Lateral variation of K/Hf ratios in Quaternary volcanic rocks of Northeastern Japan

YOSHIYUKI TATSUMI^{1*} and SHUN NAKANO²

Department of Geology, The University of Manchester, Manchester M13 9PL, England, UK¹,
and Geological Survey of Japan, Yatabe, Ibaraki 305, Japan²

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K/Hf ratios of rocks from 39 Quaternary volcanoes in NE Japan have been examined. In most volcanoes, the ratio remains constant throughout the process of magmatic differentiation, suggesting that the ratios in volcanic rocks represent those in primary magmas produced in the upper mantle. The observed lateral variation of the ratios, increasing toward the back-arc side could be influenced by two factors. The first possibility could be the result of systematic differences in the degree of partial melting, decreasing toward the back-arc side, during which process minor minerals such as zircon, sphene, perovskite, and rutile buffer the concentration of Hf in the liquid produced; the second possibility is the result of differences in K/Hf ratios of fluid phases added to the mantle wedge from the downgoing lithosphere in which serpentine and phlogopite decompose beneath fore- and back-arc regions, respectively.

INTRODUCTION

The east volcanic zone of Japanese islands consists of about 140 discrete Quaternary volcanoes. The lateral variations of chemical compositions in these volcanic rocks have been pointed out by several authors (SUGIMURA, 1960; KUNO, 1966; MASUDA *et al.*, 1975; SAKUYAMA, 1979; MASUDA and AOKI, 1979; ISHIKAWA *et al.*, 1980), and it is widely accepted that contents of incompatible elements and H₂O increase toward the back-arc side within the volcanic zone. This relationship is believed to indicate a systematic difference in the degree of partial melting of source mantle materials, which is consistent with experimental results on deduced primary basalt magma compositions for NE Japanese islands (TATSUMI *et al.*, 1983). On the other hand, the concomitant lateral variation of rare-earth element patterns (FUJITANI and MASUDA, 1981) and isotope ratios (NOHDA and WASSERBURG, 1981; NOTSU, 1983), which may suggest that differences in the chemical composi-

tions of mantle wedge materials have to be taken into account.

Recent geochemical studies have indicated that arc volcanic rocks have significantly higher values for large-ion-lithophile element (LILE)/high-field-strength element (HFSE) ratios (WOOD *et al.*, 1979; PERFIT *et al.*, 1980; ARCULUS and JOHNSON, 1981; TATSUMI and ISHIZAKA, 1982). Both LILE and HFSE would be concentrated mainly into the liquid through the process of magmatic differentiation. The LILE/HFSE ratio in a primary magma tends to remain constant until LILE- or HFSE-rich phases are separated from the magma; the ratios in volcanic rocks could therefore give a better understanding of the chemical characteristics of source mantle materials.

In this study, data on K and Hf contents (K and Hf are typical LILE and HFSE, respectively) of NE Japanese volcanic rocks have been examined, and the origin of lateral variation of K/Hf ratios is discussed.

* Present address: Department of Geology and Mineralogy, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606, Japan.

