

## Hydrogen isotopes in hornblendes and biotites from Quaternary volcanic rocks of the Kamchatka-Kurile arc

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The hydrogen isotopic composition of hornblendes (Hb) and biotites (Bi) from Quaternary volcanic rocks along the Kamchatka-Kurile volcanic arcs was measured. Volcanoes from three different tectonic environments were sampled: The Kurile chain, East Kamchatkan volcanic belt and Sredinny Ridge. Large local and regional variations were observed.

There is no correlation between  $\delta D$  values of minerals and their chemical composition, including Cl and F contents. All observed trends are caused by regional variations in the major element chemistry (Hb) or Cl and F contents (Bi). Minerals from the Kuriles and East Kamchatka are most enriched in D, have a low F content, and a high Cl content, the latter 500–1000 ppm. Hb and Bi from Sredinny Ridge are D-depleted, enriched in F (up to 1.7 wt.% in Bi) and depleted in Cl.

Based on the data set for Shiveluch and Avacha volcanoes,  $\delta D$  variations for Hb are caused mainly by degassing of the erupted material; the most degassed rocks contained the most D-depleted Hb. We believe that the maximum  $\delta D$  values correspond to isotopic equilibrium of OH-bearing minerals with a "parent magmatic water", dissolved in the melt prior to eruption. Magmatic water for the Kurile volcanoes with  $\delta D$  in the range of  $-40$  to  $-25\%$  could be derived mainly from subducted oceanic sediments. Magmatic water for the East Kamchatka volcanoes is slightly depleted in D ( $-46$  to  $-36\%$ ) and corresponds to a mixture of "devolved" water from subducted sediments and water released from altered basalts of oceanic crust. The water source of the Sredinny Ridge magmas with  $\delta D$  values in the range of  $-70$  to  $-80\%$  may not be related to oceanic slab-derived fluids; rather, they may preserve a depleted mantle isotopic signature. The regional variation of maximum D/H ratios for Hb and Bi agrees well with trends of the Sr isotopic composition and the  $^{10}\text{Be}$  content in volcanic rocks throughout the modern Kurile-Kamchatka arc.

### INTRODUCTION

Large variations in the isotopic composition of Sr, Nd, O, B, Pb and Be are found in volcanic rocks of the Kamchatka-Kurile volcanic belts, indicating that the parental arc magmas are not derived from a homogeneous mantle reservoir, but rather from a mixture of various sources (Vinogradov *et al.*, 1986; Bailey *et al.*, 1987; Zhuravlev *et al.*, 1987; Tera *et al.*, 1989; Tsvetkov *et al.*, 1991; Pokrovsky and Zhuravlev, 1991; Ishikawa and Tera, 1994; Kersting and Arculus, 1995).

Aqueous fluids derived from the dehydration of subducted oceanic crust play an important role in the process of magma generation (Delaney and Helgeson, 1978; Tatsumi *et al.*, 1986; Tatsumi, 1989; Othman *et al.*, 1989; Peacock, 1990; Avdeiko *et al.*, 1992; Giggenbach, 1992; Stolper and Newman, 1994). The participation of recycled oceanic water in the generation of arc magmas is suggested by the following observations: (1) There is an enrichment in deuterium of high-temperature magmatic gases from island arc volcanoes (Sakai and Matsubaya, 1977; Mizutani, 1978; Taran *et al.*, 1987, 1989, 1995; Symonds *et al.*, 1990;

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Giggenbach, 1992; Chiodini *et al.*, 1995) over that commonly ascribed to mantle-derived water (e.g., Taylor and Sheppard, 1986); (2) there is also an enrichment in deuterium in amphiboles from island arc volcanic rocks (Graham *et al.*, 1982; Taran *et al.*, 1989; Deloule *et al.*, 1991; Miyagi and Matsubaya, 1992); and (3) there is a high pre-eruptive water content in subduction zone magmas (Harris and Anderson, 1984; Johnson *et al.*, 1994) and high initial D/H ratios as estimated for closed or open system degassing models (Taylor *et al.*, 1983; Taylor, 1986; Newman *et al.*, 1988).

The isotopic composition of the fluid derived from a subducting slab has been discussed by several authors. The most direct estimate has been made by Poreda (1985), who showed that the water dissolved in the Mariana Trough basalts is a mixture of mantle water ( $\delta D = -70$  to  $-80\text{‰}$ ) and water derived from the oceanic slab, with  $\delta D = -25\text{‰}$ .

In this study, hydrous minerals (hornblendes and biotites) from Kamchatka-Kurile Quaternary volcanoes have been analyzed for their chemical composition (including H<sub>2</sub>O, Cl and F content) and  $\delta D$  value. The results are discussed with respect to magma-crust interaction, the origin of arc magmatic water, and the regional variation of the D/H ratio and other isotopic systems. But first we examine the general controls on the  $\delta D$  composition of hydrous minerals in magmatic systems.

#### *Processes which control the D/H ratio in Hb and Bi*

One question regarding the interpretation of the  $\delta D$  data of magmatic Hb and Bi concerns whether these minerals reflect the isotopic signature of the initial magmatic water from which they form, or do they partially or completely lose the isotopic signature of the magmatic environment due to secondary processes.

The range of  $\delta D$  values may be caused by isotopic heterogeneity of the source magmatic water (local or regional) and/or by fractionation during the life time of minerals after crystallization (Deloule *et al.*, 1991). During the initial stage of mineral formation isotopic equilibrium exists be-

tween water dissolved in the magma ("parent magmatic water") and the crystallizing minerals. Since the hydrogen isotope fractionation for "dissolved water-vapor" and "magmatic hydrous minerals-vapor" are approximately the same (10 to 30‰; Suzuoki and Epstein, 1976; Kuroda *et al.*, 1982; Dobson *et al.*, 1989), the fractionation between OH-minerals and dissolved water should be low, in the range of several permil. Therefore, the hydrogen isotope composition of OH-minerals should be close to that of the dissolved, "magmatic", water.

Regional variations in the isotopic composition of magmatic water are related to the source of the water. The water may be released mainly from the subducting oceanic slab (e.g., Giggenbach, 1992) or it may be a mixture of Mid Oceanic Ridge Basalt (MORB) water and "subducted" water, with the proportion of each endmember depending on the distance from the volcanic front (Stolper and Newman, 1994). The "subducted" water, in turn, may be a mixture of water released from the subducted oceanic sediments with  $\delta D = -30 \pm 10\text{‰}$  (Giggenbach, 1992) and water dehydrated from altered oceanic basalts (Ishikawa and Tera, 1994; Volynets, 1994; Kersting and Arculus, 1995). The hydrogen isotopic composition of altered oceanic basalts usually ranges from  $-25$  to  $-80\text{‰}$  (Alt *et al.*, 1986; Kawahata *et al.*, 1987; Kusakabe *et al.*, 1989). The water in altered basalts of the oceanic crust occurs mainly in low-temperature clay minerals which are formed in isotopic equilibrium with seawater.

The chemical composition of hydrous minerals to some extent reflects the bulk composition of the parent magma and is sensitive to pressure, temperature, oxygen and water fugacities (e.g., Helz, 1982). It is possible, therefore, that during crystallization there is a correlation between the chemical composition of OH-minerals and their  $\delta D$  value (or, the  $\delta D$  of water dissolved in the crystallizing melt).

After crystallization, during magma ascent to the surface, the  $\delta D$  values of Hb and Bi can be modified by isotopic exchange with water of dif-

ferent isotopic composition. At this stage, one of the factors governing the  $\delta D$  composition is the degassing of magma; the greater the water loss by the magma, the lower the  $\delta D$  value of the residual water in the melt (Nabelek *et al.*, 1983; Taylor *et al.*, 1983; Taylor, 1986; Qin *et al.*, 1987; Newman *et al.*, 1988; Matsuhisa, 1992), and thus the lower the  $\delta D$  value of minerals in equilibrium with the residual dissolved water will also be lower. During eruption, under "dry" magmatic conditions, Hb and Bi become unstable due to a drop of the water pressure. Partial oxidation and dehydration of minerals during and after eruption

can be accompanied by noticeable changes in isotopic composition (Graham, 1981; Kuroda *et al.*, 1988; Miyagi and Matsubaya, 1992). Deloule *et al.* (1991) have measured by ion microprobe variations up to several tens of permil in a single Hb crystal, most probably caused by a different rate of the dehydrogenization ( $H_2$ -loss by diffusion) of different parts of a crystal.

