Ionium dating of acidic volcanic rocks*

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Abstract—Concentrations of uranium, and concentrations and isotopic ratios of thorium in zircon and glass were determined for pyroclastic dacite pumices in southern Kyushu, Japan, and Io -ages were calculated. Uranium and thorium distributions in other minerals were also determined.

Uranium and thorium contents of minerals were highest for zircon and decreased in the order, zircon-apatite-glass-mafic minerals-plagioclase. Zircons showed the highest U/Th activity ratios compared with other minerals.

Io -ages obtained by glass-zircon pair for pyroclastic flows in southern Kyushu, except for Ata pyroclastic flow were consistent with ^{14}C and fission track ages and the stratigraphic sequence. Comparison of uranium and thorium concentrations in mineral constituents of acidic volcanic rocks showed that the glass-zircon pair is the most preferable for ionium dating.

INTRODUCTION

Ages of volcanic activities in the late Quaternary have been determined mostly by radiocarbon dating. The use of radiocarbon dating, however, is limited to samples younger than about 40,000y because of the relatively shorter half-life of ^{14}C . Recently the fission track dating method (SHIMA, 1967; SUZUKI, 1970; YABUKI and SHIMA, 1970; KANEOKA and SUZUKI, 1970) and the K-Ar dating method (KANEOKA and SUZUKI, 1970) were applied to the dating of volcanic rocks of the late Quaternary. However, these two methods often include considerably larger errors for late Quaternary samples than for older ones, owing to the long half-lives of radioactive nuclides involved.

Ionium (^{230}Th), decaying with its half-life of 75,200y (ATTREE *et al.*, 1962), appears to be a useful tool for the dating of late Quaternary events ranging in age from several thousand to about 200,000y. However, the ionium dating which can give more accurate dates than fission track or K-Ar datings has been carried out only on the samples of pelagic sediments (GOLDBERG and KOIDE, 1962) and corals (KAUFMAN *et al.*,

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1971). CERRAI *et al.* (1965) first attempted to apply ionium dating to volcanic products. KIGOSHI (1967) independently developed a similar dating method for igneous rocks and also TADDEUCCI *et al.* (1967) reported ^{230}Th dating of volcanic rocks. More recently, KUPTSOV *et al.* (1969) attempted ionium dating of young volcanic rocks.

The method and its fundamental requirements for ionium dating of volcanic rocks were extensively described in KIGOSHI (1967) and FUKUOKA and KIGOSHI (1970). Io-age (t) of volcanic rocks is given by

$$t = \frac{1}{\lambda} \ln \left[1 / \left(1 - \frac{Y_1 - Y_2}{X_1 - X_2} \right) \right] \quad (1)$$

where Y_1 and Y_2 are $\text{Io}(^{230}\text{Th})/\text{Th}(^{232}\text{Th})$ activity ratios in minerals (1) and (2) separated from a same rock, respectively; X_1 and X_2 are $\text{U}(^{238}\text{U})/\text{Th}(^{232}\text{Th})$ activity ratios in minerals (1) and (2), respectively; and λ is the decay constant of ^{230}Th . The accuracy of age t calculated from Eq. (1) depends on the difference between X_1 and X_2 as well as uranium and thorium contents of mineral phases. Therefore, the most accurate ages will be obtained by the mineral pair having the largest difference in U/Th activity ratios.

To find out the pair of X_1 and X_2 which gives the most accurate age, we analyzed uranium and thorium in mineral phases separated from pyroclastic dacite pumices. Based on the results, four pyroclastic flows in southern Kyushu have been dated in terms of ionium for glass and zircon pairs. The dating results have been compared with ages by other dating methods and geological evidences.

SAMPLES AND EXPERIMENTAL PROCEDURES

Rock samples used in this study are Kakuto, Ito, Ata, Ikeda and Torihama pyroclastic dacite pumices collected from southern Kyushu, Japan, Yunotani rhyolitic lava of Ontake volcano and Hotokeiwa dacitic lava of Asama volcano in central Honshu, Japan. Geological and mineralogical descriptions of the dacite pumices are given in ARAMAKI and UI (1966), ARAMAKI (1969) and UI (1971), description of the rhyolitic lava is given in K. KOBAYASHI, *et al.* (1971) and that of the dacitic lava in ARAMAKI (1963).

