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HELIUM IN LIMESTONE AND MARBLE*

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ABSTRACT

The helium and uranium content of a number of specimens of marble, Iceland spar and fossil shell of known age have been determined. The sedimentary calcite specimens contained only a small fraction of the helium expected, indicating that most of the uranium is external to the lattice. The marbles in contrast contain much more helium than is calculated from the age and the alpha activity. This appears related to the gaseous inclusions in these materials.

INTRODUCTION

This work was undertaken to evaluate the potential use of the alpha-helium method in the dating of carbonate materials. Such mineral phases as marble in metamorphic rocks, crystals of calcite associated with the gangue of hydrothermal deposits and fossil shells are common so that a means of directly dating them would have considerable value.

Earlier theoretical work has shown that reasonably perfect calcite crystals should not permit diffusion of helium at surface temperatures (Keevil, 1940). On the other hand, pioneer measurements on such materials (Keevil, 1950) showed both more and less helium than would be expected from the uranium-thorium content and the age. In view of the imposing experimental difficulties in accurately measuring the extremely small quantities of helium by the older volumetric techniques, the uncertainty in the age of the specimens and the limited selection of mineral types, further investigation was desirable. In the work described below, the helium was determined by the method of isotope dilution and the alpha activity by the radium emanation and fluorimetric techniques.

The terms "excess" and "deficiency" of helium in this study refer to the amount of helium observed compared to the amount expected from the rate of production and the age of the mineral. If either existed it was hoped that the causes could be defined so that evaluation of the potential age method could be made.

EXPERIMENTAL TECHNIQUES

Helium Determination

The helium was determined by isotope dilution using He^3 as a spike. The vacuum systems used for preparation of the He^4 standards and the He^3 spikes have been described by Damon (1956). Two He^3 spikes from

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each set of thirty were calibrated with primary He^4 standards. The average deviation from the mean of the calibrations was about 2% and indicates uniformity of He^3 pressure throughout the set.

The gas liberation and purification system is similar to that described by Damon. The carbonate samples are not actually fused but merely decrepitated at about 800° C. in which process the helium is liberated with the carbon dioxide. When the sample has begun to decrepitate, the He^3 tracer is admitted to the furnace side of the system. Since pure carbonates have such a low uranium content, it is often necessary to process 10–30 gm. samples. Thus, up to a third of a mole of CO_2 may be liberated. Essentially all the CO_2 freezes at liquid nitrogen temperatures in the large cold trap adjacent to the furnace. Other gases are pumped out of the furnace by a mercury diffusion pump specially designed to pump against high back pressures. They pass through a U-tube filled with CuO and maintained at a temperature of 600° C. where any hydrogen reacts to form water. The diffusion pump is allowed to continue pumping out the furnace side after decrepitation is complete, until a vacuum of 10^{-6} mm. of Hg is achieved in the furnace volume. Still more pumping time is allowed to ensure equilibration and quantitative transfer of helium out of the furnace. The furnace is then isolated from the sample purification side by means of a stopcock and gases condensed on the charcoal trap at liquid nitrogen temperatures are successively sublimed and recondensed as an aid to equilibration. Final purification is achieved by allowing these gases to react with metallic calcium at 700° C. When this process is completed, the helium is compressed into a sample breakseal by allowing mercury to rise into a 500 ml. reservoir at the top of which is attached the breakseal. All of the helium is thus compressed into the sample breakseal which is then detached and transferred to the sample introduction system of the mass spectrometer.

The standard deviation on individual helium measurements was 6%. Blank runs on the fusion system included mock fusions with Pleistocene coral and barnacle samples. All blanks were negative (see Table 1); however, the amount of atmospheric helium introduced to the system during the operation of the CuO furnace cannot be tolerated for very low level measurements. Hence, in the case of fossils, removal of impurities by adsorption on charcoal at liquid nitrogen temperatures must be substituted for the chemical removal of the impurities.

