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Determination of Thorium-Uranium ratio in Radioactive Minerals by α-ray Counting

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Résumé

L'évaluation du rapport de l'uranium au thorium dans les mineraux an faibles teneurs puit être permis par la discrimination spectrale des rayons α par l'emploi de l'absorbant associé au changement de la sensibilité de l'equipement.

Introduction

Age determination of granite by lead-alpha-ray method devised by LARSEN, E. E. Jr. *et al.*[1] has been followed in this country by HATUDA, Z.[2] and his co-workers since 1958. The writer also has been engaged in the measurement of α-activity in connection with the project. For an accurate dating, it is required to determine the content-ratio of thorium to uranium, as otherwise an theoretical error as large as 17 per cent in the age may be introduced[3] even by use of the approximate average values for proportions of thorium and uranium in zircon.

Radioactive minerals rich in these elements can be analysed by ordinary chemical method, while those poor in them show difficulties in determination especially of thorium content. Spectrometric analysis of gamma-rays[4] is also possible for minerals of relatively high radioactivity, as well as for less radioactive ones, if a sufficient quantity of the sample is available to give a stable spectrum pattern. For the present purpose, we cannot help giving up the gamma-ray spectrometer method, even if we could have the equipment, considering that the quite laborious work of concentrating zircon purely out of a large bulk of granite. Zircon is contained in granite about $n\times10^{-2}$ per cent in average. The method based upon nuclear track technique[5] may be appropriate for the purpose, too. The writer has devised a method which is essentially a combination of EVANS' method[6] and PEIRSON's one[7] in principle; in the former the discrimination of energies of alpha-rays are made by changing the thickness of absorber, while in the latter by changing the sensitivity of

the apparatus. The present method is superior to either of the methods in practice by the reason described later. This method requires no further equipments other than those used in counting alpha-particles from a sample of which dating is aimed.

Theory

When the thickness of a radioactive source becomes greater than the internal range of the most energetic alpha-particle emitted from the elements of the uranium and thorium series, it is called a "thick" source, and then the numbers of alpha-particles will no longer gain in count with increase of thickness or mass of the source owing to its self-absorption.

The number of alpha-counts of such thick source has been calculated by FINNEY and EVANS (1935), Mme IRENNE CURIE (1946) and PIERSON (1951). HATUDA, Z. *et al.*[8] have recently constructed a formula suitable for 4π gas-flow counter. The alpha-emissions per second per 1 cm^2 of the surface of the thick source material in radioactive equilibrium are given as the following equation.

$$n=d\mu 10^3\left[\mathrm{UI}\left\{6.21\Sigma_{\mathrm{UI}}\frac{(R_{\mathrm{UI}}-\rho-a^2)}{R_{\mathrm{UI}}-\rho}+0.28\Sigma_{\mathrm{AcU}}\frac{(R_{\mathrm{AcU}}-\rho-a)^2)}{R_{\mathrm{AcU}}-\rho}\right\}+2.06\mathrm{Th}\,\Sigma_{\mathrm{Th}}\frac{(R_{\mathrm{Th}}-\rho-a)^2}{R_{\mathrm{Th}}-\rho}\right] \quad (1)$$

where UI, Th; concentration of uranium or thorium in the source (g/g), (UI≒U),

d ; density of the source mineral,

$R_{\mathrm{UI}}R_{\mathrm{AcU}}$ and R_{Th}; alpha-ranges of each members of the U, AcU and Th series in air (cm),

μ ; ratio of range in mineral to range in air of alpha-particles,

Σ ; summations are made over the members of the U, Th and AcU series,

a ; thickness of aluminium or myler foil in terms of range of alpha-particles in air (cm),

ρ ; minimum detectable residual range of alpha-ray in air (cm),

numerical coefficients; these are calculated for the specific activity per second of uranium and thorium, and for the case of actinium, the ratio of exisetance of actinium to uranium is considered.

Usually ρ is a constant for the apparatus used, but it is parametrically variable for the proportional counter circuit provided with a pulse-amplitude discriminator.

The fundamental point to discriminate thorium from uranium by counting of alpha-particles is based on the fact that energy spectra of alpha-rays from uranium and thorium series are different and that it is capable to count selectively the alpha-particles longer than a desired range by means of absorbers or pulse-height discriminator.