Each mineral species was separated by using organic heavy liquids and an electromagnetic separator (Frantz Isodynamic Separator). For pumice samples, most of porous glass had been panned off with running water before the separation by an electromagnetic separator and by heavy liquid. Microscopic inspection on the separated zircon and other minerals gave the estimation of the purities of about 99% and over 95% respectively. Zircon samples were identified by X-ray diffraction analysis using $\text{Cu } K\alpha_1$ ($\lambda = 1.5405 \text{ \AA}$) on a Norelco diffractometer.

Uranium and thorium in minerals were determined by the neutron activation

analysis using a technique similar to that described by WAKITA *et al.* (1968).

The isotopic ratio of thorium was measured by α -ray activity ratio of thorium separated from the sample. For glass samples, 10 to 20g of a sample was decomposed with HF-HClO₄. Uranium and thorium were separated in an anion exchange resin column (Dowex 1-X8, 100 ~ 200mesh). The thorium fraction was purified by a cation exchange resin column (Dowex 50W-X8, 100 ~ 200mesh, 9mm $\times$ 50mm). Finally, the thorium was electroplated on a stainless steel disc of 1.4cm diameter. The energy spectrum of alpha rays from thorium isotopes was measured by a solid state detector (surface barrier type). For zircon samples, 2 to 130mg of a sample was decomposed by borax fusion. Zirconium was removed by precipitation with mandelic acid from 2N HCl solution of the decomposed sample. The analytical procedure after the elimination of zirconium was similar to that described above.

RESULTS AND DISCUSSION

The results of uranium and thorium analyses are shown in Table 1 with the values of Io/Th activity ratios. The results of six repeated analyses of AGV-1 showed that the errors in uranium and thorium analyses are about 8% and 4%, respectively. Therefore, over-all errors in uranium and thorium analyses are also believed to be about 8% and 4%, respectively. A stratigraphic sequence of pyroclastic flows in southern Kyushu (ARAMAKI, 1969; U₁, 1971) and its Io-ages are shown in Table 3 together with the ages obtained by other dating methods.

Uranium and thorium contents of minerals are the highest for zircon and decrease in the order, zircon-apatite-glass-mafic minerals-plagioclase (Table 1). Uranium and thorium contents of zircon are 1,000 to 3,000 times higher than those of mafic minerals and plagioclase.

In regard to the difference in U/Th activity ratios of mineral pairs, hornblende-zircon, glass-zircon, plagioclase-zircon, and hypersthene-zircon are largest for Kakuto, Ito, Ata and Ikeda, and Torihama pyroclastic dacite pumices, respectively (Table 1). However, when we consider analytical convenience, the glass-zircon pair is generally the most favorable mineral pair for ionium dating because in most cases volcanic glass has high uranium and thorium contents.

Acidic volcanic rocks usually have large quantities of glass. From the separation yield of zircon from volcanic rocks (Table 2), we can estimate zircon contents of our samples at 1×10^{-5} to $2.5 \times 10^{-3}\%$. The separation yield of zircon from Yunotani lava is only about $1 \times 10^{-5}\%$ and no zircon was obtained from Hotokeiwa lava. For these lava samples, the separation of zircon was far more difficult than for pumice samples. The estimated zircon content would be far less than the actual abundance of zircon. The separation yields of plagioclase and mafic minerals are about 0.1 to 0.5% (calculated from Table 2). For most of acidic volcanic rocks, in order to obtain an

Table 1. Uranium and thorium contents and U/Th and Io/Th activity ratios of minerals separated from pyroclastic dacite pumices in southern Kyushu