Regardless of which procedure is used, gross fusion system leaks can be effectively monitored by scanning the Ne^{20} peak during the spectrometer measurement. This is not applicable to diffusion leaks however, since neon will not diffuse significantly through quartz and vycor at elevated temperatures, whereas helium will.

TABLE 1. HELIUM CONTENT OF SPECIMENS OF CALCIUM CARBONATE

Sample	Description	Procedure used to purify helium	Blank assoc. with procedure (microliters He^4)	Total He^4 in sample (microliters)	Weight of sample (g)	He^4 (microliters/g. rock)
I. *Sedimentary or Low Temperature Origin*		Charcoal at Liq. Air temp.	.002			
KT-1	Ammonite composite from U. Cret. Pierre Shale, Mobridge, S. Dakota, Baculites (sp.)			.034± .006	10.6	.0032± .0006
SB-3	U. Cret. Belemnite from N.J. coastal plain.			<.0024	14.4	<.0002
No. 475A	Pleistocene Barnacles, Vancouver Island, British Columbia			<.0020 <.0030	13.5 10.4	<.0002 <.0003
JS-1	Iceland Spar, Joplin, Missouri			<.002	20.6	<.0002
II. *Metamorphic Origin*		CuO	.02			
IN-1	Inwood Marble, Thornwood, N.Y., crystal size ~5 mm.			.30 .88	10.4 31.6	.029± .002 .028± .002
RC-1	Pink Carbonate from Sterling Zinc Mine, Ogdensburg, N.J. 2550′ level. Avg. crystal size 5–10 mm.			.90	33.3	.027± .002
SH-3C	Same as RC-1 except sample colorless.			.61	25.6	.024± .002
G5K	Grenville marble from No. 1 pit along Rt. 7 about 4 mi. east of Deloro turnoff on Rt. 7 east of Marmora, Ont. Avg. grain size ~2 mm. contains about 3% tremolite.			4.34	8.343	.52
				6.75	10.81	.62
				11.5	22.98	.50
				18.2	39.56	.46
				7.10	11.20	.64
				12.7	26.39	.48
				18.5	33.01	.56
				25.7	47.57	.54
				6.00	12.75	.47
				5.09	9.83	.51
						Avg. .53± .02
G5K <200 mesh				2.31	10.71	Avg. .21± .02

Helium measurements were made using the first order, 60°, 6 inch radius mass spectrometer described by Carr and Kulp (1957). The present helium sensitivity of the instrument is about one millivolt per 10^{-5} s.c.c. before the molecular leak using a 10″ ohm reed lead resistor. The half time of helium before the leak is about 40 minutes. Thus fractionation of the helium isotopes through the leak can, during the course of a normal run, alter the ratio by as much as 3%. The observed ratios, however, are extrapolated back to the time of presentation of the sample before the leak, or a fixed time thereafter. Since this procedure is followed both in the initial spike calibration and in sample runs, the fractionation effect is essentially canceled. The introduction system is static leak-tested prior to liberation of the sample using the A^{40} peak and, as stated earlier, the fusion system can be checked for gross leaks by scanning the Ne^{20} peak during the course of the run. In addition, the H_2 peak is scanned to insure that there is no significant contribution to the mass-3 peak from HD.

Radium Measurement

Radium was determined by dissolving samples in phosphoric acid and counting the radon gas in equilibrium with the dissolved radium. Radium determinations were reproducible to within 10%. Assuming complete secular equilibrium in the rock, the uranium content of the rock can be calculated and compared with that measured by other techniques. The agreement is good considering the extremely low concentrations of uranium in these materials and the uncertainty in the absolute level of fluorimetric analysis (Table 2).

It appears that the radium measurement can be used to assess the helium production rate in these samples. This is largely because the average limestone has a thorium:uranium ratio of only 0.5 as compared to 3.5 for an average granite. Furthermore, any given amount of thorium produces alphas at less than one-fourth the rate of an equal amount of ordinary uranium. It would be expected then, that the total rate of helium production would be within about 10% of that predicted on the basis of uranium or radium analyses alone.

