PHYSICAL REVIEW VOLUME 74, NUMBER 3 AUGUST 1, 1948

The Radioactive Decay Constants of K^{40} as Determined from the Accumulation of Ca^{40} in Ancient Minerals

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(Received April 15, 1948)

New measurements of the rate of emission of gamma-ray energy by K^{40} give 4.9±0.1 Mev/sec. g K, in agreement with Gleditsch and Gráf. Thus the minimum value of the probability of electron capture in K^{40} is $\lambda_e = 0.062\times 10^{-9}$ yr.$^{-1}$. Spectrochemical analysis of 4 samples of lepidolite known to be 2.1×10^9 years old, as well as 22 younger lepidolites, gives a maximum value of 22, and a most probable value of 11 for the ratio of radiogenic Ca^{40} to residual K^{40} in the 2.1×10^9 year old minerals. In such an ancient mineral, the Ca^{40}/K^{40} ratio is a function not only of the probability of β-ray decay, λ_β, of K^{40} into Ca^{40}, but also the probability of transformation by electron capture, λ_e, of K^{40} into A^{40}. This is because the electron capture process may significantly deplete the K^{40}, thus tending to produce larger Ca^{40}/K^{40} ratios than would result from β-decay alone. The decay constants λ_β and λ_e reported by Bleuler and Gabriel predict $Ca^{40}/K^{40} = 152$, while Mühlhoff's λ_β predicts $Ca^{40}/K^{40} = 1.48$ for a 2.1×10^9 year old mineral. We have therefore suggested approximate corrections for the effects of β-ray scattering in the observations by Mühlhoff and by Bleuler and Gabriel on the absolute rate of emission of β-rays by K. These corrections lead to a mean value of 34 β-rays/sec. g K, or $\lambda_\beta = (0.65\pm 0.1)\times 10^{-9}$ yr.$^{-1}$. The observed value of $C^{40}/K^{40} = 11$ then leads to $\lambda_e = (0.9\pm 0.1)\times 10^{-9}$ yr.$^{-1}$, and a total half-period of $T = (0.45\pm 0.05)\times 10^9$ yr. for K^{40}. Then approximately 42 percent of the disintegrations of K^{40} are by β-ray emission to the ground state of Ca^{40}; 4 percent by electron capture to a 1.5-Mev excited state in A^{40}, and 54 percent by electron capture to the ground state of A^{40}. It is shown that these revised disintegration constants lead to a sufficiently smaller thermal output by K early in the earth's history to satisfy Birch's calculations on the possibility of an early solid terrestrial crust, and to remove arguments relating to the origin of species through gene mutations caused by intense K^{40} radiations early in the earth's history.

INTRODUCTION

DIRECT observations of the β-rays, γ-rays, and x-rays associated with the decay of ${}_{19}K^{40}$ have shown that individual atoms of this isotope transform radioactively by either of two competing processes: β-ray emission to ${}_{20}Ca^{40}$, or electron capture to ${}_{18}A^{40}$. Some, if not all, of the electron capture transitions are accompanied by γ-ray emission. Thus:

$${}_{19}K^{40} \rightarrow {}_{20}Ca^{40} + \beta^-, \quad {}_{19}K^{40} + e^- \rightarrow {}_{18}A^{40} + h\nu.$$

Much of the recent literature has been summarized by Gleditsch and Gráf.[1] The more reliable experimental estimates of the decay constants, λ_β for β-ray transitions, and λ_e for electron capture transitions, vary sufficiently widely to lead to profound uncertainties in the geophysical significance of potassium.[2]

Extreme values of the half-period, T, of K^{40} corresponding to the better direct measurements on its radioactive radiations range from $T = 16\times 10^8$ yr. obtained by Mühlhoff[3] to $T = 2.4\times 10^8$ yr. by Bleuler and Gabriel,[4] who report more than twice the absolute β-ray activity observed by Mühlhoff, and who, in addition, estimate from measurements of the x-rays that 1.9 atoms of K^{40} transform to A^{40} by electron capture for each atom of K^{40} which transforms to Ca^{40} by β-ray emission, i.e., $\lambda_e/\lambda_\beta = 1.9$.

In their measurements with Geiger-Müller counters of the β-rays and x-rays of K^{40}, both of these authors used thin sources of potassium salts, mounted on the inside of a brass cylinder. Neither made any explicit estimate of the effects of back-scattered radiation,[5] which could introduce errors of as much as 50 percent in their calibrations. Mühlhoff used the mixed α-rays and β-rays of uranium (UI, UX_1, UX_2, UII) for calibration, and may thus have obtained too high an apparent counter efficiency because of the high reflection factor for the very soft β-rays

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* The work here reported was supported in part by the Office of Naval Research in conjunction with the Laboratory for Nuclear Science and Engineering.