Locality	Mineral	U (ppm)	Th (ppm)	U/Th (activity)	Io/Th (activity)
Kakuto	glass	1.53 ± 0.04	7.34 ± 0.30	0.621 ± 0.030	0.734 ± 0.023
	hornblende	0.105 ± 0.004	0.519 ± 0.026	0.602 ± 0.037	
	apatite*2)	7.48 ± 0.23	10.3 ± 0.5	2.17 ± 0.12	
	zircon			3.20 ± 0.17*3)	
Ito	glass	2.48 ± 0.12	9.67 ± 0.44	0.766 ± 0.050	0.658 ± 0.021
	plagioclase	0.216 ± 0.007	0.435 ± 0.018	1.49 ± 0.08	
	hypersthene	0.476 ± 0.015	1.12 ± 0.05	1.27 ± 0.07	
	apatite*2)	8.84 ± 0.23	25.4 ± 1.0	1.04 ± 0.05	
	zircon	346 ± 16	293 ± 15	3.54 ± 0.25	
Ata	glass	2.07 ± 0.09	7.90 ± 0.35	0.783 ± 0.050	0.798 ± 0.022
	plagioclase	0.128 ± 0.005	1.04 ± 0.05	0.369 ± 0.022	
	hypersthene	0.0838 ± 0.004	0.419 ± 0.023	0.599 ± 0.041	
	augite	0.0924 ± 0.004	0.358 ± 0.019	0.772 ± 0.050	
	apatite*2)	2.43 ± 0.07	12.2 ± 0.4	0.595 ± 0.026	
	zircon	763 ± 13	1810 ± 70	1.26 ± 0.05	
Ikeda	glass	2.51 ± 0.06	10.7 ± 0.7	0.705 ± 0.046	
	plagioclase	0.0706 ± 0.0027	0.387 ± 0.019	0.546 ± 0.034	
	hornblende	0.404 ± 0.014	0.956 ± 0.046	1.26 ± 0.08	
	apatite*2)	13.0 ± 0.3	24.2 ± 1.1	1.61 ± 0.08	
	zircon	226 ± 5	189 ± 7	3.58 ± 0.16	
Torihamma*1)	glass	1.79 ± 0.05	8.94 ± 0.32	0.599 ± 0.027	0.663 ± 0.027
	plagioclase	0.0487 ± 0.0017	0.250 ± 0.012	0.583 ± 0.035	
	hornblende	0.108 ± 0.003	0.447 ± 0.018	0.723 ± 0.035	
	hypersthene	0.140 ± 0.005	1.14 ± 0.07	0.369 ± 0.027	
	apatite*2)	19.7 ± 0.6	19.8 ± 0.8	2.98 ± 0.15	
	zircon	230 ± 2	222 ± 10	3.10 ± 0.14	
U.S.G.S. standard rock*4) AGV-1		1.81 ± 0.15	6.16 ± 0.22		

Quoted errors are standard deviations calculated from the counting statistics.

*1) Values are derived from FUKUOKA and KIGOSHI (1970).

*2) Values are derived from TEZUKA (1972).

*3) $^{234}\text{Th}/^{232}\text{Th}$ activity ratio (cf. KIGOSHI, 1967).

*4) Averages of six analyses. Quoted errors are standard deviations.

equal amount of uranium (or thorium), the use of plagioclase or mafic minerals requires larger amounts of rock samples than does the use of zircon. Consequently, the use of zircon has the merits in the easy separation and in the simple analytical procedure which is allowed by its high uranium and thorium contents.

Io-ages obtained by the glass-zircon pair are reasonable, except for Ata pyroclastic flow. The Io-age for Ito pyroclastic flow agrees with fission track ages obtained for obsidian samples from Arasaki pumice fall deposits within the range of errors. Though Arasaki pumice fall deposits underlie Ito pyroclastic flow deposits, the time gap between both deposits was not figured out by the dating methods (SATO *et al.*, 1972). KIGOSHI *et al.* (1972) reexamined the samples which gave scattered ^{14}C -ages

Table 2. *Approximate separation yields of minerals separated from pyroclastic dacite pumices and lavas*

	Locality						
	Kakuto (pumice)	Ito (pumice)	Ata (pumice)	Ikeda (pumice)	Torihamma (pumice)	Yunotani (lava)	Hotokeiwa (lava)
total weight of separated sample	30 kg	73 kg	38 kg		73 kg	20 kg	>30 kg
plagioclase quartz		4.5 kg	2.8 kg	2.1 kg	17.8 kg		
hypersthene		150 g*	155 g*		95*		
augite			55 g*				
hornblende		550 g	860 g	190 g	51 g*	1.84 kg	147 g
magnetite					340*		24 kg
ilmenite							
zircon	415 mg	113 mg	8 mg	91 mg	1.76 g	2 mg	no yield
apatite	325 mg	110 mg	2.6 g	200 mg	2.24 g	65 mg	

* Weight of fraction having purity of above 95%.