Fluorimetric Procedure

Uranium determinations by the fluorimetric method were performed on all samples. A combination of dilution and solvent extraction was used to separate the uranium from possible interferences and quenchers. Aluminum nitrate was used as a salting agent and the uranium was extracted into ethyl acetate. The ethyl acetate was evaporated off gold dishes and the uranium then incorporated into buttons of flux containing sodium fluoride. The intensity of fluorescence was then determined using a Jarrell-Ash G-M Fluorimeter. Samples were run in groups of ten including three standards and a blank. Reproducibility was about 10% in this concentration range.

TABLE 2. MEASUREMENTS OF THE ALPHA ACTIVITY
parts per million uranium

Sample	Radium given as 10^{-12}g. Ra/g.	Calculated from Radium Content	Fluorimetric Measurement	Alpha activity of rock based on fluorimetric U analsis α's/mg./hr.
KT-1	.44± .04 (unleached)	1.2± .01	1.3± .1 (unleached)	.48± .05
	.36± .04 (leached)	1.0± .01		
SB-3			.31± .03	
			.25± .03	.10± .01
			.28± .03 Av.	
ML-1†	.31± .03	.87± .09	1.10± .10	
	.29± .03	.82± .08	1.25± .10	.44± .04 .38± .01*
	.30± .03 Av.	.85± .09 Av.	1.18± .10 Av.	
JS-1	.046± .005	.13± .01	.13± .01	
			.10± .01	
			.11± .01	
			.16± .01	.045± .005
			.12± .01 Av.	
			.19± .01 (<200 mesh, leached)	
RC-1	.0035± .0004	.010± .001		
	.0037± .0004	.010± .001	< .02	
	.0036± .0004 Av.	.010± .001 Av.	< .02	<.007
SH-3H			< .02	<.007
			< .02	
IN-1	.034± .004	.10± .001	.12± .01	
	.039± .004	.11± .001	.10± .01	.041± .004
	.037± .004 Av.	.11± .001 Av.	.11± .01 Av.	
G5K	.056± .006	.16± .02	.39± .04	
	.051± .005	.14± .01	.23± .03	.11± .01
			.27± .03	
	.054± .006 Av.	.15± .02 Av.	.30± .03 Av.	

* Isotope Dilution Method performed by J. C. Cobb, Lamont Geochemical Laboratory gave 1.02 ± .02 ppm uranium.

† Oolitic limestone from the Spergin formation (Mississippian). See Sackett 1958.

RESULTS

The sample descriptions and the helium concentrations are given in Table 1. Sample KT-1 was found to be entirely aragonite by x-ray diffraction. The sample of Pleistocene barnacles represents a blank. SB-3 and JS-1 also showed negligible helium. The reproducibility shown by samples IN-1 and G5K are satisfactory. The error given on the average of the determinations of G5K is the standard error on the mean.

The radium and uranium determinations are given in Table 2. The estimated uranium content from the fluorimetric measurements and that inferred from the radium measurement assuming radioactive equilibrium is the same within the experimental uncertainties for all samples, except the Grenville marble where the uranium content from the fluorimetric determination is double that calculated from the radium content. This implies radioactive equilibrium for all cases except the Grenville marble. The ML-1 sample was also analyzed for uranium by isotope dilution. The figure obtained agreed with the average of the uranium content calculated from the radium and fluorimetric analyses. The alpha activity of the rock was estimated in each case from the fluorimetric analyses and the assumption that the thorium content is negligible.

The alpha activity of most of these samples is too low for direct determination except in the case of KT-1 and ML-1. Using the method described by Kulp *et al.* (1952) ML-1 was counted after calibration of the system with NBS standards. The alpha activity agree with that predicted from the fluorimetric analysis within the experimental errors of both methods suggesting that the Th:U ratio was less than 0.4. This is in agreement with the result of Sackett (1958) who obtained a ratio Th:U of .15 by neutron activation analysis. The Th:U ratio is normally less than 0.5 in reasonably pure carbonates. Since the specific alpha activity of the thorium is only one-fourth that of uranium, the contribution from thorium to the total alpha activity in these samples is probably negligible.

