

RADON LEAKAGE FROM RADIOACTIVE MINERALS*

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ABSTRACT

The leakage of radon from a variety of primary and secondary uranium minerals has been measured. At room temperature pitchblende specimens show radon loss ranging from 0.064% to 16.6%; uraninite, 0.58 to 0.80%; samarskite, approximately 0.03%; carnotite, 17 to 27%; and zircon, 1.6 to 6.2%. These ranges are not maximal since only a few specimens of each type were measured, but they indicate the order of magnitude involved. Radon leakage increases with temperature such that at 150° C. it is about twice that at room temperature. Between 200 and 300° C. recrystallization ensues, reducing the internal surface area and the radon leakage.

Measurements were made under equilibrium and non-equilibrium conditions. These studies helped define the mechanism of radon leakage as one of gaseous diffusion through the microfissures of the mineral.

Application of a radon leakage correction to Pb^{206}/U^{238} ages of certain minerals brings them essentially into agreement with the Pb^{207}/U^{235} ages.

INTRODUCTION

The loss of radon from uranium minerals was first investigated at the beginning of this century in connection with studies of the various uranium and thorium decay schemes. In the process of working out the relationships between the different members of each decay series it was found that radium emanation, radon, leaked from naturally occurring minerals. This was confirmed when the daughter products were found in slightly lower abundance than expected.

Boltwood (1) obtained values of leakage ranging from 0.7% to 26% on a wide variety of uranium minerals. Lind and Whittemore (2) characterized pitchblende as leaking from three to eight per cent and carnotites from sixteen to fifty per cent.

Since these authors were interested in the decay series, they confined their attention to the material balance aspects of radon leakage relative to the other decay products. Boltwood did heat a uraninite sample in a crucible to red heat and found that after this treatment the rate of radon loss was smaller. An investigation of the mechanism of the leakage process and of the factors affecting it was not attempted in this early work.

The present study has had a three-fold objective: (1) to study the mechanism of radon leakage; (2) to measure radon leakage as a function of temperature; (3) to define the average radon leakage for each specimen of a variety of uranium minerals, particularly those to be used for age determination. The last objective is required to correct Pb^{206}/U^{238} , $Pb^{207}/$

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Pb²⁰⁶, and Pb²⁰⁶/Pb²¹⁰ ages to the proper values. Loss of radon makes the 206/238 age low and the 207/206 high, whereas the effect on the 206/210 age depends on the history of the leakage. If the radon leakage has been constant for most of the lifetime of the mineral the 206/210 age will be correct.

It is postulated that radon leakage occurs by recoil of the radon atoms at "birth" from the lattice into the microfissures of the mineral. From this point, the radon is lost by gaseous diffusion through these fissures to the surrounding country rock. The relatively long half-life of radon (Em^{222} , $t_{1/2} = 3.83$ days) gives time for a large fraction of the radon which enters the microfissures to escape. From the diffusion mechanism it is possible to calculate the leakage of the emanation isotopes from the other two decay series (thoron, Em^{220} , $t_{1/2} = 54.5$ sec.; and actinon, Em^{219} , $t_{1/2} = 3.92$ sec.). It is concluded that the leakage of these two isotopes is negligible.

EXPERIMENTAL PROCEDURE

In this investigation both equilibrium and non-equilibrium methods of measuring radon leakage were employed. All of the final results were obtained by the equilibrium method. However, the non-equilibrium methods produced results which aid in the understanding of the mechanism of radon loss.

Equilibrium Method

A suitable quantity (generally 0.5 to 30 grams) of a uranium-bearing mineral, or a rock containing such a mineral, is sealed in air in a small glass bulb. Care is taken to avoid heating the specimen while the bulb is being sealed. The bulb is stored at constant temperature for at least thirty days.

At the end of the thirty day period, the rate of leakage of radon from the specimen into the bulb should equal the rate of decay of the radon in the bulb. The reason for this steady state is that almost eight half-lives of radon will have elapsed ($t_{1/2} = 3.83$ days) and it should be in secular equilibrium with its source. The size of the minerals is such that the rate of diffusion of radon out of the specimen will have reached a steady state in this time.