Let n_0 and $n_{\rho a}$ be the numbers of counts corresponding to the measurements under the conditions (a_0, ρ_0) and (a, ρ); a being the thickness of the absorber and ρ the minimum detectable range, then the ratio of $n_{\rho a}$ to n_0 for a source containing both uranium and thorium series is expressed as follows,

$$\left(\frac{n_{\rho a}}{n_0}\right) = \frac{X_{\rho a}\mathrm{U} + X_{\rho a}\mathrm{Th}}{X_0\mathrm{U} + Y_0\mathrm{Th}} \tag{2}$$

where

$$X_{\rho a} = 6.21\Sigma_{\mathrm{UI}}\frac{(R_{\mathrm{UI}}-\rho-a)^2}{R_{\mathrm{UI}}-\rho} + 0.28\Sigma_{\mathrm{AcU}}\frac{(R_{\mathrm{AcU}}-\rho-a)^2}{R_{\mathrm{AcU}}-\rho}$$

$$Y_{\rho a} = 2.06\Sigma_{\mathrm{Th}}\frac{(R_{\mathrm{Th}}-\rho-a)^2}{R_{\mathrm{Th}}-\rho}$$

and X_0, Y_0 are the values of $X_{\rho a}$, $Y_{\rho a}$ when $\rho=\rho_0$, $a=a_0$.

$$\left(\frac{n_{\rho a}}{n_0}\right)_{\mathrm{U}} = \frac{X_{\rho a}}{X_0} \qquad \text{for} \quad \mathrm{Th} = 0$$

$$\left(\frac{n_{\rho a}}{n_0}\right)_{\mathrm{Th}} = \frac{Y_{\rho a}}{Y_0} \qquad \text{for} \quad \mathrm{U} = 0$$

$$\left(\frac{n_{\rho a}}{n_0}\right) = \frac{X_{\rho a}/X_0 + Y_{\rho a}/Y_0 \cdot Y_0/X_0 \cdot \mathrm{Th/U}}{1 + Y_0/X_0 \cdot \mathrm{Th/U}} = \frac{\left(\frac{n_{\rho a}}{n_0}\right)_{\mathrm{U}} + \left(\frac{n_{\rho a}}{n_0}\right)_{\mathrm{Th}} \cdot Y_0/X_0 \cdot \mathrm{Th/U}}{1 + Y_0/X_0 \cdot \mathrm{Th/U}} \tag{3}$$

The values of $(n_{\rho a}/n_0)$ as a function of a, ρ can be shown by the theoretical curves as seen in Fig. 1; the upper couple of curves being simply functions

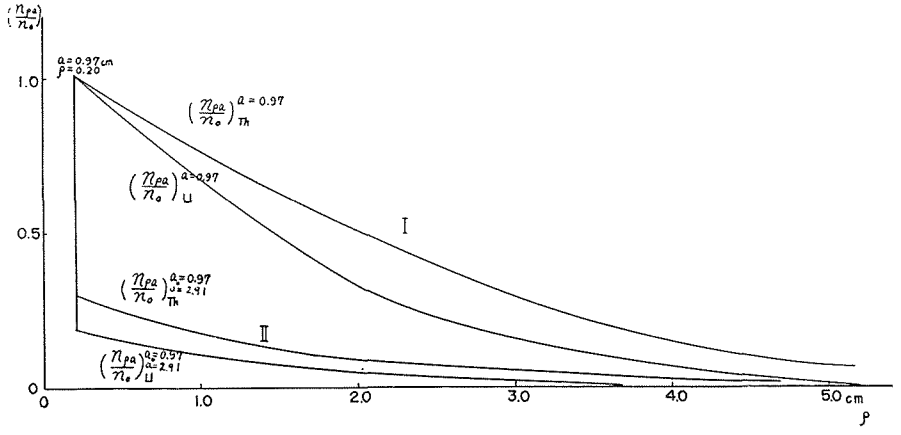

Fig. 1. Theoretical values of $(n_{\rho a}/n_0)_{\mathrm{U}}$ and $(n_{\rho a}/n_0)_{\mathrm{Th}}$ as a function of ρ.

of ρ and the lower one functions of ρ with fixed absorbers added, and in either case of them the upper curve being for the thorium series, the lower one for

the uranium series, and the curve for mixtures of the both series, will lie between the two curves in each couple.