[1] E. Gleditsch and T. Gráf, Phys. Rev. **72**, 640(L), 641(L) (1947).

[2] F. Birch, Phys. Rev. **72**, 1128(L) (1947).

[3] W. Mühlhoff, Ann d. Physik **7**, 205 (1930).

[4] E. Bleuler and M. Gabriel, Helv. Phys. Acta **20**, 67 (1947).

[5] S. Eklund, Arkiv Mate. Astron. Fysik **33A**, No. 14, 50 (1945).

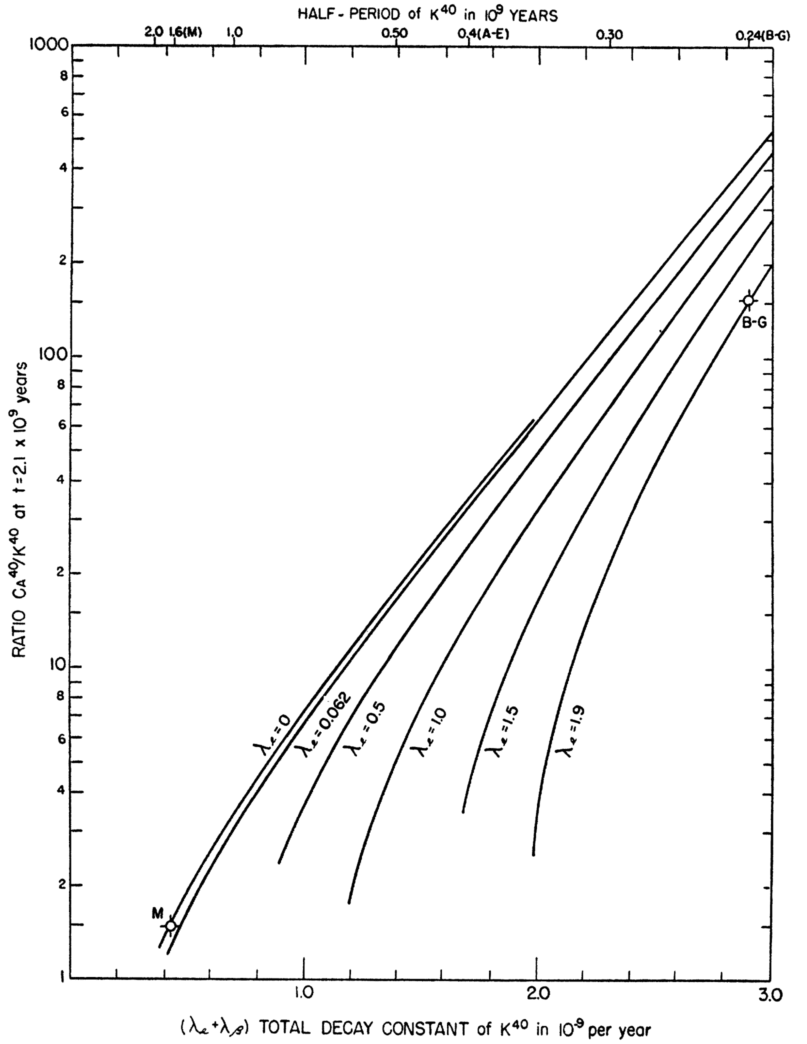

FIG. 1. Evaluation of Eq. (6) for the ratio of Ca^{40} accumulated in 2.1×10^9 years to the residual K^{40}, as a function of the total decay constant $(\lambda_\epsilon+\lambda_\beta)$, and the partial decay constant λ_ϵ for electron capture. The numerical values of the half-period $T=0.693/(\lambda_\epsilon+\lambda_\beta)$ are shown at the top, corresponding to the scale of total decay constants. The predicted values of Ca^{40}/K^{40}, using Mühlhoff's data and using Bleuler and Gabriel's data, are shown by points marked *M* and *B-G*.

of UX_1. If so, this could account for the fact that more recent evidence suggests that Mühlhoff's absolute decay rates for both K^{40} and for Rb^{87} are too low.

On the other hand, Bleuler and Gabriel obtained their calibration purely by calculation, but completely neglected back scattering, or reflection, of β-rays and x-rays. The K^{40} β-rays are thought[6–8] to have a maximum energy in the neighborhood of 1.3 Mev, and the back scattering from a thick brass source mounting may therefore add as much as 50 percent to the β-ray counting rate, as is the case[9] for the β-rays of Na^{24} which have about the same maximum energy. Back scattering of the 3.0-kev x-rays of A^{40} is difficult to estimate theoretically, but could be evaluated experimentally by studies on strong sources of other isotopes which decay by electron capture, such as Fe^{55}.

