Volcanic-related alteration and geochemistry of Iwodake volcano, Satsuma-Iwojima, Kyushu, SW Japan

S. Hamasaki

Research Center for Deep Geological Environments, Geological Survey of Japan, AIST, Central 7, 1-1-1 Higashi, Tsukuba 305-8567, Japan

Satsuma-Iwojima is located near the northwestern margin of Kikai caldera, and active Mt. Iwodake is one of the post-caldera cones. Inside the summit crater of about 300 m diameter and 50 m depth, volcanic gas with maximum temperature >800°C is discharged. At Iwodake, the rhyolite is strongly altered by volcanic vapor and acid hydrothermal solution inside and around the summit crater. The main alteration mineral assemblages at surface include quartz-tridymite-cristobalite, tridymite-cristobalite-alunite and cristobalite-(alunite) inside the summit crater and on the ank. Molybdenum blue sublimates are forming at the surface around high-temperature fumaroles inside the summit crater. The ground surface is commonly cemented by amorphous silica or cristobalite. The original rhyolite with $SiO_2 = 71$–72 wt% has been leached, resulting in a rock with maximum $SiO_2 = 97$ wt%. All major elements are leached except for TiO_2. Although LIL (large-ion lithophile) elements have leached, HFS (high eld-strength) elements appear to be immobile. Rare earth elements are considered to have been soluble as a complex with sulfate mainly in the low pH hydrothermal uid during the silici cation of the rhyolite. There is abundant Mo, Pb, Zn, Bi, Sn and much lower As in the volcanic sublimates and altered rocks inside the summit crater. By contrast, the rocks near the acid springs at the foot of the cone are As-rich, but with lower Pb, Zn, Bi and little Mo in comparison with the summit. The fractures and fumarole locations around Iwodake summit and erosional ridges on the anks re ects a NE-SW trend that is parallel to the trace of the outer ring of Kikai caldera. In addition, this is the same direction as the alignment of Shin-Iwojima, Iwodake and Inamuradake, all of which are post-caldera cones. Zones of structural weakness parallel to the caldera rim may exist, acting as pathways for the ascending volcanic gases and hydrothermal solutions. Fumarolic activity appears to be shifting gradually to the eastern part of the summit crater.

1. Introduction

Satsuma-Iwojima is an active volcano island located 40 km south of the Satsuma Peninsula in Kyushu, southwest Japan. The island is part of the Quaternary volcanic front of the Ryukyu arc. The volcanic island lies on the northwestern margin of the Kikai caldera (Matsumoto, 1937), a submarine caldera about 17 km in diameter (Fig. 1). Two post-caldera volcanoes, Inamuradake and Iwodake, occur on Satsuma-Iwojima. Iwodake is the largest volcano, with a roughly conical shape, an elevation of 704 m, and a summit crater 300 m wide and 50 m deep. Many fumaroles exist within and outside the crater, and on the volcano ank. Native sulfur was historically mined inside the crater of Iwodake, and silica stone was quarried near the summit until 1996. Various aspects of Iwodake have been long studied, for example, geology (Matsumoto, 1937; Ono *et al.*, 1982), alteration mineralogy (Yoshida *et al.*, 1976; Kimbara *et al.*, 1977), rock chemistry (Ueda and Itaya, 1981; Notsu *et al.*, 1987), the composition of the volcanic gas and hot springs (Kamada *et al.*, 1974; Nogami *et al.*, 1993; Shinohara *et al.*, 1993; Hedenquist *et al.*, 1994a) and isotopic geochemistry (Matsuo *et al.*, 1974; Matsubaya *et al.*, 1975). Saito (1998)

published a topographical map of the summit crater area.

Alteration mineral assemblages are helpful in recording the volcanic activity and its characteristics. In addition, the behavior of metals and other components related to volcanic activity provides information on the hydrothermal processes related to the formation of ore deposits (Hedenquist *et al.*, 1994a). This study contributes additional information on the mineralogy and geochemistry of alteration of Iwodake, and the geological structure inside and around the summit crater.

2. Geological Setting

The geology of the island is dominated by volcanic products related to the caldera (Fig. 1(c)). The caldera boundary intersects the island NE-SW. Pre-caldera units occur outside the caldera margin and consist of andesite-basalt (Yahazuyama) and rhyolite lavas (Nagahama). Pyroclastic products of the caldera-forming eruption (Koabiyama and Takeshima pyroclastic ow deposits) are preserved in the northwest part of the island. The eruption that accompanied the Takeshima pyroclastic deposit also ejected "Akahoya" about 6300 years ago, a well-known ne air-fall ash that is used as a standard tephra in Japan (Machida and Arai, 1978). Post-caldera units include the basaltic Inamuradake volcano and rhyolitic Iwodake volcano. Iwodake is a steep rhyolite ow-dome complex with bedded volcaniclastics, talus and a few air-fall scoria and pyroclastic ow deposits. The [14]C
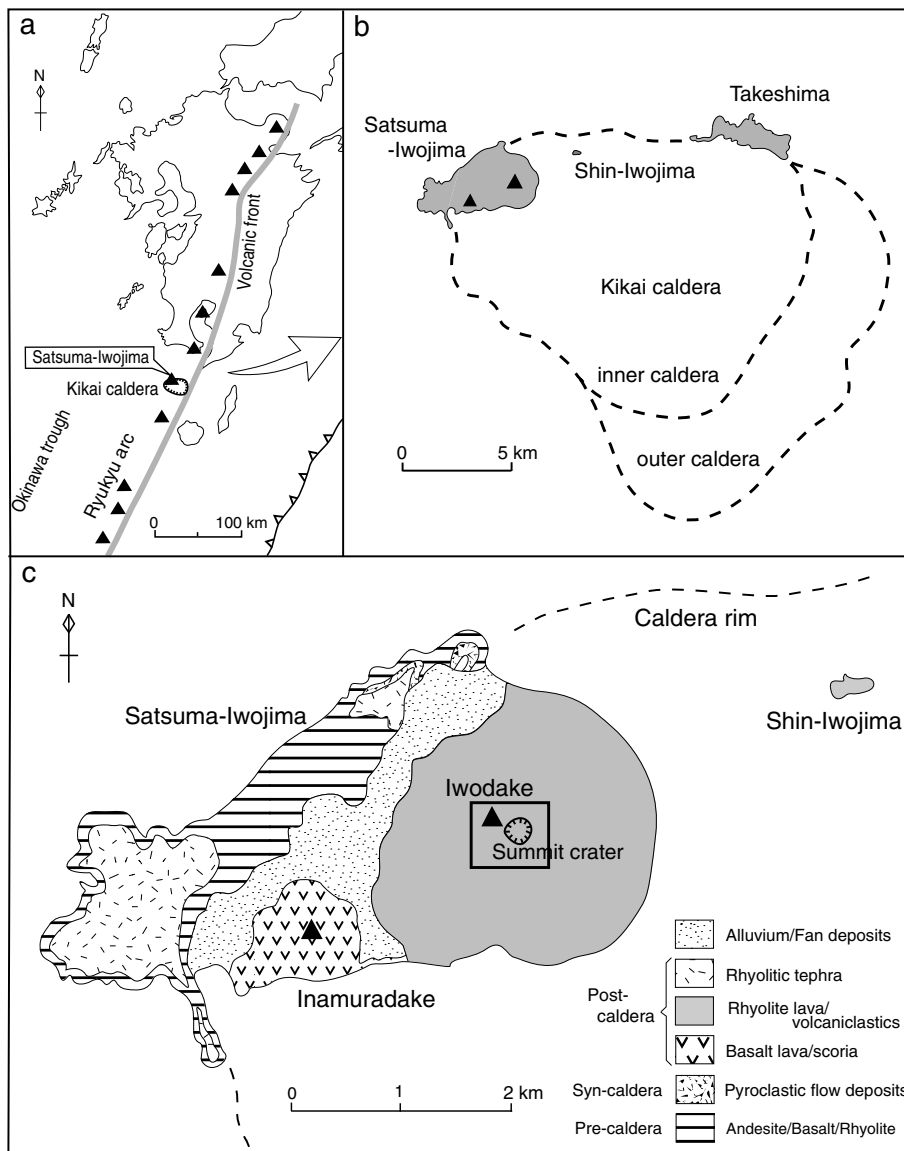
Fig. 1. a, b) Location of Quaternary volcanic front of Ryukyu arc, Kikai caldera and Satsuma-Iwojima. Kikai caldera consists of inner and outer rims. c) Geological map of Satsuma-Iwojima (simplified from Ono *et al.*, 1982). Square shows area of Figs. 2 and 3.

ages of the pyroclastic flow deposits are 1500–1300 yrBP (Ono *et al.*, 1982) and 500–600 yrBP (Kawanabe, 2000). Iwodake rhyolite overlies the Inamuradake basalt that finished eruption at the latest 3000 years ago. According to these geological and geochronological data, Iwodake started to erupt on a large scale about 3000 years ago, and subsequently erupted several times with lava, volcaniclastics and pyroclastic flows. According to an ancient document, the fumarole activity atop Iwodake has continued for more than 1000 years.