As seen in the equation (1), energy discrimination of alpha-rays is capable by changing ρ or a, or both at a time. Nevertheless from the view-point of stability, there are slight difference more or less.

The absorber placed upon the sample reduces the range of all alpha-particles, and consequently the alphas to be counted are restricted to be relatively narrow bound of energy. By this reason the method using absorber affords an advantage in stabitity for counting alpha-rays in the excellent region of the proportional characteristic of the counter. On the other hand, in the alternative method using discriminator, in which the minimum detectable range is taken as a parameter, the strict regularity has to be kept not only in counting number but also in proportionality of pulse energies almost through the full course of the counting system and relatively wide energy bound. For the proportional counter such as gas-flow counter, the slight changes in temperature, pressure, composition and velocity of gas-flow in the ionization chamber may be effective to the proportionality of the counter in some degrees, especiallyin the high energy region but not to counting capability. Such a spontaneous irregularity may be insignificant for counting much number of counts of high activity, with low pulse-height limit of discriminator, because the observed values are expressed as ratio of two numbers of counts. On the contrary, it may disturb the counting for the few number of low activity at the high pulse-height limit of discriminator. For the reason mentioned above the method of using absorber is relatively favourable for the sample of poor radioactivity. In general,

1) The use of absorber is excellent in reproducibility.
2) The larger the minimum detectable range of the instrument is, the lower is the background counts in the apparatus.

For the above two reasons, the writer adopted the method of changing a and ρ at the same time, by which the difficulties of counting poor activity have been overcome in some degrees.

From the practical point of view, the discrimination of thorium and uranium seems to obtain a satisfactory result, if ρ and a are so chosen that the difference of $(n_{\rho a}/n_0)_{\mathrm{Th}}$ and $(n_{\rho a}/n_0)_{\mathrm{U}}$ may be as large as possible, and the counts with (ρ, a) preferably numerous, and that the background due to noises may be as low as possible. Considering these, (ρ, a) the most proper value for $(\rho+a)$ is 4–5 cm in air equivalent.

Apparatus and procedure

The equipments used in the measurements are composed of a 4π gas-flow counter, a stabilised voltage source, a linear amplifier, a pulse height discriminator and scaling units.

The gas-flow counter (type PC-V Tokyo Atomic Industry Co., Ltd.) was followed by a linear amplifier which is usually operated at a half of its maximum gain ($\times 3200$) considering from the stability, and by discriminator which can be set from $3.2v$ to $100v$ for the input of the Schmidt-trigger circuit.

The discriminator is employed as the means of effectively controlling the sensitivity of the counter circuits, i.e. to vary the minimum detectable α-particle range.

The normal background of this counter equipment is about 0.1 cpm under the condition of $\rho = 0.20$ cm, but it diminishes sharply in count as value of ρ increases, e.g. to ca. 0.01 cpm when ρ is about 2.0 cm, and almost to zero when ρ is nearly 3 cm.

Experimental results and consideration

For the verification of equation (3), a series of standard samples arranged in the increasing order of Th/U required. Diluting U-less thorium mineral such as monazite and Th-less uranium mineral such as pitchblende with non-radioactive substance e.g. quartz, and mixing these in desired proportions, we may get a series of samples of varing portions of Th/U. But practically, it is not easy to get samples of exact proportion and the method requires a large quantities of them. Moreover, in this case some difficulties may arise especially from the differences of the stopping power among these three minerals. Now the writer has devised the method suitable for the present purpose instead of the mixing method stated above. Referring to Fig. 2, a uranium mineral K, and a thorium mineral M, are put in the respective half of the circular groove cut on the surface of an aluminium plate. The groove is 0.5–2 mm in width according to the bulk of the sample used. A movable screen of thin semi-circular aluminium plate is placed concentrically on the foil covering the surface of the sample, and is turned around the center of the circle. This screen acts to intercept the alpha-particles from below, while it covers the mineral K and M by a certain ratio of the area. Noting the content of uranium and thorium by U_K, Th_K, U_M, Th_M, the ratio of alpha range in mineral to that in air by μ_K, μ_M, and the density of these two mineral by d_K, d_M, respectively, we have

