Discordant Io-ages and the uranium and thorium distribution between zircon and host rocks*

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(Received April 23, 1974)

Abstract—Io-ages obtained for glass-zircon pairs which were not consistent with expected ages were discussed on the basis of uranium and thorium distribution between zircon and glass. Uranium and thorium distribution between zircon and host rocks from dacites and granites were also discussed.

Discordant Io-ages obtained for glass-zircon pairs with normal $(Th/U)_{\text{zircon}}/(Th/U)_{\text{glass}}$ ratio are explained by early stage crystallization of the zircon in the magma. Discordant Io-ages with abnormal $(Th/U)_{\text{zircon}}/(Th/U)_{\text{glass}}$ ratios suggest that the zircon was captured in the magma as xenocryst. The discrepancy between $(Th/U)_{\text{zircon}}/(Th/U)_{\text{glass}}$ ratios (about 0.19) for dacites and $(Th/U)_{\text{zircon}}/(Th/U)_{\text{whole rock}}$ ratios (about 0.12) for granites could be explained by crystallization of granitic zircon from liquid having chemical composition different from that of the whole rock of granite.

INTRODUCTION

FUKUOKA and KIGOSHI (1970) and FUKUOKA (1974) reported several Io-ages for volcanic rocks. Most of these ages agreed with other age data, such as ^{14}C -ages, fission track ages and/or stratigraphic sequence. The Io-ages for Ata pyroclastic flow in southern Kyushu and Hijiori pyroclastic flow in northern Honshu, Japan, determined for glass-zircon pairs, were two exceptions. The Io-age for Ata was discordant with the ^{14}C -ages and the stratigraphic sequence reported by ARAMAKI (1969) and UI (1971). The Io-age of Hijiori obtained for a glass-zircon pair was older than the Io-age obtained for a glass-plagioclase pair and the ^{14}C -age. The following two possibilities were given by FUKUOKA and KIGOSHI (1970) to explain these discrepancies: (I) The zircon used for the dating was captured in the magma as xenocryst. (II) The zircon

* This study has been undertaken by T.F. in partial fulfillment for the degree of Doctor of Science at Gakushuin University.

was crystallized from the magma at an early stage of magmatic crystallization. They suggested that the estimation of nearly occurred process could be made by the study of trace element distribution between zircon and host rocks.

In this paper, discordant ^{106}Ru -ages are discussed on the basis of uranium and thorium distribution between zircon and glass.

SAMPLES

The granite samples analyzed in this study were following two.

- 1) Takakumayama Granite: Biotite granodiorite collected from Kagoshima Prefecture, Kyushu, Japan.
- 2) Osumi Granite: Hornblende biotite granodiorite collected from Kagoshima Prefecture, Kyushu, Japan.

Geological descriptions for these samples are given in SHIBATA (1967).

ANALYTICAL RESULTS

Mineral separation and analytical procedure of uranium and thorium are similar to those described in FUKUOKA (1974). The analytical results are shown in Table 1. Over-all errors are estimated to be about 8 and 4% for uranium and thorium analyses, respectively (FUKUOKA, 1974).

Table 1. *Uranium and thorium contents of whole rock and zircon from granites in southern Kyushu*

Locality	Phase	U (ppm)	Th (ppm)
Takakumayama	whole rock	7.73 ± 0.18	20.8 ± 0.8
	zircon	1040 ± 40	334 ± 19
Osumi	whole rock	3.44 ± 0.15	10.9 ± 0.6
	zircon	563 ± 22	212 ± 11

Errors are standard deviations calculated from counting statistics.

DISCUSSION

The uranium and thorium inclusion in zircon is generally interpreted by the substitution of U^{4+} ($r = 0.97 \text{ \AA}$) and Th^{4+} ($r = 1.02 \text{ \AA}$) ions for Zr^{4+} ($r = 0.79 \text{ \AA}$) (e.g. GOLDSCHMIDT, 1954).