3. Distribution and Mineral Assemblages of Alteration

Numerous fumaroles exist in and around the summit crater of Iwodake (Fig. 2). The temperature of the fumaroles varies from about $100°C$ to $>800°C$ (Shinohara *et al.*, 1993). The vapor in the fumaroles consists mainly of water and volcanic gases such as SO_2, HCl, CO_2, H_2S and

HF (Matsubaya *et al.*, 1975). The distribution of the fumaroles is focused in the NE-SW direction (Fig. 2). The original rock of Iwodake is rhyolite lava and volcaniclastic products. The alteration minerals in the main samples collected for this study are listed in Table 1. The main alteration mineral zones and mapped structures in the summit area, including the Ohtanibira and Kotake silica quarry remnants, are shown in Fig. 3.

3.1 Inside the summit crater

Inside the summit crater, the fumaroles are widely distributed. The Ohachi vent (Shinohara *et al.*, 1999) has been active since 1996, with a diameter increasing to 50 m, and now degasses the largest amount of volcanic gas. The maximum temperature of the vent was $862°C$ in 1997 (G.S.J. and Kyoto University, 1998). The texture of the altered rock here poorly preserves that of the original ryholite, and very strongly residual silicified rocks are porous to friable. The residual silicified rock is composed mainly of
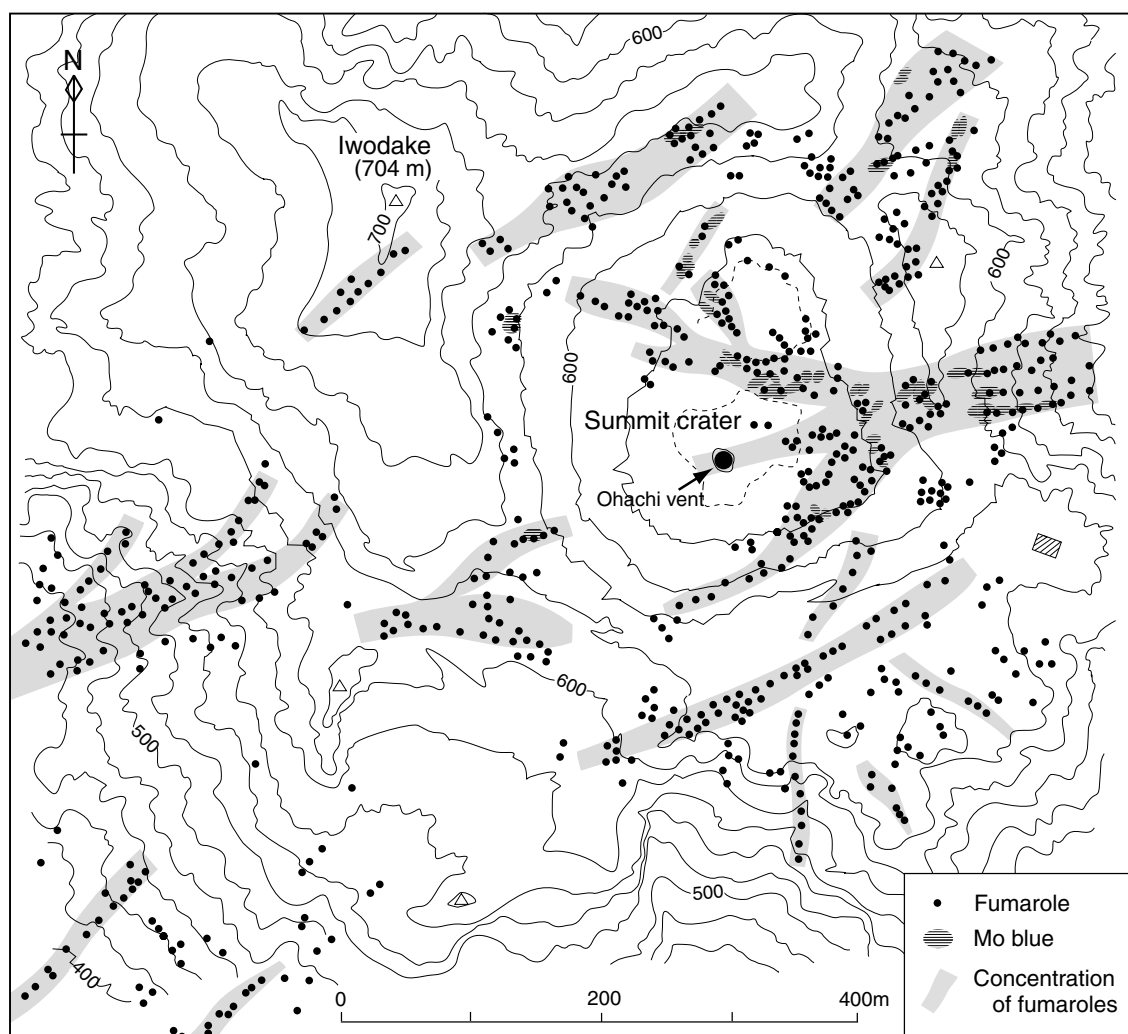
Fig. 2. Distribution of fumaroles around the Iwodake summit crater. Topographic map is from Saito (1998).

quartz, α-cristobalite, tridymite (low-temperature type) and native sulfur. A blue sublimate, called molybdenum blue, covers residual silicified rock adjacent to high-temperature fumaroles (Fig. 4(a)), and quartz is also more abundant. Molybdenum blue is an amorphous hydrate with Mo^{5+} and Mo^{6+} (Yoshida et al., 1972) that has been documented near high-temperature fumaroles. Compared to the center of the crater, the walls of the crater contain less quartz and more tridymite. Alunite and clay minerals have not been documented inside the crater or on the crater wall.

3.2 Outside the summit crater

Numerous fumaroles also occur outside the summit crater. The main alteration minerals in this area are α-cristobalite and tridymite, together with lesser amounts of native sulfur, sometimes alunite and rare quartz. Overall, residual silicification outside the crater is less intense than inside. By contrast, alunite is abundant outside of the crater. On the ground surface clay minerals were not found around the summit crater.

Outside the crater walls, the abandoned Ohtanibira and Kotake silica quarries provide good views of the altered rhyolite. Alunite filling the matrix of talus is also commonly observed at the quarries. At an outcrop in Kotake,

located about 10 m under the original surface at an elevation of 620 m, similar amounts of cristobalite and alunite are present. At an outcrop in Ohtanibira, located more than 50 m under the original surface at an elevation of 600 m and farther from the summit crater rim, alunite is much more abundant.

3.3 Flank

Some fumaroles also occur on the flank of the volcano, although they are fewer than inside and around the summit crater (Fig. 2). Compared with the summit, flank fumaroles seem to consist largely of water vapor, based on their odor. The alteration mineralogy on the flank is mostly cristobalite, and sometimes accompanied by amorphous silica, rare alunite and kaolinite.

