[American Journal of Science, Vol. 255, December 1957, P. 697-704]

ARGON IN MICA AND THE AGE OF THE BERYL MT., N. H., PEGMATITE*

PAUL E. DAMON and J. LAURENCE KULP

ABSTRACT. A^{40} and K^{40} measurements on specimens of margarite (calcium mica) from two Appalachian localities and potassium micas associated with the Beryl Mt., N. H., pegmatite and associated country rocks are used to show the probable absence of appreciable primary argon in these minerals. The age of the Beryl Mt. pegmatite and associated regional metamorphism appears to be 323 ± 10 m.y.

INTRODUCTION

The potassium-argon method of age determination requires that the following conditions be met in order to obtain absolute ages: (1) The decay constant must be known: (2) the A^{40} produced by K^{40} decay during the life of the mineral must be quantitatively retained: (3) no significant A^{40} should be incorporated in the mineral at the time of its formation. Recent interlaboratory comparisons indicate that the analytical techniques are adequate (Carr and Kulp, 1957: Baadsgaard, Goldich, Nier and Hoffman, 1957). The decay constants are discussed below: they now appear reasonably well established by both physical and geological methods. Comparison of K^{40}/A^{40} ages on micas from a number of localities with uranium-lead and rubidium-strontium ages (Wetherill, Wasserburg, Aldrich and Tilton, 1956; Carr and Kulp, 1957: Goldich, Baadsgaard and Nier, 1957) has indicated that this mineral commonly retains all its argon, although there are cases where loss occurs, presumably due to thermal effects during the history of the mineral (Gast, Kulp and Long, in press).

It has been known for a half century that beryl invariably contains more helium than has been produced by the decay of uranium and thorium within the mineral subsequent to its formation (Strutt, 1908). More recently Aldrich and Nier (1948) have reported an excess of primary argon as well as helium in several essentially potassium free beryls. Wasserburg et al. (1956, p. 157) have called attention to this phenomena as a possible source of error in the K-A age method, but they have concluded that the available evidence, although not definitive, does not indicate the presence of inherited argon in mica. The discovery of excess (primary) argon and helium in the lattices of cordierite, tourmaline and some amphiboles (Damon and Kulp, in press), as well as in beryl, has pointed up the necessity of further investigation of this phenomenon in micas which otherwise appeared to be suitable for age work. The Beryl Mt., New Hampshire, pegmatite was chosen as the prime locality for further investigation because (1) excess gas had already been demonstrated in several minerals from this deposit (Strutt, 1911); (2) the deposit was young and, (3) age work by isotopic methods was very limited in this metamorphic district.

Two types of measurements were made in an attempt to define the possible existence of primary argon in micas: (1) A^{40} concentration in non-potassium micas and (2) A^{40}/K^{40} ratios on micas of differing potassium content from the same pegmatite where excess argon in beryl had been demon-

* Lamont Geological Observatory Contribution No. 267.

strated. The study of the non-potassium micas would show in general whether the mica-type lattice incorporates appreciable primary gas. The second study, although somewhat less sensitive, would show whether excess argon is present in potassium-micas in a normal pegmatite-country rock environment.

ANALYTICAL TECHNIQUES

The experimental techniques used in this laboratory to determine the potassium and argon content of minerals have been described by Carr and Kulp (1957) and Damon and Kulp (1957). Briefly, radiogenic argon (A^{40}) is released from the mineral in vacuum by direct fusion without flux. The radiogenic argon is equilibrated with a known amount of A^{38}, purified and completely recovered on charcoal at liquid nitrogen temperature, and the isotopic ratio is measured on a mass spectrometer to determine the amount of A^{40} present in the mineral.

Potassium analyses of the mica samples were made by Ledoux and Co. using a wet chemical method (Kallman, 1956). The potassium content of the albites was determined by flame photometry, and an upper limit was set on the potassium content of the beryls by a modification of the radiochemical method (Damon and Kulp, in press) first described by Gaudin and Pannell (1948). The analytical precision given for the results in table 1 has been determined from a large number of replicate measurements from previous work in this laboratory.