Now, the seal on the bulb is broken and the radon flows to an evacuated one-liter flask. The volumes of the bulb and the flask are known with sufficient accuracy so that the fraction of the radon in the flask can be defined to better than 1%. An aliquot of radon is transferred from the one-liter flask to a four-liter ionization chamber. The chamber is then filled with dry nitrogen (which has been stored at least thirty days to permit any radon originally present to decay) to a pressure of 76 cm. of mercury. Three such aliquots are taken for three chambers.

The alpha pulses, which occur in the ionization chamber as the result of the decay of radon and its daughters, are amplified and counted according to the method described by Bate, Volchok and Kulp (3). In general, the aliquots are about 0.5% of the total radon in the one-liter flask. This is sufficient to give count rates on the order of 200 to 1000 cph. Backgrounds are constant at about 20 cph. The absolute efficiency of the counting tech-

nique has been determined by the use of radium solutions of known concentration obtained from the U. S. Bureau of Standards.

Three hours after the chamber has been filled, the radon is in equilibrium with its decay products. The chamber is usually counted overnight. The radon activity in the specimen bulb at the time the seal was broken can be calculated from the counting data as follows:

Let

t_0 = time gas phase removed from mineral.

t_1 = time (in hrs.) from t_0 to start of counting.

t_2 = time (in hrs.) from t_0 at which counting is stopped.

N = number of atoms of radon in the gas phase (a subscript referring to the corresponding time).

λ = decay constant of radon (in hours).

$$N_1 = N_0 e^{-\lambda t_1} \quad (1)$$

$$N_2 = N_0 e^{-\lambda t_2}. \quad (2)$$

Subtracting

$$N_0 = \frac{N_1 - N_2}{e^{-\lambda t_1} - e^{-\lambda t_2}}. \quad (3)$$

The difference $(N_1 - N_2)$ = number of radon atoms that decayed in the counting interval. This difference is obtained experimentally by correcting the counts obtained in the interval for counter efficiency and daughter contribution. Hence, equation (3) gives the number of radon atoms initially present in the gas phase. At equilibrium (i.e. t_0), the rate of decay of these atoms = rate of diffusion from the mineral. The latter essentially is equal to the rate at which radon atoms enter the gas phase in the internal volume of the mineral.

Since

$$-\frac{dN_0}{dt} = N_0 \lambda \quad (4)$$

or

$$\frac{dN_0}{dt} = \frac{(N_2 - N_1)\lambda}{e^{-\lambda t_1} - e^{-\lambda t_2}}. \quad (5)$$

Now, the rate of production of radon in the mineral grains can be assumed to be equal to the rate of decay of the uranium (i.e., secular equilibrium). Therefore

$$\frac{dN_u}{dt} = N_u \lambda_u = N_{Rn\lambda_{Rn}} \quad (6)$$

where N_u is the number of uranium atoms in the specimen and $N_{Rn\lambda_{Rn}}$ is the rate of production of radon in the mineral.

$$N_u = \frac{\text{Weight } U}{238} \times 6.02 \times 10^{23} \times \frac{138}{139}. \quad (7)$$

The ratio 138/139 corrects for the U^{235} which is included in the original uranium analysis.

The radon leakage is,

$$L = \frac{N_0}{N_{RN}}, \quad (8)$$

or

$$\% L = (100) \frac{(N_2 - N_1)\lambda}{N_u \lambda_u (e^{-\lambda t_1} - e^{-\lambda t_2})} \quad (9)$$

when N_u is obtained from (7). Radon leakage is defined in (9) as the loss of radon per hour divided by the rate of production of radon from radium per hour.

Non-equilibrium Experiments

The non-equilibrium experiments were conducted in two ways—the sample was evacuated prior to accumulation or the sample was flushed with a flow of nitrogen at room temperature prior to accumulation.

Vacuum Technique

In this technique the specimen is placed in a small bulb which is part of the vacuum system. The sample bulb is evacuated four times to a pressure of less than 1 mm. Each time it is filled again to one atmosphere with dry, "old," nitrogen. This removes any radon in the container as well as some of the radon in the microfissures. After the last flush, the sample is isolated under one atmosphere of nitrogen for a definite time interval ranging from 3 to 120 minutes. At the end of this accumulation period, the N_2 and the radon which has leaked out of the mineral are flushed into the previously evacuated ionization chamber. The procedure from this point parallels that for the equilibrium method.

Flow Technique

The specimen is placed in a tube through which flows dry, old nitrogen. After the N_2 flows through for some time, the tube is isolated for the radon to accumulate. After this, the nitrogen flush is resumed, but the gases now go into the evacuated ionization chamber. The process and calculations from this point on are the same as for the vacuum technique.