The alpha activities reported in Table 2 are 10^{-1} to 10^{-3} times that for typical granitic rocks.

HELIUM LOSS IN ROCKS AND MINERALS

Keevil (1940) has treated the diffusion of helium in various crystal lattices from a theoretical point of view. In the absence of suitable experimental data such an approach is necessary to estimate potential losses of helium.

Distances of approach of helium to neighboring ions in a crystal lattice depend on weak attractive forces resulting from perturbations or induced polarizations ($\sim$130 cal/g mole) and important repulsive forces which change sharply with distance and which determine the effective "size" of the helium atom. Equilibration separation from oxygen corresponds to an interatomic distance of about 2.3 Å and to bring the helium atom within the range corresponding to an effective helium radius of .95 Å would require 13 k cal/mole. Experimentally determined values indicate that this is a minimum radius but even this is large compared with spacings in most crystal structures. This is indicated by the fact that diffusion experiments with glasses show that the diffusion rate is strongly dependent on the radius of the inert gas (T'sai and Hogness, 1932). In silica glass the average pore openings larger than the helium atom are about 1.3 Å in radius. It is generally true that if the channels are less than 2 Å in diameter the energy of activation to move helium along the channel is very high and rises sharply with decreasing channel width. In old glasses that have partially recrystallized it has been observed that the rate of diffusion is greatly reduced. When glasses completely recrystallize with disappearance of the larger metastable holes, the activation energy would be expected to greatly exceed that which the helium atom possesses as the result of its thermal agitation

$$\left(\bar{E}_{km} = \frac{3}{2} kT\right).$$

On the other hand, the helium atom impinges, with some energy, on the potential barrier between it and the next potential valley with a frequency which is very high ($\sim 10^{13}$ sec^{-1}) throughout the entire course of geologic time. Knowing the frequency of vibration and taking $e^{-E/kT}$ as the probability that, at any instant, a given helium atom possesses enough energy to get it over an opposing potential hill of height E, the number of times a helium atom vibrating between two such hills could surmount one in any length of time can be calculated. The probable distance of diffusion of a helium atom in a crystal in any time is then, according to the Einstein relation, the product of the time, the mean path length from one valley to the next, and the average velocity of the vibrating helium atom. Keevil (1940) performs these calculations considering the effect of thermal motion of the bordering ions in temporarily widening the channel so that the helium atom might pass. There is required synchroneity of vibration of all the ions away from the channel rim while at the same time the helium atom possesses enough energy to allow it to pass through the temporarily widened channel. The probability that all this will happen is the product of two terms. The first is the probability that all the n atoms around the rim will vibrate a given distance away from the rim at a given moment and is, of course, the nth power of the probability that this will occur for any one individual which in turn depends on the vibrational force constant of the ions. The second is the probability that at just this moment the helium atom will possess enough energy to get it through the channel before it narrows again. At any temperature this product, which represents the key rate determining step in the diffusion process, reaches a maximum value at a certain vibrational amplitude. Because Keevil (1940) uses this vibrational amplitude corresponding to the highest diffusion rate and because of the relation used for dependence of repulsive force on distance, his calculations can be regarded as conservative. Even so, they indicate that the diffusion path of a helium atom through most crystal lattices at 600° K. during geologic periods of time would only be a few interatomic distances long.