DECAY CONSTANTS

K^{40} decays by competing processes to A^{40} (K capture with associated gamma emission) and Ca^{40} (beta decay). At any time the fraction which decays to A^{40} is given by the ratio of the decay constant for K electron capture (λ_e) to the total decay constant ($\lambda_e + \lambda_\beta$) where λ_β is the decay constant for the beta transition. The amount of K^{40} which has decayed during a past time t measured from the Present is simply $K^{40}\ (e^{(\lambda_e+\lambda_\beta)t} - 1)$, and so the amount of A^{40} produced during time t is:

$$A^{40} = \frac{\lambda_e}{(\lambda_e + \lambda_\beta)} K^{40}\ (e^{(\lambda_e + \lambda_\beta)t} - 1)$$

or, solving for the time:

$$t = \frac{1}{\lambda_e + \lambda_\beta} \ln \left(1 + \frac{A^{40}}{K^{40}} \frac{(\lambda_e + \lambda_\beta)}{\lambda_e} \right)$$

Data on the necessary constants have been reviewed (Carr, Damon, Broecker and Kulp, 1956) covering the period up to late summer of 1955. The average of all reasonably accurate determinations from 1948 to the present, recalculated where necessary to conform to the latest knowledge of the decay scheme, gave $\lambda_\beta = 4.92 \times 10^{-10}$ and $\lambda_e = 0.574 \times 10^{-10}$ or 28.6 ± 0.9 dps/gm K and 3.33 ± dps/gm K for the beta and gamma activities respectively. Subsequently McNair, Glover and Wilson (1956) reported 27.6 ± .4β/g. sec. and 3.41 ± .10γ/g. sec. using proportional and scintillation spectrometry. Wetherill (1957), using refined scintillation technique and calibration against Co^{60} and Na^{24} gamma standards, obtained 3.39 ± 0.12

γ/g. sec. Backenstoss and Goebel (1955) reported 3.50 ± .01 γ/g. sec. using scintillation spectrometry and calibration with Pr^{142}, Co^{60} and Fe^{59}. For absolute geochronometry the uncertainties in these constants are still larger than is desired. By giving most weight to the most recent measurements of both beta and gamma determinations the authors have chosen 3.4 γ/g. sec. and 28 β/g. sec. for computation and consider them accurate to ± 5 percent. These correspond to $\lambda_e = 0.58 \times 10^{-10}$ and $\lambda_\beta = 4.8 \times 10^{-10}$ which will be used in this paper.

Wetherill et al. (1956) have calculated λ_e by a comparison of A^{40}/K^{40} ratios on minerals dated by concordant U-Pb and Th-Pb isotope ratios. They obtained $\lambda_e = 0.557 \pm .026 \times 10^{-10}$ assuming a value of $\lambda_\beta = 4.72 \times 10^{-10}$, the latter not being at all critical. This is a useful approach as the measured A^{40}/K^{40} age is more sensitive to λ_e in young minerals (<1. b.y.). Since the possibility of limited argon loss cannot be eliminated and the U-Pb ages for the three youngest localities used by Wetherill et al. are not certain to more than 3-5 percent, it seems better to use the most probable decay constants determined by direct physical means. Unless this is done, other potentially significant processes such as diffusion of argon from the minerals may be obscured.

The original data in this paper are given in terms of the A^{40}/K^{40} ratio because this is a directly measured quantity independent of the choice of decay constants.

ARGON CONTENT OF MARGARITE

Two specimens of margarite (calcium mica) were analyzed in an effort to detect lithospheric argon that may have been trapped in the mica structure at the time of mineral formation (table 1). These samples have a probable age of about 350 m.y.

TABLE 1

Argon Content of Two Specimens of Margarite

Locality	A^{40}* microliters per gram S.T.P.	K %	A^{40}/K^{40}
Ashland, N. C.*	<.001	<0.05	—
Unionville, Pa.**	~.004	~0.15	~.034

* 30 gram samples were fused. The A^{40} content has been corrected for atmospheric contamination (~.002 microliters per gram).

** from Emery and Corundum Co. Property, Ashland, N. C.

*** from Corundum Hill, Unionville, in the township of Newland, Chester Co., Pa.

Muscovite and biotite specimens of rocks of about this age contain .08 to .15 microliters per gram (Carr and Kulp, 1957). It appears from table 1 that margarite does not permit appreciable A^{40} to be built into the crystal at the time of mineral formation ($<1 \times 10^{-6}$ scc./g). A less likely interpretation is that the interlayer position in margarite permits loss by diffusion and thus an original excess of argon would not be detected.

