Chemical compositions and K-Ar ages of Pliocene volcanic rocks along Aimagawa river, western Gunma, central Japan

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(Received July 19, 1989; Accepted November 29, 1989)

From the area along the Aimagawa river in western Gunma, central Japan, 12 samples were collected for the determination of K-Ar ages and chemical compositions. X-ray fluorescence and instrumental neutron activation analysis methods were applied to determine major and trace elements, respectively.

Based on the K-Ar ages, the rock samples were divided into two groups having 4.5Ma and 2.0Ma. Although transformation of magnetite to maghemite, possibly due to high temperature oxidation, was observed among the samples, there is no apparent inconsistency between stratigraphic relation and the K-Ar ages, suggesting that such oxidation gave no effect on the K-Ar ages.

No large variation is observed in chemical compositions for both major and trace elements. Among the trace elements, lithophile elements such as rare earth elements and Zn show small variations in their abundances. The samples with K-Ar ages of 4.5Ma yield La/Yb ratios larger than 2.5 as chondrite-normalized values, while the remaining samples (*ca.* 2.0Ma) give values smaller than 2.0, suggesting a difference in the degree of partial melting between the two stages of magmatism. In contrast to the lithophiles, Cr, Ni, and Co show relatively large variations. Chromium shows a positive correlation with ³⁶Ar. Non-radiogenic Ar must have been trapped in some Cr-bearing mineral(s) (chromite and/or clinopyroxene?).

INTRODUCTION

A large amount of volcanic rocks of late Tertiary to early Quaternary ages prevails in the western region of Gunma Prefecture. Though geological studies including stratigraphy have been performed by many investigators (Akima Collab., 1975, 1976; Motojuku Collab., 1970), chronological studies have been done only in limited areas (Ozima *et al.*, 1968; Kaneoka *et al.*, 1979). Recently a large number of K-Ar age data are being accumulated for the volcanic rocks in this region, making it possible to discuss the sequence of volcanic activity chronologically (Nomura and Kosaka, 1987; Nomura and Ebihara, 1988).

In the Japanese Islands, it is not rare for Quaternary and especially Tertiary volcanic rocks that their K-Ar data are not consistent with the stratigraphical relation, because of some disturbances in the K-Ar system. Hydrothermal alteration producing 'green tuff' in Miocene is one of the main factors which caused such a disturbance in Tertiary volcanic rocks. However, some other mechanisms such as mass fractionation of Ar and excess ⁴⁰Ar have also been asserted for possible factors (e.g. Kaneoka, 1980; Itaya and Nagao, 1988). Ebihara *et al.* (1984) reported chemical compositions and K-Ar ages of Tertiary volcanic rocks of northeast Japan and discussed their geochemical features in comparison with those of Quaternary volcanic

rocks. It is, however, very limited for Tertiary rock samples that K-Ar dating and chemical analysis including trace elements were carried out simultaneously for the same samples. Hence, it is needed that reliable data of both chemical compositions and K-Ar ages are accumulated for the same rocks to discuss the geochemical characteristics of the Tertiary volcanism in the Japanese Islands.

In this study, in order to examine the systematics among chemical compositions, K-Ar ages and stratigraphy in volcanic rocks of late Neogene, we selected the area along the Aimagawa river (Aimagawa Formation) in western Gunma, where stratigraphy had already been studied in detail (Akima Collab., 1975). Rock samples were collected systematically, of which K-Ar ages and chemical compositions were determined. In the determination of major and trace elements, X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) methods were used, respectively. We compare K-Ar ages with stratigraphy and consider whether and how the K-Ar system has been disturbed in this area. Setting the absolute time scale to the Aimagawa Formation, we describe the change in chemical compositions of the rocks with time.

SAMPLES

In the north boundary of the Kanto mountainland, volcanic rocks of Neogene age are widely distributed. Twelve rock samples in total were collected from individual members of the Aimagawa Formation, which is distributed in the area along the Aimagawa river, western Gunma (Fig. 1). The Aimagawa Formation is divided into four members: Yakehoda in the lowest, Odaira, Tsunoochi, and Omine in the uppermost (Akima Collab., 1975), and lie over the Itahana Formation. The lower part of the Itahana Formation includes fossils of marine species of Miocene age, while the upper part consists of continental sediments, indicating that the sea level changed during the Itahana Formation. The studied area and sampling localities are illustrated in Fig. 1. Sample numbers and rock types are summarized in Table 1. All the rock samples are two-pyroxene andesite lavas except for one two-pyroxene andesite dyke (Am 2). Stratigraphic relations of samples used in this study are shown in Fig. 2.