It is improbable that helium is "exsolved" since it is present in such low quantities. Thus it has never been possible to correlate helium "retentivity" with helium content except where minerals are actually metamict. Some loss might be expected where alpha tracks end in minute cracks resulting from substitution of different sized ions or from surface tension during growth. These cracks may be spaced on a very fine scale down to about 10^{-6} cm., but, barring reflection phenomena at phase boundaries, there is no reason to expect the per cent of the alpha tracks which end in these cracks to exceed the volume per cent of the mineral represented by the cracks and this is very low. If cracks were present with a spacing of 10^{-6} cm. throughout a crystal, and a sharp rise in structural strength at these edge lengths for some crystals indicates that this may be the case, the diffusion constants are still about a factor of 10,000 too low at 300° to allow much diffusion; but at 600° it would be significant. The barrier height implied in this calculation is based on measured distances between oxygen atoms and is about a factor of ten higher than the lower limit set by Rayleigh for calcite; but ordinarily, since the diffusion rate is such a sensitive function of channel width, it is not only the equilibrium interatomic distance between oxygen atoms but also the ability of the oxygens to vibrate about this mean position that determines the diffusion rate. Thus critical factors include the force constant for vibration of oxygen atoms and the effect of local distortion due to the presence of the large foreign helium atom in the structure.

All attempts to force helium through common minerals, including calcite, have failed. Rayleigh (1936) succeeded in setting a lower limit on the activation energy of 21.5 k cal/mole. Unfortunately, calculations based on a non-rigid lattice model show that it is still just possible that, if the activation energy is no greater than this, the diffusion distances might, in geologic time, approach the crack spacing in the crystal. Rayleigh also had determined the activation energy for mica at a similar value but was later able to raise the limit to 47 k cal/mole which prohibits significant helium diffusion in mica perpendicular to the cleavage. It is important to note that all of the experimental results on diffusion through minerals were negative which means that the activation energy is probably higher than 21.5 k cal/mole. At least, although they are not very definitive, the experimental data accumulated to date have not contradicted the theoretical conclusions of Keevil. Diffusion theory and experiment, then, indicate negligible helium loss by diffusion through ordinary crystal lattices in geologic time.

In contrast, essentially all of the helium age determinations made during the last thirty years seem to indicate that, in most rock forming minerals, the ratio of observed helium to expected helium is less than unity. This suggests that the answer lies in the location of the uranium atoms.

If the activity is surficially concentrated (Hurley, 1956), in intergranular microcrystals of uranium and thorium minerals in igneous rocks, in association with a free organic phase in sediments or merely on grain boundaries, the helium from this uranium-thorium and their decay products would be expected to leave the rock. Thus even if the helium produced within the calcium carbonate lattice were quantitatively retained, the ratio of observed to expected helium would be less than unity.

DISCUSSION

It may be seen from Table 3 that the specimens of calcium carbonate crystal formed at low temperature all show a deficiency of helium, whereas those found in a metamorphic environment show an excess of helium.

The alpha activity and the helium content are taken from Tables 1 and 2.

Probable ages were assigned to the samples on the basis of regional U-Pb and K-A dates. The absolute ages assigned to the fossils are consistent with an age of 90 m.y. for the base of the Santonian (U. Cret.)

TABLE 3. HELIUM RETENTION IN FOSSIL SHELLS AND LOW TEMPERATURE DOG-TOOTH SPAR

Sample	Alpha Activity α's/mg./hr.	Geologic Age	Expected He^4 content mic./g.	Measured He^4 content mic./g.	% Retained
KT-1	.48 ± .05	90	.014 ± .001	.0032 ± .0006	22
SB-3	.10 ± .01	90	.0030 ± .0003	< .0002	< 7
JS-1	.045 ± .005	100	.0015 ± .0007	< .0002	< 13
		Helium Excess in Marble			
					(% Excess)
G5K	.11 ± .01	1040	.041 ± .004	.53 ± .03	~1200
IN-1	.041 ± .004	360	.0050 ± .0005	.029 ± .002	~ 600
RC-1	< .007	850	< .002	.027 ± .002	> 1000
SH-3C	< .007	850	< .002	.024 ± .002	> 1000

(Kulp, 1959). Concordant U-Pb dates on zircon and uraninite indicate a probable date of about 1040 for the Grenville event (Eckelmann and Kulp, 1957). Potassium-argon ages on Sterling Hill micas give an age of about 850 m.y. (Long and Kulp, 1959) for the last major metamorphism of the area. Potassium-argon ages on phlogopite from the Inwood marble and surrounding rocks (Long and Kulp, in press) indicate a major event at about 360 m.y. It is possible that the Inwood marble was formed as early as 850 m.y. and that the 360 event did not heat the rock sufficiently to cause loss of helium. The fact that the 360 event produced widespread pegmatites, however, points to a significant metamorphic event. It is also possible that the Sterling Hill marbles may have been produced at about 1100 m.y. ago and survived the 850 m.y. event. As will be shown below, the uncertainties in the true age are not critical to the argument.