#### GEOLOGICAL SETTING AND SAMPLE LOCATION

The Kamchatka-Kurile arc system extends over 2000 km and is associated with the subduction of

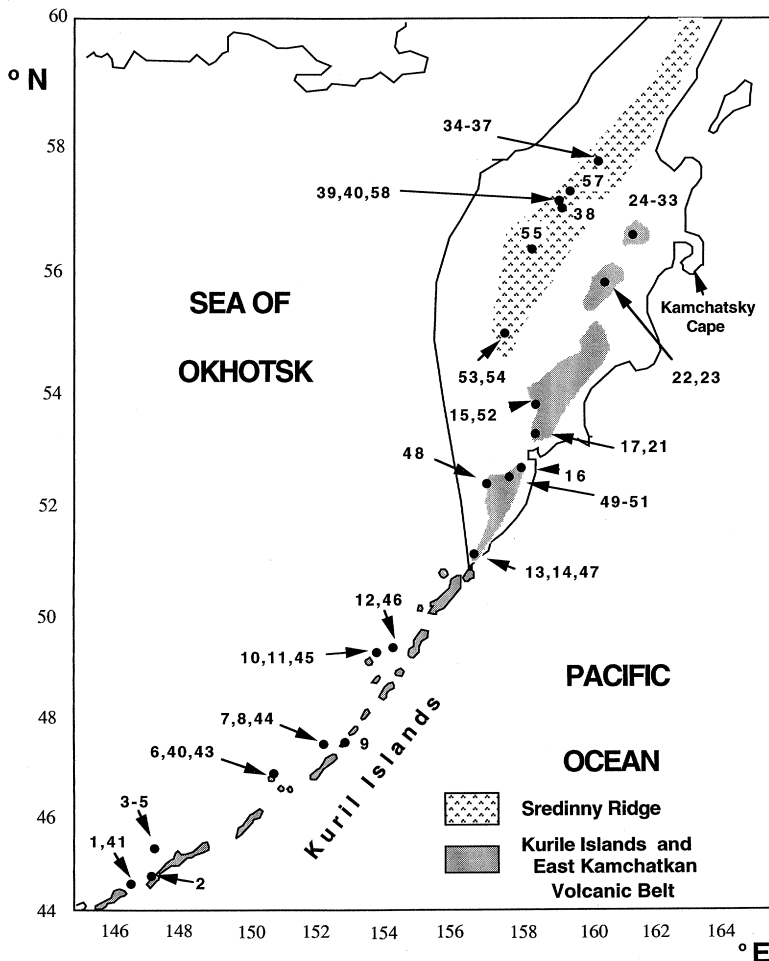


Fig. 1. Location of samples collected from Quaternary volcanoes in Kamchatka and the Kurile islands. The numbers correspond to data in Table 1. Also shown are main volcanic belts: Sredinny Ridge, East Kamchatkan volcanic belt and Kurilian chain.

the Pacific Plate at the Kurile-Kamchatka trench. About 100 active volcanoes of the Kurile islands and Eastern Kamchatka form a modern volcanic belt with two chains, frontal and rear-side, like most subduction zones with a rather low angle of slab subduction (Marsh, 1979). This belt acquired its present configuration in Late Miocene-Early Pliocene, when a new northern branch of the Kurile-Kamchatka trench was formed from the latitude of Avacha Bay to the Kamchatsky Cape (Legler, 1977). In Late Pliocene-Quaternary time volcanoes in the Kamchatka segment of the arc formed solely under subaerial conditions. In the Kurile segment, subaerial volcanoes (dominant in the frontal zone) coexist with submarine volcanoes (dominant in the rear-arc zone).

Quaternary volcanoes of Sredinny Ridge form a third volcanic chain ~200 km behind the modern volcanic front. The source of magmas for the Sredinny Ridge Quaternary volcanoes is still the subject of discussion. This chain may represent the volcanic front of an older (Middle Miocene?) arc system (Legler, 1977; Watson and Fujita, 1985; Volynets, 1994), and in the Early Pliocene (Late Miocene?) volcanism in the Sredinny Ridge apparently lost its connection with the subduction process. However, volcanic activity continued here until the Late Holocene, because volcanic processes tend to exhibit greater inertia than tectonic processes (Legler, 1977; Volynets, 1994). Tatsumi *et al.* (1994) believe that Quaternary volcanoes of Sredinny Ridge form a "third" chain of the modern subduction zone with a distinct condition of magma generation caused by partial melting of K amphibole-bearing peridotites in the down-drug hydrous layer at the base of the mantle wedge.

Figure 1 shows the volcanic chains and location of Quaternary volcanoes where samples were collected. All samples from the Kurile islands were collected during the cruise of the RV "Vulcanolog".

Amphiboles and micas are typical, though not abundant, minerals of the Quaternary volcanics from the Eastern Kamchatka-Kurile arc and Sredinny Ridge (Volynets *et al.*, 1975, 1987, 1989). These minerals occur as phenocrysts as well

as in the groundmass of the rocks. Rocks containing these minerals occur in the rear-arc zone of the modern volcanic belt (Opala and Kupol volcanoes, and submarine volcanoes of the Kurile chain), and in the Sredinny Ridge, whereas in the frontal zone of the modern volcanic belt anhydrous mafic minerals predominate. However, amphibole-bearing rocks are also present in the frontal part of arcs, in transverse structures associated with across-arc faults (Avachinsky volcanic group) and in large volcanic centers (Shiveluch and Bezymyanny volcanoes). The Quaternary lavas of Northeast Japan are also characterized by similar mineral zonation (Sakuyama, 1979).

#### SAMPLE PREPARATION AND ISOTOPIC ANALYSIS

The alteration of minerals results in a change from green Hb and Bi in pyroclastic deposits and pumice flows to brownish Hb and reddish Bi in lava flows, lava domes and dikes. We selected for analysis rock samples without visible alteration; we have not analyzed series of minerals which were essentially red to brown in color or altered to opaque minerals (see also, Miyagi and Matsubaya, 1992). The phenocrysts of Hb in intermediate and acid lavas from Kamchatka and the Kuriles range from 0.5 to 1.5 mm in size, though there are Hb megacrysts up to 40-mm long. The separation of minerals from rocks was performed using crushed samples weighing 10–20 kg, or from concentrates weighing 0.5–1.0 kg. Heavy liquid and magnetic separation techniques were used to separate Hb and Bi, and samples were also hand picked under a microscope. Gently-crushed Hb megacrysts were also cleaned under the microscope. This separation technique generally resulted in greater than 90% mineral purity, but in some cases Hb and pyroxene were not completely separated.

High-purity separates of Hb (200–300 mg) and Bi (150–200 mg) were pre-heated at 250°C under vacuum for 2–4 hours to remove absorbed and interlayered water, then were heated to 1200°C. All the samples melted at this temperature. Any hydrogen gas produced by dehydration of miner-

als and reduction of water was oxidized to water by reaction with CuO at 600°C. All the water was then reduced to hydrogen gas by reaction with uranium or zinc metal, and uranium also used to collect the hydrogen. The volume of hydrogen gas was measured manometrically to determine the water content of each sample. The isotopic composition of the hydrogen gas was measured by a modified Varian GD-150 or Finnigan Mat 251 mass spectrometer. The reproducibility of  $\delta D$  analyses is within  $\pm 3\%$ .

Cl and F contents were measured by electron microprobe using a JXA-5 analyser (Volynets *et al.*, 1989) with the detection limit of 0.02 and 0.05 wt.%, respectively.

## RESULTS AND DISCUSSION

### *Isotopic and chemical composition of minerals*

Hydrogen isotope compositions, and water, Cl and F contents for 58 samples of Hb and Bi from 22 volcanoes are summarized in Table 1. The variations in  $\delta D$  throughout the Kuriles and Kamchatka are large, even for rocks from a single volcano (e.g., Shiveluch and Avacha). The  $\delta D$  value does not correlate with the bulk rock composition, but there is a tendency for an increase in the  $\delta D$  value of pyroclastic material, as also noted by Miyagi and Matsubaya (1992). Available microprobe analyses of minerals and their structural formulas are presented in Tables 2 and 3. Water, Cl and F contents, as well as  $\delta D$  values from Table 1 are added for completeness.