The samples Am 1 and Am 2 were taken from the Yakehoda and Odaira Members, respectively. Am 2 was collected at the highest elevation along the Aimagawa river. The Odaira

Table 1. Sampling sites and rock types of samples studied in this work

Sample name	Member*	Sampling site	Rock type**
Am 1	Yakehoda	36°25'09"N 138°43'22"E	
Am 2	Odaira	36°25'02"N 138°42'27"E	
Am 3	u-Tsunoochi	36°24'44"N 138°45'31"E	cont. c-g. px. phenocryst
Am 4	l-Tsunoochi	36°25'17"N 138°44'00"E	cont. pl. phenocryst
Am 5	l-Tsunoochi	36°25'25"N 138°43'53"E	} glassy andesite
Am 6	l-Tsunoochi	36°25'19"N 138°43'35"E	
Am 7	u-Tsunoochi	36°25'29"N 138°43'51"E	} cont. c-g. px. phenocryst
Am 8	u-Tsunoochi	36°25'22"N 138°44'04"E	
Am 9	Omine	36°25'23"N 138°44'07"E	} cont. pl. phenocryst f-g. andesite
Am 10	Omine	36°25'31"N 138°44'07"E	
Am 11	Omine	36°25'23"N 138°44'10"E	
Am 12	Omine	36°24'56"N 138°44'43"E	
Am 13***	Omine	36°24'53"N 138°45'37"E	

*u-: upper, l-: lower.

**two-pyroxene andesite lava except for Am 2 (two-pyroxene andesite dyke).

cont.: containing, c-g.: coarse-grained, px: pyroxene, pl: plagioclase, f-g.: fine-grained.

***Only K-Ar age was determined for Am 13 (Nomura and Ebihara, 1988).

Fig. 1. The studied area and sampling locality of rock samples.

Member contains gravels of diorite at the lowest layer and overlies unconformably the Yakehoda Member. Am 2 was taken from a dyke of two-pyroxene andesite called 'Jujo-gantai', which is intruding into the Yakehoda Member.

The Tsunoochi Member is divided stratigraphically into two parts; the upper and the lower Tsunoochi Members. Am 7 and Am 8 are from the upper lava and Am 3 is from the lower lava in the upper Tsunoochi Member. These three samples contain coarse-grained pyroxene phenocrysts. Am 5 and Am 6 are from the upper lava of glassy andesite in the lower Tsunoochi Member. Am 4 is from the lower

lava, which contains plagioclase phenocrysts in contrast with Am 5 and Am 6.

Am 9, Am 10 and Am 12 were taken from the same lava flow of fine-grained andesites called "Beniizawawa-lava" in the Omine Member. (Am 13 also was sampled from the same lava flow at about 5 km east of the sampling site of Am 12, Nomura and Ebihara, 1988). Am 11 is from a lava overlying a tuff breccia above the Beniizawawa lava. These four rock samples from the Omine Member contain a small amount of plagioclase phenocrysts.

age (Ma)	Formation	Member	K-Ar age (Ma)
-1	Kennomine		
-2	Aimagawa	Omine	Am 11:2.1(1) Am 10:2.1(1), Am 9:2.1(1), Am 12:2.0(1)
		Tsunoochi (upper)	Am 7:2.5(7), Am 8:2.4(3)
		(lower)	Am 3:1.8(3)
-3		Odaïra	Am 5:2.0(1), Am 6:1.9(1)
			Am 4:2.2(2)
-4			
			Am 2:4.5(7)
-5		Yakehoda	Am 1:4.5(7)

Fig. 2. Comparison of stratigraphic relation with K-Ar ages. Values in parentheses indicate estimated errors (1σ) and correspond to the last figures of K-Ar ages.