On the basis of the ages and the alpha activities listed in Table 3, the "expected" helium content of the rock is calculated. This is the amount of helium produced in the rock by radioactive decay since its formation. The per cent "excess" helium is defined as

$$\frac{\mathrm{He}_{\mathrm{measured}} - \mathrm{He}_{\mathrm{expected}}}{\mathrm{He}_{\mathrm{expected}}} \times 100.$$

Likewise in case the mineral contains less than the expected amount and hence has lost helium, the per cent retained is,

$$\frac{\mathrm{He}_{\mathrm{measured}}}{\mathrm{He}_{\mathrm{expected}}} \times 100.$$

The results on the fossil shells KF-1 and SB-3 show that most of the uranium must be located on the surface of grains or in association with the organic phase. Since the ammonite composite, KT-1, is still aragonite the loss of helium cannot be explained by loss during recrystallization of the primary calcium carbonate to calcite. Some evidence for the surficial uranium may be the lower radium content observed for KT-1 after leaching with acid (Table 2). In most cases, as in JS-1, it is unlikely that leaching can be sufficiently selective to determine the fraction of uranium in surficial sites.

The dog-tooth spar from the Joplin, Missouri lead deposits was surely formed at low temperature and atmospheric pressure. It shows loss of at least 85% of its helium if the time of formation is accepted. The latter is probably uncertain by a factor of two but this does not alter the picture.

It is concluded that the helium produced from the uranium atoms and their decay products in the calcite or aragonite lattice is quantitatively retained. In shells and other low temperature products this may represent only a small fraction of the total helium generated in the sample in the course of its geologic history, thus accounting for the low retentivity.

Since the ratio of external to internal uranium is highly variable, no retentivity factor can be defined to correct the experimental He/U ratio to the actual one for the system as a whole throughout its geological history. As a result it appears that the helium age method cannot be used in sedimentary carbonates. It is probable that this conclusion applies to all minerals with low uranium content and high internal surface area.

The results on the helium content of a selected group of marbles indicate that there may generally be a large excess of helium. The Grenville sample (G5K) has twelve times the helium expected from the uranium content. The samples from New Jersey Highlands (RC-1 and SH-3C) appeared to have an equally large excess but here the uranium analysis is too low to permit an accurate estimate to be made. The sample from the Inwood marble shows six times the expected helium content.

TABLE 4. EXCESS HELIUM AND ARGON IN MARBLES AND BERYL

Sample	He^4 micro'iter /g.	He^4/A^{40}
G5K	.53	>2000
G5K (<200 mesh)	.21	
IN-1	.029	
SH-3C	.024	
RC-1	.027	
Average of 12 beryls (Damon and Kulp, 1958)	27	21±15

The presence of "excess" helium in these samples is evidence for the inherent high retentivity of the calcite lattice. Under magmatic-metamorphic conditions it appears that helium can be trapped in inclusions in the growing calcite crystals. The quantity that is trapped is far less than is observed in beryl and cordierite lattices (Damon and Kulp, 1958) which contain channels of sufficient size to incorporate large foreign ions readily. For example, the Grenville marble shows 10 times less non-radiogenic helium than the average beryl (Table 4). This is probably present in small vacuoles in the calcite since all of these marbles showed liquid-gas inclusions frequently localized on sharply defined planes traversing intergrain boundaries. Microscopic examination of a <200 mesh fraction revealed some tendency to preferred breakage along these inclusion-rich planes. Thus it was not surprising that grinding to less than 200 mesh decreased the helium content by more than a factor of two.