Amphiboles are calcic, referred to as hornblendes (Wones and Gilbert, 1982), and according to their aluminum content can be divided into pargasite-hastingsite series (mainly from andesites and basaltic andesites), hornblende series (mainly from acid rocks), and tremolite-ferroactinolite series (from some acid Kurile rocks). Hornblendes from alkali andesites and basaltic andesites of Sredinny Ridge contain a significant fraction of the kaersutite endmember. The  $x_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Mg} + \text{Al})$  atomic ratio in Hb ranges from 0.26 to 0.32. Mica compositions correspond mainly to aluminous biotites, with the  $x_{\text{Fe}}$  in analyzed samples

ranging from 0.21 to 0.36. Biotites from alkali rocks of Sredinny Ridge are Mg-poor and Ti-rich, with mole fraction of titanobiotite up to 0.18 and  $x_{\text{Fe}} = 0.35\text{--}0.38$ .

### *Relationships between $\delta D$ , water, Cl, and F contents*

One of the principal secondary processes after the crystallization of Hb and Bi, and the most undefinable in terms of hydrogen isotope composition, is the oxidation and dehydration during magma ascent and eruption when the minerals become unstable as a result of magma degassing or due to a gradual cooling of the erupted material. The water content for most of the samples (Table 1) is less than the stoichiometric value (about 2 wt.% for Hb and 4 wt.% for Bi). Less oxidized, green minerals in pumice and fine-grained pyroclastics contain more water and can be considered to have quenched during rapid cooling. As was shown experimentally by Miyagi and Matsubaya (1992), a noticeable modification of the  $\delta D$  value in Hb and Bi occurs when  $\geq 40\%$  of the water is lost, i.e., at a water concentration less than about 1.2 wt.% in Hb and 2.4 wt.% in Bi. "Self-oxidation" (in vacuum) leads to a strong enrichment in D, whereas oxidation by air results in a strong depletion in D (Miyagi and Matsubaya, 1992).

The Cl and F microprobe data as well as the H<sub>2</sub>O content determined for minerals (the latter by the volumetric method; all data from Table 1) are plotted versus  $\delta D$  values on Fig. 2. Water contents less than 1.3 wt.% for Hb and 2.5 wt.% for Bi are shown by the dashed lines. Isotopic compositions which lie below these lines may be affected by dehydration and post-magmatic alteration of minerals.

In our case there are only a few Hb samples with less than 1.2 wt.% water. Some of the dehydrated Bi samples from Sredinny Ridge volcanoes contain a considerable amount of F, substituting for the hydroxyl. In at least two of them (5485, Khangar, and AA-1023, Amanina, marked on the  $\delta D\text{-H}_2\text{O}$  plot, Fig. 2), the water loss is the result of the partitioning of OH-F-Cl between minerals

Table 1. Isotopic composition of hydrogen and contents of water, chlorine, and fluorine in Hb and Bi from Quaternary volcanic rocks of the Kurile-Kamchatka region. Numbers of sites correspond to those in Fig. 1.

No.	Sample	Volcano	Rock composition	Type	$\delta D$ , VSMOW (‰)	H <sub>2</sub> O, Cl, F		
						H <sub>2</sub> O	Cl	F
						weight (%)		
<b>Hornblendes</b>								
KURILE ISLANDS								
1	V17-31/1	8.17*	dacite	d	-40	2.2	0.08	0.01
2	V17-615	Lvinaya Past	dacite	pyr	-46	1.79	0.08	0.14
3	V17-26/5	8.10	bas. and.	d	-73	1.6	0.06	0.03
4	V17-26/4	8.10	bas. and.	d	-61	1.55	0.04	0.02
5	V17-26/2	8.10	bas. and.	d	-62	1.21	0.05	0.0
6	V17-13/1	6.10	rhyodacite	d	-53	1.77	0.11	0.02
7	V24-2/1	5.1	andesite	d	-25	1.49	0.04	0.0
8	V24-35/1	5.1	andesite	d	-57	1.75	0.03	0.0
9	V25-35/9	4.3	andesite	d	-48	1.52	0.05	0.0
10	V17-51/1	3.1	bas. and.	d	-44	2.0	0.02	0.0
11	V17-51/3	3.1	bas. and.	d	-37	1.56	0.06	0.0
12	V25-46/1	2.8	andesite	d	-26	1.41	0.07	0.0
KAMCHATKA								
<i>Eastern Kamchatkan Volcanic Belt</i>								
13	TDG-91/1	Dikyi Greben	dacite	pyr	-37	1.92	0.12	—
14	TDG-91/2	Dikyi Greben	dacite	pyr	-42	1.76	0.16	—
15	5504	Kupol	dacite	dome	-58	1.13	0.02	0.0
16	VL-667/3	Medvezhia	rhyodacite	pyr	-45	1.79	0.12	0.06
17	6870	Avacha	bas. and. mc	pyr	-65	2.18	—	—
18	29232	Avacha	andesite	dyke	-81	1.8	—	—
19	31801	Avacha	bas. and.	dyke	-73	1.49	—	—
20	31800	Avacha	andesite	pyr	-51	1.81	—	—
21	AMK-1945	Avacha	andesite	pyr	-36	1.85	—	—
22	B-8204	Bezmyanny	andesite	pyr	-47	1.05	—	—
23	M-1031	Bezmyanny	andesite	pyr	-57	1.30	—	—
24	SHV-8	Shiveluch	andesite	pyr	-46	1.36	—	—
25	5706	Shiveluch	andesite	pyr	-58	1.53	—	—
26	SHV-88/2	Shiveluch	andesite	dome	-79	1.79	—	—
27	5711/3	Shiveluch	andesite	dyke	-94	1.40	—	—
28	V-610	Shiveluch	basalt	dyke	-49	1.89	—	—
29	1314	Shiveluch	andesite	pyr	-58	1.80	—	—
30	1315	Shiveluch	andesite	pyr	-55	1.60	—	—
31	1316	Shiveluch	andesite	pyr	-56	1.30	—	—
32	V-614	Shiveluch	amphibolite	xen	-47	1.86	—	—
33	V-611	Shiveluch	amphibolite	xen	-50	1.61	—	—
<i>Sredinny Ridge</i>								
34	TT-995	Tekletunup	andesite	lf	-115	1.33	0.04	0.03
35	TT-1003	Tekletunup	dacite	pyr	-111	1.6	0.06	0.02
36	TT-1003A	Tekletunup	dacite	dome	-112	1.73	0.05	0.03
37	AA-1052/2	Tekletunup	dacite	dome	-85	1.69	0.05	0.07
38	6833/4	Bolshoy	trachyandesite	lf	-73	1.16	—	—
39	6962	Bol. Ketepana	bas. and.	lf	-79	1.15	0.02	0.03
40	KT-618/10	Bol. Ketepana	bas. and.	dyke	-66	1.06	—	—

Table 1. (continued)

No.	Sample	Volcano	Rock composition	Type	$\delta D$ , VSMOW (‰)	H <sub>2</sub> O		
						weight (%)		
<b>Biotites</b>								
KURILE ISLANDS								
41	V17-31/1	8.17	dacite	d	-56	2.13	0.13	0.04
42	V15-88/1	6.10	rhyodacite	d	-40	2.19	0.14	0.16
43	V17-13/1	6.10	rhyodacite	d	-61	3.0	0.15	0.06
44	V24-2/1	5.1	andesite	d	-42	2.67	0.09	0.04
45	V17-51/1	3.1	andesite	d	-45	3.18	0.25	0.08
46	V25-46/1	2.8	andesite	d	-44	3.14	0.18	0.06
KAMCHATKA								
<i>Eastern Kamchatkan Volcanic Belt</i>								
47	TDG-91/1	Dikiy Greben	dacite	pyr	-52	3.40	0.26	—
48	86-204/2	Opala	rhyolite	pyr	-47	3.06	0.1	0.08
49	VL-675/1	Barkhatnaya	rhyolite	pyr	-75	2.46	0.1	0.05
50	VL-676/1	Barkhatnaya	rhyolite	pyr	-75	3.0	0.09	0.16
51	VL-676/1a	Barkhatnaya	hyolite	pyr	-85	2.0	0.09	0.34
52	5504	Kupol	dacite	dome	-58	3.0	0.14	0.29
<i>Sredinny Ridge</i>								
53	5485	Khanger	hyolite	lf	-72	2.16	0.09	0.97
54	5440	Khanger	dacite	lf	-108	1.75	0.08	0.64
55	ES-786	Uxichan	trachydacite	lf	-93	2.0	0.07	0.67
56	AA-1023	Amanina	syenite	dyke	-80	1.8	0.03	1.7
57	7047	Napana	syenite	dyke	-106	1.66	0.02	0.53
58	KT-619	Bol. Ketepana	bas. and.	dyke	-86	2.63	0.05	0.04

\*Number of site for dredged submarine rocks (Avdeiko et al., 1992).