EXPERIMENTAL

K-Ar dating

K-Ar dating for six samples (Am 6, Am 8, Am 9, Am 10, Am 11 and Am 12) was carried out at Okayama University of Science (hereafter OUS). K-Ar ages for the remaining samples were measured commercially at the Central Research Institute, Mitsubishi Metal Corporation (hereafter MMC). Experimental procedures at OUS, which are essentially the same as those at MMC, are described briefly here.

About 10 g of each rock sample was crushed in a hardened steel mortar and sieved to $-60+80$ mesh (about $300\mu\text{m}$ in diameter). Adhering fine particles were removed by rinsing in acetone. 0.5 to 1 g of sieved sample was weighed, wrapped in Al foil and introduced into an extraction line. The amount of radiogenic ^{40}Ar was determined by means of the isotope dilution method using ^{38}Ar as a spike. Mass discrimination of Ar isotopes was corrected by measuring air Ar. For the decay constant of ^{40}K and isotopic ratio of K, those recommended by Steiger and Jäger (1977) were used. Analytical and calculation methods of K-Ar ages have been

described in Nagao *et al.* (1984) and Nagao and Itaya (1988).

For the determination of K content, about 1 g of the identical sample that was used for Ar measurement was ground in an agate mortar to the grain size finer than $50\mu\text{m}$. About 100 mg of this powdered sample was dissolved in hydrofluoric acid and nitric acid using a teflon bomb. Potassium content was determined by the flame photometry. Analytical procedures including dissolution of samples were repeated twice. Replicate analyses were reproducible within 2%.

X-ray fluorescence (XRF) analysis

A portion of the sample next to that used for K-Ar dating was taken for the determination of chemical composition by XRF and INAA. 5–10 g of each sample was ground in an agate mortar to the grain size finer than about $80\mu\text{m}$. About 400 mg of this sample was weighed, mixed with lithium borate of the amount of exactly 10 times greater than the sample weight as a flux, and fused in an electric oven to make a glass bead for XRF analysis. Analysis was carried out at the Earthquake Research Institute, University of

Tokyo, using Rigaku Geiger Flex system 3080 E3. Standard samples, JG-1, JB-1, JA-1, JB-2, JB-3, JGb-1, JR-1 and JR-2, prepared and supplied by the Geological Survey of Japan (GSJ) (Ando *et al.*, 1987), were used for the determination of major elements.

Instrumental neutron activation analysis (INAA)

For INAA, about 50–100 mg of the sample prepared for chemical analysis was heat-sealed doubly into clean plastic bags (1 cm × 1 cm). For rare earth elements (REEs) and U, standard samples were prepared by taking known amounts of standard solutions (prepared by dissolving appropriate reagents) onto filter papers of the same size as rock samples, dried and heat-sealed doubly in plastic bags. For the remaining elements, standard rock samples, JB-1 of GSJ (Ando *et al.*, 1987) and W-1 of the US Geological Survey (Flanagan, 1973), were used as reference standards.

Rock samples along with standards were put into a capsule and irradiated for 12 h at a thermal neutron flux of $1.5 \times 10^{12} \text{ cm}^2 \text{ sec}^{-1}$ in the TRIGA II reactor of the Institute of Atomic Energy, Rikkyo University. Samples were analyzed non-destructively. Measurements were repeated several times at Tokyo Metropolitan University after appropriate cooling intervals using planar- and coaxial-type pure Ge detectors hooked up with a computer-assisting multi-channel analyzer (Seiko EG & G).

RESULTS AND DISCUSSION

Reliability of analytical data

Analytical results of K-Ar dating, XRF and INAA are summarized in Table 2. Two pairs of samples (Am 7 and 8, and Am 5 and 6) were collected from the same lavas belonging to the upper and the lower Tsunoochi Members, respectively, and one sample was measured at OUS and the other at MMC for each pair. No significant difference in K-Ar ages is observed between the determinations of the two laboratories. This suggests that K-Ar ages obtained at OUS and

MMC are reliable.

In data of INAA, analytical errors due to counting statistics are given. Potassium contents of the samples used for K-Ar dating do not always agree with those determined by XRF, because the samples used for dating were prepared by sieving, hence can not represent the bulk. In volcanic rocks, iron is in divalent state in part and in trivalent state in other part. XRF, as well as INAA, can yield only a value of the total iron. For XRF, elemental abundances are usually presented in the form of oxides in divalent state (Table 2). Since the water content can not be determined by XRF analysis, the total abundances of the remaining elements analyzed are normalized to 100%.