THEORY AND MECHANISM OF RADON LEAKAGE

The fraction of radon generated which escapes from a mineral is dependent on the *total* surface area, the temperature, and the nature of the aggregate of mineral grains. Consider first the simplest case of isolated, homogeneous, fissure-free grains of spherical shape. The emission of such a single grain is a sum of the contributions from recoil and diffusion in the solid phase. Near room temperature the contribution from diffusion of radon in a nearly perfect crystal is entirely negligible, having values for the diffusion coefficient, D , of less than 10^{-22} cm²/sec. Even at several hundred degrees the diffusion contribution is of little importance (Keevil, 4).

A thorough theoretical investigation of the rate of escape of emanation from solids has been made by Flügge and Zimens (5). The theory given below follows their development, although the experimental investigation of the mechanism is entirely new.

If a mineral grain has a constant concentration C of radium, the number of atoms of radon generated per cc. per sec. will be $C\lambda_{Ra}$ which will equal the number of radon atoms decaying per cc. per sec. in the mineral plus the number that escape. Consider a grain of radius r_0 . For geometrical

reasons exactly one-half of the radon atoms generated in the surface monolayer will escape, the other half will be driven back into the grain. Of the radon atoms formed within a shell of thickness R , the recoil range, only a fraction (which must be less than $\frac{1}{2}$) will be able to escape. It can be shown that the fraction of radon atoms formed in a shell of radius r (where $r_0 - R \leq r \leq r_0$) which will escape is

$$q(r) = \frac{2rR - (r_0^2 - R^2) + r^2}{4Rr}$$

The total number of atoms escaping by recoil, N_r will be

$$N_r = C\lambda_{\text{Ra}}4\pi \int_{r_0-R}^{r_0} q(r)r^2 dr = C\lambda_{\text{Ra}}4\pi \left(r_0^2 R - \frac{1}{12} R^3 \right)$$

Dividing by $\frac{4}{3}\pi r_0^3 C\lambda_{\text{Ra}}$, the total number of radon atoms formed per second, will give F_r , the fraction emitted due to recoil.

$$F_r = \frac{3}{4} \frac{R}{r_0} - \frac{1}{16} \left(\frac{R}{r_0} \right)^3 \quad \text{for } 2r_0 \geq R.$$

If $2r_0 < R$, every radon atom formed will escape by recoil. R is of the order of 10^{-6} cm. for radon in minerals.

Consider the effect of total surface area on this relationship. If the density of pitchblende is taken as 10g/cc., a pitchblende composed of isolated homogeneous spheres of radius such that the surface area is 1.0m²/gm, the pitchblende would have a leakage rate (due to recoil) of about 2.5%. Actually the pitchblende is not composed of isolated spheres of UO₂, but rather is a highly irregular aggregate of microcrystals. This leads to a high total surface area, but the internal fissures are very narrow and tortuous. Therefore, a certain fraction of the radon atoms ejected from the crystals into the internal volume decay in the fissures before escaping to the exterior of the mineral. Under such conditions the observed leakage from the mineral as a whole must be less than the actual release of radon from the solid phase, but will be proportional to the total surface area.

Whatever detailed mechanism is assumed for radon leakage, the following experimental results must be satisfied.

(1) An equilibrium, or quasi-equilibrium, situation is reached in 30 days. Longer times of accumulation do not yield higher leakage rates (Table 1).

(2) Increasing the external volume surrounding the mineral from 5 cc. to 1 liter has no effect on the apparent leakage in the equilibrium (30 day) experiments. This, along with the temperature effect listed under (6), indicates that the partial pressure of radon in the external volume is negligible compared to that in the internal volume.

TABLE 1. RADON LEAKAGE AS A FUNCTION OF ACCUMULATION TIME
(Sample K-1-28)

| Waiting Period (Days) | % Leakage |
|--------------------------|----------------|
| 40 | 3.2 ± .1 |
| 53 | 3.5 ± .2 |
| 227 | 3.4 ± .1 |
| | Av. = 3.3 ± .1 |

(3) A bulb containing a sample was connected to another bulb of equal volume by way of a stopcock and the stopcock was left open for the 30 day experiment. At the end of the experiment the stopcock was closed and the radon in the two bulbs measured separately. The radon concentration in each bulb was found to be the same, proving that a negligible additional quantity of radon is flushed out of the mineral during the evacuation to the ionization chamber after a 30 day accumulation.