*d* - dredged sample, *lf* - lava flow, *pyr* - pyroclastic material, *dome* - lava dome, *mc* - megacryst, *xen* - xenolith, *bas. and.* - basaltic andesite.

and fluid (melt?) rather than by oxidation.

There is no correlation between  $\delta D$  and H<sub>2</sub>O concentration for Hb. Points for Sredinny Ridge volcanoes form a separate field with lower  $\delta D$  values, while the compositions of Kurilian and East Kamchatkan volcanoes are distinct and scatter with a wide range of  $\delta D$  and H<sub>2</sub>O values. This latter group of data, in turn, form two overlapping fields with the range of -94 to -36‰ for East Kamchatka and -73 to -25‰ for Kuriles with no trend (arithmetic mean of  $\delta D = -52‰$ ).

For Bi there are also three overlapping clusters of points on the  $\delta D$ -H<sub>2</sub>O plot. The first field, for the Kuriles, has  $\delta D$  values ranging from -40 to -61‰. The second field for East Kamchatka has slightly lower  $\delta D$  values (-85 to -47‰). The third field for Sredinny Ridge has  $\delta D$  in the range

of -108 to -72‰ and lower water contents.

The lack of correlation of  $\delta D$  and H<sub>2</sub>O is not surprising; the data scatter can be the result of many superimposed factors, including the regional and local heterogeneity of the magmatic fluid composition and the rate of magma degassing during ascent and eruption. Alteration (dehydration) of Hb probably does not play a significant role; points with the lowest water content fall in the main range of  $\delta D$  variation. In contrast, for Bi, the lowest  $\delta D$  values correspond with the lowest water content. Almost all Sredinny Ridge points fall below the 2.5 wt.% water line and in this case the observed correlation could be a result of post-magmatic alteration of Bi. These samples, except the two marked with a high F content, as well as Hb samples with less than 1.3 wt.% of water, are

Table 2. Microprobe analyses of selected hornblendes

Sample No.	V17-615	V17-31/1	V17-13/1	V17-51/1	TDG-91	31800	31801	6870	5504	1314	1315	5706	6962	6833/4	KT-618
SiO <sub>2</sub>	48.03	47.96	49.79	45.17	48.02	43.31	42.27	42.74	47.47	43.62	45.01	47.74	39.48	38.60	39.25
TiO <sub>2</sub>	1.4	1.02	1.04	1.88	1.33	1.76	2.19	1.50	1.64	1.90	1.49	1.33	2.36	3.80	2.77
Al <sub>2</sub> O <sub>3</sub>	6.6	7.75	6.43	7.97	6.32	11.93	11.05	11.41	9.04	9.87	9.45	9.70	13.05	12.75	14.50
FeO	12.4	13.74	11.68	13.37	12.40	13.21	13.08	12.56	12.43	11.20	10.63	11.76	12.91	12.40	11.58
MgO	14.78	13.22	15.66	13.59	15.25	0.02	0.19	14.94	15.03	14.49	15.39	14.25	14.39	14.54	13.90
MnO	0.48	0.73	0.66	0.40	0.41	14.52	13.45	0.11	0.38	0.21	0.25	0.25	0.12	0.10	0.09
CaO	10.83	10.88	10.57	11.12	10.64	10.65	10.95	12.06	9.84	11.22	11.24	10.23	11.94	12.52	11.80
Na <sub>2</sub> O	1.51	1.2	1.22	1.46	1.52	2.61	2.45	2.40	1.76	2.38	2.38	2.20	2.19	2.45	2.44
K <sub>2</sub> O	0.17	0.47	0.28	0.88	0.44	0.21	0.13	0.34	0.90	0.47	0.34	0.60	1.26	0.96	1.05
Total	97.12	97.7	98.00	96.24	98.43	98.22	95.76	98.06	98.49	95.36	96.48	98.41	97.80	98.12	97.38
<i>n</i>	2	9	8	4	12	5	7	6	6	4	5	6	6	8	4
H <sub>2</sub> O*	1.79	2.2	1.77	2.00	1.91	1.49	1.81	2.18	1.13	1.80	1.60	1.53	1.16	1.15	1.06
Cl	0.08	0.08	0.11	0.02	0.12	—	—	—	0.02	—	—	—	0.02	—	—
F	0.14	0.01	0.02	—	—	—	—	—	0.0	—	—	—	0.03	—	—
<i>Number of ions per 24 atoms of oxygen</i>															
Si	7.40	7.40	7.55	7.10	7.41	6.57	6.57	6.67	7.19	6.82	6.95	7.20	6.17	6.02	6.02
Al	0.60	0.60	0.45	0.90	0.59	1.43	1.43	1.33	0.81	1.18	1.05	0.80	1.83	1.98	1.98
Al	0.60	0.81	0.70	0.58	0.56	0.78	0.70	0.77	0.80	0.65	0.67	0.92	0.57	0.36	0.71
Fe	1.65	1.77	1.48	1.76	1.60	1.70	1.68	1.64	1.57	1.47	1.37	1.48	1.69	1.62	1.53
Mg	3.39	3.04	3.54	3.19	3.51	3.12	3.28	3.47	3.39	3.39	3.54	3.20	3.35	3.38	3.26
Ti	0.16	0.12	0.12	0.22	0.15	0.26	0.20	0.15	0.19	0.22	0.17	0.15	0.28	0.45	0.33
Ca	1.78	1.80	1.72	1.87	1.76	1.82	1.89	2.02	1.60	1.89	1.86	1.65	2.00	2.02	1.99
Na	0.45	0.36	0.36	0.45	0.45	0.74	0.77	0.73	0.37	0.773	0.71	0.54	0.66	0.74	0.75
K	0.03	0.09	0.05	0.18	0.09	0.03	0.04	0.05	0.17	0.09	0.07	0.01	0.25	0.19	0.21
<sup>x</sup> Fe	0.29	0.31	0.26	0.32	0.28	0.30	0.30	0.28	0.27	0.27	0.25	0.27	0.30	0.30	0.28
δD	-46	-40	-53	-44	-37	-73	-51	-65	-58	-58	-55	-58	-79	-73	-66

*Analyses in weight percent. n is number of microprobe analyses averaged. Fe determined as total FeO.*

*\*H<sub>2</sub>O was analyzed by volumetry.*

*Data for TDG-91 are from Bindeman (1993); analyses 31800, 31801 and 6870 (Avacha volcano) are from M. Puzantov, IVGG.*