Fe and Na were determined by both XRF and INAA. In Table 3, data for these elements by XRF and INAA are compared with each other. In this table, elemental abundances are expressed in the form of elements. No large discrepancy between the two analytical methods is seen for both elements, although Na data by INAA seem to be slightly high, suggesting some small systematic errors to be involved either in XRF or INAA for this element. Table 3 clearly shows that analytical errors due to neglecting the water content and the difference in valency of Fe are not significant.

K-Ar ages of the Aimagawa Formation and their consistency with stratigraphy

In Fig. 2 compared is a stratigraphic relation with K-Ar ages for the samples studied in this work. No large inconsistency is observed between them. In this section, described is chronology of the Aimagawa Formation based on K-Ar ages in the descending order of stratigraphy.

Omine Member: Among samples from the Omine Member, Am 10, Am 9 and Am 12 were collected from the same lava flow. This lava is thought to have flowed from Mt. Omine volcano, the crater of which was located roughly 1 km north-northwest of the sampling site of Am 10. It was observed under a microscope that about 30–50% of magnetite in Am 10 was

Table 2. Analytical results of K-Ar dating, XRF and INAA for Aimagawa samples

	Am 11	Am 10	Am 9	Am 12	Am 7	Am 8
K-Ar dating ^a	(OUS)	(OUS)	(OUS)	(OUS)	(MMC)	(OUS)
age(Ma) ^b	2.1(0.1)	2.1(0.1)	2.1(0.1)	2.0(0.1)	2.5(0.7)	2.4(0.3)
K(%)	0.63	0.83	0.89	0.66	0.59	0.47
rad. ⁴⁰ Ar(10 ⁻⁸ cc STP/g) ^c	5.0	6.6	7.2	5.2	5.6	4.3
atm. ⁴⁰ Ar(%) ^d	60	61	67	57	84	86
³⁶ Ar(10 ⁻¹⁰ cc STP/g)	2.59	3.47	4.83	2.32	9.73	8.98
total Ar(10 ⁻⁸ cc STP/g)	13	17	22	12	35	31
XRF ^e						
SiO ₂	60.4	63.7	64.5	59.9	56.8	56.8
Al ₂ O ₃	18.7	17.4	17.3	18.6	17.5	17.5
CaO	7.21	5.92	5.52	7.43	8.20	8.12
FeO	5.84	5.21	4.83	5.99	8.16	8.25
MgO	1.96	1.39	1.34	2.13	4.25	4.34
Na ₂ O	3.95	4.22	4.30	3.94	3.15	3.16
K ₂ O	0.83	1.02	1.07	0.85	0.68	0.67
TiO ₂	0.86	0.83	0.82	0.86	0.91	0.91
MnO	0.10	0.088	0.079	0.12	0.15	0.13
P ₂ O ₅	0.18	0.20	0.21	0.18	0.17	0.17
INAA ^f						
Fe(%) (0.17–0.35)	4.50	3.89	3.73	4.50	6.34	6.41
Na(%) (0.36–0.45)	3.05	3.36	3.46	2.99	2.34	2.34
Rb(3.3–13)	15.3	18.1	20.9	14.9	13.2	13.8
Cs(4.1–13)	0.33	0.62	0.68	0.21	0.30	0.25
Sr(2.8–6.2)	344	315	312	347	366	351
Ba(1.2–5.2)	260	311	307	249	204	207
Sc(0.11–0.16)	19.2	17.7	17.8	19.0	25.4	25.2
Hf(1.3–3.9)	2.39	2.86	2.99	2.26	1.89	1.91
Ta(6.2–27)	0.18	0.22	0.21	0.17	0.17	0.18
Cr(0.41–2.6)	17.0	21.0	26.0	10.0	58.3	48.4
Ni(5.1–27)	11.8	12.8	17.2	10.5	45.7	35.6
Co(0.35–0.97)	14.6	11.4	11.4	15.0	27.2	26.4
Zn(1.3–2.5)	67.8	65.3	67.9	66.0	78.1	77.7
La(1.3–2.2)	10.9	8.32	8.47	6.33	5.67	5.61
Ce(0.75–2.4)	16.9	19.5	20.7	16.2	14.3	13.6
Nd(1.9–5.1)	12.8	14.9	16.6	12.1	10.7	10.5
Sm(0.74–0.81)	3.78	4.21	4.43	3.38	2.94	2.93
Eu(2.5–4.2)	1.15	1.21	1.28	1.08	0.96	0.97
Tb(2.7–9.7)	0.70	0.77	0.79	0.62	0.56	0.53
Yb(0.90–3.2)	2.64	3.18	3.41	2.44	2.00	1.90
Lu(2.9–7.7)	0.46	0.56	0.59	0.44	0.38	0.28
Th(1.1–5.4)	1.02	1.25	1.35	0.96	0.73	0.76
U(5.0–37)	ND ^h	ND	0.42	ND	0.19	0.27

