uranium yield concordant ages.

Ages based on helium were also determined for some Tertiary Pelecypod shells from near Plum Point, Maryland

(Table 1), which are thought to be of lowermost Miocene or Oligocene age. The ages are in rough agreement with estimates based on stratigraphy, and there is in any event no suggestion of extensive loss of helium.

Helium ages of an Eocene gastropod also are compared (Table 1) with a stratigraphic estimate of age; there is no agreement, and yet the stratigraphic estimate is known to be highly reliable. It is difficult to explain this extreme anomaly in view of the agreement of ages based on helium with independent estimates of age for younger shells and corals. The possibility that surface mineralization by uranium may be responsible for the low helium age can be discounted; essentially the same data came from a similar but acid-leached specimen.

Both concordant *(10)* and highly discordant *(11)* helium ages have been previously reported for Paleozoic and Mesozoic carbonates. The observation of both essentially concordant and highly discordant helium ages despite the limited sampling is therefore not surprising.

In summary, helium content has correlated quantitatively with uranium content for suites of aragonitic shells of equal age. In addition, helium contents of C^{14}-range and recent shells were found to be typically negligible relative to helium contents of comparable shells from the same localities that were 10^5 to 10^7 years old. In virtually all instances where reliable "control" ages were available, ages based on helium proved equal to or lower than "control" ages, whether these were established by Th^{230}:U^{234} dating (in the $< 3 \times 10^5$ year range) or by stratigraphy ($>$ 1 million years).

On the basis of these observations we conclude that, in the absence of recrystallization, the helium content of young aragonites is typically equal to the total alpha-flux in them since their formation. This means that no significant contribution to the total helium content normally results from incorporation of primary helium at the time of formation of biogenic carbonate. It also means that contribution of helium from old detritus can easily be reduced to negligible levels for samples such as we examined. Thus it appears that determinations of age from helium, such as we describe, can provide reasonably reliable minimum estimates of age for aragonitic samples.

These observations are not surprising in view of the fact that the two most probable violations of the assumptions of the method (secondary addition of uranium and diffusive loss of helium) would both tend to lower helium ages from the true values. For both shell and coral, the greatest negative deviations of ages based on helium from true ages appear in the older samples ($> 10^7$ years), suggesting that diffusive loss of helium may have reached significant proportions for these. In any event, the general agreement between helium and Th^{230}:U^{234} ages for the Pleistocene shells and corals indicates that diffusive loss of helium was probably negligible in such instances. We should point out that some of the older coral and shell samples also yielded reasonable helium ages despite the fact that they were up to 100 times older than the Pleistocene samples for which helium and ionium ages were compared.

Secondary addition of uranium appears to be the most serious potential problem in the method, especially for Pleistocene samples. It is known that many old mollusk shells exhibit U^{234}:U^{238} activity ratios very much greater than 1.00, even though they are tens of U^{234} half-lives old and should therefore show U^{234}:U^{238} activity ratios of 1.00 within experimental error *(12)*. This means that even though net addition of uranium may have ceased, a significant amount of isotopic exchange of uranium with the environment must have gone on in such cases during the last million years.

It is obvious from electron photomicrographs *(13)* that domains of intact aragonite in mollusk shells do not normally extend for distances exceeding a few microns, and that interstitial organic domains are less than 0.1 μ thick. Since the alpha range in solids is tens of microns, it might be expected that helium distribution or retention in such a structure would not be dependent on whether alpha emitters were located in the aragonitic "bricks" or in the extremely thin bands of interstitial organic material between the bricks. However, if the alpha emitters are located in such interstitial sites and if, as a result, a significant amount of exchange of uranium takes place between shell and environment, the helium-production rate at any time in the past can no longer be accurately estimated from the measured content of U^{238}. In such an instance, even though the helium content of the shell might still accurately represent the integrated alpha flux, the age could not be accurately determined from the measured contents of helium and uranium. It is also probable that the Th^{230}:U^{234} age of the shell may be likewise affected by such addition or exchange of uranium; if all uranium were added in an episode late in the history of the fossil, the helium and Th^{230}:U^{234} methods might yield the same age (or t_0 for the system). Yet this age might not represent the time of formation of carbonate. Since no absolute estimates of age are available for these Pleistocene samples other than the Th^{230}:U^{234} ages, it is difficult to estimate the seriousness of the above problem. Virtually the only other means of estimating the absolute age of such young samples would be the K-Ar method, results of which might be compared with U:He ages in a few exceptional Pleistocene localities where fossil aragonite and appropriate igneous phases could be stratigraphically related.

It may be possible to evaluate the seriousness of this effect from the consistency of He:U ratios or ages for several samples (in a suite) having vastly different uranium contents, as well as on the basis of agreement with ionium ages.

In conclusion, it appears that He-U ages in shells and corals are essentially equivalent to ionium ages of these materials except for the greater range of the helium method. It is unlikely that an isolated age on a given shell would yield a reliable estimate of the fossil age. However, within the limitations imposed by our sampling, it appears that the helium method may be of use in Pleistocene geochronology when suites of aragonitic fossils are obtained and when other types of geologic or isotopic information are available.