Table 1. SiO_2 , K and Hf contents of samples

Volcano	SiO_2	K ($\times 10^3$)	Hf	K/Hf ($\times 10^3$)	Ref.
Shiretoko-Iwo	60.69	13.0	4.5	2.9	1
Rausu	61.76	11.5	4.1	2.8	1
Atosanupuri	64.26	6.89	3.6	1.9	1
Mashu	65.73	6.23	3.0	2.1	1
	72.96	8.88	3.7	2.4	
Kutcharo	54.14	3.40	1.1	3.1	1
	71.25	15.9	5.6	2.8	
Akan	52.43	4.23	0.9	4.7	1
	65.87	12.1	3.6	3.4	
Daisetsu	54.73	12.0	2.7	4.4	1
	56.72	13.7	2.7	5.1	
	56.99	12.2	2.9	4.2	
Shikaribetsu	59.16	10.5	2.5	4.2	1
	61.26	11.5	3.5	3.3	
Tokachi	46.79	6.56	1.6	4.1	1
	53.41	10.9	2.6	4.2	
Shokanbetsu	55.41	11.1	2.6	4.3	1
Niseko	59.93	14.9	2.6	5.7	1
	60.35	13.4	3.0	4.5	
Yotei	57.84	8.22	2.7	3.0	1
	57.89	8.88	3.4	2.6	
	58.23	8.38	3.6	2.3	
	63.45	11.1	4.8	2.3	
Usu	49.36	1.49	0.9	1.7	1
	52.81	3.57	1.1	3.2	
	53.21	4.40	1.5	2.9	
Oshima-oshima	49.90	15.9	2.4	6.6	1
	55.56	14.9	2.9	5.1	
	61.72	27.2	3.7	7.4	
Oshima-kojima	60.46	15.3	3.2	4.8	1
Hakkoda	58.67	7.22	2.2	3.3	2
Iwaki	59.23	12.5	3.0	4.2	2
	60.11	10.7	3.3	3.2	
Towada	50.27	2.47	1.3	1.9	2
	55.09	3.24	1.8	1.8	
	55.85	3.24	1.7	1.9	
Hachimantai	52.85	2.66	1.1	2.4	2
	54.38	5.23	1.7	3.1	
	55.79	4.40	1.6	2.8	
	57.85	6.39	2.5	2.6	
	58.09	7.06	2.7	2.6	
	60.21	8.30	2.7	3.1	
	61.39	10.1	3.7	2.7	
	62.24	13.0	4.1	3.2	
	67.68	12.0	5.1	2.4	
	68.61	14.8	4.7	3.1	
Moriyoshi	55.36	8.72	2.7	3.2	2
	61.28	11.5	4.1	2.8	
Kampu	54.78	9.30	3.2	2.9	2
	55.47	9.80	2.5	3.9	
Iwate	52.38	2.66	1.2	2.2	2
	52.84	3.24	1.1	2.9	
	53.42	3.07	1.2	2.6	
	54.11	5.23	1.5	3.5	
	59.60	9.38	2.9	3.2	
	59.82	7.97	2.5	3.2	
	60.45	6.23	2.2	2.8	
	60.58	10.0	3.4	2.9	
	62.71	10.8	3.8	2.8	
Akita-komagatake	49.06	2.91	0.94	3.1	2
	49.37	1.83	0.99	1.8	
	52.13	4.15	1.5	2.8	

To be cont'd.