a: name of institute where K-Ar dating was carried out is shown in parentheses; OUS=Okayama University of Science, MMC=Mitsubishi Metal Corporation.

b: Values in parentheses indicate estimated errors (1 σ).

c: radiogenic ⁴⁰Ar.

d: atmospheric ⁴⁰Ar (relative to total Ar).

e: in %.

f: in ppm, otherwise indicated. Values in parentheses are ranges of error (%) due to counting statistics.

g: doubtful.

h: not determined (below detection limit).

Table 2. (continued)

	Am 3	Am 5	Am 6	Am 4	Am 2	Am 1
K-Ar dating ^a	(MMC)	(MMC)	(OUS)	(MMC)	(MMC)	(MMC)
age(Ma) ^b	1.8(0.3)	2.0(0.1)	1.9(0.1)	2.2(0.2)	4.5(0.5)	4.5(0.7)
K(%)	0.74	0.74	0.67	0.62	0.74	0.66
rad. ⁴⁰ Ar(10 ⁻⁸ cc STP/g) ^c	5.1	5.7	5.0	5.2	12.8	11.4
atm. ⁴⁰ Ar(%) ^d	75	67	64	72	83	86
³⁶ Ar(10 ⁻¹⁰ cc STP/g)	5.17	3.97	3.01	4.65	20.4	24.1
total Ar(10 ⁻⁸ cc STP/g)	20	17	14	19	75	81
XRF ^e						
SiO ₂	58.4	56.7	62.2	59.8	62.7	58.3
Al ₂ O ₃	17.7	19.6	19.3	19.1	16.5	16.9
CaO	7.41	8.49	6.88	7.36	6.52	7.93
FeO	7.41	7.45	4.54	5.93	5.62	7.33
MgO	3.47	2.36	0.88	2.24	3.34	4.55
Na ₂ O	3.66	3.38	4.14	3.79	3.56	3.18
K ₂ O	0.74	0.74	0.94	0.66	0.82	0.75
TiO ₂	0.93	1.02	0.85	0.89	0.61	0.83
MnO	0.13	0.12	0.084	0.10	0.11	0.13
P ₂ O ₅	0.20	0.18	0.18	0.16	0.15	0.16
INAA ^f						
Fe(%)	5.76	5.79	3.53	4.61	4.50	5.96
Na(%)	2.72	2.51	3.07	2.81	2.84	2.54
Rb	14.3	14.9	16.5	11.1	18.1	20.0
Cs	0.27	0.31	0.51	0.26	0.64	0.45
Sr	348	408	331	343	336	331
Ba	233	216	331	208	266	265
Sc	22.3	25.2	17.3	18.8	17.3	25.7
Hf	2.41	2.03	2.87	2.45	2.51	2.16
Ta	0.20	0.22	0.24	0.28	0.32	0.23
Cr	30.0	27.8	16.9	16.0	69.0	95.4
Ni	27.5	18.6	11.9	11.1	31.8	35.9
Co	23.6	19.4	10.3	16.3	18.4	27.2
Zn	79.3	80.4	67.6	75.9	68.8	82.9
La	6.73	7.24	9.45	6.39	8.04	7.34
Ce	17.8	16.1	20.0	15.8	19.9	17.9
Nd	13.5	(62.7) ^g	16.8	12.6	12.0	11.8
Sm	3.60	3.40	4.58	3.60	2.84	2.94
Eu	1.17	1.07	1.29	1.16	0.93	0.95
Tb	0.74	0.62	0.92	0.70	0.51	0.50
Yb	2.58	2.00	3.01	2.56	1.97	1.97
Lu	0.46	0.34	0.59	0.47	0.36	0.37
Th	0.94	1.05	1.22	0.81	1.47	1.38
U	0.26	ND	0.25	0.27	0.45	0.45