3.4 Ground surface around the crater and the flank

Around the summit crater and on the flank of Iwodake, silicification, as silica addition, of volcaniclastics, ash and talus is observed on the surface far from fumaroles (Fig. 4(b)). Although the thickness of the silica-added layer is variable, it is usually greater than several tens of cm. Silicification becomes weaker at lower elevations. The silica-added layer is composed of amorphous silica and cristobalite.
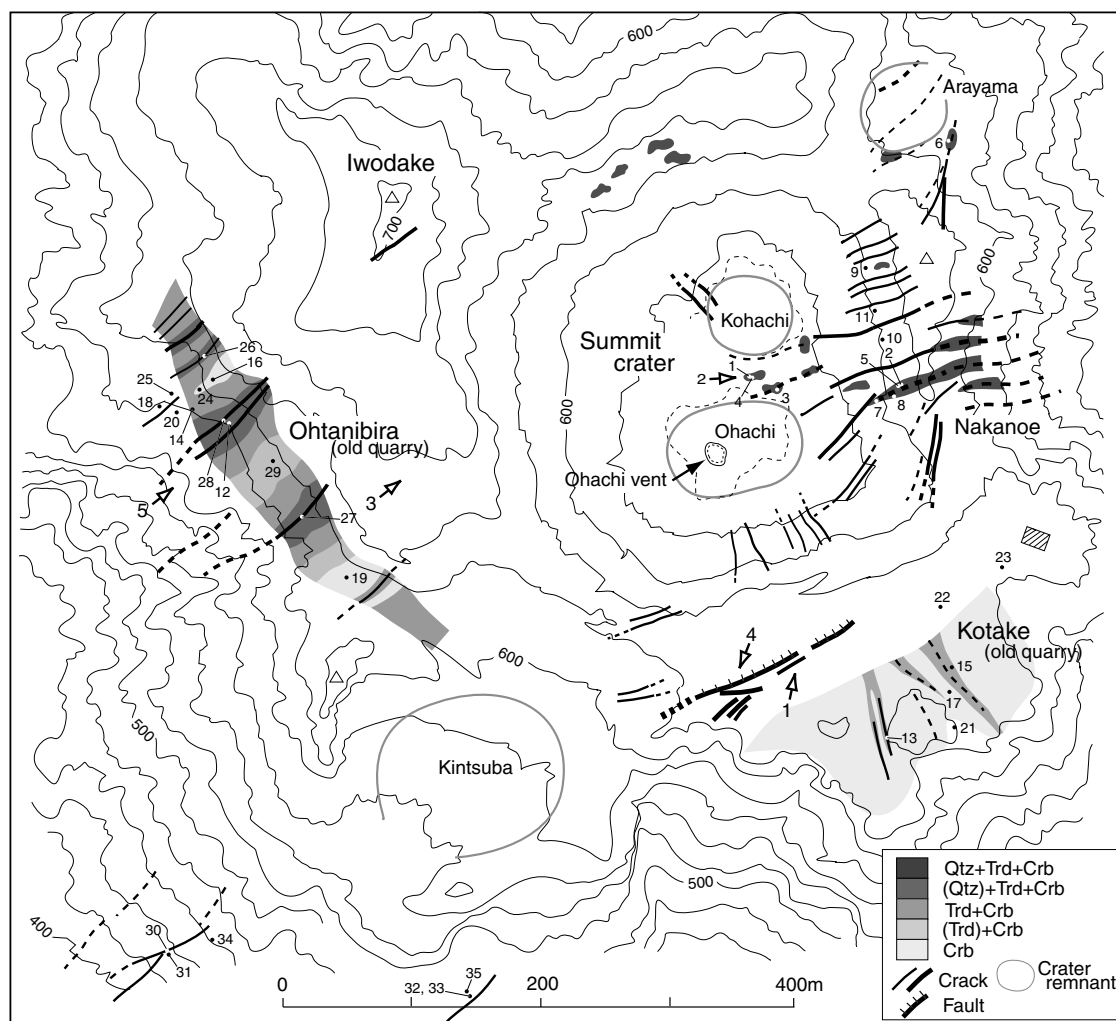
Fig. 3. Distribution of fractures and strongly altered zones around the Iwodake summit crater. Minerals in legend show alteration mineral assemblages. Numbered arrow shows photograph number and angle of Fig. 4. Thick and thin lines refer to different widths of fractures, and broken line shows an inferred fracture. The fault near arrow no. 4 indicates the northern downfaulted side.

3.5   Fractures

There are many fractures with varying widths inside and around the summit crater. Although the fractures are typically less than 20 cm wide, some open fractures up to 60 cm wide are offset about 80 cm down to the north on the southern side of the crater rim (Fig. 4(c)). Some groups of sulfur chimneys are also present along the fractures (Fig. 4(d)).

Fractures occur in two principal directions, NE-SW and NW-SE. The NE-SW direction is much clearer. The Ohtanibira and Kotake silica stone quarries expose cross sections more than 250 m and 200 m wide and about 40 m and 15 m high, respectively. In addition, there is a good cross section in the Nakanoe area along the eastern wall inside the summit crater. There are many NE-SW fractures in these areas, which acted as conduits of hydrothermal solution, and alteration zones have developed vertically along the fractures (Figs. 3 and 4(e)). The alteration zoning outward from the central fracture is characterized by the following pattern: (quartz)-tridymite-αcristobalite, tridymite-αcristobalite, (tridymite)-αcristobalite and αcristobalite. Quartz occurs locally along open fractures. In addition,

many amorphous silica veins fill cracks up to 3 cm wide in the silicified rocks. There are also NW-SE fractures inside and around the summit crater, but they are few and not as abundant as the NE-SW fractures.

4.   Chemistry of Altered Rocks

Table 2 shows the major and trace elements, including rare earth element (REE) content, of altered rock, and Table 3 shows the metal content of selected samples. Unaltered rocks and a variety of altered rocks representative of various locations inside and around the summit crater of Iwodake volcano were chosen for the purpose of understanding the chemical behavior of elements during hydrothermal alteration, including rocks from the flank, near fractures and molybdenum blue-bearing rock.

4.1   Major element

Figure 5 shows major element variations versus SiO_2. Unaltered rocks of Iwodake are rhyolite with 71–72 wt% SiO_2. The rhyolite has been leached of most components except silica by acidic magmatic-hydrothermal fluids, with the residual silica reaching 97 wt% SiO_2. The Al_2O_3, Fe_2O_3 and

Table 1. Alteration mineral assemblages inside and around the summit crater and on the flank of Iwodake.

No.	Sample	Locality	occurrence	S	Qtz	Trd	αCrb	Alu	Am. Si	Pl
1	SIJ-2	Inside summit crater	Mo blue center	+	+++	++++	++++			
2	022403-1	(central part)	Mo blue center	+	++++	++	++			
3	022409-1		Mo blue center		++	+	+++			
4	SIJ-1		Mo blue		++	+++	+++			
5	022403-2		Mo blue	−	+++	++	+			
6	022401-3		Mo blue (Arayama)		++	++	++			
7	98110813	Inside summit crater	Fine crumbly silicified rock	−	+++	+++	+++			
8	98110923	(crater wall)	Fine crumbly silicified rock	+	+++	+++	+++			
9	98110916		Coarse crumbly silicified rock	+	+	++++				
10	98110919		Strongly silicified rock	+	++	++++	+++			
11	98110917		Medium silicified rock	+	+	−	+++			
12	98110801	Around summit crater	Strongly silicified rhy. lava	−	+	+++	+++			
13	99112111		Strongly silicified rhy. lava			+	++++		−	
14	98110802		Medium silicified rhy. lava			++	++++		+	
15	99112104		Medium silicified rhy. lava			++	+++		+	
16	98110805		Weakly silicified rhy. lava				+++		−	
17	99112103		Weakly silicified rhy. lava			++	+++		+	
18	98110804		Weakly silicified rock			+	++++		+	
19	98111011		Weakly silicified rock				+++		+	
20	98110803		Unaltered rhyolite lava			+	+++			++
21	99112102		Unaltered rhyolite lava		+	++	++			++
22	98111113	Below the surface	Sediment by meteoric water			−	+++	+	−	
23	98110811-1	(Kotake; <10 m)	Matrix of talus breccia				+	+++		
24	98111134	Below the surface	Matrix of talus breccia				+	++++		
25	98111121	(Ohtanibira; <40 m)	Matrix of talus breccia				−	++++		
26	99112011′	Along fracture	Strongly silicified rock		+	+++	+++		−	
27	98111014′	(around summit crater)	Crumbly silicified rock		++++	++	++		−	
28	98110801′	Amorphous silica vein	White vein						++	
29	98111005	(around summit crater)	White vein	−		−	+++		+	
30	99112004	Amor. silica. v. (flank)	White vein			−	+		++	
31	99112003	Flank	Coarse crumbly silicified rock		−	−	++++		−	
32	98111004		Coarse crumbly silicified rock		−	−	++++		−	
33	98111003		Matrix of talus sediment				+++	−	+	
34	98111001		Matrix of talus sediment				++++		−	
35	98111003′		Layered boundary of talus sediment				+++		+	

++++: abundant, +++: common, ++: local, +: rare, −: very rare.

S: native sulfur, Qtz: quartz, Trd: tridymite, αCrb: α-cristobalite, Alu: alunite, Am. Si: amorphous silica, Pl: plagioclase.