Table 3. Microprobe analyses of selected biotites

Sample No.	V17-31/1	V17-13/1	V17-51/1	86-204/2	TDG-91/1	5504	5485	5440	7047	AA-1023	KT-619
SiO <sub>2</sub>	37.31	37.32	36.45	37.00	38.19	37.36	38.13	37.38	34.30	34.37	37.50
TiO <sub>2</sub>	3.76	3.62	4.35	3.73	3.85	3.70	4.09	4.12	9.89	9.15	2.98
Al <sub>2</sub> O <sub>3</sub>	14.17	13.93	13.76	14.31	14.01	13.96	14.98	14.01	14.67	13.45	16.70
FeO	16.28	14.08	15.03	15.81	13.61	16.99	14.42	15.92	15.89	16.47	11.10
MgO	13.34	14.97	14.43	13.38	15.57	16.06	14.90	15.01	10.38	10.76	17.90
MnO	0.34	0.27	0.16	0.53	0.46	0.33	0.35	0.37	0.17	0.16	0.08
CaO	0	0.01	0	0.02	0	0.93	0.21	0.60	0	0	1.30
Na <sub>2</sub> O	0.64	0.61	0.63	0.77	1.23	0.94	1.16	1.10	0.78	0.48	0.51
K <sub>2</sub> O	9.29	8.92	9.39	9.18	8.08	6.85	8.13	8.28	9.25	9.35	7.88
Total	95.13	93.83	94.30	94.73	95.00	97.02	96.37	96.79	95.33	94.19	95.95
<i>n</i>	7	8	5	8	7	5	8	6	7	7	4
H <sub>2</sub> O*	2.13	3.10	3.18	3.06	3.40	3.00	2.16	1.75	1.66	1.80	2.63
Cl	0.13	0.15	0.25	0.10	0.26	0.14	0.09	0.08	0.02	0.03	0.05
F	0.04	0.06	0.08	0.08	—	0.29	0.97	0.64	0.53	1.70	0.04
<i>Number of ions per 12 atoms of oxygen</i>											
Si	3.08	3.09	3.03	3.07	3.10	3.00	3.06	3.02	2.84	2.9	2.96
Al	0.92	0.91	0.97	0.93	0.90	1.0	0.94	0.98	1.16	1.10	1.04
Al	0.46	0.45	0.38	0.47	0.44	0.32	0.48	0.36	0.27	0.24	0.52
Fe	1.12	0.98	1.04	1.10	0.92	1.14	0.97	1.08	1.10	1.16	0.73
Mg	1.64	1.84	1.79	1.65	1.88	1.95	1.92	1.77	1.81	1.78	2.20
Ti	0.23	0.23	0.27	0.23	0.23	0.22	0.25	0.25	0.62	0.58	0.18
Ca	0	0.001	0	0.002	0	0.08	0.02	0.05	0	0	0.11
Na	0.10	0.10	0.10	0.12	0.20	0.14	0.18	0.17	0.13	0.08	0.08
K	0.98	0.94	1.00	0.97	0.84	0.70	0.83	0.85	1.00	0.98	0.79
<i>x</i> <sub>Fe</sub>	0.35	0.30	0.32	0.34	0.29	0.33	0.29	0.34	0.35	0.36	0.21
$\delta D$	-56	-61	-45	-47	-52	-68	-72	-108	-106	-80	-86

Analyses in weight percent. *n* is number of microprobe analyses averaged. Fe determined as total FeO.

excluded from further discussion.

There is no correlation between  $\delta D$  and either Cl or F for Hb; however, there are obvious trends for Bi. The Cl and F contents of Hb from Sredinny Ridge and the F content of Hb from Kuriles and East Kamchatka in most of the samples are very low, close to the detection limit of the microprobe spot analyses. The Hb samples with higher Cl concentrations from Kuriles and East Kamchatka scatter randomly in the range of 0.02 to 0.15 wt.%. There is a slight positive correlation in Bi samples between  $\delta D$  and Cl, whereas there is no  $\delta D$ -F correlation (excluding samples with a low H<sub>2</sub>O content from Sredinny Ridge).

The H<sub>2</sub>O-Cl-F correlations are shown in Fig. 3. The only clear trend in the data points is an increase in Cl content in Bi as the water content approaches its stoichiometric value. Dehydrated Bi from Sredinny Ridge also shows a high F content.

In summary, there is a slight difference in the  $\delta D$  values of Hb, and  $\delta D$  and volatile content of Bi between Kurile and East Kamchatka volcanoes. There is a significant difference in these values for Sredinny Ridge volcanoes, although low water content makes interpretation difficult. There is a tendency for the Bi most enriched in water to have a high  $\delta D$  value, low F content and high Cl content (above 1000 ppm). Hb with close to stoichiometric water content from the Kuriles and East Kamchatka contains about 500 ppm Cl, and low F. Even at high water concentrations (>1.5 wt.% for Hb and >3 wt.% for Bi) the variations in  $\delta D$  are large (90 and 50‰, respectively) and must be caused by processes other than syn- or post-eruptive oxidation and dehydration.

The main feature of these data is the presence of three overlapping, but clearly distinct clusters of points (see Fig. 2, the H<sub>2</sub>O- $\delta D$  plot, where all

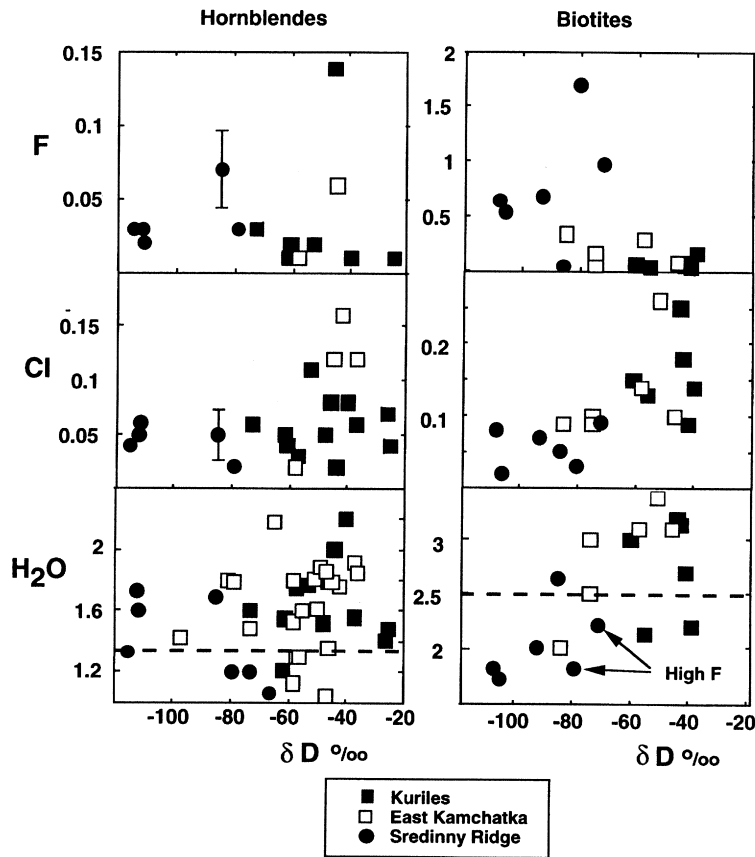


Fig. 2. Hydrogen isotope composition vs.  $H_2O$ , Cl and F content in Hb and Bi. Dashed lines on  $H_2O$ - $\delta D$  plots correspond to the  $H_2O$  content limit (1.3 wt.% for Hb and 2.5 wt.% for Bi) estimated from experiments of Miyagi and Matsubaya (1992); see text for discussion. Minerals with low water contents may be isotopically altered due to dehydration and oxidation processes. Error bars are shown for F ( $1\sigma$ ) and Cl ( $2\sigma$ ) on the Hb plots.

data are shown) with approximately equal ranges of  $\delta D$  values for Hb and Bi and showing a systematic enrichment in D from the Sredinny Ridge to Kurilian magmas.

#### *Correlations between $\delta D$ of minerals and their chemical composition*

Figure 4 shows the relationships between  $\delta D$  of Hb and Bi and their chemical composition. The main trends for Hb are a positive correlation between  $\delta D$  and  $SiO_2$  and a negative correlation between  $\delta D$ ,  $Al_2O_3$  and  $Na_2O$ . There is no correlation between hydrogen isotopic composition of a mineral and its Ti, Ca, Mg, and Fe contents and  $x_{Fe}$  values (only the  $\delta D$ -MgO plot is shown on Fig.

