MEMOIRS OF THE COLLEGE OF SCIENCE, UNIVERSITY OF KYOTO, SERIES B,
Vol. XXXIII, No. 2 Geology and Mineralogy, Article 1, 1966

A Trial Method of Determining Uranium and Thorium Content of Rocks in Radioactive Disequilibrium by Neutron Activation Analysis (1)

By

Zin'itiro HATUDA, Susumu NISHIMURA* and **Tetsuji ASAYAMA***

Geological and Mineralogical Institute, University of Kyoto

(Received June 30, 1966)

Abstract

The uranium and thorium content of some basic lavas has been determined by using the neutron activation method. These lavas revealed radioactive disequilibrium by means of alpha- and gamma-ray spectra interpretation. The uranium content of some lavas in younger historical ages has been found to be smaller than that calculated from their radium content assuming the radioactive equilibrium, while their Th/U ratios are in average value for such rocks.

1. Introduction

The uranium and thorium content of rocks and meteorites has been determined by a few workers by neutron activation analysis. This method is believed to be effective for the determination of uranium and thorium at the sub-microgram level in basic rocks and meteorites[1),2),3)].

Usually the direct radiometric method is used[4),5),6)] on the assumption that the samples are in radioactive equilibrium, but it is noteworthy that not a few samples of rocks in nature are in radioactive disequilibrium. Among them are lavas presumably suffered from various geochemical processes.

The radioactive disequilibrium feature of the sample with high content of uranium and thorium is easily found by the alpha- and gamma-rays spectrometry, while that of the sample with low content of them as rocks will not be so. In the latter case, the determination of uranium requires other methods. The authors have adopted the method in which the rock samples are first activated by the neutron bombardment and subjected to the spectrometry after an optimum period of cooling during which most of the produced short-lived nuclides are decayed

* Department of Geological Sciences, University of Osaka Prefecture.

away. The irradiation was carried out in the hydraulic tubes of the reactor of the Research Reactor Institute of Kyoto University.

The authors acknowledge the support of the followings in this research: Assist. Prof. S. IWATA and the members of the Research Reactor Institute of Kyoto University for the facilities of the irradation and the gamma-ray measurements, and Prof. S. SHIMIZU of the Institute for Chemical Research of Kyoto University, for alpha-ray measurements. Finally this investigation has been partly supported by the financial aids of the Scientific Research Expenditure of the Ministry of Education, and of the Co-operated Use of the Research Reactor of Kyoto University.

2. Nuclear Data

Table 1 lists the relevant nuclear data for the nuclides produced by slow neutron irradiation of the natural isotope mixture of uranium and thorium.

Table 1. Nuclear data for uranium and thorium

$^{232}Th\ (n,\gamma)\ ^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U \rightarrow \cdots\cdots$

$^{238}U\ (n,\gamma)\ ^{239}U \rightarrow {}^{239}Np \rightarrow {}^{239}Pu \rightarrow {}^{235}U \rightarrow \cdots\cdots$

Nuclide	Half-life	Type of disintegration and its energy (MeV)
^{233}Th	22.12 m	β^-: 1.245 γ : 0.0292(2.1%), 0.0869(2.7%), 0.171(0.7%)
^{233}Pa	27.0 d	β^-: 0.15(37%), 0.254(58%), 0.568(5%) γ : 0.301(22*), 0.313(150*), 0.341(6*)
^{233}U	1.65×10^5 y	α : 4.773(14.9%), 4.816(83.5%), 4.717(1.6%) γ : 0.0428(0.05%), 0.0561(0.01%)
^{239}U	23.54 m	β^-: 1.21 γ : 0.0736
^{239}Np	2.346 d	β^-: 0.070(22%), 0.327(35%), 0.382(21%), 0.439(16%), 0.723(6%) γ : 0.1064(50*), 0.2099(9*), 0.2284(28*), 0.2546(0.6*), 0.2777(31*), 0.2856(1.4*), 0.3161(3.3*), 0.3344(4.4*)
^{239}Pu	2.44×10^4 y	α : 5.069(10.7%), 5.134(16.8%), 5.147(72.5%)

* relative intensity

3. Experimental

3.1.1. Description of samples

The samples used in the present study are listed in Table 2. They are lavas from volcanoes in Kyûshû District with one exception of lava from Hakone in Kanagawa Prefecture. The Sakurajima lavas are classified according to the time of eruption: Bummei eruption (1475–6), An'ei eruption (1779), Taishô eruption (1914) and Shôwa eruption (1946). The magma of Shôwa lava may be the

residual of Taishô lava, considering from the feature of eruptions and the results of the chemical analyses[7].

Table 2. Samples used in the uranium and thorium determinations

Sample	Time of eruption	Rock type	Locality
Sakurajima			
Bummei lava	1475–6	Two pyroxene andesite	Mochiki, East part of Sakurajima
An'ei lava	1779	Hyperthene andesite	Yumoto, East part of Sakurajima
Taishô lava	1914	Two pyroxene andesite	Akamizu, West part of Sakurajima
Shôwa lava	1946	Two pyroxene andesite	Kurokami, East part of Sakurajima
Kirishima lava	? historic	Two pyroxene andesite	Iôdani Spa
Aso lava	? historic	Two pyroxene andesite	Central crater
Hakone lava	? Quaternary	Two pyroxene andesite	Hakone Pass

3.1.2. Preparation of samples for irradiation

The rock is pulverized to the fineness to pass through a 80 mesh sieve. After having been dried in an oven at 110°C for several hours, it is put into a desiccator for cooling. 0.2 g of the pulverized rock is put into a silica ampoule, then sealed at a diminished pressure. The ampoule is made of silica tubing whose internal diameter is 4 mm, cleaned over night in aqua regia, rinsed several times with demineralized water and dried in an oven at 110°C for three hours.