K_2O all show similar patterns of depletion. These components decrease with increasing SiO_2 content as leaching becomes more intense. The CaO, Na_2O, MgO and MnO contents also show common depletion patterns, and are totally leached at about SiO_2 85 wt%. P_2O_5 is not fully depleted, and the TiO_2 content in lava remains constant. These data indicate that all major elements except for TiO_2 and P_2O_5 have been essentially leached at a SiO_2 content of 90 wt%.

4.2 Trace elements

Figure 6 shows selected trace element variations versus SiO_2 for the same altered samples as shown in Fig. 5. The Sr, Rb, Sc, Y, Th and V all decrease with increasing silica content. Compared with the major elements, the decrease is more gradual with full depletion not occurring until maximum 97 wt% SiO_2. The Ba, Zr, Nb and Hf show no clear pattern or is almost constant.

4.3 REE

Figure 7 shows REE patterns for altered rocks. Patterns in Fig. 7(a) are chondrite-normalized, and patterns in Fig. 7(b) are normalized to unaltered rhyolite from Iwodake. Unaltered to strongly silicified rocks of rhyolite samples lava-1 and lava-2 show a different of degree alteration in the same lava unit. Two unaltered samples show identical chondrite-normalized REE patterns. The chondrite-normalized REE patterns of all altered samples show almost equal depletion in all REE except for Eu, which decreases more rapidly with increasing intensity of silicification. In the same samples, the negative Eu anomaly, which is weak in the unaltered rhyolites, becomes greater. The unaltered rhyolite-normalized patterns show the transition of the REE depletion well, particularly Eu. It appears that Eu is almost entirely leached once the SiO_2 content reaches about 90 wt%. These patterns also show that leaching of light REEs is slightly greater than the heavy REEs.

4.4 Metal contents

The concentrations in ppm of several metals for representative samples are shown in Fig. 8. There is a greater degree of variability among metals than major or trace el-
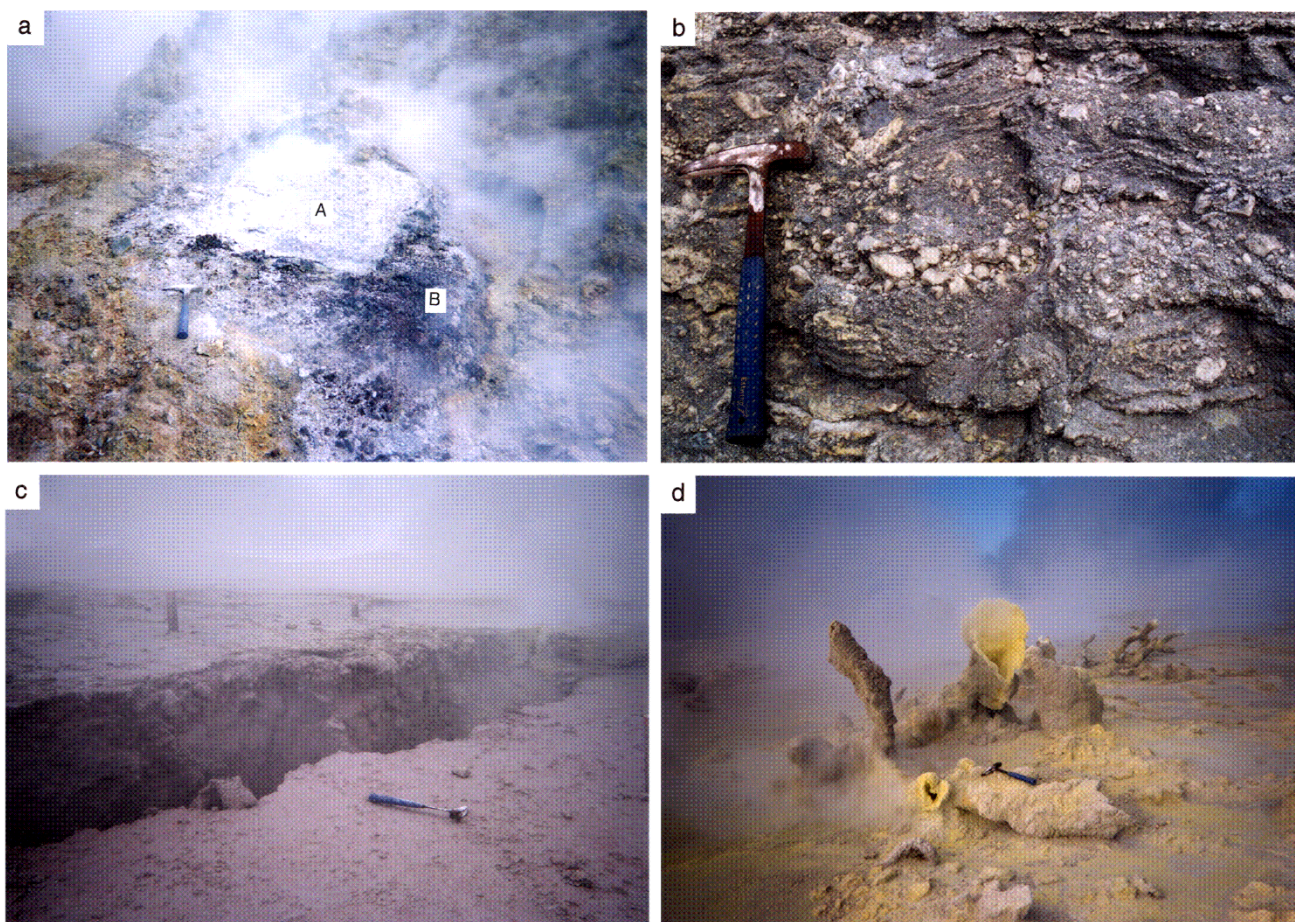
Fig. 4. a) Molybdenum blue sublimate inside the summit crater. A is the white central part having an abundant amount of secondary quartz, B is a typical blue part where many metals precipitated. b) Layered volcaniclastic rocks with matrix cemented by amorphous silica on the surface. c) Fault with ENE direction on the south side of the summit crater rim. The fault opened to a maximum width of about 60 cm, and the northern side has a maximum of 80 cm downfault. d) A group of sulfur chimneys developed in the ENE direction on the south of the summit crater.

ements. The highest concentrations occur in samples from molybdenum blue sublimate areas (Figs. 8(a), (b)). In these samples, Hg, As, Sn, W, Mo, Pb, Zn and Bi are all high, with the last four showing concentrations of several hundred ppm. In the silicified breccia inside the crater (Fig. 8(c)), Mo, Pb, Bi and As are strongly enriched relative to the unaltered rhyolite (Fig. 8(f)). Amorphous silica (Fig. 8(d)) has high Zn, some Pb and no other metals. Strongly altered rhyolite lava (Fig. 8(g)) has a small amount of Zn, Pb, Cu and Mo with no other elements compared with the unaltered rhyolite lava. Samples of silicified matrix of talus near the pH 1.5 Higashi hot spring have abundant Fe and Hg, and anomalous amounts of As, Pb and Zn. Hedenquist *et al.* (1994a) reported several ppm As, Pb, Mo, Sn, slightly lower Zn, 10^{-2} ppm Sb, Cu and 10^{-6} ppm Au in high-temperature ($>700°$C) fumarolic vapor. The relative contents of Pb, Zn, Mo and Sn, except for As and Mo, in the molybdenum blue sublimates are almost similar to their proportions in the high-temperature fumaroles, with the former showing concentrations of 10 to 10^3 times the latter.

5. Discussion and Conclusion
5.1 Alteration minerals
Figure 9 shows assemblages of the alteration minerals inside and around the summit crater and on the flanks of Iwodake. Overall, the alteration mineral sequence of quartz-tridymite-cristobalite $\rightarrow$ tridymite-cristobalite-alunite $\rightarrow$ cristobalite-(alunite) is zoned from the inside to the outside of the summit crater and down the flank, respectively. Quartz is dominant particularly near the molybdenum blue sublimates. These assemblages, except for alunite, are also observed zoned around fractures (Figs. 3 and 4(e)). Therefore, the intensity of alteration depends on the location with the summit crater, and proximity to fractures inside and outside the crater. In general, native sulfur occurs as a volcanic sublimate near the fumaroles regardless of location inside or outside the summit crater. Molybdenum blue sublimates are produced only near high-temperature fumaroles, as mentioned above. Yoshida *et al.* (1972) calculated thermodynamically that a fumarole temperature of more than 500°C is necessary to form the molybdenum blue, which is consistent with its occurrence.