4). There are three separate fields of points for samples from the Kuriles, East Kamchatka and Sredinny Ridge, similar to the plots for volatile components (Fig. 2). One point for East Kamchatka with a maximum  $\delta D$  value in Hb represents Dikiy Greben volcano; this is the southernmost volcano in the Kamchatka peninsula, and is considered to belong to the Kurilian segment of the volcanic belt (Shantser and Shapiro, 1984). Therefore, the observed trends may be caused by the regional heterogeneity in both the chemical composition of the parent magmas and the isotopic composition of magmatic water during crystallization of minerals.

In contrast to Hb data, there are no general

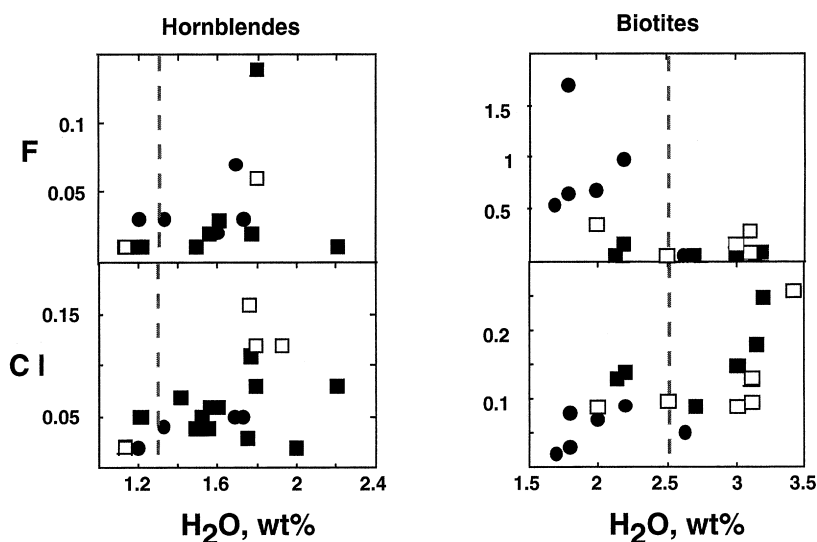


Fig. 3. Relationship between water, Cl, and F contents (wt.%) in hornblendes and biotites. The symbols are the same as in Fig. 2.

trends between chemical and isotopic composition for Bi (Fig. 4). Points for the Kuriles and East Kamchatka form a group with a slight decrease in  $\text{SiO}_2$  and MgO contents and an increase in  $\text{K}_2\text{O}$  content for the minerals enriched in D.

#### Variations of Hb $\delta D$ values due to magma degassing

In the magmatic environment, the main process causing D/H variations in OH-bearing minerals before, during and just after an eruption is magma (lava) degassing (Nabelek *et al.*, 1983; Taylor *et al.*, 1983; Taylor, 1986; Qin *et al.*, 1987; Anderson and Fink, 1989; Matsuhisa, 1992; Anderson *et al.*, 1995). Hb and Bi in magma are likely to be in isotopic equilibrium with water dissolved in the melt, and/or with aqueous fluid released from the magma (Suzuoki and Epstein, 1976; Kuroda *et al.*, 1988). The fractionation factor  $\Delta D$  (melt-vapor) was experimentally determined to range from 10 to 50‰ for melts of varying composition (Kuroda *et al.*, 1982; Ritchen *et al.*, 1986; Taylor, 1986; Dobson *et al.*, 1989), such that the residual water dissolved in the melt will be progressively depleted in deuterium with decreasing water content. Such an isotopic effect for “in situ” degas-

ing of magma was demonstrated using natural volcanic glasses or whole rock samples by Taylor *et al.* (1983), Newman *et al.* (1988), Taylor (1992), Anderson and Fink (1989), and Anderson *et al.* (1995). Thus the  $\delta D$  values of OH-bearing minerals from volcanic rocks should also reflect a variation in the  $\delta D$  composition of magmatic water.

We measured the  $\delta D$  values and water content of Hb for several samples from Shiveluch and Avacha volcanoes and also the water content (and  $\delta D$  values in a few samples) of the groundmass of the rocks containing these minerals. The pyroclastic rock groundmass consists mainly of glass with microphenocrysts, whereas the dome and dyke samples are “glassy” (Table 4). The results of  $\delta D$  and  $\text{H}_2\text{O}$  content of Hb and the groundmass versus  $\text{H}_2\text{O}$  content in groundmass are shown in Fig. 5. Both data sets for Hb and groundmass are consistent with the trends expected for magma degassing (Taylor, 1986, 1992). Isotope data for rock samples (“glass”) suggest an open-system degassing trend, with extrapolation indicating that the initial bulk water content in the magma was 4 wt.%, the initial  $\delta D$  value was between  $-40$  and  $-50$ ‰ and the melt-vapor isotope fractionation

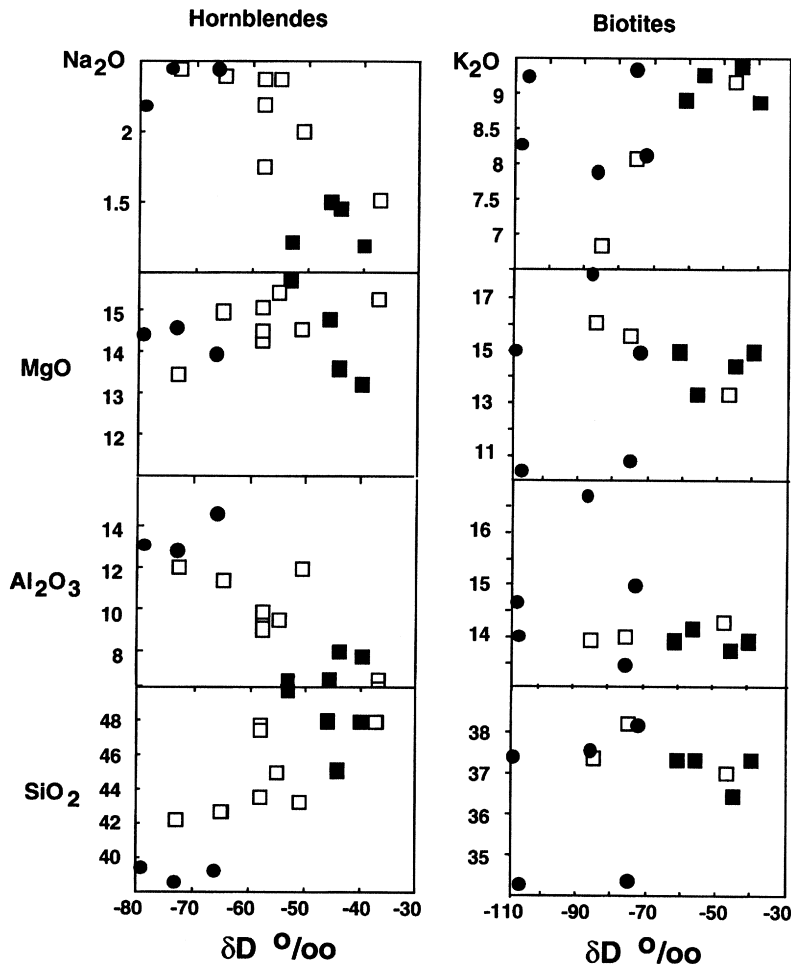


Fig. 4. Hydrogen isotope composition vs. chemical composition of minerals (Table 2). All concentrations are in weight %. The symbols are the same as in Fig. 2.

factor was 40‰ (Fig. 5). However, this value of the fractionation factor was experimentally determined at magmatic temperature only for dissolved water in form of hydroxyl groups, at a low (<0.5 wt.%) water concentration (Dobson *et al.*, 1989). At higher water contents, when part of water in the melt is present in the form of molecular water (Stolper, 1982), the bulk fractionation factor is lower, 20–25‰ (Taylor, 1986; Dobson *et al.*, 1989), and a combined (two-stage) open-system degassing curve with the same initial water content and initial  $\delta D$  values will be shifted slightly to higher  $\delta D$  values.

There is an uncertainty in both the initial wa-

ter composition and the bulk fractionation factor, but the estimated range of initial  $\delta D$  values for magmatic water is close to maximum values in the Avacha and Shiveluch Hb.  $\delta D$  values of Hb decrease with the loss of the bulk water content much more smoothly than those for groundmass. This could be due to a kinetic effect of isotopic exchange between minerals and water during eruption (during fast cooling re-equilibration is not complete). There is no correlation between water content in groundmass and coexisting Hb (Fig. 5). Therefore, the dehydration of Hb does not play a significant role in the variation of  $\delta D$ .