Table 3. *Results of ionium dating for pyroclastic flows in southern Kyushu compared with ^{14}C and fission track ages*

Stratigraphic sequence	Io-age (Y.B.P.)	^{14}C -age or fission track age (Y.B.P.)
Ito	53,000 $\pm$ 8,600	22,000 $\pm$ 850 (GaK-211) ¹⁾
		16,350 $\pm$ 350 (GaK-473) ²⁾
		23,400 $\pm$ 800 (GaK-558) ³⁾
		29,600 $\pm$ 1,800 (GaK-2621) ⁴⁾
		21,500 $\pm$ 700 (GaK-3513) ⁵⁾
		22,000 $\pm$ 700 (GaK-3516) ⁵⁾
		21,200 $\pm$ 700 (GaK-3517) ⁵⁾
		8,760 $\pm$ 250 (TK-59) ⁶⁾
		2,460 $\pm$ 350 (TK-60) ⁶⁾
		38,900 $\pm$ 2,100 (TK-75) ⁷⁾
		26,800 $\pm$ 500 (TK-77) ⁷⁾
		26,000 $\pm$ 695 (N-638) ⁸⁾
		31,000 $\pm$ 9,000 fission track ⁹⁾
		38,000 $\pm$ 6,700 age
		41,000 $\pm$ 10,400
Ata	> 161,000	24,500 $\pm$ 900 (GaK-472) ¹⁰⁾
		23,800 $\pm$ 1,200 (GaK-3366) ¹¹⁾
		37,600 $\pm$ 200 (GaK-4047) ¹²⁾
Kakuto	109,000 $\pm$ 16,000	> 50,000 (701210) ¹³⁾
		> 33,000 (GaK-660) ¹⁴⁾
Torihamma	145,000 $\pm$ 27,000	

1) GOHARA (1965), 2) ARAMAKI (1965), 3) ISSHIKI *et al.* (1965), 4) HOSHINO (1971), 5) KIGOSHI *et al.* (1972), 6) SATO *et al.* (1971), 7) H. KOBAYASHI *et al.* (1971), 8) YOKOYAMA (1971), 9) SATO *et al.* (1972), 10) ARAMAKI and UI (1965), 11) UI (1972), 12) ONO (1973), 13) TANEDA and MIYACHI (1971), 14) ARAMAKI (1969).

reproduced in Table 3 and concluded that the most probable ^{14}C -age for Ito pyroclastic flow was about 22,000 Y.B.P. If it is the case, the Io-age for Ito pyroclastic flow may be slightly older than the ^{14}C -age. The Io-age for Kakuto pyroclastic flow is consistent with ^{14}C -ages. The Io-age for Ata pyroclastic flow, on the other hand, is much older than the ^{14}C -ages (Table 3). This Io-age is also older than Io-ages for Kakuto and Torihama pyroclastic flows which underlie Ata pyroclastic flow deposits. This suggests that the Io-age for Ata does not show actual eruption time. The details of this discordant Io-age are discussed in FUKUOKA and KIGOSHI (1974). Except the Io-age for Ata pyroclastic flow, all other Io-ages are consistent with the stratigraphic sequence.

In conclusion, (1) Io-ages for Ito, Kakuto and Torihama pyroclastic flows are in agreement with ^{14}C and fission track ages and consistent with the stratigraphic sequence. (2) It is suggested that when volcanic glass and zircon are available, this pair is the best for ionium dating among all possible combinations of minerals in acidic volcanic rocks. The large difference observed in this study between U/Th activity ratios in coexisting glass and zircon is extensively discussed elsewhere (FUKUOKA and KIGOSHI, 1974) on the basis of partitioning behaviors of uranium and thorium.

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