Thus, surface alteration at Iwodake is classified mainly into two types. The first type of alteration occurs inside and around the summit crater and formed by strongly acid solution or fumarole, consisting of residual silica accompanied by native sulfur and molybdenum blue. The strongly acid hydrothermal solution is formed by condensation of

Table 2. Chemical composition of major, trace and rare earth elements of representative altered whole rocks. Abbreviation of rhy. means rhyolite.

|	Unaltered rhyolite lava		Weakly silicified rhy. lava		Medium silicified rhy. lava		Strongly silicified rhy. lava		Fine crumbly silicified rock (crater)		Coarse crumbly silicified rock (ank)		White center of Mo blue	
Sample No.	98110803	99112102	98110805	99112103	98110802	99112104	98110801	99112111	98110813	98110923	99112003	98110004	022403-1	022409-1
No. (Table 1)	20	21	16	17	14	15	12	13	7	8	31	32	2	3
SiO_2 (wt%)	71.09	71.91	83.70	90.34	91.24	90.12	97.04	92.55	95.58	94.61	90.38	87.96	85.71	97.50
TiO_2	0.60	0.59	0.75	0.74	0.65	0.80	0.72	0.73	0.68	0.69	0.94	1.24	0.85	0.22
Al_2O_3	14.29	14.22	6.04	0.93	1.12	1.03	0.45	1.11	1.41	1.26	2.81	3.95	2.42	0.73
Fe_2O_3	3.10	3.18	1.00	0.34	0.17	0.19	0.09	0.16	0.15	0.14	0.28	0.39	0.51	0.09
MnO	0.06	0.06	0.02	0.01	<0.01	<0.01	0.00	<0.01	<0.01	0.00	0.01	0.01	<0.01	<0.01
MgO	0.43	0.55	0.05	0.02	<0.01	0.01	<0.01	0.02	<0.01	<0.01	0.03	0.04	0.03	<0.01
CaO	2.50	2.61	0.27	0.05	0.05	0.05	0.02	0.07	0.04	0.04	0.22	0.18	0.69	0.04
Na_2O	4.39	4.29	0.35	0.21	0.29	0.25	0.15	0.22	0.17	0.17	0.33	0.40	0.27	0.04
K_2O	2.10	1.98	0.62	0.14	0.06	0.04	0.05	0.08	0.11	0.08	0.19	0.46	0.74	0.13
P_2O_5	0.11	0.11	0.03	0.02	0.03	0.02	0.01	0.02	0.03	0.02	0.04	0.06	0.04	0.03
LOI	1.28	0.55	7.55	7.35	6.67	7.64	1.88	5.47	2.29	3.42	4.96	5.74	8.61	1.48
Total	99.95	100.05	100.38	100.15	100.29	100.17	100.42	100.43	100.46	100.43	100.19	100.42	99.85	100.25
Rb (ppm)	61	54	58	4	15	6	<2	8	8	4	20	36	87	7
Sr	180	184	36	28	12	24	4	13	9	9	24	45	57	4
Zr	182	177	216	190	123	121	60	146	185	184	197	339	205	113
Ba	416	396	439	488	510	420	435	330	494	461	941	651	645	66
Y	37	41	29	18	6	9	2	8	5	5	9	14	12	4
Nb	5	5	6	6	6	6	5	6	6	6	9	7	5	<1
Hf	5.1	5.1	6.0	5.6	4.3	3.9	1.4	4.3	5.2	5.1	5.6	8.4	5.1	2.7
Ta	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.8	0.5	0.6
Sc	15	15	6	2	2	1	<1	1	3	2	2	4	3	<1
V	33	36	12	5	10	9	6	8	8	7	7	13	12	<5
Co	2	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ga	14	13	6	1	1	1	<1	1	2	1	2	5	3	1
Ge	<1	<1	<1	<1	<1	<1	<1	<1	15	<1	<1	<1	<1	<1
Tl	0.3	0.2	0.7	<0.1	0.3	<0.1	<0.1	<0.1	0.9	1.5	0.2	0.5	35.0	54.6
La	15.5	16.2	12.2	5.3	2.6	6.5	0.5	2.3	1.6	1.5	4.2	8.7	5.5	0.6
Ce	35.3	36.7	28.1	10.5	5.2	10.5	0.7	6.6	2.6	2.4	8.5	18.0	10.8	1.2
Pr	4.34	4.45	3.29	1.33	0.50	0.99	0.06	0.63	0.25	0.24	0.99	2.04	1.22	0.14
Nd	19.3	20.0	13.8	6.2	1.9	4.0	0.3	2.6	1.0	1.0	4.2	8.7	5.1	0.6
Sm	4.5	4.9	3.3	1.9	0.5	1.1	<0.1	0.8	0.3	0.3	1.1	2.0	1.3	0.2
Eu	1.25	1.22	0.46	0.12	0.09	0.20	<0.05	0.18	<0.05	<0.05	0.15	0.32	0.32	<0.05
Gd	4.6	5.3	3.4	1.9	0.5	1.1	<0.1	0.8	0.4	0.4	1.1	2.0	1.3	0.2
Tb	0.9	1.0	0.7	0.4	0.1	0.2	<0.1	0.2	<0.1	<0.1	0.2	0.4	0.3	<0.1
Dy	5.8	6.3	4.2	2.8	0.8	1.5	0.2	1.1	0.6	0.6	1.3	2.2	1.7	0.4
Ho	1.2	1.4	0.9	0.6	0.2	0.3	<0.1	0.2	0.2	0.1	0.3	0.4	0.4	<0.1
Er	4.0	4.3	3.1	2.0	0.6	1.1	0.2	0.9	0.6	0.6	0.9	1.4	1.2	0.4
Tm	0.63	0.67	0.49	0.33	0.10	0.17	<0.05	0.14	0.10	0.10	0.15	0.21	0.19	0.06
Yb	4.2	4.3	3.2	2.2	0.7	1.1	0.3	1.0	0.8	0.7	1.0	1.4	1.3	0.5
Lu	0.68	0.72	0.55	0.35	0.12	0.19	0.06	0.17	0.14	0.14	0.16	0.21	0.22	0.09
Th	6.7	6.8	6.7	5.6	2.2	2.6	0.8	2.0	1.7	1.8	2.2	3.5	3.9	0.9
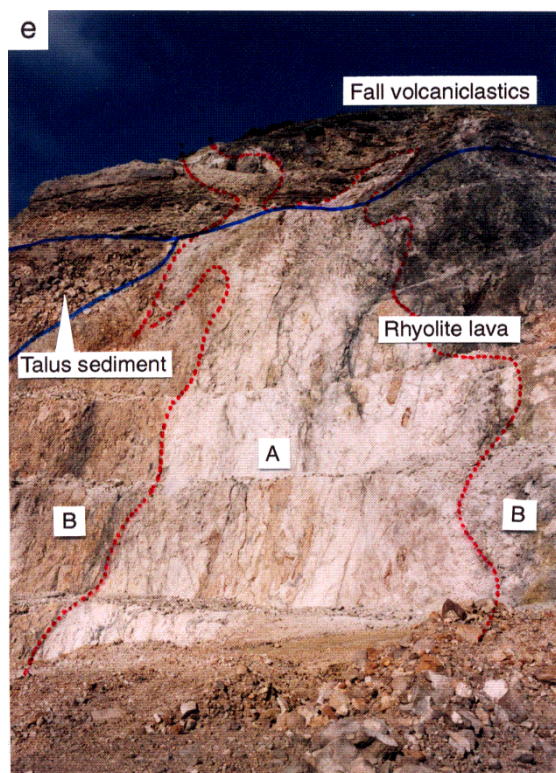
Fig. 4. e) Residual silicified zone along the fractures at the old Ohtanibira quarry. The height of the cliff is about 40 m, and the silicified zone of A is 10–15 m wide. A and B show alteration mineral assemblages of (quartz)-tridymite-cristobalite and tridymite-cristobalite, respectively.

Fig. 5. SiO_2-major element variation diagram of altered whole rocks.

volcanic vapor into ground water, based on isotopic data (Shinohara *et al.*, 1993). A similar origin of acidity is also indicated at many high-sulfidation type deposits (Vennemann *et al.*, 1993; Hedenquist *et al.*, 1994b; Arribas *et al.*, 1995) and active acid crater lakes (Christenson and Wood, 1993). The second alteration type occurs as silica addition by low-temperature and much less acidic solutions on the flanks of the volcano and at the ground surface. For example, the silica cementation of volcaniclastics, ash and talus matrix observed on the surface far from the fumaroles is probably caused by silica addition. Around the summit crater, meteoric water penetrates into the already silicified rock, is heated and dissolves silica from volcanic glass at depth. After the temperature of the solution decreases silica is precipitated during flow toward the flanks. The silica-cemented surface consists mostly of amorphous silica or cristobalite. Some amorphous silica veins also form by flow of low-temperature silica-rich solution.