Volcano	SiO ₂	K ($\times 10^3$)	Hf	K/Hf ($\times 10^3$)	Ref.
Akita-komagatake	54.90	4.98	1.9	2.6	
Chokai	54.56	16.2	4.5	3.6	2
	55.93	15.6	5.0	3.1	
Gassan	56.58	14.6	3.3	4.4	2
Nekoma	60.26	4.8	2.8	1.7	2
Bandai	58.67	11.5	3.7	3.1	2
	58.70	8.30	2.8	3.0	
	58.97	9.21	3.7	2.5	
	60.51	9.96	3.5	2.8	
Naeba	55.0	7.14	3.0	2.4	3
	57.3	7.89	2.8	2.8	
	58.6	8.05	2.8	2.9	
	60.0	14.7	4.3	3.4	
	60.7	14.6	5.0	2.9	
	60.8	15.2	4.4	3.5	
	60.8	14.8	5.2	2.8	
	61.4	17.8	5.2	3.4	
	61.5	16.0	5.2	3.1	
Myoko	51.07	8.72	1.4	6.2	4
	52.35	8.22	1.4	5.9	
	53.89	12.0	1.6	7.5	
	55.99	10.5	1.7	6.2	
	59.06	15.2	2.4	6.3	
	60.59	15.8	2.4	6.6	
	63.93	17.7	2.8	6.3	
Kurohime	49.45	5.98	1.1	5.4	4
	52.41	7.22	1.8	4.0	
	54.89	8.22	1.5	5.5	
	57.00	7.55	1.7	4.4	
	57.69	11.2	2.5	4.5	
	59.25	11.8	2.6	4.5	
Asama	54.3	6.31	1.7	3.7	5
	55.2	4.15	1.2	3.5	
	56.7	5.89	2.3	2.6	
	56.8	7.80	2.8	2.8	
	57.3	7.55	2.0	3.8	
	58.5	6.14	1.9	3.2	
	58.5	7.97	2.3	3.5	
	59.5	10.5	2.5	4.2	
	59.6	9.05	3.4	2.7	
	61.5	11.0	2.7	4.1	
	62.4	12.2	3.1	3.9	
	62.8	11.7	2.8	4.2	
	69.1	16.1	3.7	4.4	
	73.0	19.8	4.2	4.7	
	73.1	20.1	4.5	4.4	
Yatsugatake	48.21	6.14	1.8	3.4	4
	53.77	6.72	2.1	3.2	
	54.50	9.80	3.0	3.3	
	60.72	16.8	3.7	4.5	
	62.78	19.5	3.5	5.6	
	65.11	15.9	3.2	5.0	
Shirouma-oike	56.3	17.1	2.7	6.3	4
	60.1	18.4	3.6	5.1	
	60.2	18.9	4.4	4.3	
Tateyama	61.93	21.0	4.2	5.0	4
	63.80	22.1	5.2	4.3	
Washibadake-	56.53	13.3	3.2	4.2	4
Kumonotaira	58.13	17.8	3.7	4.8	
Norikura	56.31	14.0	3.5	4.0	4
	58.56	16.5	3.8	4.3	
	58.91	15.1	3.8	4.0	
	59.00	18.0	3.6	5.0	
	59.14	17.9	4.0	4.5	

To be cont'd.

Volcano	SiO ₂	K (× 10 ³)	Hf	K/Hf (× 10 ³)	Ref.
Norikura	59.22	16.9	3.8	4.4	
	60.82	19.4	4.2	4.6	
	62.06	19.4	4.3	4.5	
	63.12	21.3	4.3	5.0	
Ueno	54.18	8.55	4.8	1.8	4
	55.02	8.80	4.1	2.1	
Hakusan	57.43	16.0	4.0	4.0	4
	58.30	16.1	3.6	4.5	
	60.55	17.3	3.7	4.7	
	61.43	18.3	3.7	4.9	
	61.49	17.0	3.8	4.5	

SiO₂ is given in wt.%, and K and Hf in ppm.

References, 1: MASUDA *et al.*, 1975; 2: MASUDA, 1979; 3: HASENAKA, 1978; 4: NAKANO, 1983; 5: OKAMOTO, 1979.

SAMPLES

Data of K and Hf contents are available for rocks from 39 Quaternary volcanoes (MASUDA *et al.*, 1975; HASENAKA, 1978; MASUDA, 1979; OKAMOTO, 1979, NAKANO, 1983) which cover the west end of the Kurile arc, the NE Japanese arc, and the northern end of the Izu-Bonin arc. Hf values measured by instrumental neutron activation analyses and K values by wet chemical or X-ray fluorescence analyses are referred to. The analytical error is about 10% for Hf and less than 10% for K (e.g., MASUDA *et al.*, 1974; MATSUMOTO and URABE, 1980). The compiled data are listed in Table 1 together with SiO₂ contents. No attention has been paid to rock types and phenocrystic mineral assemblages.

RESULTS AND DISCUSSION

K/Hf variation in a volcano K/Hf ratios are shown in Fig. 1 for four representative volcanoes from which relatively many data are available. With only one exception, the K/Hf ratio in a single volcano remains constant through a wide range of magmatic compositions (see also Table 1); in Yatsugatake (YT) volcano, the ratio becomes higher in more acidic rocks, which may be caused by the effective separation of a Hf-rich phase such as zircon. It is unlikely that K- or Hf-rich phases are fractionated from magmas of basaltic compositions, and the above observation suggests that K/Hf ratios of most volcanic rocks are equal to or very close to those in

primary magmas. If this is the case, a K/Hf ratio of a single rock from one volcano could be used in the discussion.