It seems qualitatively clear that Bleuler and Gabriel's decay constants λ_β and λ_ϵ may both be appreciably too high and the corresponding half-period too short, because of neglect of back scattering from the source mounting. Calculations based on the fragmentary counting data included in Bleuler and Gabriel's paper, suggest that their net β-ray counting rates were about

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[6] W. J. Henderson, Phys. Rev. **71**, 323(L) (1947).

[7] B. Dželepow, M. Kopjava, and E. Vorobjov, Phys. Rev. **69**, 538(L) (1946).

[8] O. Hirzel and H. Wäffler, Helv. Phys. Acta **19**, 216 (1946).

[9] W. C. Peacock, Thesis, Mass. Inst. of Tech. (1944).

180 counts per minute, while their estimate of $\lambda_e/\lambda_\beta=1.9$ was based on a change of only about 3 counts per minute when argon and carbon tetrachloride mixtures were used to absorb the A^{40} x-rays which follow electron capture in K^{40}. Clearly, their important experiment should be repeated, using enriched K^{40}, with counters which have been calibrated for both β-ray and γ-ray sensitivity through the use of isotopes whose decay schemes and absolute disintegration rates have been measured by other methods.[*]

Using amounts of Co^{60} whose absolute decay rate has been determined by β-γ coincidence methods, we[10] have compared the absolute rate of emission of γ-ray energy from K^{40} with that of Co^{60}, by using copper screen cathode Geiger-Müller counters whose sensitivity is proportional to quantum energy and whose response is therefore proportional to γ-ray energy flux. It is found that 1 gram of ordinary (unenriched) potassium emits 4.9 ± 0.1 Mev of γ-rays per second. New measurements of the quantum energy in progress, but in the meantime we may use the current values[1,8] of about 1.5 Mev. Thus, we estimate $4.9/1.5=3.3$ quanta per second per gram of potassium, in substantial agreement with the value found by Gleditsch and Gráf.[1] If every electron capture transition of K^{40} resulted in the emission of one photon, then the minimum decay constant of K^{40} for electron capture would be:

$$\lambda_e=0.062\times10^{-9}\ \text{yr.}^{-1}. \tag{1}$$

For comparison, the β-ray counting results of Mühlhoff correspond to:

$$\lambda_\beta=0.434\times10^{-9}\ \text{yr.}^{-1},$$

and the β-ray and x-ray counting results of Bleuler and Gabriel correspond to:

$$\lambda_\beta=1.0\times10^{-9}\ \text{yr.}^{-1},\quad \lambda_e=1.9\times10^{-9}\ \text{yr.}^{-1}.$$

Table I. Calcium content (mean of 3 to 4 determinations on each sample) and geological age of 26 samples of lepidolite.

No.	Locality	Percent Ca	Age ($\times10^6$ yr.)
1	Falcon Island, Lake of the Woods, S.E. Manitoba	0.019	2100
2	Silver Leaf Mine, along Winnipeg River, S.E. Manitoba	0.018	2100
3	Silver Leaf Mine, along Winnipeg River, S.E. Manitoba	0.032	2100
4	Along Winnipeg River, S.E. Manitoba	0.023	2100
5	Pala, California	0.0012	110
6	Pala, California	0.0023	110
7	Buckfield, Maine	0.008	270
8	Newry, Maine	0.016	270
9	Norway, Maine	0.014	270
10	Topsham, Maine	0.009	270
11	Mt. Mica, Maine	0.08	270
12	Auburn, Maine	0.01	270
13	Haddam, Connecticut	0.005	270
14	Middleton, Connecticut	0.02	270
15	Portland, Connecticut	0.011	270
16	Dixon, New Mexico	0.015	~850
17	Brown Derby, Colorado	0.008	~850
18	Brown Derby, Colorado	0.005	~850
19	Black Hills, South Dakota	0.006	~850
20	Black Hills, South Dakota	0.008	~850
21	Black Hills, South Dakota	0.015	~850
22	Okongava Ost 72, Karibib, South West Africa	0.013	~850
23	Karibib, South West Africa	0.008	~850
24	Albrecht's Höhe, Karibib, South West Africa	0.022	~850
25	Warmbad, South West Africa	0.0032	~850
26	Omaruru, South West Africa	0.006	~850