This example shows that the main process

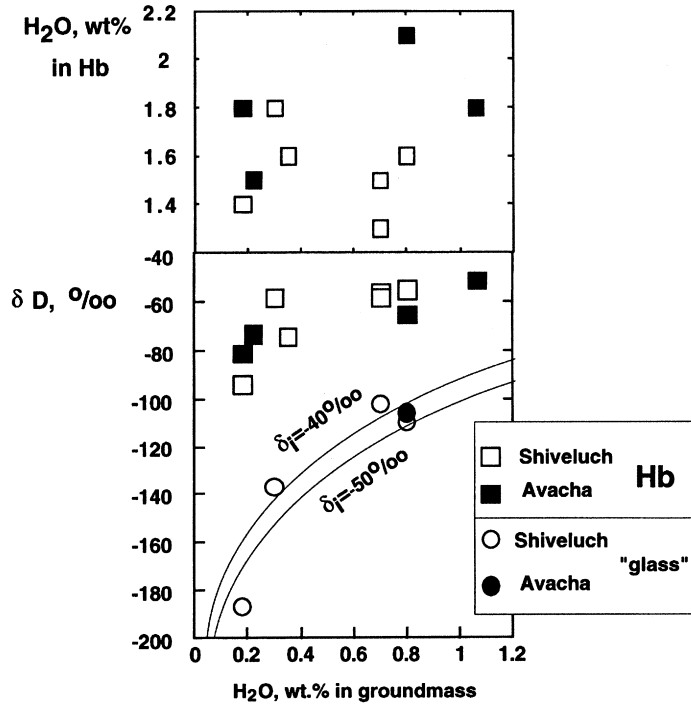


Fig. 5. Correlation between  $\delta D$  values in hornblende and groundmass ("glass") and  $H_2O$  content in ground mass of the host rocks, showing a trend of D depletion for minerals and groundmass corresponding to a loss of water in erupted rocks. Data for Shiveluch and Avacha volcanoes, East Kamchatka. The two curves shown were constructed using the fractionation factor  $\alpha_{vapor-melt(OH)}$  value of 1.040 (Dobson et al., 1989), an initial water content of 4 wt.% and initial  $\delta D$  values of magmatic water of  $\delta_i = -50$  and  $-40\text{‰}$ .

Table 4. Hydrogen isotope ratio and water content measured on Hb and groundmass from rocks of Shiveluch and Avacha volcanoes (abbreviations from Table 1)

No. of sample	Type of rock	Amphiboles		Groundmass	
		$\delta D$ (‰)	$H_2O$ (wt.%)	$\delta D$ (‰)	$H_2O^+$ (wt.%)
<i>Shiveluch volcano</i>					
M-1314	pyr	-58	1.8	-137	0.3
M-1315	pyr	-55	1.6	-106	0.8
M-1316	pyr	-56	1.3	-102	0.7
5706	pyr	-58	1.5	—	0.7
88/1	dome	-74	1.6	—	0.35
5711/3	dyke	-94	1.4	-184	0.18
<i>Avacha volcano</i>					
29232	dyke	-81	1.8	—	0.18
31801	dyke	-73	1.5	—	0.22
31800	pyr	-51	1.8	—	1.06
6870	pyr	-65	2.1	-110	0.80

controlling  $\delta D$  values of Hb in volcanic (erupted) rocks is the degassing of magma (lava). The most D-enriched samples are most representative of the initial magmatic  $\delta D$  value (see also Miyagi and Matsubaya, 1992). We conclude, therefore, that the relationship between water content and  $\delta D$  values of groundmass and coexisting Hb indicates the initial magmatic  $\delta D$  value for Shiveluch and Avacha Hb is in the range of  $-50$  to  $-40\%$ .

#### ISOTOPIC COMPOSITION AND ORIGIN OF MAGMATIC WATER IN THE KURILE-KAMCHATKA ARC

Hydrogen isotope data for Hb and Bi from Quaternary volcanic rocks of the Kuriles and Kamchatka range widely (Table 1, Figs. 2 and 4), reflecting a complex magmatic water genesis; causes of the variation may include the original magmatic source, magma degassing and post-magmatic alteration of minerals. We exclude  $\delta D$  values of minerals with less than "critical" water contents (1.3 wt.% for Hb and 2.5 wt.% for Bi; Fig. 2) and consider only the maximum  $\delta D$  for each volcano or group of volcanoes in close proximity as being representative of the  $\delta D$  value of magmatic water. This leaves us with the following ranges in  $\delta D$  for the three regions:  $-40$  to  $-25\%$  for Kurile islands,  $-46$  to  $-36\%$  for East Kamchatka, and  $-111$  to  $-85\%$  for Sredinny Ridge. Ranges for the Kuriles and East Kamchatka are similar, but with a systematic lighter maximum  $\delta D$  values for Kamchatkan volcanoes (Figs. 2 and 4).

The potential fluid sources participating in arc magma generation, and controlling the variations in isotopic composition of unaltered OH-bearing minerals, include: (1) MORB-type mantle water,  $\delta D = -75 \pm 5\%$  (Craig and Lupton, 1976; Kyser and O'Neil, 1984) and (2) water released from the subducted slab as a result of dehydration of the downgoing material. Giggenbach (1992) suggested the accumulated marine sediments are the main source of fluid that contributes to magma generation in the mantle wedge, with a  $\delta D$  isotopic composition of  $-30 \pm 10\%$ . On the other hand,

Ishikawa and Tera (1994) concluded on the basis of boron isotopic composition and B/Be systematics of the Kurile and Kamchatka volcanic rocks that the contribution from subducted sediments is  $<10\%$ , and that the main source of magmatic fluid is altered oceanic crust.

We measured the  $\delta D$  of water extracted from eight samples of altered submarine basalts of Kamchatsky Cape, which are considered to be a fragment of the oceanic crust incorporated into the accretionary complex (Zinkevich and Tsukanov, 1993). The alteration mineralogy is dominated by zeolites, amphiboles, chlorites and serpentine minerals. The average  $\delta D$  value for these basalts is  $-67 \pm 4\%$  and water content is  $2.8 \pm 0.3$  wt.%. Dehydration above  $400^\circ\text{C}$ , when the subducting slab is deep beneath the volcanic front (Toksoz *et al.*, 1971; Delaney and Helgeson, 1978; Van den Benkel and Wortel, 1987) should be accompanied by  $<20\%$  fractionation (Graham *et al.*, 1984; Cole *et al.*, 1987). Thus, if we assume that the subducted slab beneath the modern Kamchatka-Kurile arc was altered to a similar extent as the Kamchatsky Cape basalts, the hydrogen isotopic composition of water released from the subducted oceanic slab (but not from sediments) can be estimated to have a  $\delta D$  value  $\sim -50\%$ . This is lighter than the  $-30\%$  value of Giggenbach's "devolved" water, or the  $-25\%$  value of the "slab component" according to Poreda (1985) and Stolper and Newman (1994), but close to the  $-53\%$  estimated by Dobson and O'Neil (1987) by analysis of boninite glasses from the Mariana island arc.

Our range of  $-40$  to  $-25\%$  for magmatic water of Kurile islands lies within the range of Giggenbach's "devolved" water signature. A relatively high Cl content in Hb and Bi from Kuriles also suggests the involvement of subducted seawater in Kurilian magmas. By contrast, the  $\delta D$  range of  $-46$  to  $-36\%$  for East Kamchatka corresponds to a mixture of water from altered oceanic basalts and water from subducted sediments as a source of magmatic water for the East Kamchatka volcanoes. High-temperature volcanic gas condensates from Kurile islands are also systematically enriched in D in comparison with conden-

sates from Kamchatkan volcanoes ( $-17$  to  $-12\%$  for Kudryavy volcano and  $-22\%$  for Chorny volcano, Kuriles, against  $-30$  to  $-28\%$  for Avacha and Bezymianny volcanoes, Kamchatka (Taran, 1992; Taran *et al.*, 1995).