(4) On the other hand, if a mineral which has been at atmospheric pressure for at least 30 days, is flushed with nitrogen at atmospheric pressure to remove radon from the external volume, then isolated to accumulate radon for 10 minutes at atmospheric pressure, and finally the gas phase evacuated into an ion chamber, the radon leakage measured in such a procedure is too high. This indicates that an appreciable quantity of the radon in the internal volume was carried out with the nitrogen when the mineral was evacuated. The reason that the radon from

TABLE 2. LEAKAGE AS A FUNCTION OF PREVIOUS HISTORY
(Sample K-1-28)

| Date | Duration of accumulation time (minutes) | % Leakage | Prior Treatment |
|---------|--|-----------|-------------------------------|
| 7/13/53 | 4.29 | 1.95 | No prior flush |
| 7/14 | 4.38 | 1.45 | Single evacuation on 7/13 |
| 7/16 | 4.42 | 1.23 | Evacuation on 7/13 and 7/14 |
| 7/18 | 4.42 | 1.27 | Evacuation on 7/13, 14 and 16 |
| 7/20 | 4.50 | .84 | Four successive evacuations |
| 7/21 | 4.46 | .79 | Four successive evacuations |
| 7/22 | 4.40 | .68 | Four successive evacuations |
| 7/23 | 4.49 | .89 | Four successive evacuations |
| 7/24 | 4.56 | 1.18 | Four successive evacuations |

the interior is measurable in this case but not in experiment (3) is simply due to the much greater quantity of radon in the external gas phase in experiment (3).

(5) A mineral is repeatedly exposed to one atmosphere of nitrogen and evacuated. Then, after a ten minute accumulation at atmospheric pressure, the gas phase is evacuated to the ion chamber.

In this case the measured radon leakage may be higher or lower or equal to the equilibrium leakage depending on the relation of the efficiencies of the evacuations. If the last of the repeated evacuations is more efficient than the one at the end of the accumulation, the apparent radon leakage will be low. If it is less efficient, the apparent leakage will be high. Since it is difficult to control this effect, the method is not usable for quantitative leakage measurements. Table 2 shows the type of variation obtained under two conditions: (A) the sample was not flushed prior

TABLE 3. COMPARISON OF RADON LEAKAGE MEASURED BY THE EVACUATION AND EQUILIBRIUM METHODS

| Sample | % Leakage | |
|--------|------------|-------------|
| | Evacuation | Equilibrium |
| K-1 | 2.9 | 3.1 |
| K-4 | ~0.1 | .03 |
| K-7 | 8.5 | 6.7 |
| K-8 | 2.1 | 8.6 |
| K-9 | 1.9 | 1.6 |
| K-14 | .086 | .064 |
| K-15 | 2.7 | 1.3 |

to accumulation and, (B) the sample was evacuated four times in rapid succession prior to accumulation. The identical sample was used successively and remained in vacuum between runs. All of these measurements were made on the same sample. These evacuations reduce the partial pressure of radon in the internal volume—at least in that portion which is connected with the external volume through orifices that are wide compared to several molecular diameters. The outrush of nitrogen due to the pressure gradient carries out much more radon than would leave the internal volume in the same time interval by gaseous diffusion at one atmosphere of nitrogen inside and outside.

Table 3 shows the variation from the true (equilibrium) leakage rate obtained for a few representative samples by using the evacuation technique.

(6) If a mineral at atmospheric pressure and room temperature is isolated for 10 minutes while the temperature is raised, say from 25° C. to 100° C., radon leakage occurs which is far larger than the equilibrium value at the higher temperature. This appears due to the sudden expulsion of the expanded nitrogen in the internal volume which carries with it some of the radon. It cannot be due merely to the increase of the diffusion coefficient, or the partial pressure of radon which accompanies the temperature rise. Table 4 shows this effect for two consecutive series of runs using the evacuation technique. Prior to the first series the mineral had been left at room temperature and atmospheric pressure for several weeks so that equilibrium could be attained. There was a one day interval between series "A" and "B". The equilibrium value for this mineral is 3.3%.