Now that some potassium minerals are available whose measured geological age equals or exceeds the proposed range of values of the half-period of K^{40}, the opportunity has arisen to estimate the decay constants of K^{40} by an experiment whose effective duration is of the order of 10^9 years, instead of a few days or months. This involves, of course, observations of the accumulated Ca^{40} and A^{40}, instead of short measurements of the radiations of K^{40}. If there were N_0 atoms of K^{40} per gram of mineral at the time ($t=0$) of formation of the mineral, then the number of K^{40} atoms remaining at the present time, t, is:

$$N=N_0\exp[-(\lambda_\beta+\lambda_e)t]. \tag{2}$$

The number of Ca^{40} atoms formed will be:

$$Ca^{40}=(N_0-N)\lambda_\beta/(\lambda_\beta+\lambda_e), \tag{3}$$

the number of A^{40} atoms formed will be:

$$A^{40}=(N_0-N)\lambda_e/(\lambda_\beta+\lambda_e)=Ca^{40}(\lambda_e/\lambda_\beta), \tag{4}$$

while the total amount of decay products formed is, of course, equal to the K^{40} which has decayed, or:

$$Ca^{40}+A^{40}=N_0-N=Ca^{40}(1+\lambda_e/\lambda_\beta). \tag{5}$$

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[*] *Note added in proof, 15 June 1948:* R. W. Stout, in an unpublished B.S. thesis under Prof. M. Deutsch at M. I. T., has just obtained a preliminary value of 30 ± 6 disintegrations per second per gram K for the absolute β-ray specific activity of normal unenriched K, by β-ray counting on KCl sources which have been internally standardized through the addition of known activities of Na^{24}, whose maximum β-ray energy is almost identical with that of K^{40}.

[10] R. D. Evans and R. O. Evans, Rev. Mod. Phys. **20**, 305 (1948).

Combining Eqs. (2) and (5), and writing K^{40} for N, we have, for the Ca^{40}/K^{40} ratio in a mineral of age, t:

$$Ca^{40}/K^{40} = [\lambda_\beta/(\lambda_e+\lambda_\beta)]\{\exp[(\lambda_e+\lambda_\beta)t]-1\}. \quad (6)$$

As described below, we have observed a Ca^{40}/K^{40} ratio of about 11 in lepidolites of 2.1×10^9 years of age. Figure 1 is a plot of the Ca^{40}/K^{40} ratio to be expected in a mineral of age $t=2.1\times10^9$ yr., for various values of the total decay constant $(\lambda_e+\lambda_\beta)$ and a series of particular values of the probability, λ_e, of electron capture transitions. The two points plotted on Fig. 1 show the Ca^{40}/K^{40} ratios to be expected on a basis of Mühlhoff's decay constant for K^{40} ($Ca^{40}/K^{40}=1.48$, marked *M*) and on a basis of Bleuler and Gabriel's decay constants ($Ca^{40}/K^{40}=152.$, marked *B–G*).

CHOICE OF A SUITABLE POTASSIUM RICH MINERAL

Some minerals of the mica group commonly contain only traces of calcium, in particular types like muscovite and lepidolite. Thus, chemical analyses of lepidolite invariably report calcium as either a trace or as absent; see, for example, analyses of lepidolite by Stevens.[11] An inspection of the spectra of 28 specimens of lepidolite and 2 of muscovite which had been recorded for making age determinations by the strontium-rubidium spectrochemical method,[12] showed that in general the intensities of the calcium lines were weak, and in most instances corresponded to about 0.01 percent in the magnitude of the calcium content. This magnitude is very small, and with reasonable fortune it should be possible to utilize lepidolite and probably also muscovite, for the determination of Ca^{40}/K^{40} ratios, provided very ancient specimens of known age are obtainable.

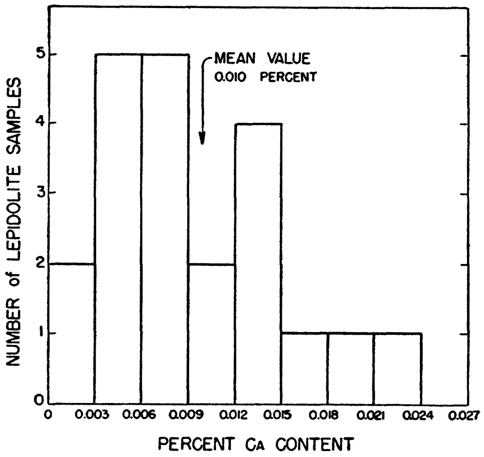

FIG. 2. Distribution histogram of the Ca content of 21 lepidolites, samples 5 to 10, and 12 to 26 of Table I. The oldest samples in this group have an age of 0.85×10^9 years, and should have accumulated only 0.001 percent Ca^{40}, using the decay constants $\lambda_e=1.0\times10^{-9}$ yr.$^{-1}$ and $\lambda_\beta=0.7\times10^{-9}$ yr.$^{-1}$.