Few clay minerals have been documented at the surface of the summit or flank. In addition, alunite is also uncommon inside the summit crater. Alunite fills the matrix of talus sediments to depth of several tens of meters around the summit crater, indicating alteration by acid aqueous solution (Hemley *et al.*, 1969). The Al and K of alunite was probably leached and transported by acid solution, and permeated into the subsurface. According to Yoshida *et al.* (1976) and Kimbara *et al.* (1977), alunite and clay minerals were produced mainly below the water table, more than 50 m below the surface, based on alteration in several cores drilled
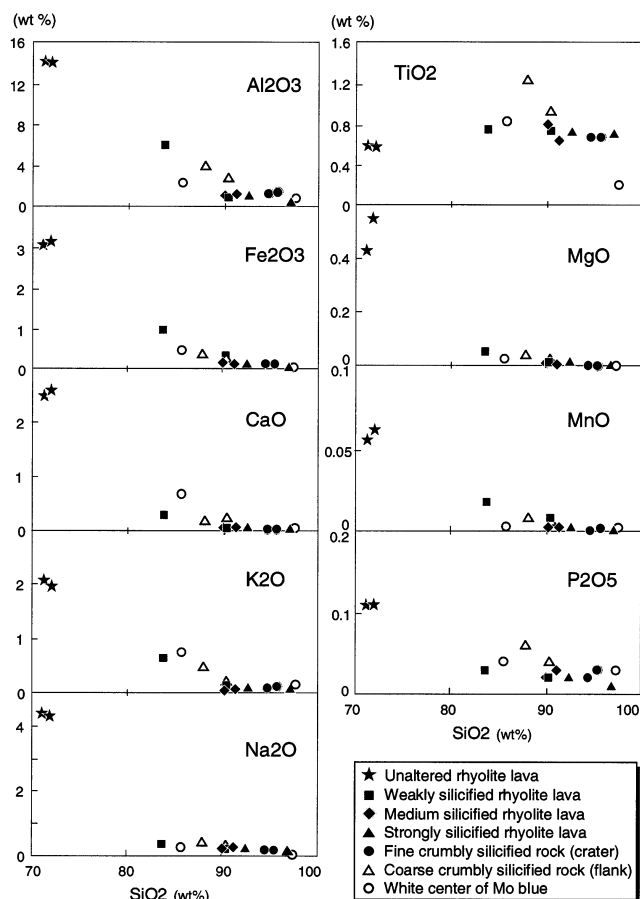
at the foot of Iwodake. The abundant silica minerals with little alunite inside the summit crater and on the crater wall is most likely caused by the rare existence of liquid water inside the summit crater.

5.2   Geochemistry of alteration process

During hydrothermal alteration, the unaltered rhyolite of $SiO_2 = 71$–72 wt% was leached to form a residual silicified rock with >90 wt% SiO_2. Most major elements, except for TiO_2 and P_2O_5, have been largely leached during the process (Fig. 5). Hedenquist *et al.* (1994a) provides evidence for the isochemical dissolution of fresh Iwodake rhyolite by the acidic water. The Al_2O_3, Fe_2O_3 and K_2O contents are completely leached at about 90 wt% SiO_2, and CaO, Na_2O, MgO and MnO are also depleted at about 85 wt% SiO_2. Thus K is less mobile than other alkali elements such as Ca and Na, consistent with the slightly smaller amount of K in the acidic water of Hedenquist *et al.* (1994a). Although trace elements such as Rb, Sr, Sc, Y, Th and V have been leached almost completely, Ba, Zr, Nb and Hf are present at concentrations close to original values (Fig. 6). Therefore LIL (large-ion lithophile) elements, except for Ba, and III B group elements in periodic table such as Sc, Y and Th have been leached. The Ba has not been mobilized despite its large ionic radius. All HFS (high field-strength) elements have been immobile.

All chondrite-normalized REE's show almost equal depletion without fractionation, except for Eu, with increasing of
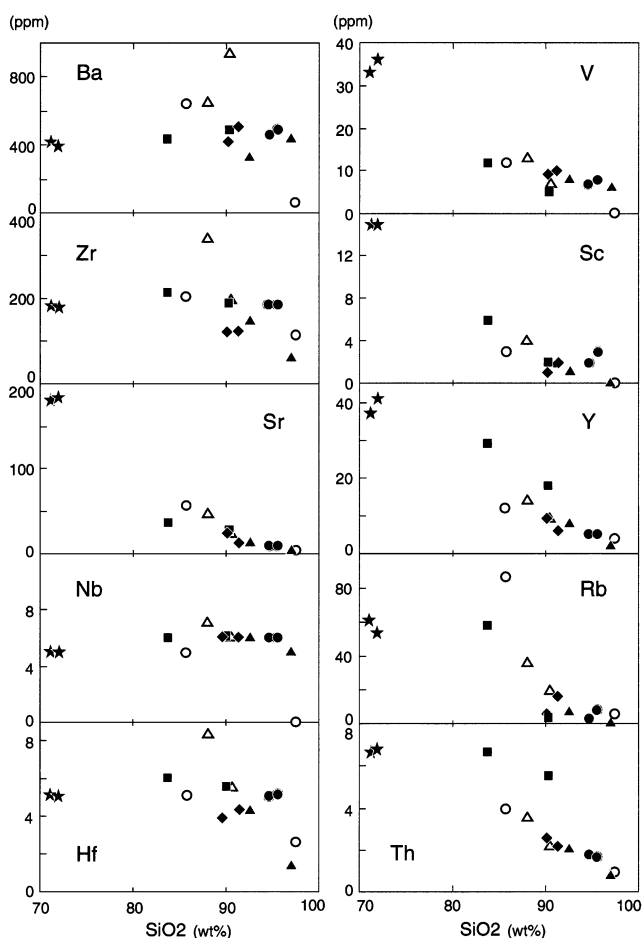
Fig. 6. SiO₂-trace element variation diagram of altered whole rocks. Legend is same as the Fig. 5.

Rhyolite lava-1
★ unaltered (SiO2=71.09 wt%)
◆ weakly silicified (83.7 wt%)
■ medium silicified (91.24 wt%)
▲ strongly silicified (97.04 wt%)

Rhyolite lava-2
☆ unaltered (SiO2=71.91 wt%)
◇ weakly silicified (90.34 wt%)
□ medium silicified (90.12 wt%)
△ strongly silicified (92.55 wt%)

Fig. 7. REE pattern of altered rhyolite lava normalized to chondrite (a) and unaltered rhyolite (b) of Iwodake.

silici cation (Fig. 7(a)). Such depletion in the silici ed samples may be caused by the absence of secondary minerals, such as alunite or clay minerals, which can host the REE in their structures. But the unaltered rhyolite-normalized patterns reveal that leaching of light REEs is slightly greater than the heavy REEs (Fig. 7(b)). Fulignati *et al.* (1999) also reported REE depletion pattern without fractionation in silicic facies. On the other hand, Arribas *et al.* (1995) showed an obvious depletion of heavy REEs in leached, vuggy quartz of high-sul dation ore deposits.