When the exchange equilibria

and

hold at the growth of zircon crystals, the equilibrium constants K_{Th} and K_U are given as follows:

$$K_{Th} = \frac{(Th/Zr)_s}{(Th/Zr)_l} \quad (2) \quad K_U = \frac{(U/Zr)_s}{(U/Zr)_l} \quad (2')$$

where s and l denote solid and liquid phases, respectively. The partition coefficient of a specified element between two phases is given by the ratio of the concentrations in both phases. For instance, the partition coefficient of uranium D_U is given by $D_U = (U)_s/(U)_l$. Because we have no direct information on the concentration of the specified element in liquid phase in equilibrium with solid phase, this value is supposed to be nearly equal to the concentration in glass (in the case of dacite) or in whole rock (in the case of granite). The partition coefficients of zirconium, uranium and thorium (D_{Zr} , D_U , and D_{Th}) between zircon and glass or whole rock show the relation of D_{Zr} (ca. 2,000 ~ 5,500)* $> D_U$ (ca. 100 ~ 200) $> D_{Th}$ (ca. 15 ~ 30) (see Table 2). This order is in accord with the ionic radii of Zr^{4+} , U^{4+} and Th^{4+} ions. Dividing (2) by (2'), we obtain:

$$\frac{K_{Th}}{K_U} = \frac{(Th/U)_s}{(Th/U)_l} = \frac{D_{Th}}{D_U} \quad (3)$$

Table 2. Partition coefficients of uranium and thorium between zircon and glass or whole rock, and $(Th/U)_{zircon}/(Th/U)_{glass \text{ or whole rock}}$ ratios

Locality	Partition coefficient		$\frac{(Th/U)_{zircon}}{(Th/U)_{glass}}$
	D_U	D_{Th}	
Kakuto *2)			0.194 ± 0.015
Ito *2)	140 ± 9	30.3 ± 2.1	0.217 ± 0.021
Ata *2)	369 ± 17	229 ± 14	0.620 ± 0.047
Ikeda *2)	90.0 ± 2.9	17.7 ± 1.3	0.196 ± 0.015
Dacite Torihama *2)	129 ± 4	24.8 ± 1.4	0.193 ± 0.012
Hijiori *3)			0.180 ± 0.004
Pm-I (Ontake)–① *3), *4)			0.198 ± 0.029
Pm-I (Ontake)–② *3), *4)			0.246 ± 0.007
Pm-I (Ontake)–③ *3), *4)			0.0974 ± 0.0036
Summer Lake *3)			0.172 ± 0.007
Granite Takakumayama	135 ± 6	16.1 ± 1.1	0.119 ± 0.009 *1)
Osumi	164 ± 10	19.4 ± 1.4	0.119 ± 0.011 *1)

All errors are calculated only from counting statistics.

*1) $(Th/U)_{zircon}/(Th/U)_{whole \text{ rock}}$

*2) Calculated from the values given by FUKUOKA (1974).

*3) Calculated from the values given by FUKUOKA and KIGOSHI (1970).

*4) See Fig.1.

* FUKUOKA and SEKI (1973). Calculated from zirconium content of glass coexisting with zircon.

Since the dependences of K_{Th} and K_U on temperature, pressure and also on the major element composition of the system might be similar, the ratio given by Eq. (3) would not depend so strongly on these factors as K_{Th} and K_U .

The $(Th/U)_{zircon}/(Th/U)_{glass}$ ratios (about 0.19) of dacites show good agreement with each other, except those of Ata dacite and zircons ② and ③ in Pm-I from Ontake volcano (Table 2). The $(Th/U)_{zircon}/(Th/U)_{whole\ rock}$ ratios (about 0.12) of granites are lower than the $(Th/U)_{zircon}/(Th/U)_{glass}$ ratios of dacites (Table 2). This may be explained either by crystallization of zircon from thorium-poor magma after crystallization of thorium-rich minerals (such as thorite and monazite) or by removal of uranium-rich fractions from the liquid phase after crystallization of zircon. The latter explanation is consistent with the explanation by NAGASAWA (1970). He suggested that the zircon in Takakumayama granite crystallized from a liquid phase more enriched in heavy rare earth elements than the whole rock granite.