transformed to maghemite. Am 13 from the same lava flow was sampled at a farther site from the crater and has little oxidation with less than 5% of magnetite transformed to maghemite. Degree of oxidation thus seems to decrease from Am 10 to Am 13 through Am 12 with increase of the distance from the crater, suggesting a high temperature oxidation by terrestrial heat due to

volcanic activity of Mt. Omine.

K-Ar ages of Am 10, Am 9 and Am 12 agree well with each other within their error ranges (2.1 ± 0.1 Ma) and a K-Ar age of Am 13 (2.0 ± 0.1 Ma, Nomura and Ebihara, 1988) also falls in this range, indicating the eruption age of the Beniiwazawa-lava to be about 2.0Ma. Such an agreement also suggests that high temperature

Table 3. Comparison of Fe and Na data between XRF and INAA

Sample name	XRF(%)		INAA(%)		XRF/INAA	
	Fe	Na	Fe	Na	Fe	Na
Am 11	4.54	2.93	4.50	3.05	1.01	0.96
Am 10	4.05	3.13	3.89	3.36	1.04	0.93
Am 9	3.75	3.19	3.73	3.46	1.01	0.92
Am 12	4.65	2.92	4.50	2.99	1.03	0.98
Am 7	6.34	2.34	6.50	2.54	0.98	0.92
Am 8	6.41	2.34	6.42	2.54	1.00	0.92
Am 3	5.76	2.72	5.90	2.97	0.98	0.92
Am 5	5.79	2.51	5.92	2.70	0.98	0.93
Am 6	3.53	3.07	3.60	3.34	0.98	0.92
Am 4	4.61	2.81	4.81	3.03	0.96	0.93
Am 2	4.37	2.64	4.50	2.84	0.97	0.93
Am 1	5.70	2.36	5.96	2.54	0.96	0.93

oxidation caused no effect on the K-Ar ages. Am 11, sampled from the lava overlying the Beniiwazawa lava, has a K-Ar age of 2.0 ± 0.1 Ma, indicating that these two lavas erupted with a short interval.

Tsunoochi Member: Although a K-Ar age of Am 3 (1.8 ± 0.3 Ma) from the lower lava in the upper Tsunoochi Member is apparently younger than those of Am 7 (2.5 ± 0.7 Ma) and Am 8 (2.4 ± 0.3 Ma) from the upper lava, it can not be concluded that there is a real discrepancy in K-Ar ages among these samples, considering the fairly large errors involved.

K-Ar ages of samples from the lower Tsunoochi Member (Am 5: 2.0 ± 0.1 Ma, Am 6: 1.9 ± 0.1 Ma, and Am 4: 2.2 ± 0.2 Ma) seem to be slightly younger than those from the upper Member. A mean value of K-Ar ages for the former (2.0 ± 0.1 Ma), however, is essentially the same as that for the latter (2.2 ± 0.3 Ma). These mean values are also indistinguishable from that for samples taken from the Omine Member (2.1 ± 0.1 Ma).

Odaira and Yakehoda Members: Although no age data are available so far for the boundary between the Aimagawa and the preceding Itahana Formations, it has been inferred on the basis of stratigraphy and some other geological data that the deposition of Aimagawa Formation started about 5 Ma ago (Nomura and Ebihara, 1988). Am 2 and Am 1 collected from the Odaira and

the Yakehoda Members, respectively, yield essentially the same K-Ar ages of 4.5 Ma. Hence, although these two members are in the relation of unconformity (Akima Collab., 1975), the time gap between them seems to be not so large.