The association of calc-alkaline and tholeiitic rocks in a single composite volcano is common

Fig. 1. K-Hf relations for four volcanoes in NE Japan. Numbers indicate K/Hf ratios (averaged value ± 1 sigma). MK, Myoko; KH, Kurohime; YT, Yatsugatake; HM, Hachimantai. Open and closed circles in HM show tholeiitic and calc-alkaline rock series, respectively. The K/Hf ratio in a single volcano remains constant, and there is no difference in K/Hf ratios between tholeiitic and calc-alkaline rock series. In Yatsugatake volcano (YT), the K/Hf ratio does not remain constant during the process of chemical differentiation and becomes higher in more acidic rocks (along the broken line on the figure), which is only one exception within volcanoes examined in this study (see text).

in NE Japan, and two principal mechanisms have been proposed to explain the association; two different processes of magmatic differentiation from the common parental basalt magma including magma mixing in calc-alkaline rocks (KUNO, 1950, 1968; SAKUYAMA, 1983), and different parental magmas for each rock types (KUSHIRO and SATO, 1978; MASUDA and AOKI, 1979). As shown in Fig. 1, there is no difference in K/Hf ratios between calc-alkaline and tholeiitic series, suggesting that the parental magmas for these two series have the same K/Hf ratios. This observation favors the hypothesis that just one parental magma exists for a single volcano.

K/Hf variation within an arc Figure 2 shows the lateral distribution of K/Hf ratios in NE Japanese Quaternary volcanoes. On the figure, the K/Hf ratio for a single volcano is the averaged value of all rocks from the volcano listed on Table 1. To remove the added complexity of a changing ratio during later stages of magmatic differentiation, we have chosen only compositions from each source which have constant ratio, i.e., which plot on a straight line with an inclination of 45° in a log-log plot (see Yatsugatake volcano in Fig. 1). As indicated in Fig. 2, an across-arc lateral variation is observed in K/Hf ratios; the ratio in a back-arc region magma is higher than that in a fore-arc region magma. The lateral variation could be caused by three factors, which are examined below.

Effect of crustal contamination: Contamination of mantle-derived magma by assimilation of crustal rocks has often been discussed (KUNO, 1950; ARCULUS and JOHNSON, 1981). As the K/Hf ratio remains constant at different degrees of magmatic differentiation (i.e., at different degrees of crustal contamination), (1) K and Hf contents of crustal materials should be much lower than those of primary magmas, or (2) K/Hf ratios in crustal materials should be equal to those in primary magmas. The first possibility is improbable as several studies of Japanese crustal rocks (e.g., ANDO *et al.*, 1974) suggest that their K and Hf concentrations are roughly

Fig. 2. Lateral variation of K/Hf ratios in NE Japan. ●, volcanoes with the ratio below 3,000; ◐, 3,000-4,000; ⊕, 4,000-5,000; ○, beyond 5,000. The K/Hf ratio is higher in the inner-arc region than in the outer-arc region.

equal to those of Quaternary volcanic rocks. The second possibility is also unlikely, as K/Hf ratios of crustal materials may be higher than those observed in rocks from fore-arc volcanoes ($<3,000$); for example, typical granodiorite in NE Japan (ANDO *et al.*, 1974) and the post-Archaean crustal material after TAYLOR (1979) have K/Hf ratios of 10,000 and 5,600, respectively. Furthermore, if the lateral variation is caused by the crustal contamination, the K/Hf ratios in crustal materials have to change systematically toward the back-arc side; this may be unrealistic. It can thus be concluded that the effect of crustal contamination on K/Hf ratios of arc magmas is not likely to be significant.