Lepidolite usually contains about 10 percent K_2O (8.3 percent K) and invariably the potassium content lies within ±5 percent (1/20) of this value; see for example, Stevens[11] analyses, which includes a sample from the Silver Leaf pagmatite (see Table I samples 2 and 3). According to Nier[13] 0.011 percent of potassium is K^{40}, and thus in lepidolite, 0.00091 percent K is K^{40}. The possible slight variation of ±5 percent in the K_2O content of lepidolite is considered insignificant for the purpose of this investigation.

AGE OF SOME ANCIENT LEPIDOLITE SPECIMENS

Several lepidolite specimens of pre-Cambrian age were available. Unless, however, extremely ancient specimens can be used, it is doubtful whether an investigation of this type could be employed with a reasonable chance of success. Thus, in specimens of middle pre-Cambrian age (850×10^6 years), several of which were available, only about 0.001 to 0.003 percent Ca^{40} would be generated, depending on the values assumed for the decay constants of K^{40}. These quantities are extremely small and, consequently, interference from common calcium will almost certainly be excessive. Recently, Ahrens[14] has been able to establish beyond reasonable doubt that the age of pegmatites from southeast Manitoba, Canada, is extremely great; using the available data (five Sr^{87}/Rb^{87} age determinations and two Pb^{207}/Pb^{206} age determinations), an age of 2100 $\times10^6$ years was assigned to these pegmatites. At this extreme age, sufficient quantities of Ca^{40} would have been generated in leipdolite now containing 0.00091 percent K^{40} to permit spectrochemical analysis.

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[11] R. E. Stevens, Am. Min. **23**, 607 (1938).

[12] L. H. Ahrens, Bull. Geol. Soc. Am., in press (1948).

[13] A. O. Nier, Phys. Rev. **50**, 1041 (1936).

[14] L. H. Ahrens, Nature **160**, 874 (1947).

ANALYTICAL

A spectrochemical procedure was employed for determining calcium quantitatively: a brief description of the procedure is as follows.

To avoid the use of synthetic standards, a specimen of lepidolite (Pala, California) was chosen, the calcium content of which was extremely low (~0.002 percent); CaO was added to this base material to provide standards containing up to 0.32 percent Ca. After admixture of each standard (1 part) with the purest carbon powder available (2 parts) each specimen was arced to completion, using d.c. arc anode excitation. From these spectra, a working curve was prepared, by means of which the calcium contents of the unknowns were determined after each had been prepared and arced as described before. Reproducibility was reasonably good, and the standard deviation was about ±10 percent per single determination. Unfortunately, below about 0.02–0.03 percent Ca, the blank error, due in part to the small amount of calcium in the Pala lepidolite and in the main to calcium impurity in the carbon, became serious; consequently, the limit of experimental error for specimens containing 0.01–0.03 percent Ca is considered to be about ±30 percent. Below 0.01 percent Ca, calcium determinations were made indirectly, using hydrofluoric acid residues (see Ahrens[12]) of lepidolite. By using some HF residues of lepidolite, which are relative rich in calcium and are of known calcium content, as secondary standards, calcium determinations could be made on specimens containing 0.001–0.01 percent Ca.

ANALYTICAL RESULTS

In Table I, the calcium contents of 4 specimens of lepidolite from southeast Manitoba are given; in addition, quantitative data are also provided for 22 other specimens of lepidolite so as to obtain a reasonably accurate indication of the quantities of calcium likely to be found in lepidolite.

Excluding the s.e. Manitoba specimens and specimen No. 11, the high calcium content of which is quite exceptional, the mean calcium content of 21 specimens is 0.010 percent. Figure 2 is a frequency-distribution histogram of the Ca content of these 21 samples. In the 11 pre-Cambrian specimens (age = 850×10^6 years) which also average 0.010 percent Ca, the radiogenic calcium is probably 0.001 percent, and has a maximum value of 0.003 percent even if one uses Bleuler and Gabriel's decay constants. Consequently, the mean non-radiogenic calcium content in lepidolites is of the magnitude 0.008 to 0.010 percent.