TABLE 4. INITIAL RADON LEAKAGE AFTER TEMPERATURE INCREASE

Sample K-1-28

Equilibrium temperature (200° C.) attained after 20 min.

| | Time from Room Temperature (Hours) | % Leakage |
|-------|--|-----------|
| Run A | 0:37 | 10.5 |
| | 1:36 | 6.1 |
| | 2:56 | 3.9 |
| Run B | 1:00 | 5.6 |
| | 2:14 | 3.2 |
| | 26:14 | 2.9 |
| | 53:00 | 3.2 |

(7) If equilibrium experiments are carried out as a function of temperature, the rate of radon leakage increases somewhere between $T^{3/2}$ and T^2 . Results on three representative minerals are shown in Table 5. These data will be discussed in more detail later.

The temperature coefficient of the radon leakage strongly suggests that the rate determining step is that of gaseous diffusion (Jost, 6) since the rate of escape from the solid by recoil is essentially temperature independent and at temperatures of less than 400° C. the rate of diffusion in the solid is negligible. However, the diffusion coefficient for radon in air at room temperature, D , is .12 cm.²/sec in an unrestricted volume. Hence, the diffusion is essentially immediate in the external volume. On the other hand, empirical D values for the rate of escape of radon from various materials have ranged as low as 10^{-22} cm.²/sec. Thus the actual rate is determined by gaseous diffusion through pores of very limited

cross sectional area. Consequently, a considerable fraction of the radon atoms ejected into the internal volume may decay before they have time to diffuse into the external volume.

For a given mineral the uranium concentration, surface area, cross sectional area, internal volume, and temperature determine the partial pressure of radon in the internal volume. Since the partial pressure of radon in the external volume is always essentially zero, the effective rate of radon loss from the geometrical surface of the mineral is determined only by the partial pressure of radon in the interior, the temperature,

TABLE 5. EFFECT OF TEMPERATURE ON RADON LEAKAGE
(Equilibrium values)

| Sample | Temperature (° C.) | % Leakage |
|--------|-----------------------|-----------|
| K-1-28 | 25 | 3.3 ± .1 |
| K-1-28 | 100 | 5.1 ± .3 |
| K-1-28 | 140 | 5.5 ± .5 |
| K-1-28 | 200 | 5.8 ± 1.0 |
| K-1-28 | 320 | 2.6 ± .3 |
| K-6 | 25 | 2.5 ± .3 |
| K-6 | 85 | 3.5 ± .5 |
| K-6 | 200 | 9.6 ± 1.2 |
| K-6 | 320 | 3.6 ± .1 |
| K-14 | 25 | .06 ± .01 |
| K-14 | 200 | .16 ± .03 |
| K-14 | 320 | .44 ± .04 |

and the cross sectional area available for leakage. All three factors will influence the rate of diffusion.

There are then two ways to measure the actual radon leakage. First, to flush the external gas phase at one atmosphere, accumulate for a known interval of time, and then flush this quantity of radon out of the external volume at atmospheric pressure into a counter. Second, accumulate the radon for a sufficiently long period of time (i.e., 30 days) so that equilibrium is established between the number of radon atoms being emitted from the geometrical surface of the mineral per unit time and the number decaying in the external volume per unit time. Only the latter procedure has been employed in the present study.

Any non-equilibrium experiment involving evacuation of the sample and short accumulation times will yield variable apparent leakages depending on the previous history of the mineral and the efficiency of the evacuation.

If the internal volume and the total surface area can be measured, the average life of a radon atom in the internal volume and the partial pressure can be calculated. Both of these measurements are physically possible. A reconnaissance surface area determination by the *BET* gas adsorption method using the apparatus and procedure described elsewhere (Kulp and Carr, 7) on one pitchblende which had a leakage of several per cent, gave a surface area of about a square meter per gram in good agreement with theory. Further support for the large internal surface area of these pitchblendes is afforded by the data of Table 6 which shows that increasing the geometrical surface area does not change the leakage. This shows the external surface area to be a negligible fraction of the total surface area.

TABLE 6. VARIATION OF RADON LEAKAGE WITH SIZE OF SPECIMEN

| Sample Number | | % Leakage |
|---------------|--------------------------|-----------|
| K-1-L | Single Piece (34.8 gms.) | 3.0±0.4 |
| K-1-28 | Between 28 and 48 Mesh | 3.3±0.1 |
| K-1-48 | Between 48 and 100 Mesh | 3.0±0.6 |
| K-1-200 | Finer than 200 mesh | 3.8±0.5 |

RADON LEAKAGE MEASUREMENTS AT ROOM TEMPERATURE

The data obtained by measuring the radon leakage of a variety of minerals at room temperature are given in Tables 7 and 8.