At relatively low temperature (<300°C) and low pH with an abundance of sulfur, sulfate can be the major species of the REE complex (Wood, 1990; Lewis *et al.*, 1998). In contrast, at a pH of 2 and high activity of sulfate, even the very high content of chloride species does not appear to affect the complexing of REE (Lewis *et al.*, 1998). The volcanic gases from Iwodake lead to a high content of sulfate and chloride but low ratio of sulfate to chloride (Matsubaya *et al.*, 1975; Shinohara *et al.*, 1993). In addition, the acid hot springs with a pH <2 around Iwodake also show similar chemical characteristics to the volcanic gases (Kamada *et al.*, 1974; Shinohara *et al.*, 1993). The presence of alunite beneath Iwodake also indicates a high activity of sulfate in the acid solution. Therefore, the REE most likely was complexed mainly by sulfate in the low pH hydrothermal uid during
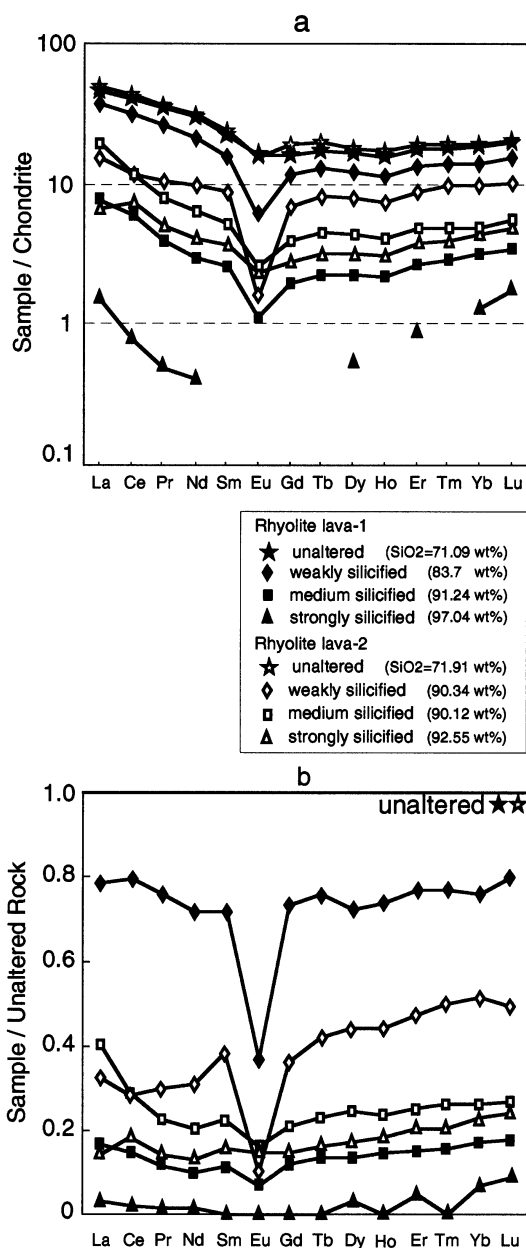
the silici cation of Iwodake rhyolite. In addition, sulfate species preferentially complex with the light REEs in a low pH uid (Lewis *et al.*, 1998; Johannesson and Lyons, 1995), consistent with the result of this study (Fig. 7(b)). A high activity of uoride also affects complexing with heavy REEs (Lewis *et al.*, 1997, 1998). However, the very high sulfate to uoride ratios in the volcanic gases and acid spring water of Iwodake are considered to have little affect on REE complexing. The large Eu negative anomaly is perhaps caused by the leaching of Eu-rich plagioclase.

There are high contents of As and Pb and slightly lower Mo and Sn in high-temperature (>700°C) fumaroles of Iwodake (Hedenquist *et al.*, 1994a). By contrast, Mo and Pb and slightly less Bi, Zn and Sn are concentrated in the molybdenum blue sublimates (Figs. 8(a), (b)). The metal content pattern between the rock samples near the acidic Hi-

Table 3. Metal content of representative altered whole rocks.

ppm	Inside of summit crater								
	White center of Mo blue		Mo blue			Silici ed breccia with sulfur matrix		Fine crumbly silici ed rock	
	022403-1	022409-1	SIJ-1	022403-2	022402-3	98110909	98110914	98110813	08110923
No. (Table 1)	2	3	4	5	6			7	8
Au (ppb)	29	<2	<2	2	<2	<2	<2	<2	<2
Ag	1.5	1.1	12.6	4.3	9.1	<0.2	<0.2	<0.2	<0.2
As	32	4	70	4	143	8	20	11	16
Sb	0.4	0.2	1.5	<0.2	0.9	0.3	0.4	<0.2	<0.2
Bi	120	113	3650	0.3	209	32.3	29.5	3.2	12.2
Cu	67	7	15	29	14	7	6	7	6
Pb	743	66	6750	65	1100	24	56	25	23
Zn	695	5	18	1860	224	10	8	7	7
Mo	364	34	4390	78	7820	39	89	36	33
Cd	7.4	2.7	45.4	7.6	38.9	0.5	0.7	0.7	0.6
Hg (ppb)	553	187	1360	345	630	<10	25	<10	<10
Sn	82	37	442	<10	188	<10	12	<10	<10
W	59	<10	22	13	116	<10	12	<10	<10
Se	2.4	<0.1	27.2	<0.1	25.6	4.9	2.6	<0.1	<0.1
Te	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe (%)	0.32	0.03	0.35	1.12	25.5	0.02	0.06	0.09	0.09
Ti	3780	1130	3560	4650	1800	818	9140	2670	2540

ppm	Around summit crater						Around summit		Flank		Higashi hot spring	
	Strongly silici ed rhyolite lava		Weakly silici ed rhyolite lava		Unaltered rhyolite lava		Amorphous silica vein			Crumbly silici ed	Silici ed matrix of talus sediment	
	08110801	99112111	08110805	99112103	98110803	99112102	98110801′	98111005	99112004	98111004	98111135	99111909
No. (Table 1)	12	13	16	17	20	21	28	29	30	32		
Au (ppb)	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Ag	<0.2	0.4	0.2	<0.2	0.3	<0.2	<0.2	<0.2	<0.5	0.5	0.5	<0.2
As	<1	<1	1	<1	3	2		<1	<1	<1	52	57
Sb	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4
Bi	<0.1	<0.1	0.5	<0.1	5.3	1.0	<0.1	<0.1	<0.1	<0.1	10.8	7.6
Cu	2	4	3	3	4	13	1	2	1	3	3	4
Pb	12	9	19	12	23	21	10	2	4	20	25	14
Zn	20	13	36	22	65	136	86	4	4	16	30	29
Mo	4	3	5	6	5	<1	<1	<1	<1	5	<1	8
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hg (ppb)	<10	<10	<10	494	292	162	<10	<10	<10	413	607	151
Sn	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
W	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Se	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Te	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe (%)	0.03	0.12	0.63	0.24	1.95	2.1	<0.01	<0.01	0.04	0.3	10.9	25.2
Ti	4300	4400	4470	4640	3480	3550	16	1100	513	7020	2390	1290

gashi spring (Fig. 8(e)) and acidic spring water at the foot of Iwodake (Hedenquist *et al.*, 1994a) are similar. The trend of acidic spring water and the high-temperature fumaroles (Hedenquist *et al.*, 1994a) are similar except for Au and Cu. In the molybdenum blue and rocks inside the summit crater, Mo concentration is high, whereas As is low despite its high concentration in the high-temperature fumaroles and acid spring water (Figs. 8(a), (b), (c)). Therefore, except for precious metals such as Au and Cu, most metals have been leached and transported to the foot of Iwodake. Inside the summit crater, Mo was largely deposited as molybdenum blue sublimate from the high-temperature fumaroles, whereas most As discharged together with volcanic gases. The very high Fe concentration in the rock samples near the Higashi spring (Fig. 8(e)) was caused by leaching from surrounding rocks during the movement of the acidic water toward the foot of the mountain.