The Io -age of Ata pyroclastic flow obtained directly for glass-zircon pair was much older than the ^{14}C -ages (FUKUOKA, 1974). This Io -age is also older than the Io -ages for Kakuto and Torihama pyroclastic flows which underlie Ata pyroclastic flow. The plotted points of ^{230}Th and ^{238}U of the zircon from Ata pyroclastic flow pumice lie on the isochron of $t = \infty$ (Fig. 1). In the case of Ata pyroclastic dacite, the partition coefficients of uranium and thorium are abnormally high and also the $(Th/U)_{zircon}/(Th/U)_{glass}$ ratio is high compared with those in other dacites (Table 2). This makes it difficult to connect the zircon in this dacite with zircons in other dacites in the genetic history. Since zircon has high melting point ($2,550^\circ C$; POLDERVAART, 1956), the zircon in this dacite would have been brought as xenocryst from wall rocks which

Fig. 1. $^{230}Th/^{232}Th$ v. $^{238}U/^{232}Th$ plot and isochrons
Numbers indicated for zircons of Pm-I correspond to the numbers in Table 2.

might have no genetic relation with the dacite. The $(\text{Th}/\text{U})_{\text{zircon}}/(\text{Th}/\text{U})_{\text{glass}}$ ratio for zircon ② of Pm-I from Ontake volcano is higher than those for zircons from many other dacites (Table 2). The plot of this zircon does not lie on the isochron (Fig.1). This zircon seems to have been also captured in the Pm-I magma as xenocryst. For the dacitic zircon, the value of the $(\text{Th}/\text{U})_{\text{zircon}}/(\text{Th}/\text{U})_{\text{glass}}$ ratio seems to be reliable as a measure to estimate the genetic relation between zircon and dacite.

Though the zircon in Hijiori pyroclastic dacite pumice shows a normal $(\text{Th}/\text{U})_{\text{zircon}}/(\text{Th}/\text{U})_{\text{glass}}$ ratio of about 0.19 (Table 2), the plot of the zircon does not lie on the isochron of Hijiori pyroclastic flow (Fig.1). The glass and this zircon pair presents an Io-age of about 50,000 ~ 60,000y. The time gap between this age and the Io-age obtained for glass-plagioclase pair (8,800y; FUKUOKA and KIGOSHI, 1970) may show the difference between the time of crystallization of the zircon in the Hijiori dacite magma and the time of eruption of Hijiori pyroclastic flow. Because it is considered that the zircons crystallized from magma at an early stage of crystallization of igneous rocks (LARSEN and POLDERVAART, 1957).

CONCLUSION

(1) The glass-zircon pair of Ata pyroclastic dacite and the glass-zircon ② pair of Pm-I from Ontake volcano gave discordant Io-ages and showed abnormal $(\text{Th}/\text{U})_{\text{zircon}}/(\text{Th}/\text{U})_{\text{glass}}$ ratios. This seems to suggest that these zircons were captured in the magma as xenocrysts. (2) The glass-zircon pair of Hijiori pyroclastic flow gave a discordant Io-age and showed a normal $(\text{Th}/\text{U})_{\text{zircon}}/(\text{Th}/\text{U})_{\text{glass}}$ ratio (about 0.19). This seems to suggest the early stage crystallization of the zircon in the magma.

ACKNOWLEDGMENTS

The authors are much grateful to Prof. H. NAGASAWA of Gakushuin University for his useful suggestions; to Prof. S. ARAMAKI of the Earthquake Research Institute, University of Tokyo and Dr. T. UI of Yamagata University for sample collections and their useful geological suggestions; to Dr. A. TEZUKA and Mr. M. MORIOKA of Gakushuin University for aid in neutron activation analysis. This work was supported in part by grants from Matsunaga Science Foundation.

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