ARGON CONTENT OF POTASSIUM MICAS AND OTHER MINERALS OF THE BERYL MT. PEGMATITE

The Beryl Mt. pegmatite has been intruded into the schistose amphibolites and interbedded metasediments comprising the Littleton formation about 0.8 miles south of the village of South Acworth in the Keene pegmatite district of New Hampshire (Cameron et al., 1954). A sketch map of the Beryl Mt. area is shown in figure 1. Most of the minerals studied came from the main pit

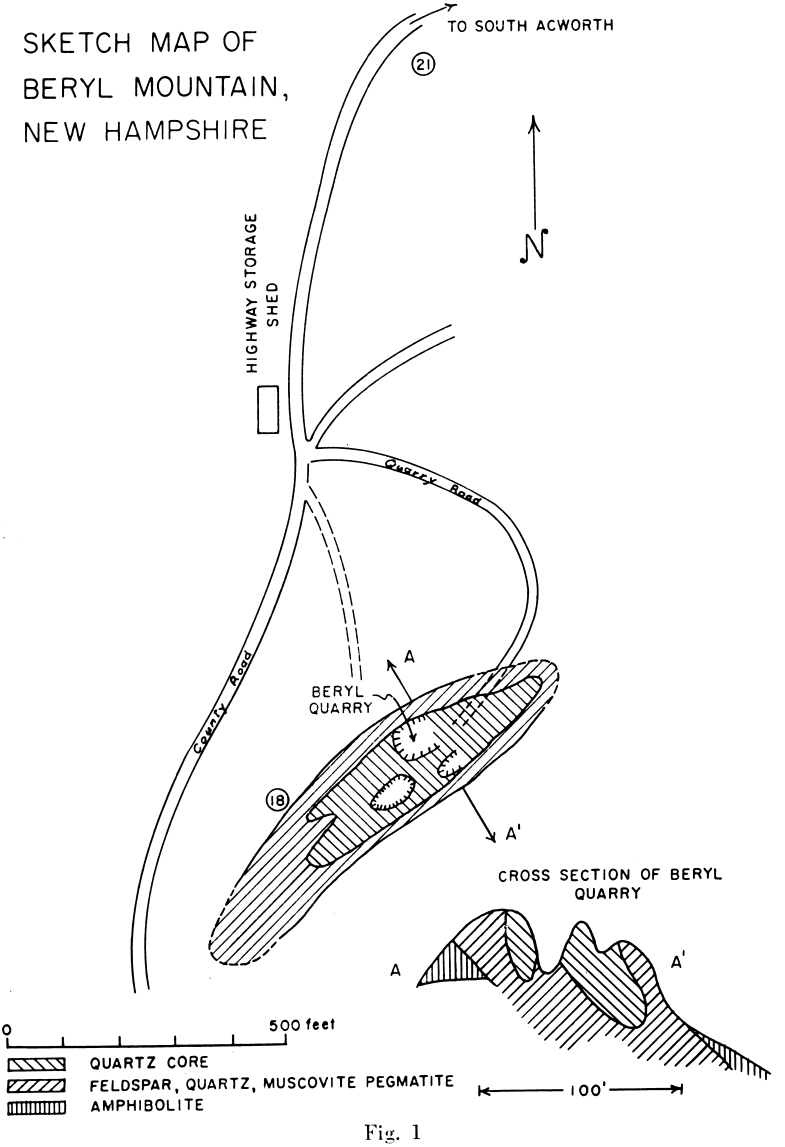

Fig. 1

where the pegmatite is best exposed and in which beryl is abundant. The pegmatite has a core of massive white and rose quartz. The core is flanked by an intermediate zone consisting primarily of perthite and quartz which contains large cylindrical crystals of albite, large books of wedge mica and crystals of green and yellow-brown beryl up to 5 feet in length. The intermediate zone, which is about 25 feet to 50 feet wide, grades into a wall zone consisting primarily of coarse graphic granite but containing small clusters of biotite, sooty black crystals of tourmaline and small garnet dodecahedrons. The origin of the pegmatites in the Keene district, according to Cameron et al. (1954), is either from underlying bodies of the New Hampshire magma series (Concord granite), or from the concordant injections of Bethlehem gneiss that occur abundantly in the Littleton formation.