The leakage from pitchblende varies from .064% to 16.6% depending on the structure of the specimen. The 16.6% leakage was obtained from a rock containing extremely finely dispersed pitchblende. The Contact Lake pitchblende occurs in narrow wavy bands up to .02 mm. across. The Marysvale, Utah, sample which gave a 7.5% leakage was a fine powder consisting of aggregates less than .03 mm. in diameter. The Sunshine Mine material is somewhat coarser, having an average grain diameter of .05 mm. The Eldorado Mine sample which had only 0.27% leakage was relatively massive, commonly showing unfractured areas up to 0.2 mm. in diameter. The Nicholson sample K-19 is similar to K-18 in polished sections. The lowest leakage was obtained from K-14 which was colloform pitchblende in hematite-carbonate gangue. The pitchblende is banded, the inner zones being largely unfractured. The width of the bands may be as large as 0.7 mm. Samples K-30 through K-68 are all pitchblende concentrates without detailed polished section descriptions. The radon leakage for these samples lies in the range of the more completely described samples above.

The radon leakage for a representative set of uranium-bearing minerals is shown in Table 8. The uraninite falls in the range of the more massive

pitchblende samples. The carnotite is very high as expected for a porous, poorly-crystallized, secondary uranium mineral. The considerable leakage obtained from the zircon samples is somewhat surprising since the samples were single crystals with well-formed faces. The specimen from

TABLE 7. RADON LEAKAGE OF PITCHBLENDE SPECIMENS

| Sample Number | Location | Size | % Leakage |
|---------------|---|---|-------------|
| K-1 | Sunshine Mine, Idaho; 3100 ft. level | 28-48 mesh | 3.1 ± .4 |
| K-6 | Rickards Mine, Gilpin Co., Colorado | Lump with silicates | 2.5 ± .3 |
| K-7 | Contact Lake, N.W. Terr., Canada | Lump with silicates | 6.7 ± .1 |
| K-8 | German and Belcher Mine, Central City, Colorado | Lump with silicates | 8.6 ± .2 |
| K-9 | Katanga, Belgian Congo | Massive pitchblende | 1.61 ± .05 |
| K-13 | Marysvale, Utah; 300 ft. level | Powder | 7.5 ± .7 |
| K-14 | Eagle Mine, L. Athabasca, Canada; 200'-300' level | Pea size | .064 ± .008 |
| K-15 | Joachimsthal | Pea size | 1.3 ± .1 |
| K-18 | Eldorado Mine, Gt. Bear Lake, Canada; 913 Stope | Pea size | 0.27 ± .08 |
| K-19 | Nicholson Mine | Pea size | 0.34 ± .05 |
| K-21 | Upper Huronian Iron Formation, Michigan | Very finely disseminated in silicate matrix | 16.6 ± .3 |
| K-30 | Pitch Ore Group | Pitchblende concentrate | 2.9 ± .4 |
| K-32 | Martin Lake Mine, Canada | Pitchblende concentrate | .23 ± .02 |
| K-34 | Rix (Leonard Series) Adit, Goldfields, Canada | Pitchblende concentrate | .72 ± .05 |
| K-45 | Ace Mine, L. Athabasca, Canada | Pitchblende concentrate | 1.90 ± .09 |
| K-48 | Ace Mine, 1st level, L. Athabasca, Canada | Pitchblende concentrate | 2.51 ± .07 |
| K-54 | Ace Mine, L. Athabasca, Canada | Pitchblende concentrate | 4.3 ± .4 |
| K-55 | Ace Mine, L. Athabasca, Canada | Pitchblende concentrate | 0.26 ± .03 |
| K-68 | Lee Lake, Loc-Larange, Saskatchewan | Pitchblende concentrate | 5.2 ± .3 |

Brazil had about three times the α activity and was considerably more metamict than the one from Madagascar.

RADON LEAKAGE AS A FUNCTION OF TEMPERATURE AND PRESSURE

As shown in Table 5 the radon leakage of radioactive minerals increases with temperature up to 200° C. with a functional relationship of

about $T^{3/2}$ indicative of a gaseous diffusion process. The increase in leakage is largely due to the increase of the diffusion coefficient with temperature, although the partial pressure of radon may also contribute.