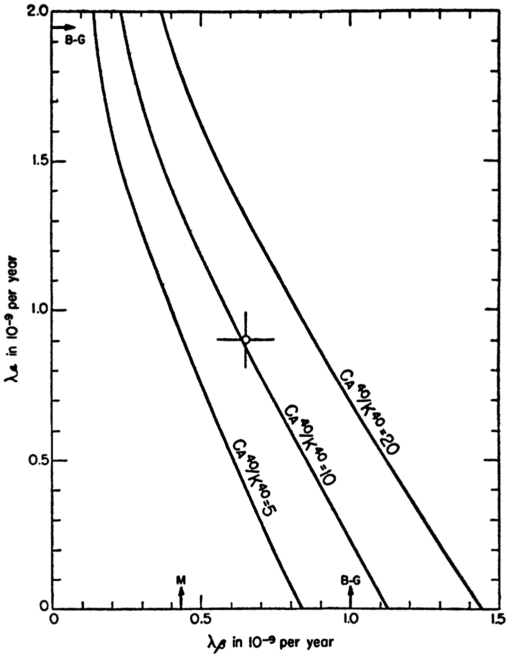

FIG. 3. The three curves show the simultaneous values of λ_e and λ_β of K^{40} which in 2.1×10^9 years will give Ca^{40}/K^{40} ratios of 5, 10, and 20. Measured values of λ_β and λ_e are shown by arrows marked *M* for Mühlhoff and *B-G* for Bleuler and Gabriel. Taking a value of $\lambda_\beta=(0.65\pm0.1)\times10^{-9}$ per year, and our observed ratio $Ca^{40}/K^{40}=11$, leads to $\lambda_e=(0.9\pm0.1)\times10^{-9}$, as shown by the single point near the middle of the graph.

All four specimens of lepidolite from s.e. Manitoba are characteristically high in calcium. Furthermore, the three specimens of lowest calcium content contain essentially the same amount of calcium (0.020 percent). This evidence strongly indicates that a significant portion of the total calcium in these 3 samples is radiogenic. It may be added further, that the high calcium content of these specimens provides the first direct indication of the formation of Ca^{40} from the decay of K^{40}; it will be recalled that although β-activity of K^{40} is well established and hence Ca^{40} should be generated, no proof of the accumulation of Ca^{40} in old, potassium-rich minerals has been made previously.

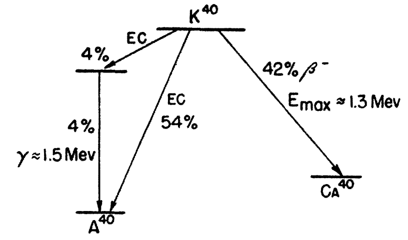

FIG. 4. Decay scheme of K^{40}, according to Eqs. (1), (7), and (8). Approximately 54 percent of the disintegrations of K^{40} appear to be by electron capture to the ground state of A^{40}.

Arrangements have been made with Professor A. O. Nier to perform a mass-spectrometric analysis of Ca to be separated chemically from a new larger sample of ancient lepidolite from the Winnipeg River area. Professor Nier estimates that as little as 5 percent radiogenic Ca^{40} can be successfully measured, when mixed with 95 percent non-radiogenic Ca, by measurements of the Ca^{44}/Ca^{40} ratio. When available, these measurements will greatly reduce the uncertainties in our interpretation of the data of Table I. Also, Professor P. M. Hurley is collaborating in securing A^{40} analyses of lepidolites and of other selected minerals. It is to be noted that the A^{40} content would be of the order of 0.1 cc per gram in an ancient ($\sim 2\times 10^9$ yr.) lepidolite, and could not possibly have been retained quantitatively. Consequently, definitive studies of A^{40} accumulation must be made either on very young lepidolites, or on minerals containing less potassium. It seemed unwise, however, to delay further the publication of the present results, both because of current general interest in the K^{40} problem and because Dr. Ahrens is moving from the Massachusetts Institute of Technology to England.

We may reasonably assume that sample No. 3 of Table I contains a larger quantity of non-radiogenic Ca than the other three ancient samples, whose average Ca content is 0.020 percent. Deducting 0.010 percent as an average non-radiogenic Ca content of lepidolite (Fig. 2), we have an estimated excess Ca content of 0.010 percent for samples 1, 2, and 4, which is assumed to be Ca^{40}. It is to be noted that the maximum possible Ca^{40} content of these 3 samples would be 0.020 percent if we made the unreasonable, but limiting, assumption that they contain no non-radiogenic Ca. Taking the K content of lepidolite as 8.5 ± 0.5 percent, and hence the K^{40} content as 0.00091 ± 0.00005 percent, the most probable value of the Ca^{40}/K^{40} ratio is $0.010/0.00091=11$. The maximum possible ratio, assuming that all the Ca is radiogenic Ca^{40}, and adding the reasonable geochemical assumption that no Ca is lost during geological time, is $0.020/0.0091=22$. This value could be raised further only by invoking our estimated limit of error of 30 percent in the Ca analysis.