TABLE 2

Argon in the Beryl Mt. Pegmatite

Sample Number	Mineral	A^{40}* microliters per gram S.T.P.	K %	A^{40}/K^{40}	Apparent Age m.y.
A. *Micas*					
BMD-16m	muscovite	0.120 0.123	8.39 8.70	0.0209 0.0208	329±13 328±13
BMD-3b	muscovite	0.118	8.48	0.0203	321±13
BMD-15	muscovite	0.0995	7.22	0.0202	319±13
BMD-10	muscovite and biotite from xenolith	0.0969 0.0879	6.88 6.87	0.0206 0.0188	327±13 299±13
BMD-18a	biotite from contact zone	0.0696 0.0735	6.47 6.69**	0.0160	258±10
BMD-21	impure biotite from Littleton	0.0245	1.67	0.0215	338±15
			Average (18a omitted)		323±6
B. *Other Minerals*					
BMD-16p	perthite	0.0897	10.4	0.0136	238±10
BMD-3a	albite	0.0074	0.39 0.42**	0.026	402±94
BMD-3d	albite	0.0064	0.37	0.025	390±85
BMD-9	beryl	0.045	<0.05	>1.3	
BMD-2d	beryl	0.056	<0.1	>0.8	

* Radiogenic A^{40} after correction for atmospheric contamination. The correction varied from a few percent for muscovite up to 20 percent for albite.

** Analyzed by E. Oslund and C. O. Ingamells of the Univ. of Minnesota, Rock Analysis Laboratory.

Decay Constants $\lambda_e = 0.58 \times 10^{-10}$ yr.$^{-1}$; $\lambda_\beta = 4.8 \times 10^{-10}$

Analytical precision:

micas and perthite: $A^{40} = \pm 3.3\%$ s.d., $K = \pm 3\%$ s.d.
$A^{40}/K^{40} = \pm 4.3\%$ s.d.

albite: $A^{40} = \pm 20\%$ s.d. (est.); K determined by flame photometry (S. Kallman—Ledoux, mc) $= \pm 10\%$; $A^{40}/K^{40} = \pm 22\%$.

The results are given in table 2. The measured ages of three book muscovite samples from the main pit (BMD-16m, BMD-3b and BMD-15) and a mixture of muscovite and biotite separated from a xenolith of country rock enclosed in the pegmatite (BMD-10) are in excellent agreement despite a difference in potassium content of 25 percent. The agreement of the pegmatite and xenolith ages also shows that the country rock mica does not have any "inherited" argon from its existence prior to pegmatite intrusion. The beryl sample BMD-9, which like BMD-2d shows a large quantity of primary argon, was in direct contact with muscovite BMD-3b. Even in this case the muscovite shows no evidence of excess argon.

Biotite (BMD-18a) taken from the contact zone between the amphibolite country rock and the western side of the pegmatite shows an anomalously low age. X-ray examination of this specimen shows it to be partly chloritized which probably accounts for the low argon content. Further evidence of alteration was the unusual quantity of water and other volatiles released during fusion of this sample.

The perthite sample (BMD-16p) shows the usual (Wetherill, Aldrich and Davis, 1955; Carr and Kulp, 1957, Goldich, Baadsgaard and Nier, 1957) loss of argon. The albite samples appear to give the correct age, although the errors are large due to the low potassium content. The apparently higher retention of argon in albite compared with perthite is in contrast with the observation of Wasserburg and Hayden (1956) but may be merely the result of included veinlets of sericite (fine muscovite) which may contribute most of the potassium content.

AGE OF THE BERYL MT. PEGMATITE AND SURROUNDING ROCKS

The potassium-argon age of biotite separated from the Littleton formation about a quarter of a mile from the Beryl Mt. pegmatite was 338 ± m.y. which agrees with the pegmatite age within the experimental error. Table 3 compares the K/A ages from the Beryl Mt. pegmatite with lead-alpha ages on zircons, xenotime and monazite for the major units of metamorphic rocks in the area.

TABLE 3

Comparison of A^{40}/K^{40} Age of Beryl Mt. Muscovites with Pb/α Ages for the Oliverian and New Hampshire Magma Series

Geologic Formation	Age m.y.	Method and number of Analyses	Analyst This paper
Beryl Mt. Pegmatite	323	A^{40}/K^{40}: ave. for 5 micas	Lyons*
Concord Granite	330	Pb/α: ave. for 2 zircons, 1 xenotime and 1 monazite	Lyons*
Bethlehem Gneiss	317	Pb/α: ave. for 1 monazite and 1 zircon	
Oliverian magma series	322	Pb/α: ave. for 3 zircons	Lyons*

* See Faul (1954) p. 268.