Effect of degree of partial melting: The crystal/liquid distribution coefficients, D , of K and Hf are much smaller than unity for major mantle materials, that is, olivine, orthopyroxene, and clinopyroxene (GILL, 1981), and both elements behave as incompatible elements during the process of partial melting of mantle peridotites. $D_{\text{Hf}}^{\text{cpX}}$ is, however, higher than $D_{\text{K}}^{\text{cpX}}$, so the K/Hf ratio in a primary magma should decrease with increasing degree of partial melting, especially as far as the residual material is lherzolite. On the basis of melting experiments of materials of NE Japanese primary basalt compositions (TATSUMI *et al.*, 1983), residual materials of back- and fore-arc region magmas are likely to be lherzolite and harzburgite, respectively. Therefore, differences in the degree of partial melting may play a partial role in causing the observed lateral variation. In a simple mathematical model of partial melting, the concentration of an element in a liquid phase formed by equilibrium partial melting is expressed as follows.

$$\frac{C_l}{C_o} = \frac{1}{\bar{D}_i + F(1 - \bar{D}_i)}$$

where C_l and C_o are the concentrations of an element i , in the liquid and the original solid, respectively. F is a liquid fraction and is equal to degree of partial melting, and $\bar{D}_i$ is a bulk partition coefficient defined as:

$$\bar{D}_i \equiv \sum_j^n D_i^j X_j$$

where D_i^j is a partition coefficient of an element i , between the liquid and a phase j , X_j is the fraction of phase j in the original solid and n is number of phases. According to the above equation, the following equation can be obtained.

$$R(F) \equiv \frac{(K/Hf)_l}{(K/Hf)_o} = \frac{\bar{D}_{\text{Hf}} + F(1 - \bar{D}_{\text{Hf}})}{\bar{D}_{\text{K}} + F(1 - \bar{D}_{\text{K}})}$$

Assuming that $D_{\text{K}}^{\text{ol}} = 0.01$, $D_{\text{K}}^{\text{opx}} = 0.01$, $D_{\text{K}}^{\text{cpX}} = 0.02$, $D_{\text{Hf}}^{\text{ol}} = 0.01$, $D_{\text{Hf}}^{\text{opx}} = 0.10$, $D_{\text{Hf}}^{\text{cpX}} = 0.25$, $X_{\text{ol}} = 0.6$, $X_{\text{opx}} = 0.25$, $X_{\text{cpX}} = 0.15$, $F_{\text{fore-arc}} =$

0.30, and $F_{\text{back-arc}} = 0.05$, which may be the most realistic values (GILL, 1981; TATSUMI *et al.*, 1983), we get R to be 1.9 and 1.1 for the back-arc and the fore-arc region magmas, respectively. Thus it can be estimated that the K/Hf ratio in a back-arc primary magma should be about 1.6 times higher than that in a fore-arc magma. The K/Hf ratios in NE Japanese volcanic rocks, however, increase by a factor of up to 4. Therefore, the lateral variation of the ratio cannot be caused only by the buffering effect of clinopyroxene during the partial melting process.

Figure 3 shows K, Hf-SiO₂ relations of NE Japanese volcanic rocks. As pointed out by previous studies, the lateral variation of K contents has clearly been recognized, and is attributed mainly to differences in the degree of partial melting; on the other hand, there is no systematic difference in Hf contents between volcanoes in fore- and back-arc regions. In such discussions using SiO₂ variation diagram, attention must be paid to the fact that rocks with the

Fig. 3. K, Hf-SiO₂ relations in NE Japanese volcanic rocks. Open and closed circles indicate rocks with K/Hf ratios above and below 4,000 (i.e., in the inner- and outer-arc regions), respectively. There is no systematic difference in Hf contents between these two types of volcanic rocks.