THE DECAY CONSTANTS OF K^{40}

The decay constants of K^{40} reported by Bleuler and Gabriel predict a Ca^{40}/K^{40} ratio of 152 for a mineral of 2.1×10^9 years age. This is 7 times the maximum possible value obtained in our measurements, and 14 times our most probable value of $Ca^{40}/K^{40}=11$. Reference to Fig. 1 shows that the observed Ca^{40}/K^{40} ratio is consistent with a range of total decay constants $(\lambda_e+\lambda_\beta)$ between 1.2 and 2.2×10^{-9} per year with λ_e between 0 and 1.9×10^{-9} per year.

In the introduction we pointed out that the omission of corrections for back scattering of β-rays from the brass source holders has the effect of making Mühlhoff's value of $\lambda_\beta=0.434\times 10^{-9}$ per year too low, and also of making Bleuler and Gabriel's value of $\lambda_\beta=1.0\times 10^{-9}$ per year too high. Thus the true value probably lies between these two limits, and may be close to 0.65×10^{-9} per year if we arbitrarily assign a 50 percent back-scattering error to each of these direct measurements.

Figure 3 shows three curves of constant Ca^{40}/K^{40} ratios obtained from Eq. (6), and bracketing the values observed from the Manitoba lepidolites, plotted against λ_β and λ_e as independent variables, for $t=2.1\times 10^9$ years. Taking:

$$\lambda_\beta=(0.65\pm 0.1)\times 10^{-9} \text{ per year,} \qquad (7)$$

and $Ca^{40}/K^{40}=11$, leads to the value:

$$\lambda_e=(0.9\pm 0.1)\times 10^{-9} \text{ per year,} \qquad (8)$$

or a total decay constant and half-period for K^{40} of:

$$\lambda_e+\lambda_\beta=(1.55\pm 0.15)\times 10^{-9} \text{ per year,} \qquad (9)$$

$$T=(0.45\pm 0.05)\times 10^9 \text{ years.} \qquad (10)$$

These estimated probable errors have the usual significance of denoting even odds that the true value lies within or outside the limits specified. Similarly, the "limit of error" would be given its usual value of 3 probable errors, and would specify a band having a 96 percent chance of containing the true value.

DISCUSSION

The numerical values suggested in Eqs. (7) to (10) will, of course, be subjected to further improvement by independent measurements of A^{40} accumulation in K minerals, and by new measurements of the x-rays and β-rays from samples of K enriched in K^{40}. As it may be a year or so before suitably enriched samples become available, it is worth noting that the disproof of Bleuler and Gabriel's decay constants requires also the modification of Birch's and of Gleditch and Gráf's conclusions.

The decay scheme of K^{40}, with revised branching ratios corresponding to Eqs. (1), (7), and (8), is shown in Fig. 4. The specific activity of ordinary potassium (0.011 percent K^{40}) would then be 34 β-rays per second per gram of potassium.

The total heat production per gram of ordinary potassium is then: 4.9 Mev/sec. for the γ-rays, plus approximately[15] 0.49 ± 0.06 Mev per β-ray or $34\times 0.49=16.6$ Mev/sec. for the β-rays. This amounts to a total of about 22 Mev/sec., or 26×10^{-6} cal. per year per gram of potassium. This estimate of the heat output should replace the early value of 5×10^{-6} cal./yr. g by Evans and Goodman,[16] which was based on Mühlhoff's decay constant, Anderson and Neddermeyer's[17] β-ray energy, and Gray and Tarrant's[18] gamma-ray emission, all three of which were too low in the light of more recent measurements. This revised heat output also replaces Gleditch and Gráf's value of 38×10^{-6} cal./yr. g, which uses Bleuler and Gabriel's decay constants. Birch[2] has pointed out that Bleuler and Gabriel's short half-period of 0.24×10^9 years, if accepted, would require re-evaluation of a number of important geophysical problems. In particular, the heat output[1] of potassium 1 to 1.5×10^9 years ago would have been too great to have permitted a permanent crust to exist on the earth. Our value of the half-period of K^{40} is essentially twice that of Bleuler and Gabriel, and of course leads to very much lower values of the heat production at times comparable with the age of the earth. Illustrative numerical values are given in Table II, where it is seen, for example, that our estimate of the heat production by potassium 2×10^9 years ago is only about 5 percent as large as Gleditch and Gráf's value. Even if our smaller values are confirmed by further work on the radioactive properties of K^{40}, the heat production by radioactive decay 2×10^9 years ago would have been due mainly to K^{40}, which would then have exceeded the heat production by uranium and thorium[16, 19] in all classes of igneous rocks.