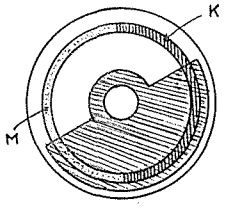

Fig. 2. Sample holder used for varying the exposed areas of the two minerals.
M: monazite
K: kobeite
Semi-circular sector (shaded part) is a movable screen

$$\frac{n_{\rho a}}{n_0} = \frac{md_K\mu_K(X_{\rho a}U_K + Y_{\rho a}Th_K) + (1-m)d_M\mu_M(X_{\rho a}U_M + Y_{\rho a}Th_M)}{md_K\mu_K(X_0U_K + Y_0Th_K) + (1-m)d_M\mu_M(X_0U_M + Y_0Th_M)} \qquad (4)$$

where m is the ratio of the exposed area to the whole area of the mineral K.

Then the effective ratio, Th to U for the alpha-particle radiometry, that is, ratio corrected for the difference of mass stopping power between M and K, is,

$$\frac{\mathrm{Th}_K+\gamma_{d\mu}\cdot \mathrm{Th}(1-m)/m}{\mathrm{U}_K+\gamma_{d\mu}\cdot \mathrm{U}_M(1-m)} \qquad (5)$$

where $\gamma_{d\mu}$ is equal to $d_M\cdot\mu_M/d_K\cdot\mu_K$, i.e., the ratio of absorption factor of mineral M to that of K.

Kobeite (μ_K; 4.24×10^{-4}, d_K; 4.6, U_3O_8; 5.34%, ThO_2; 1.25%) and monazite (μ_M; 5.1×10^{-4}, d_M; 5.8, U_3O_8; 0.29%, ThO_2; 6.33%) are chosen as the standard minerals. The effective ratio Th/U calculated by equation (5) and the values of $\frac{n_{\rho a}}{n_0}$ by equation (4) corresponding to each step of rotation by 15° in angle of the screen are shown in the Table 2.

Peirson has experimentally verified the propriety of equation (3) partialy using radioactive 4% U_3O_8; source areas of 20 cm^2; corresponding to about 1500 cpm, from the part of function of ρ at the different two settings of the pulse-amplitude discriminator. But for the case of weak radioactivity, for example, 5% U_3O_8 or 6% ThO_2; source area of 0.2 cm^2, i.e., about 100–30 cpm or less, the method of varying ρ becomes practically unsuitable, owing to the slight fluctuations which were relatively lager at the high gains of the discriminator. These fluctuations are similar in character neither to the radioactive one nor to the straggling of range, and the major causes of it, perhaps, result partially from the character of counter and partly from the changes in stability of electronic circuits. For the eliminations of this fluctuations the combined method of absorber with discriminator was adopted.

Some measurements with different absorbers and discriminator ranges, were put to the tests, using two series of radioactive source, fairly weak (200–70 cpm) and weak (70–20 cpm). The conditions of measurements and their results are shown in Table 1 and 2, where the experiments 1A, 2B and 3C, (under the source activity of 200–70 cpm), result in fair success, but under weak activity (70–20 cpm), good result has been obtained only from the combination method of absorber with discriminator (5D). The activity of 20 cpm above-mentioned

Table 1

Source activity			fairly weak 200–70 (α/cm^2/m)		weak 70–20 (α/cm^2/m)		
Experiment No.			1A	2B	3C	4D	5D
condition of measurement	1st (a_0, ρ_0)	a_0 (cm)	0.50	0.50	0.97	0.97	0.97
		ρ_0 (cm)	0.20	0.20	0.20	0.20	0.20
	2nd (a, ρ)	a (cm)	0.50	0.50	2.91	2.91	2.91
		ρ (cm)	2.5	2.5	0.20	0.20	1.0