same SiO_2 contents have not undergone the same degree of solidification (fractional crystallization). However, even if this effect is taken into account using the estimation of degree of fractionation (WRIGHT and DOHERTY, 1970; TATSUMI *et al.*, 1983), it should be noted that the Hf contents of primary basalt magmas are roughly constant. If Hf contents are constant in primary magmas produced by partial melting of different degrees, D_{Hf} should be nearly unity on the basis of the equation (1). As mentioned before, however, D_{Hf} is much smaller than unity for major constituent minerals of mantle peridotites. Therefore, minor minerals with D_{Hf} much higher than unity would have to be present as residual phases. Candidates with such distribution coefficients are zircon, sphene, perovskite, and rutile. Also, the existence of such minor phases in residual mantle wedge

materials could explain the fact that subduction zone magmas are systematically more depleted in HFSE than are oceanic magmas. According to GREEN (1981), those minerals can be stable on partial melting of relatively higher degrees under hydrous conditions, and are likely to occur in subduction zones.

Effect of fluid phase from downgoing lithosphere: It has been suggested that the downgoing lithosphere could release a fluid phase to cause partial melting of mantle wedge materials (MCBIRNEY, 1969; FYFE and MCBIRNEY, 1975; TATSUMI *et al.*, 1983). The fluid phase should be formed by the breakdown of hydrous minerals in the descending slab, and it may contain considerable amounts of some elements in addition to H_2O ; for example, SiO_2 and LILE can be dissolved in H_2O to a certain extent at high pressures (NAKAMURA and KUSHIRO, 1974;

Fig. 4. Stability limit of serpentine, talc, clinocllore, and phlogopite in the NE Japanese downgoing lithosphere. Temperature distribution at the top of the slab and 5 km below the top are given by A and B, respectively. Serpentine and phlogopite play an important role in the supply of the fluid phase to the mantle wedge beneath the inner- and outer-arc regions, respectively.

RYABCHIKOV and BOETTCHER, 1980; TATSUMI *et al.*, 1984). Therefore, the fluid phase may have a serious effect on the compositions of arc magmas, and the stability fields of hydrous minerals in the downgoing slab have to be carefully examined. In general, the stability of hydrous phase depends mainly on temperature, and it is important which geothermal model is chosen for the temperature distribution in the slab. We have used the geotherm after TATSUMI *et al.* (1983), because it can explain most reasonably the generation of arc magmas. As hydrous minerals would exist in layer 3A or 3B of oceanic lithosphere (SCHREIBER and FOX, 1973; WOOLLARD, 1975), the temperature distribution within a subducting slab should also be taken into account. The thermal model by HONDA (1983) which was based on the temperature distribution in the mantle wedge deduced by TATSUMI *et al.* (1983), was selected for this purpose. These geotherms are shown in Fig. 4.

In the NE Japanese volcanic arc, the pressure at the depth of Wadati-Benioff zone is more than 40 kb. On the basis of the results of high pressure experiments and thermodynamic calculations, clay minerals and amphiboles are believed to break down at pressures below 40 kbars (NISHIKAWA *et al.*, 1969; MERRILL and WYLLIE, 1975; DELANY and HELGESON, 1978), and they could not be directly related to the production of arc magmas. On the other hand, serpentine, talc, clinocllore, and phlogopite in the slab would decompose at pressures between 40 and 70 kb (KITAHARA *et al.*, 1966; YAMAMOTO and AKIMOTO, 1977; STAUDIGEL and SCHREYER, 1977; KUSHIRO *et al.*, 1967; DELANY and HELGESON, 1978, TATSUMI *et al.*, 1984). Of these minerals, serpentine may have been produced by the alteration of peridotitic minerals, that is it may exist below the surface of the downgoing lithosphere. In contrast, phlogopite could be formed at the top of the slab by the reaction of sediment-derived muscovite with amphibole or chlorite. From Fig. 4, therefore, it is suggested that serpentine and phlogopite could play an important role in the supply of water to the mantle wedge beneath the fore-

and back-arc regions, respectively. It should be noted that phlogopite may dehydrate to release potassium with H₂O; that is, the following reaction could occur in the slab beneath the back-arc region;

The K/Hf ratio in a fluid phase released from phlogopite, therefore, should be higher than that from serpentine, and this may cause the lateral variation of the ratio in arc magmas together with the difference in the degree of partial melting.

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