It appears that the last major metamorphic event in this region took place about 325 m.y. ago, that the pegmatites and the Concord granite were

formed at the time of the regional metamorphism rather than later and that they are probably earlier than the Upper Devonian-Carboniferous age suggested on geologic grounds by Cameron et al., 1954. In any case the potassium-argon date on the Beryl Mt.-Littleton rocks places an upper limit to the time of deposition of the Littleton formation. If the Holmes-Marble (Marble, 1950) time scale is accepted, these results would make the Littleton deposition and metamorphism pre-Devonian. On the other hand if the Littleton deposition is taken as Oriskany (Lower Devonian) in age as the fossil assemblage indicates (Billings, 1937)—a more plausible approach—this may be a new and important control point in establishing the absolute post-Cambrian time scale. It would then be concluded that the Silurian-Devonian boundary is at least 330-340 m.y. ago.

Appendix

Description of Beryl Mountain, N. H., Pegmatite Samples

BMD-2d	Beryl, surrounded by 1/4" mica, smoky quartz and a large albite crystal. See Damon and Kulp (in press).
BMD-3a	Albite associated with quartz and beryl containing sericite veinlets near contact of quartz core with quartz-mica-feldspar intermediate zone.
BMD-3b	Large books of muscovite about 6 inches wide associated with quartz, albite and beryl; sample was carefully hand-picked to remove all visible impurities.
BMD-3d	Albite similar to BMD-3a.
BMD-9	Beryl, in contact with BMD-3b. See Damon and Kulp (in press).
BMD-10	Mixed muscovite and biotite from xenolith of quartz-mica schist containing nearly equal amounts of clean, unaltered, biotite and muscovite; garnet occurs as an accessory; one patch of tourmaline parallel to schistosity was visible in thin section; sample was pure except for a few small crystals of garnet.
BMD-15	Muscovite from graphic granite; several mms. in width; sample was separated by sieving and purified by hand-picking; obtained from main beryl pit in area where the intermediate pegmatite zone grades into the coarse graphic granite.
BMD-16m	Muscovite samples from a large book about 12 inches wide and 6 inches thick was free of inclusions and associated with perthite and quartz.
BMD-16p	White to honey-yellow perthite adjacent to BMD-16m containing a small amount of sericite in thin veins visible in thin section.
BMD-18a	Biotite from contact zone between western pegmatite and amphibolites near county road (fig. 1). Hand specimens nearest the contact contained about 40 percent hornblende, 15 percent biotite; remainder was primarily quartz and feldspar. Thin section of rock nearest contact, where biotite sample was obtained, showed that the grains were not well aligned but, rather, occurred in swirls and eddies with evidence of flow. Thin section from rock 10 feet from the contact showed well aligned, finer grains, no evidence of movement, no biotite but considerable fine-grained clean muscovite, much more quartz, less hornblende and scattering of opaques. Because of the coarseness of the biotite at the contact there was no difficulty in removing the hornblende by sieving. Remaining impurities were removed by heavy liquid separation (tetrabromethane) and water washing (panning).
BMD-21	Impure biotite concentrate from country rock, a quarter of a mile N from the pegmatite in a pasture beside the county road (fig. 1). It was similar to the amphibolites near contact of the pegmatite, but contained less amphibole; quartz and feldspar were the principal constituents; small amount of garnet. Sample was prepared by sieving; sericite was present but was removed by the sieving; heavy liquid separation (tetrabromethane) and water washing were used to remove amphibole. Later examination showed that considerable impurities remained, including amphibole, which contribute, in part, to the low potassium content.

CONCLUSIONS

1. The absence of measurable primary argon in calcium micas or in sets of potassium micas of differing potassium content suggests that primary argon is not a significant source of error in the potassium-argon dating method.

2. The time of regional metamorphism and pegmatite intrusion in the region near Beryl Mt., New Hampshire appears to be 323 ± 10 m.y. ago.

ACKNOWLEDGMENTS

This investigation was supported by the Research Division, Atomic Energy Commission under Contract AT(30-1)-1669. The authors wish to acknowledge the assistance of Philip A. Kluft, Charles W. Giffin and Leon E. Long in making the measurements. Bruno J. Giletti and Alan Walton assisted during several field trips to Beryl Mt.