The sharp decrease in radon leakage at 320° C. is due to a phase change (recrystallization) presumably to U_3O_8 as shown by Kerr (8) which occurs somewhere between 200 and 400° C. depending on the nature of the pitchblende. This effect is enhanced in air but the reaction occurs even in

TABLE 8. RADON LEAKAGE OF VARIOUS MINERALS

| Sample Number | Mineral | Description | Source | % Leakage |
|---------------|------------|--------------|--|---------------|
| P-2 | Uraninite | Lump | Flat Rock Mine, Spruce Pine, N.C. | .58 ± .09 |
| P-3L | Uraninite | Lump | Crabtree Creek, Yancey Co., N.C. | .80 ± .08 |
| K-3 | Samarskite | Lump | Mitchell Co., N.C. | 0.026 ± 0.008 |
| K-4 | Samarskite | Lump | Wiseman Mine, Beaver Creek, Mitchell Co., N.C. | 0.030 ± 0.002 |
| LL-1 | Autunite | Flakes | Mt. Painter, So. Australia | 5.9 ± .3 |
| LL-2 | Carnotite | Disseminated | Camp Marvel, Naturita, Colo. | 17.3 ± 1.0 |
| LL-5 | Carnotite | Disseminated | Copper Prince Mine, Rock Creek, Colo. | 27.1 ± 0.8 |
| Z-16 | Zircon | Crystal | Brazil | 6.2 ± 0.1 |
| LL-6 | Zircon | Crystal | Ambotofotsky, Madagascar | 1.59 ± 0.13 |
| K-73 | Brannerite | Pea Size | Crocker's Well, So. Australia | 6.0 ± 0.3 |

vacuum since all pitchblende contains appreciable UO_3 due in part to auto-oxidation as the uranium decays into lead.

U_3O_8 has not been reported in natural uraninites so it may be presumed that at least those that have been studied by x-ray diffraction techniques have not been subjected to temperatures exceeding 200–300° C. since they were emplaced. To obtain the integrated radon leakage for the life history of a mineral it is necessary to measure the leakage as a function of temperature up to the temperature at which phase changes occur and to estimate the thermal history of the mineral.

In this study no experimental attempt has been made to assess the effect of pressure. The pressure effect on the velocity of radon atoms in the gas phase would be quite trivial. On the other hand, if the fissures were closed, the leakage would be reduced in proportion to the cross sec-

tional area available for diffusion. However, the evidence suggests that most of the lifetime of the mineral has been spent at temperatures less than 200° C., which is equivalent to a depth of about 7 km. At this depth rocks are still quite porous and unmetamorphosed, hence, it is not likely that the pressure effect is an important one. An independent confirmation of this conclusion comes from the application of radon leakage to correct the 206/238 ages as will be discussed in the following section. The radon leakage correction never overcorrects the age, which would be the case if the average radon leakage during the life of the mineral was measurably less than that observed in the laboratory at one atmosphere confining pressure.

APPLICATION TO AGE DETERMINATION

As has been pointed out in some detail (Kuip, Bate and Broecker, 9) the leakage of radon from radioactive minerals can explain several of the important and consistent anomalies in the ages obtained from the isotopic ratios Pb^{206}/U^{238} , Pb^{207}/U^{235} , Pb^{207}/Pb^{206} , and Pb^{206}/Pb^{210} . In almost all of the reported ages based on these ratios, the 206/238 age is lower than the 207/235. The 207/206 age which is dependent on these two is exponentially affected by slight differences in the ratio, hence the loss of small quantities of radon make this age very high. It is only for minerals older than 1×10^9 years that the percentage error in the 207/206 age due to radon loss approaches the error in the 206/238 age.

The 206/210 age bears a more complex relation to the radon leakage since Pb^{210} occurs below radon in the uranium decay series. Therefore, if the radon leakage has remained constant throughout the life of the mineral the 206/210 age will be correct. If the leakage was much higher during most of the history of the mineral than it was during the past million years, the age derived from this ratio will be low and will approach the 206/238 age. In most cases the 206/210 age will be between the 206/238 and 207/235 ages.