5.3 Direction of alteration and geological structure

The fractures in the summit crater wall and around the crater have two trends, NE-SW and NW-SE, with the fractures of the NE-SW trend dominant (Fig. 3). Yoshida *et al.* (1976) also suggested the same directions for two structural lines under Iwodake volcano. Many fumaroles and molybdenum blue sublimates are also concentrated along the NE-SW trend (Fig. 2). Figure 10(a) shows zones of concentrated fractures, based on the distribution of fumaroles, fractures and alteration areas around the summit crater of Iwodake. Major erosion of the ank also develops along the same direction as concentrated fractures. In addition, concentration area of fractures (Fig. 10(b)) is parallel to the caldera rim and the trend of Shin-Iwojima, Iwodake and In-amuradake, which are post-caldera cones. Therefore, it is likely that fractures parallel to the caldera rim are pathways for the ascending volcanic gases and hydrothermal solution (Hamasaki, 1999). Indeed, Ketsunohama coast-line, which
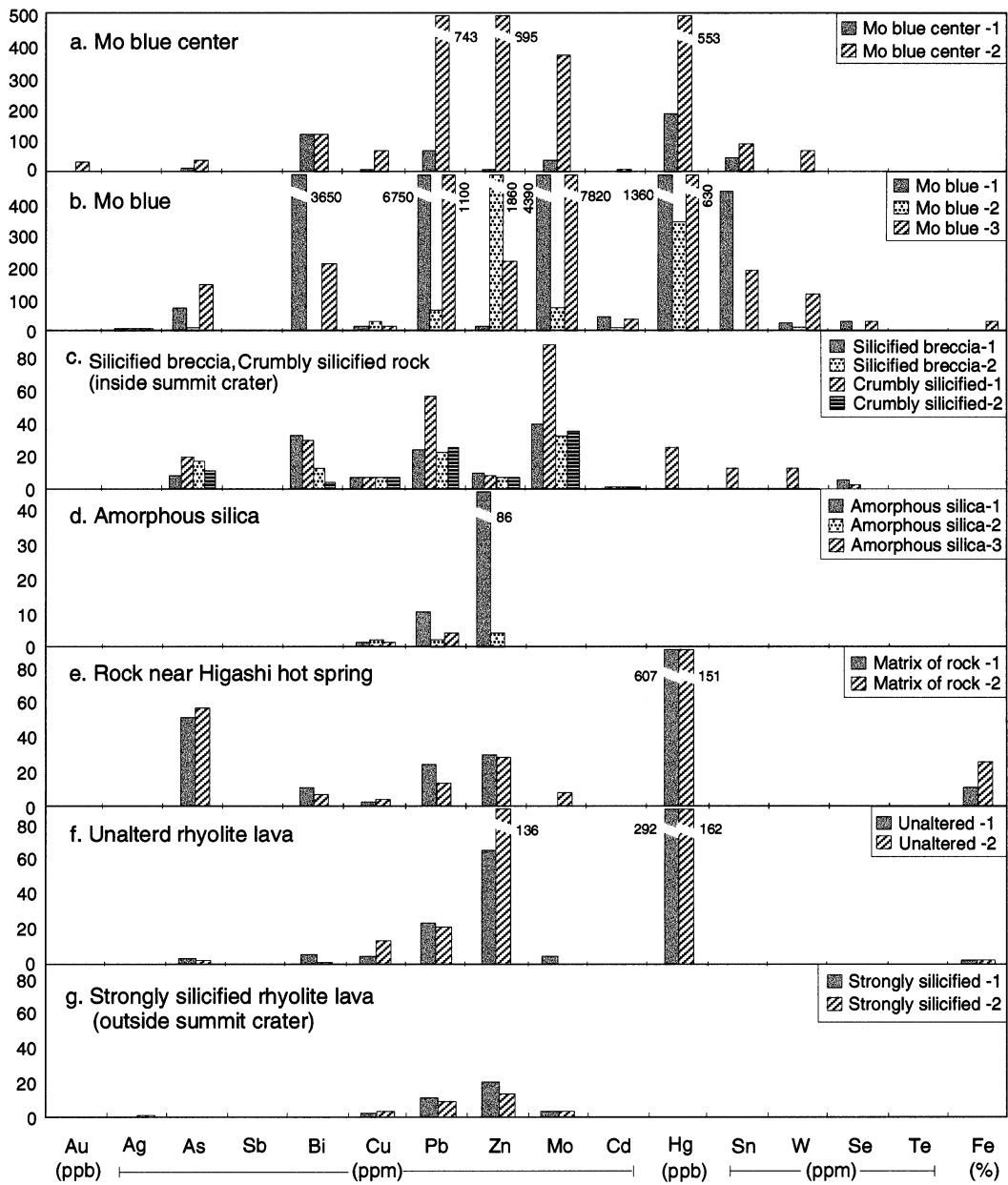
Fig. 8. Metal content diagram of altered whole rocks.

Fig. 9. Mineral assemblages of altered rocks near and on the surface of Iwodake volcano.
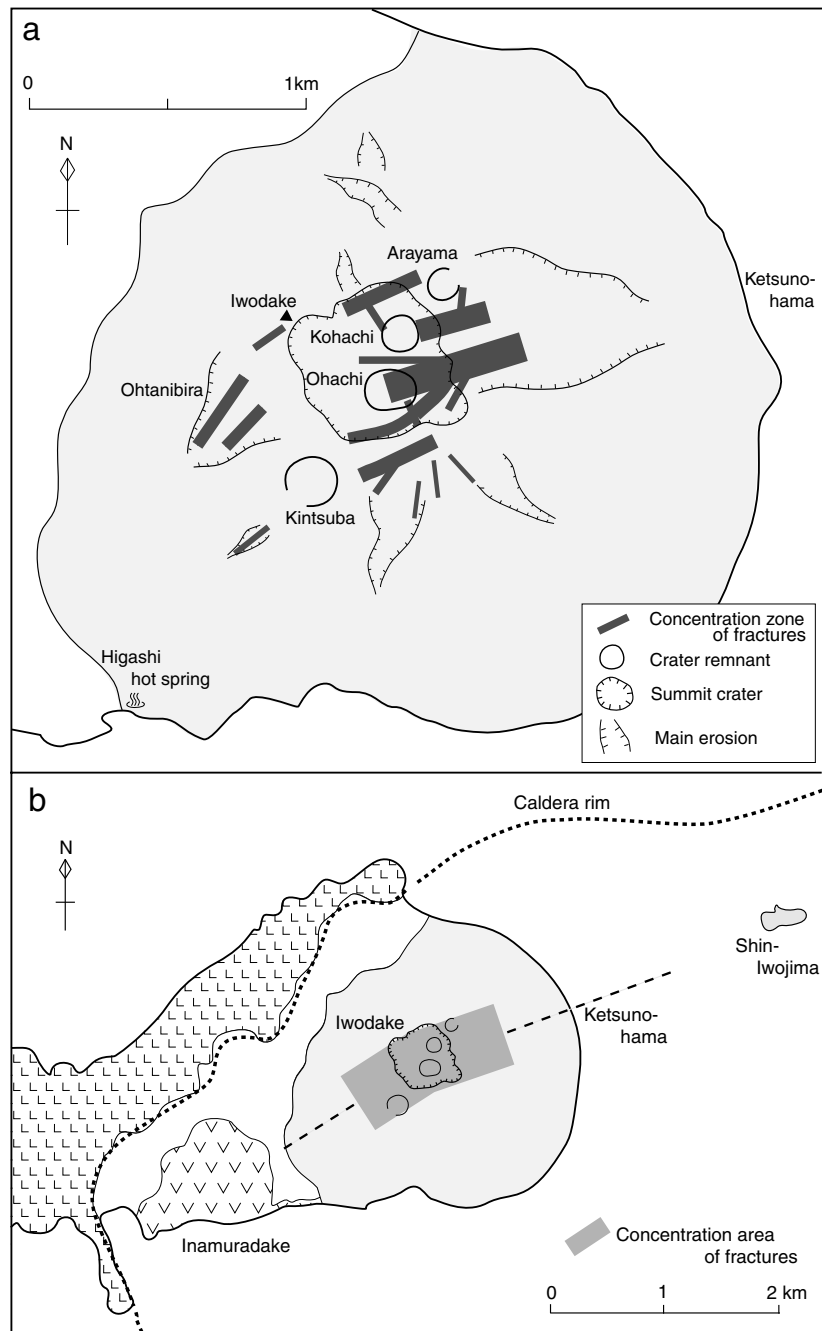
Fig. 10. a) Zone of concentrated fractures determined by the distribution of the fumaroles, fractures and altered areas around the summit crater of Iwodake. Main eroded topography also shown. b) Relation of area of fractures around Iwodake to the Kikai caldera rim.

has the most hot springs, also lies between Shin-Iwojima and Inamuradake. Futhermore, high anomalies of CO_2 content in the soil occur not only at the caldera rim but on the Ketsunohama coast and between Iwodake and Inamuradake (Shimoike *et al.*, 2000). These facts support the possibility that there is tectonic line along Shin-Iwojima, Iwodake and Inamuradake.

The direction of fractures on the western side of the summit crater, including Ohtanibira, is NE-SW and changes to ENE-WSW on the eastern side. In addition, several crater remnants around the summit, such as Kintsuba, Kohachi and Arayama plus the active Ohachi crater, lie along the domi-

nant NE-SW direction (Fig. 10(a)). Alteration evidence indicates that Ohtanibira was an area of high-temperature fumaroles, although activity is now weak. High-temperature fumaroles are now located inside and on the eastern side of the summit crater. Therefore, it appears that several craters once located along the NE-SW direction, and volcanic gases were also discharged along the same direction fractures. This direction of fractures has now changed to ENE-WSW and the active fumarolic area moved to the eastern part of the summit crater.

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S. Hamasaki (e-mail: hamasaki-st@aist.go.jp)