TABLE II. Calculated heat production by the K^{40} associated with 1 gram of K^{39} and K^{41}, i.e., heat production per gram of *residual* potassium, as a function of geological time, t, measured backwards from the present, for two values of the half-period T, and of the present heat output H_0 per gram of potassium.

	Time t in 10^9 years					
	0	0.5	1.0	1.5	2.0	2.5
10^{-6} cal./yr. g K if[1] $T=0.24\times 10^9$ yr. and $H_0=38\times 10^{-6}$ cal./yr. g K	38.	162.	690.	2920.	12500.	53200.
10^{-6} cal./yr. g K if $T=0.45\times 10^9$ yr. and $H_0=26\times 10^{-6}$ cal./yr. g K	26.	57.	122.	388.	577.	1260.

From the standpoint of the general theory of forbidden β-ray transformations, it was thought[20] some years ago that accurate knowledge of the β-ray energy and the half-period of K^{40} would be crucial in deciding between the tensor and polar vector interactions, because it is known[21] that the nuclear angular momentum of K^{40} is 4, while that of Ca^{40} is probably zero. Marshak[22] has shown, however, that this is actually not the case, and that the shape of the β-ray spectrum, not its maximum energy, is destined to become the decisive evidence in settling the form of the interaction. Thus, the present results do not modify existing β-ray theory.

The average potassium content of mammalian tissues is about 0.11 percent, and varies in

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humans from 0.19 mg K/g of blood serum to 4.20 mg K/g red blood cells. The average potassium content of sea water is 0.39 mg/g of water. Because this is only about 2.6 percent of the K which has been released by the decomposition of crustal rocks, it is assumed that the remainder has been adsorbed and is to be found in sedimentary deposits. Thus, the K content of the oceans may be assumed to have been at substantially its present concentration for at least the major portion of the earth's history. Suggestions have reappeared[23] recently concerning the possible early importance of the radiations from K^{40} on mutations and on the origin of species. Taking 4.9 Mev of γ-radiation plus 16.6 Mev of β-radiation per second per gram of potassium as the present rate of energy release, it can be shown from the ordinary principles of radiation dosage[24, 25] that the K content of sea water now produces, on organisms whose dimensions are small compared with the range of the β-rays of K^{40}, a tissue dosage of only 1.4×10^{-5} rep./day. Taking the half-period of K^{40} as 0.45×10^9yr. and the K constant of ocean water as constant with respect to time, the corresponding tissue dosage 1.0×10^9 yr. ago would have been 0.066×10^{-3} rep./day, while 2.0×10^9 yr. ago the dosage would have been 0.31×10^{-3} rep./day. These are very small dosages, and can hardly be held accountable for any significant degree of mutation induced by radiation. By way of comparison, the cosmic radiation at sea level gives[24] a tissue dosage of 0.10×10^{-3} rep./day. On the other hand, a total dosage of about 50 rep. per generation is required to double the natural mutation rate in lower organisms.

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PHYSICAL REVIEW VOLUME 74, NUMBER 3 AUGUST 1, 1948

Effect of Large Quadrupole Interactions on Nuclear Radiofrequency Spectra at Twice Larmor Frequency

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(Received April 17, 1948)

The work of B. T. Feld and W. E. Lamb [Phys. Rev. **67**, 15 (1945)] on the effect of a nuclear electrical quadrupole moment on the radiofrequency absorption spectrum of a heteronuclear diatomic molecule in a magnetic field is extended to a special case not considered by them. This is a case in which the electrical quadrupole interaction energy is so large that even in magnetic fields of several thousand gauss the magnetic interaction energies are small compared to the electrical quadrupole interaction energy. In this case it is shown theoretically that for a spin of $\frac{3}{2}$ there are certain circumstances under which a maximum of absorption will occur at double the Larmor frequency instead of at the Larmor frequency and will have a field and molecule dependence similar in many ways to a resonance at the Larmor frequency. This result has the important implication that special care must be used in identifying the radiofrequency resonance absorption spectra or an error of a factor of two in the value of a nuclear magnetic moment can easily be made. The approximate shape and intensity of the radiofrequency absorption spectrum under these circumstances is calculated in order that a comparison of the theoretical shapes and intensities with the experimental ones can be used as a means of recognizing if an absorption is a double Larmor frequency one.

I. INTRODUCTION

DETAILED consideration has been given by Feld and Lamb[1] to the effect of a nuclear electrical quadrupole moment on the radiofrequency absorption spectra of heteronuclear diatomic molecules in magnetic fields as such spectra are observed in the molecular beam resonance method.[2–4] Although Feld and Lamb[1]

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* Part of this work was done at Columbia University.

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