In all cases, the correction for radon leakage improves the agreement of the ages. The minimum correction can be obtained by simply measuring the leakage at room temperature. On the other hand, the correction derived from the radon leakage at the average temperature at which the mineral has existed for its history should give complete agreement unless other factors are influencing the isotopic ratios.

Since the half-life of radon is 3.83 days while that of thoron is 5.45 sec. and actinon 3.92 sec., the quantity of these two cousins which will leak will be 10^{-4} and 10^{-5} times as much as radon respectively. It is clear, therefore, that of these three noble gases only radon leakage need be considered in age determination work.

A few selected age determinations are shown in Table 9.

The ages are given uncorrected for radon leakage, corrected for the radon leakage at room temperature and in two cases (K-6 and K-14) for the experimental values at higher temperatures. The Gilpin County pitchblendes which have presumably had average temperatures during their geologic history of some 100° C. or less, yield good agreement in the isotopic ages when corrected for radon leakage. The correction for room temperature radon leakage for the Katanga sample is not quite

TABLE 9. EFFECT OF RADON LEAKAGE ON AGES FROM VARIOUS ISOTOPIC RATIOS
(Ages in Millions of Years)

| Lamont Sample No. | Locality | % Radon Leakage | 206/238 | 207/235 | 207/206 | 210/206 |
|-------------------------|--|--------------------|-----------|-----------|-----------|-----------|
| K-6 | Gilpin Co., Colo. | U | 55 ± 2 | 64 ± 15 | — | 61 ± 3 |
| | | (25° C.) 2.5 | 56 ± 2 | — | — | — |
| | | (100° C.) 4.0 | 57 ± 2 | — | — | — |
| K-8 | Central City, Colo. | U | 51 ± 1 | 56 ± 5 | — | 58 ± 3 |
| | | (25° C.) 8.6 | 55 ± 1 | — | — | — |
| | | (100° C.) 12* | 57 ± 1 | — | — | — |
| K-9 | Katanga, Bel- gian Congo | U | 575 ± 4 | 595 ± 5 | 630 ± 40 | — |
| | | (25° C.) 1.6 | 585 ± 4 | — | 595 ± 40 | — |
| K-7 | Contact Lake | U | 840 ± 5 | 960 ± 15 | 1220 ± 50 | 864 ± 35 |
| | | (25° C.) 6.7 | 896 ± 5 | — | 1100 ± 45 | — |
| K-14 | Eagle Mine, 200'-300', L. Athabasca, Canada | U | 1425 ± 10 | 1450 ± 20 | 1530 ± 40 | 1448 ± 35 |
| | | (25° C.) .06 | 1425 ± 10 | — | — | — |
| | | (150° C.) .1 | 1430 ± 10 | — | 1525 ± 40 | — |

* Estimated from K-6.

enough to bring agreement, but this value is probably only about half of that for the average temperature for the life of the pitchblende.

The radon leakage of the Contact Lake specimen is high even at room temperature. By analogy with other similar specimens, taking into account the average temperature estimated at 150° C., the actual integrated leakage should approach 15% which would bring the 206/238 and 207/206 ages into line with the 207/235. This suggests that leaching of uranium or lead has been negligible. It is noteworthy that in this case, the uncorrected 210/206 age agrees with the uncorrected 206/238 age. This is

expected whenever the average radon leakage for the mineral is much greater than the present room temperature leakage.

The Eagle Mine sample is an unusually compact specimen, showing low radon leakage. The integrated radon leakage would only have to be about 1.5% to account for the discrepancies in the ages.

The importance of radon leakage in age determination can also be seen in the results obtained on minerals of intermediate radioactive content analyzed for uranium and lead by isotope dilution techniques by Aldrich et al. (11). For zircons from the Essonville granite and the Cape granite, the radon leakage required to bring the 206/238 up to the 207/235 age would be 3% and 7%, respectively. It is noteworthy that the required radon leakage for these zircons lies approximately within the range shown by the zircons measured in this study.

It is concluded that radon leakage measurements are necessary in order to estimate the correction to be applied to 206/238 ages. If this is done as a function of temperature, if the average temperature of the mineral can be approximated, and if no leaching has occurred, the 207/206 age agrees with the corrected 206/238 and the 207/235 age for a considerable variety of specimens. If leaching is absent it appears that the 207/235 age is the most reliable. Conversely, if these three isotopic ages agree after correction for the radon leakage, leaching of uranium and lead are probably absent.

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