Table 2

Propositions of exposed areas of the two minerals M & R	corrected Th/U	1A	2B	3C	4D	5D
		$(n_{\rho a}/n_0)$	$(n_{\rho a}/n_0)$	$(n_{\rho a}/n_0)$	$(n_{\rho a}/n_0)$	$(n_{\rho a}/n_0)$
12/12 M+ 0 K	22.68		0.1741			
11/12 M+ 1/12 K	10.68			0.3052	0.2886	0.1763
10/12 M+ 2/12 K	6.86	0.1418	0.1691	0.2985		
9/12 M+ 3/12 K	4.72	0.1336				
8/12 M+ 4/12 K	3.44	0.1260		0.2707		
7/12 M+ 5/12 K	2.58	0.1178				
6/12 M+ 6/12 K	1.97	0.1090	0.1407	0.2427	0.1823	0.1285
5/12 M+ 7/12 K	1.50			0.2426		
4/12 M+ 8/12 K	1.14					
3/12 M+ 9/12 K	0.85			0.2224		
2/12 M+10/12 K	0.60		0.1104		0.1937	0.1006
1/12 M+11/12 K	0.41			0.2208	0.2100	0.1276
0 M+12/12 K	0.24		0.1054		0.1963	0.1272
Calculated values of $\left(\frac{n_{\rho a}}{n_0}\right)_U$ & $\left(\frac{n_{a\rho}}{n_0}\right)_{Th}$ (least squares method)		0.0710 0.1760	0.1098 0.1845	0.1109 0.1949	0.1644 0.3206	0.1025 0.1960
Approximate values from the theoretical curves: $\left(\frac{n_{\rho a}}{n_0}\right)_{Th}$		0.155	0.200	0.200	0.266	0.178
Deviation from theoretical one		−0.021	−0.015	+0.005	+0.054	+0.018
Judgment		fairely good	good	very good	fairely bad	good
Method		discriminator only		absorber only		combined absorber with discriminator

in this case is nearly equivalent to that of zircon of 500 α/mg/hr (in source area of about 0.5 cm^2).

Practical process of measuring Th/U

Using several standards of varying ratios of Th to U, which are preferably of nearly the same order of radioactivity with the samples to be tested, countings of alpha-particles are made with the conditions (ρ_0, a_0) and then (ρ, a) to obtain n_0 and $n_{\rho a}$. The alpha-particle countings of the sample concerned are made between those of the standard samples. The each value of $\frac{n_{\rho a}}{n_0}$ thus obtained and its corresponding Th/U values of standard samples are used in equation (3) as the variables for the calculation by the method of least squares.

From equation (3)

$$\frac{n_{\rho\alpha}}{n_0}\left(1+\frac{Y_0}{X_0}\frac{\mathrm{Th}}{\mathrm{U}}\right)=\frac{X_{\rho\alpha}}{X_0}+\frac{Y_{\rho\alpha}}{Y_0}\frac{Y_0}{X_0}\frac{\mathrm{Th}}{\mathrm{U}}$$

this may be written as $y=ax+b$

where y represents the left term of the above equation considering Y_0/X_0 as a definite value, x does $\frac{Y_0}{X_0}\cdot\frac{\mathrm{Th}}{\mathrm{U}}$, and a, b is $\frac{Y_{\rho\alpha}}{Y_0}$, $\frac{X_{\rho\alpha}}{X_0}$ respectively,. The most plausible values for $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{Th}}$ and $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{U}}$, will be obtained by the method of least squares regarding a and b as the unkown in the observation equation.

In order to get the satisfactory result the values of $(n_{\rho\alpha}/n_0)_{\mathrm{Th}}$ and $(n_{\rho\alpha}/n_0)_{\mathrm{U}}$ thus obtained, must be coincident with those obtained by theoretical computation. In practice, to decide the absolute value of ρ is not necessary the examination can be tried at the theoretical curves of Fig. 1, that is, the decision is made by the examination putting one value of the obtained $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{Th}}$ or $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{U}}$ at the corresponning point on the curves and locking over again the coincidance of the other of $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{U}}$ or $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{Th}}$ with the corresponding point on the other curve for the same point of the axis in the figure. When the grave disagreement would be found between them, or the probable error in the least squars method too great, the whole measurement at that time must be put out of consideration. On the contrary, once these two values of $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{Th}}$, $\left(\frac{n_{\rho\alpha}}{n_0}\right)_{\mathrm{U}}$ are recognized to be favorable, then Th/U of testing samples would be easily obtained from the equation (3).

Conclusion

Methods of determining thorium-uranium ratio in weakly radioactive minerals have been tested experimentally. The combination method of changing the thickness of absorber and sensitivity of apparatus provides satisfactory counting accuracy. Systematic errors were avoided by the calibration with standard samples. Statistical errors in the determinations of Th/U of a mineral of activity (500 α/mg/hr) were found to be less than $\pm 7.4\%$ with a counting 3 hours.

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