If the uranium were fairly homogeneously distributed in the rock, the produced helium should be even more so because of the range of the alpha particles. Hence for nearly perfect crystals the loss of helium on grinding should not be significant unless the resulting fragments were of unit cell dimensions. The observed loss confirms the conclusion that the excess helium is largely located in inclusions. If significant diffusion had occurred it might be expected that the helium would be more homogeneously distributed.

It is particularly interesting to note that after grinding, the helium content of the Grenville limestone dropped by more than a factor of two although a significant fraction of the inclusions remained intact. Thus it appears that it may be possible to obtain an approximation to the true age of marbles from the uranium/helium ratio under certain conditions, particularly if the sample had only large inclusions and no small ones. Nevertheless, the method does not appear to have much practical value due to the large uncertainties involved.

A single determination of the argon content of the Grenville specimen indicates a much higher ratio of helium to argon than the average for the beryls formed in the pegmatite environment. Possibly this reflects the U/K ratio of the immediate environment during metamorphism but more measurements would be required to establish this hypothesis.

CONCLUSIONS

1. The gross helium retentivity in shells and sedimentary carbonate crystals appears to be small and highly variable. Although the actual retentivity of the calcite lattice is considered to be essentially 100%, the low gross retentivity is due to the high ratio of external to internal uranium.

2. Coarse-grained marbles appear to retain their helium quantitatively, but "excess helium" is present due to fluid inclusions containing gases present in the metamorphic environment. Upon grinding, the marble may break along the planes containing the fluid inclusions and thus reduce the helium/uranium ratio.

3. The helium method does not appear to be a practical geochronometer for carbonates.

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REFERENCES

CARR, D. R. AND KULP, J. L. (1957), The potassium-argon method of geochronometry: *Geol. Soc. America Bull.*, **68**, 763–784.

DAMON, P. E. (1956), Helium and argon in the lithosphere and atmosphere: Ph.D. thesis, Dept. of Geology, Columbia University.

——— AND KULP, J. L. (1958), Excess helium and argon in beryl and other minerals: *Am. Mineral.*, **43**, 433–459.

ECKELMANN, W. R. AND KULP, J. L. (1957), Uranium-lead method of age determination, Part II: North American Localities: *Geol. Soc. America Bull.*, **68**, 1117–1140.

HURLEY, P. M. (1956), Variations in isotopic abundances of strontium, calcium and argon and related topics: *M.I.T. Annual Progress Report for 1955–56, U. S. Atomic Energy Commission Contract AT (30-1)-1381.*

KEEVIL, N. B. (1940), Interatomic forces and helium in rocks: *Proc. Am. Acad. Arts and Sci.*, **73**, No. 11, 311–359.

——— (1950), Radioactivity and mineral deposits: *Am. Mineral.*, **35**, 816–833.

KULP, J. L., HOLLAND, H. D. AND VOLCHOK, H. L. (1952), Scintillation alpha counting of rocks and minerals: *Amer. Geophys. Union Trans.*, **33**, No. 1, 101–113.

——— (1959), Absolute age determination of sedimentary rocks: *Proc. Fifth World Petroleum Congress, Section I, Paper 37*, 689–704.

LONG, L. E. AND KULP, J. L. (in press), Isotopic age study of the metamorphic history of the Manhattan and Reading Prongs: *Geol. Soc. America Bull.*

RAYLEIGH, J. W. S. (1936), Studies on the passage of helium at ordinary temperature through glasses, crystals, and organic materials: *Proc. Roy. Soc. (London)*, **156**, Series A, 350–357.

SACKETT, W. M. (1958), Ionium-uranium in marine deposited calcium carbonates and related minerals: Ph.D. thesis, Dept. Chemistry, Washington University, St. Louis, Mo.

T'SAI, L. S. AND HOGNESS, T. (1932), The diffusion of gases to fused quartz: *Jour. Phys. Chem.*, **36**, 2595.

Manuscript received April 21, 1960.