Variation in chemical composition of lava

As stated in the previous section, both Am 1 and Am 2 from the Odaira and the Yakehoda Members have K-Ar ages of 4.5 Ma significantly older than the samples from the Tsunoochi and the Omine Members which have nearly the same K-Ar ages of 2 Ma. Including Am 1 and Am 2, however, there is no large variation in chemical compositions for both major and trace elements except for a few cases (cf. Table 2). Among major elements, only Mg shows a large variation with a maximum to minimum abundance ratio of 5.2. Following is Fe, which shows a maximum to minimum ratio of 1.8, yielding a variation of FeO/MgO ratio ranging from 3.8 to 1.6 (Table 4). On the contrary, such ratios as Na₂O/CaO and (CaO+Na₂O+K₂O)/Al₂O₃ remain nearly constant. Among trace elements, Cr, Ni, Cs, Co, and Lu show variations exceeding 2 as a maximum to minimum ratio. Among them, Cr shows the largest variation of 9.6.

Yakehoda and Odaira Members: Both Am 1 and Am 2 have characteristic features in chemical compositions as follows; (i) FeO/MgO ratio ranges from 1.7 to 1.6, being characteris-

Table 4. Elemental ratios in samples from Aimagawa Formation

	Am 11	Am 10	Am 9	Am 12	Am 7	Am 8	Am 3	Am 5	Am 6	Am 4	Am 2	Am 1
(La/Yb) _c [*]	(2.8)**	1.8	1.7	1.8	1.9	2.0	1.8	2.5	2.1	1.7	2.7	2.5
FeO/MgO	3.0	3.8	3.6	2.8	1.9	1.9	2.1	3.2	5.2	2.7	1.7	1.6
Na ₂ O/CaO	0.54	0.71	0.78	0.53	0.38	0.40	0.49	0.40	0.60	0.51	0.55	0.40
(CaO+Na ₂ O+K ₂ O)	12.0	11.2	10.9	12.2	12.0	12.0	11.8	12.6	12.0	11.8	10.9	11.9
S***/Al ₂ O ₃	0.64	0.64	0.59	0.66	0.69	0.68	0.67	0.64	0.62	0.62	0.66	0.70

*chondrite-normalized values.

**doubtful.

***S=CaO+Na₂O+K₂O.

tically small compared with that of the remaining samples, (ii) REEs are more fractionated, and (iii) non-radiogenic Ar and Cr are highly enriched. The last two features will be discussed in detail in the later section.

Tsunoochi Member: Among rock samples from the lower Tsunoochi Member, Am 4 is quite different from Am 5 and Am 6 in mineralogy. Such a difference, however, seems to be reflected neither in chemical compositions nor in norm values. REE abundance patterns are rather exceptional. Am 4 shows a smaller fractionation between light and heavy REEs than that of Am 5 and Am 6 (Table 4). Am 5 and Am 6 were sampled from the same lava flow but their chemical compositions are not the same. Am 6 is depleted in Fe, Mg, Sc and Co, and enriched in Ba and REE, while Am 5 is depleted in Si and enriched in Ca and Sr. Both samples are commonly enriched in Al. FeO/MgO ratio varies among the three samples. Am 6 yields a high ratio of 5.2, possibly due to an exceptionally low value of 0.88% for MgO. The remaining two samples give consistent values around 3 (2.7 and 3.2), which are clearly distinct from those of Am 1, Am 2 and the samples from the upper Tsunoochi Member.

Among the samples from the upper Tsunoochi Member, Am 3 was sampled from the lava overlain by the lava for Am 7 and Am 8. For major elements, consistency is $\pm 10\%$, except for Mg. Am 3 is relatively enriched in lithophile elements such as REEs, Ba and Hf. Am 7 and Am 8 sampled from the same lava flow show an excellent agreement in chemical com-

positions, which is contrast to the disagreement between Am 5 and Am 6 taken from the same lava flow in the lower Tsunoochi Member. FeO/MgO ratios vary from 1.9 to 2.1, which is smaller than those of the samples from the lower Tsunoochi Member.