3.1.3. Preparation of standard for irradiation

The comparison technique is adopted in the present activation analysis. In order to minimize the differential effect of neutron self-shielding and flux enhancement, it is desirable to choose the comparator sample as much akin as possible to the sample to be assayed in chemical composition and physical property. As such a comparator sample (monitor) the Deccan Trap (NBS) (0.7 ppm U, 2.8 ppm Th) is used in this study. 0.2 g of this comparator sample is enampouled under a diminished pressure just the same manner with the sample to be assayed.

3.2. Irradiation conditions

The samples and monitor sealed separately in silica tubes are placed side by side in an aluminium container for irradiation. The irradiation is made in the hydraulic tube of the reactor, in a flux of thermal neutron of 2×10^{13} n/cm^2/sec. The duration of irradiation is 10 hours.

For the correction of the effect of fast neutron, *cadmium ratio* is used.

3.3. Gamma-ray spectra resolution

The content of ^{233}Pa and ^{239}Np in irradiated samples is determined by gamma-ray spectrometry about two weeks and two months after irradiation. The gamma-activity is measured by means of a single thallium-activated sodium iodide crystal, with associated electronic equipment in conjunction with a single channel pulse-height analyser (Aloka, PSM 802, TDC 4) and a 512 multi-channel instrument (RCL). The ability for resolving gamma-ray spectra has basic importance for the success of instrumental activation analysis. For the resolution *graphical technique* is used as it is considered to be most appropriate.

3.4. Alpha-ray spectrometry

As a trial, thin source method of alpha-activity measurement was adopted for the samples from Sakurajima. To prepare a *thin source*, both the assayed and monitor samples were treated with fluoric and nitric acids in a platinum crucible after irradiation, and then the resultant solution was deposited on a nickel plate by evaporation. To insure the escape of radioelement, gamma-ray spectrometry was carried out before and after the chemical treatment, and the correction was made by utilizing ^{59}Fe peak.

The alpha-ray spectrometric assay was made twice about a month and nine months after the irradiation. All the samples were subjected to the alpha-ray spectrometry as a *thick source* by means of a 4π proportional flow-counter using PR gas, the procedure having been fully described by HATUDA and NAGAI[8].

4. Results and Discussions

The results obtained hitherto are listed in Table 3. The results for uranium and thorium content with thin source were rejected as the number of alpha particle counted was insufficient considering from the statistical point of view. For uranium content the values by alpha-ray spectrometry with thick source are cited. For the thorium content, the obtained values by alpha- and gamma-ray spectrometry gave the same figures within the experimental error, differing in the second decimal place. The figures shown under the heading eq. U are calculated values from radium content previously determined by one of the authors (T.A.) on the assumption of radioactive equilibrium between uranium and radium.

As shown in the table, Th/U ratio ranges from 2.33 to 3.72 with the average of 3.11, which may be reasonable for basic lavas. So far as the obtained data are concerned, the radium content of these lavas is highly excessive contrary to the expectation, as the time elapsed since their eruption is shorter than that required for the radioactive equilibrium between uranium and radium. The discussion

of this problem is left for the next report.

Table 3. Uranium and thorium content and equilibrium quantity of uranium calculated from radium content

Sample	U (ppm)	Th (ppm)	Ra content* (10^{-12} g/g)	eq. U (ppm)	Th/U
Sakurajima					
Bummei lava	0.9	3.0	0.72	2.1	3.34
An'ei lava	0.8	2.2	0.58	1.7	2.75
Taishô lava	0.7	2.1	0.46	1.3	3.00
Shôwa lava	0.9	2.8	0.50	1.4	3.11
Kirishima lava	0.7	2.6	0.59	1.7	3.72
Aso lava	0.4	1.4	0.61	1.8	3.50
Hakone lava	0.6	1.4	0.16	0.5	2.33

* Radium content determined by T. ASAYAMA[7].

References

1) HAMAGUCHI, H., G.W. REED and A. TURKEVICH: Geochim. Cosmochim. Acta, **12,** 337–347 (1957).
2) MORGAN, J.W. and J.E. LOVERING: Geochim. Cosmochim. Acta, **28,** 405–417 (1963).
3) FILLEY, R.H.: Geochim. Cosmochim. Acta, **26.,** 49–51 (1965).
4) HURLEY, P.M.: Bull. Geol. Soc. Am., **67,** 395–404 (1956).
5) ADAMS, J.A.S.: Nat. Rad. Envir., Rice Univ. Semicentennial Pub., 485–497 (1964).
6) HATUDA, Z. and S. NISHIMURA: Mem. Coll. Sci., Univ. Kyoto, **B, 31,** 215–226 (1965).
7) ASAYAMA, T.: Mem. Fac. Ind. Arts, Kyoto Tech. Univ., **2-B,** 53–69 (1953).
8) HATUDA, Z. and J. NAGAI: Mem. Coll. Sci., Univ. Kyoto, **B, 28,** 527–538 (1962).