REFERENCES

Aldrich, L. T. and Nier, A. O., 1948, The occurrence of He^3 in natural sources of helium: Phys. Rev., 74, p. 1590-1594.

Baadsgaard, H., Goldich, S. S., Nier, A. O., and Hoffman, J. H., 1957, The reproducibility of A^{40}/K^{40} age determinations: Trans. Am. Geophys. Union, v. 38, p. 539-542.

Backenstoss, G., and Goebel, K., 1955, Die Zahl der γ-Quanten des Kaliums: Z. Naturforsch., Band 10a, p. 920-924.

Billings, M. P., 1937, Regional metamorphism of the Littleton-Moosilauke area, New Hampshire: Geol. Soc. Am. Bull., v. 48, p. 463-565.

Cameron, E., et al., 1954, Pegmatite investigations 1942-1945: New England: U. S. Geol. Survey Prof. paper 255, 349 p.

Carr, D. R., Damon, P. E., Broecker, W. S., and Kulp, J. L., 1956, The potassium-argon age method: Natl. Research Council pub. 400 (Proceedings of the Second Conference on Nuclear Processes in Geologic Settings), p. 109-113.

Carr, D. R., and Kulp, J. L., 1957, The potassium-argon method of geochronometry: Geol. Soc. Amer. Bull., v. 68, p. 763-784.

Damon, P. E. and Kulp, J. L., 1957, Determination of radiogenic helium in zircon by stable isotope dilution technique: Am. Geophys. Union Trans. (in press for Nov.)

————, (in press), Excess helium and argon in beryl and other minerals: submitted for publication to the Am. Mineralogist.

Faul, H., et al., 1954, Nuclear Geology: New York, John Wiley and Sons, table 9, p. 168.

Gast, P. W., Kulp, J. L., and Long, L. E. (in press for 1958), Absolute age determinations of early Precambrian rocks in the Big Horn Basin and S. E. Manitoba: Geol. Soc. Amer. Bull.

Gaudin, A. M. and Pannell, J. H., 1948, Radioactive determination of potassium in solids: Anal. Chem. 20, p. 1154.

Goldich, S. S., Baadsgaard, H. and Nier, A. O., 1957, Investigation in A^{40}/K^{40} dating: Am. Geophys. Union Trans., v. 38, p. 547-551.

Kallman, S., 1946, Determination of sodium and potassium in silicates; Ind. and Engr. Chem. Anal. Ed. 18, p. 678.

Marble, J. P., 1950, Report of the Committee on the Measurement of Geologic Time for 1949-1950: Div. of Geol. and Geog., Natl. Research Council, 18.

McNair, A., Glover, R. N., and Wilson, H. W., 1956, The decay of potassium-40: Phil. Mag., v. 1, p. 199-211.

Strutt, R. J., 1908, Helium and radioactivity in rare and common minerals: Roy. Soc. London Proc., v. A80, p. 572-594.

————, 1911, The accumulation of helium in geological time, IV: Royal Soc. London Proc. A, v. 60, p. 56-57.

Wasserburg, G. J. and Hayden, R. J., 1956, A^{40}/K^{40} dating: Natl. Research Council Pub. 400 (Proceedings of the Second Conference on Nuclear Processes in Geologic Settings), p. 131-134.

Wasserburg, G. J., Hayden, R. J. and Jensen, K. J., 1956, A^{40}-K^{41} dating of igneous rocks and sediments: Geochim. et Cosmochim. Acta, v. 10, p. 153-165.

Wetherill, G. W., 1957, Radioactivity of potassium and geologic time: Science, v. 126, p. 545-549.

Wetherill, G. W., Aldrich, L. T., and Davis, G. L., 1955, A^{40}/K^{40} ratios of feldspars and micas from the same rocks: Geochim. et Cosmochim. Acta, v. 8, p. 171-172.

Wetherill, G. W., Wasserburg, G. J., Aldrich, L. T., Tilton, G. R., and Hayden, R. J., 1956, Decay constants of K^{40} as determined by the radiogenic argon content of potassium minerals: Phys. Rev. v. 103, p. 987-989.

LAMONT GEOLOGICAL OBSERVATORY
COLUMBIA UNIVERSITY
PALISADES, NEW YORK