Omine Member: The chemical composition of Am 12 is quite different from those of Am 9 and Am 10, though these samples were collected from the same lava flow. Such a disagreement may imply the heterogeneity of a lava flow in chemical composition. Am 11, though being sampled from a different unit of lava flow, shows a good agreement with Am 12 in chemical composition. Only Cr and Cs show a scatter exceeding the analytical uncertainty. Thus, it is suggested that both samples (or two lavas from which both samples were collected) were derived from the same magma or magmas of similar chemical compositions. In this case, it is supposed that Am 9 and Am 10 were erupted earlier than Am 12 and that the chemical composition of lava (or magma) changed after the eruption of Am 9 and Am 10. FeO/MgO ratios in the samples from the Omine Member vary from 2.8 to 3.8, being larger than those for other samples (Table 5). There seems to be an apparent difference in FeO/MgO ratio between Am 9, 10 (3.6–3.8) and Am 11, 12 (2.8–3.0), suggesting a discontinuity in the degree of magmatic differentiation between these two groups.

Some features in chemical composition of lava REEs: Among trace elements, lithophile elements such as REEs and Zn show small varia-

Fig. 3. Chondrite-normalized REE abundance patterns for the samples analyzed in this study. For samples Am 3 to Am 12, only the range of variation in abundance patterns is shown, because the patterns are roughly parallel to each other.

tions of their abundances among the samples. In Fig. 3, chondrite-normalized REE abundance patterns are shown for the samples analyzed in this work. The REE abundances in unfractionated chondrites (Anders and Ebihara, 1982) were used for normalization. For the samples except for Am 1 and Am 2, only the range of variation in abundance patterns is shown, because the patterns are roughly parallel to each other. Taking the chondrite-normalized values, Am 1 and Am 2 yield La/Yb ratios larger than 2.5, while the remaining samples give values smaller than 2.0. Such a difference observed in the REE abundance patterns might have resulted from the difference in degree of partial melting of source material. Aside from Am 1 and Am 2, other samples also show a small variation in the relative abundances of REEs: La/Yb ratios decrease from the lower Tsunoochi, through the upper Tsunoochi, to the Omine Members, suggesting that degree of partial melting or fractional crystallization of magma gradually changed from early to late stage of eruption.

Chromium: In contrast to the lithophile elements, Cr, Ni and Co show relatively large variations in their abundances among the samples. Correlation coefficients (r) among these samples are 0.84 for Ni-Cr, 0.88 for Ni-Co and 0.72 for Co-Cr. It is interesting to note that there is a strong positive correlation between Cr and ^{36}Ar ($r=0.92$), as shown in Fig. 4. This figure also shows that each stratigraphic member has quite distinct Cr and Ar contents: both contents increase in the order of the Omine and the lower Tsunoochi Members, the upper Tsunoochi Members and the Odaira and the Yakehoda Members. An excellent correlation ($r=0.96$) is observed for the samples from the Tsunoochi and the Omine Members of which K-Ar ages are about 2Ma.

One possible explanation of the correlation between Cr and ^{36}Ar is that Cr-bearing mineral(s) is the host phase for non-radiogenic Ar in lava. Chromium is thought to be present in trivalent state (Cr^{+3}) in a magma, and taken into solid phase(s) from the liquid magma during frac-

Fig. 4. Relationship between Cr and ^{36}Ar . There is a strong positive correlation between these two variables ($r=0.92$). An excellent correlation ($r=0.96$) is observed among the samples from the Tsunoochi and Omne Members, of which K-Ar ages are about 2Ma.

tional crystallization, presumably making a solid solution in magnetite and/or clinopyroxene. The nearly constant ratios of Cr to non-radiogenic Ar for all the samples except Am 1 and Am 2 suggest that non-radiogenic Ar was taken into Cr-bearing mineral(s) under the constant physico-chemical conditions. To verify this possibility, it is required to measure the concentration of non-radiogenic Ar in Cr-rich separates.

Acknowledgments—We are grateful to S. Aramaki, Earthquake Research Institute, University of Tokyo for the XRF analysis. Following persons are thanked for their experimental assistances; T. Miura (INAA), T. Okada (K-Ar dating) and T. Kitazume (sample preparation). We are also indebted to the reactor com-

mittee of the University of Tokyo for the use of the reactor facilities of Rikkyo University. Constructive reviewing by I. Kaneoka and an anonymous reviewer are highly acknowledged. This research was supported in part by Grant-in-Aid for Scientific Research (No. 61420014), defrayed by the Ministry of Education, Science and Culture, Japan.

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