The identification of the water source for Sredinny Ridge volcanoes with a maximum  $\delta D$  value of about  $-80\%$  is not so straightforward. If these volcanoes are of a "continental" type (Volynets *et al.*, 1995), there may be a mantle source to account for the "light" water of  $\delta D = -60$  to  $-80\%$ . If these volcanoes are the "third" volcanic belt (back arc?) of the modern subduction zone (Tatsumi *et al.*, 1994), the magmatic water may be a mixture of mantle water and water released as a result of the decomposition of K-amphibole with unknown isotopic composition. And finally, if this belt is related to the older, presently inactive subduction zone (Legler, 1977; Volynets, 1994), the depletion in D of hydrous mineral is difficult to explain.

#### REGIONAL DISTRIBUTION OF Hb AND Bi HYDROGEN ISOTOPIC COMPOSITION VERSUS Sr AND Be ISOTOPIC VARIATIONS

Many authors have tried to establish a pattern in the Sr isotope composition of the magmatic products of the Kamchatka-Kurile arc, and to link this to the geological structure of the region (Vinogradov *et al.*, 1986; Bailey *et al.*, 1987; Zhuravlev *et al.*, 1985, 1987; Volynets *et al.*, 1988; Pokrovsky and Zhuravlev, 1991; Volynets *et al.*, 1995). A small but noticeable difference between frontal arc and rear arc was observed, with an increase of  $^{87}\text{Sr}/^{86}\text{Sr}$  to the north and to the south of central Kurile islands (Fig. 6). Tera *et al.* (1989) and Tsvetkov *et al.* (1991) reported the first data on the  $^{10}\text{Be}$  distribution in modern lavas over the complete Kamchatka-Kurile arc. The  $\delta D$  variations from Hb and Bi along the Kamchatka-Kurile region are compared with the corresponding distributions of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{10}\text{Be}$  values in Fig. 6. The central part of the Kuriles is characterized by the highest  $\delta D$ , low  $^{87}\text{Sr}/^{86}\text{Sr}$  values and high  $^{10}\text{Be}$  concentrations. The same rocks, from the same

submarine Kurilian volcanoes, contain both the maximum  $^{10}\text{Be}$  contents and the highest  $\delta D$  values of Hb. To the north and south of this area, towards Kamchatka and Hokkaido, the rocks are enriched in radiogenic strontium, but are depleted in  $^{10}\text{Be}$  and depleted slightly in deuterium. Sredinny Ridge rocks are characterized by relatively high strontium ratios and low  $\delta D$  values. There are no data on  $^{10}\text{Be}$  for these rocks.

The increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  can be explained by

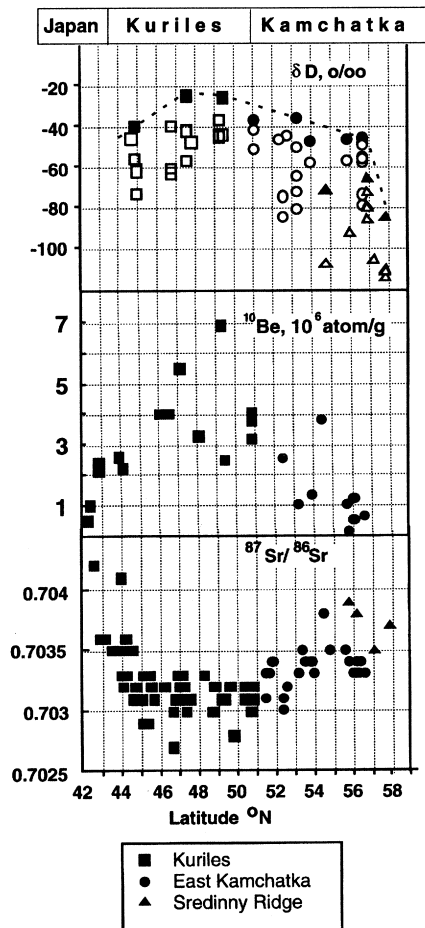


Fig. 6. Distribution of  $\delta D$  values in Hb and Bi along the Kamchatka-Kurile arc compared with Sr isotope and  $^{10}\text{Be}$  distribution in volcanic rocks. The sources of data for  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{10}\text{Be}$  are given in the text. Closed symbols connected by a dashed line correspond to maximum  $\delta D$  values for a volcano or volcanic group (see text).

the interaction between magma and rocks of the continental crust forming the basement of Kamchatka and Hokkaido. Tsvetkov *et al.* (1991) suggested that the lower  $^{10}\text{Be}$  concentration in modern volcanic rocks from East Kamchatka may have resulted from a slower ascent of magmas through thick continental crust (leading to radioactive decay), and by dilution of the original arc magmas with  $^{10}\text{Be}$ -free crustal material.

An alternative explanation could be a more appreciable contribution of the altered basalts to the lower  $^{10}\text{Be}$  content and higher Sr isotope ratio in magmas of East Kamchatka. This idea is partially supported by Pb isotope data. Pb isotope ratios in East Kamchatka volcanics are close to the MORB-type (low-radiogenic, Kersting and Arculus, 1995). This suggests that mantle and (or) oceanic basalts are contributing to the generation of magma (this seems to be particularly true for the Klyuchevskoy group of volcanoes, including Bezymianny).

For Kurile volcanoes the subducted sediments and their "devolved" water (Giggenbach, 1992), with  $\delta D$  close to  $-30\text{‰}$ , are likely to be one of the main sources of the volatiles. For the East Kamchatkan segment of the arc (to the north of Avacha volcano?; Fig. 6), a mixture of water from both sedimentary and altered basalts may supply to the magma generation zones; in this case, water having  $\delta D \sim -50\text{‰}$  from the oceanic crust is predominant.

The reason for such a heterogeneity of the subducted water sources may involve varying amounts (i.e., thickness) of the sediments subducted beneath the Kuriles and Kamchatka. And in turn, this could be related to a different age of the oceanic lithosphere which subducts north and south of the arc (less than 100 Ma to the north of Avacha volcano and greater than 130 Ma in the Middle Kuriles; Renkin and Sclater, 1988), and/or to a variable proportion of sediment that is subducted versus the amount that is incorporated into the accretionary wedge (Kita *et al.*, 1993).

The data for the Sredinny Ridge volcanoes suggests the depleted mantle as a main source of magmatic water, but lack of data on other isotopic

systems and a low water content in most Hb and Bi samples makes the interpretation difficult.

## CONCLUSIONS

There is a large scatter of  $\delta D$  values for Hb and Bi from Quaternary volcanic rocks along Kamchatka-Kurile volcanic belts. The principal trends recognized from the data presented include: (1) There is no correlation between  $\delta D$  values of minerals and their chemical composition, including Cl and F contents. All trends are caused by regional variations in the major element chemistry (Hb) or Cl and F contents (Bi). (2) There is a relation between  $\delta D$  values and the degree of magma degassing for Hb from Shiveluch and Avacha, the largest andesitic volcanoes in Kamchatka. (3) We did not find trends related to the alteration (oxidation and hydration) of minerals.

The Hb and Bi that are most enriched in deuterium for a volcano or a volcano group and have the highest water contents are most representative of the isotopic composition of the initial magmatic water. Magmatic water for the majority of the Kurile volcanoes has a hydrogen isotopic composition ranging from  $-40$  to  $-25\text{‰}$  and could be derived mainly from subducted oceanic sediments. For East Kamchatkan volcanoes the magmatic water is slightly depleted in deuterium ( $-46$  to  $-37\text{‰}$ ) and corresponds to a mixture of "devolved" water from subducted marine sediments and water released from altered basalts of oceanic crust.

The regional variation of maximum D/H ratios for Hb and Bi agrees well with that for trends of the Sr isotopic composition and the  $^{10}\text{Be}$  content in volcanic rocks throughout the modern Kurile-Kamchatka arc. The source of fluid with lower  $\delta D$ , higher Sr isotope ratios and low  $^{10}\text{Be}$  content may be altered oceanic crust; if so, it can be concluded that beneath East Kamchatka and the Kuriles there is a variable contribution to the "subducted fluid" from subducted marine sediments and altered basalts of the second layer of the oceanic crust.



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