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Carbon Abundances in Chondritic Meteorites

Abstract. *Combustion analyses of total carbon in chondritic meteorites indicate a fractionation of this element between the various types of chondrites. The median values for the percentage of carbon by weight are 0.40 for enstatite chondrites, 0.09 for olivine-bronzite chondrites, and 0.08 for olivine-hypersthene chondrites. Olivine-pigeonite chondrites show great variations in their carbon contents.*

The abundances of carbon have been determined in 18 chondritic meteorites by a combustion technique. Powdered samples ranging from 0.25 to 1 g in weight were burned in an oxygen atmosphere in a LECO induction furnace. One gram of iron chips and 1 g of copper chips were added to accelerate the reaction. The combustion products were carried in the oxygen stream through a MnO_2 trap to remove any SO_2 formed, and through a catalyst furnace to convert any carbon monoxide to carbon dioxide. The total CO_2 produced was determined by a modified Orsat technique (see *1*) in a LECO model 572-100 carbon analyzer, by dissolving the CO_2 from the oxygen carrier in a caustic solution and measuring the volume of CO_2 lost.

The technique gives reproducible and accurate results, as indicated by the results on two Thorn Smith steel standards. Four analyses of one standard ranged from 0.41 to 0.43 percent carbon by weight, as compared with the standard value of 0.40, and four analyses of the second standard ranged from 0.50 to 0.51, as compared with the standard value of 0.49.

The data obtained from the abundances of carbon in enstatite, olivine-bronzite, olivine-hypersthene, and carbonaceous and noncarbonaceous olivine-pigeonite chondrites are given in Table 1. Replicate analyses on the same batch of powdered meteorite for selected samples provide an index of the reproducibility of the method.

Previous determinations of carbon in chondrites have been largely limited to the three classes of carbonaceous chondrites and the enstatite chondrites. The presence of carbon in most of these meteorites is readily apparent and hence conducive to analysis. Carbonaceous chondrites of the rarer types were not analyzed in this investigation because of their rarity and the apparently reasonable values obtained in previous analyses. Values obtained by other investigators (*2–5*) for the same meteorites analyzed in this investigation are indicated in Table 1.

As indicated by Table 1 and Fig. 1, in which carbon abundances reported here and abundances for carbonaceous chondrites reported by Boato (*3*) and Wiik (*4, 5*) are plotted, individual meteorites within a given classification generally show a broad range of values. This type of distribution makes a calculated mean for a meteorite group of questionable value for comparison purposes; each individual meteorite should be considered separately, and representative specimens for each class should be used in comparisons. For the specimens used in this investigation, the median values for the carbon content were: enstatite chondrites, 0.40; olivine-bronzite chondrites, 0.09; olivine-bronzite chondrites, 0.09; olivine-hypersthene chondrites, 0.08. These values are close to those selected by Craig (*6*) for the average carbon content of the olivine-bronzite (high-iron group) chondrites of 0.07 and the olivine-hypersthene (low-iron group) chondrites of 0.03 and the average value of 0.29 percent carbon selected by Wood (*7*) for the enstatite chondrites. It is interesting to note the parallelism of the carbon abundances in the chondritic meteorites with the abundances of Hg, Tl, Pb, and Bi as noted by Reed *et al.* (*8*). These volatile elements are relatively depleted in the ordinary olivine-bronzite and olivine-hypersthene chondrites as compared to the enstatite, olivine-pigeonite, and carbonaceous chondrites.

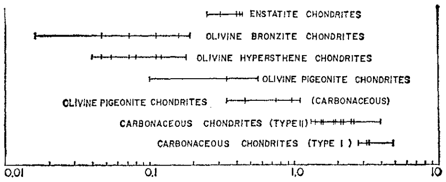

Fig. 1. Carbon distribution in chondrites (percentage by weight).

Table 1. Abundances of carbon in meteorites.

Meteorite	Abundance (% by wt.)	Previous results (% by wt.)
Enstatite chondrites		
Hvittis	0.25	
Khairpur	.31	0.41 (*5*)
Abee	.40	.38 (*2*)
Indarch	.41	.4 (*3*)
		.31 (*4*)
		.43 (*4*)
Atlanta	.43	.50 (*5*)
Olivine-bronze chondrites		
Allegan	.014	
	.018	
Richardton	.040	0.02 (*3*)
	.040	
	.046	
	.049	
	.052	
	.052	
Forest City	.072	0.08 (*3*)
	.072	
Saline	.11	
	.12	
Kesen	.15	
	.15	
	.16	
	.16	
Beardsley	.19	
Olivine-hypersthene chondrites		
Bruderheim	.040	
New Concord	.040	
	.046	
Leedey	.054	
Dhurmsala	.072	
	.085	
Marion, Iowa	.080	
	.085	
Farmington	.11	
	.11	
Ergheo	.11	
	.12	
Modoc	.18	
	.18	
Olivine-pigeonite chondrites		
Karoonda	.10	
Chainpur	.57	
Mokoia (carbonaceous)	.75	0.84 (*3*)
		.65 (*3*)
		.47 (*4*)

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