Geochemistry of volcanic gases and hot springs of Satsuma-Iwojima, Japan: Following Matsuo

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The chemical and isotopic (D, 18O, 34S) compositions were determined for 19 fumarolic gases, 11 hot spring waters and 3 meteoric waters collected from Satsuma-Iwojima volcanic island, Japan. The fumarolic gases discharge over a wide range of temperature (from 877 to 99°C), but are likely to be derived from a common parent gas with a deduced composition of (µmol/mol): H2O:975000, CO2:3800, total S:9800 (with an average oxidation state of 3.4), HCl:5800, HF:300, H2:5000, CO:15, He:0.05, Ar:0.25, and N2:60. The variation in gas composition from different fumaroles may largely be explained in terms of re-equilibration at lower temperature, addition of earlier deposited elemental S and mixing with meteoric waters at shallow depths. The chemical and isotopic composition of the highly acid hot spring discharges, pH 1.2 to 1.8, indicate that they are formed through absorption of Cl-depleted volcanic gas into local groundwaters in close to equal amounts.

INTRODUCTION

“At the present time, we have no account for the high δD values of the fumarolic condensates” (Matsuo et al., 1974).

Matsuo et al. (1974) reported δD and δ18O values for high-temperature fumarolic condensates of Iwodake volcano, Satsuma-Iwojima, Japan. These were among the first isotopic analyses of discharges from a subduction-related volcano. The δD values of −27 to −17‰ and δ18O values of +7.3 to +9.5‰ are heavier than those of the local meteoric water. While the δ18O values are similar to those of “primary magmatic water” (Taylor, 1979), the δD values are more than 20‰ heavier. Matsuo et al. (1974) explained the high δ18O values as being the result of oxygen isotope exchange with the volcanic rocks. Although they clearly stated that there was “no evidence for seawater mixing”, the high δD was not accounted for. Following the accumulation of isotope data for fumarolic discharges from volcanoes over the past twenty years, these apparent anomalously high δD values are now recognized to be characteristic of waters associated with subduction-related magmatism with δD values of −20±10‰ (Kusakabe and Matsubaya, 1986; Taran et al., 1990; Giggenbach, 1992a).

High temperature fumarolic gases (>700°C) have discharged from the summit area of Iwodake for at least the past 30 years (Kamada, 1964). The chemical and isotopic composition of the fumarolic gases and hot spring waters have been studied by several groups (Kamada, 1964; Matsuo et al., 1974; Matsubaya et al., 1975).

In this paper, we discuss variations in the composition of the volcanic gases in terms of a number of possible differentiation processes, and deduce the probable composition of the
parent gas. The origin of the hot spring waters is also discussed on the basis of their chemical and isotopic compositions.

**GEOLOGY**

Satsuma-Iwojima is a volcanic island and forms part of the largely submerged rim of the Kikai caldera located about 50 km south of Kyushu, Japan (Fig. 1). Ono et al. (1982) summarized the geologic history of the area. The caldera-forming eruptions ceased about 6300 years ago, followed by the formation of the Iwodake rhyolitic dome (704 m), and the basaltic cone of Inamuradake (236 m). The eruptive activity of Iwodake continued until about 1200 years ago. Historic literature (Heike-monogatari) describes the fumarolic activity and sulfur mining at the summit area about 800 years ago. Therefore, it is likely that intense fumarolic activity has been present since Iwodake ceased erupting (Kamada, 1964). Over this long period of quiescent degassing, no volcanic eruptions were recorded until submarine activity in 1934 formed the new small rhyolitic island of Shin-Iwojima, 3 km east of the main island.

**SAMPLING AND ANALYTICAL METHODS**

The sampling survey was conducted from 23 to 28 October, 1990, covering the locations shown in Fig. 1. Most of the fumaroles lie within the 400 m wide summit crater, and only a few low-temperature fumaroles (<110°C) are located on the lower flanks of the volcano. A new fumarolic area called Ohachi-oku (meaning “innermost part of a big bowl”), with temperatures up to 877°C, was recently discovered on the south-southwest margin of the crater floor where there were no high-temperature fumaroles about 25 years ago (Yoshida, M., pers. commun.).

Sampling and analytical methods of the volcanic gases and hot spring waters are essentially the same as those reported by Giggenbach and Goguel (1989). Differential analysis of SO₂ and H₂S was not attempted, but the total S content and average oxidation state of the sulfur species were measured. Sulfur isotopic values are those of total S in the sample.

To avoid the possibility of reaction between the gas and sampling equipment, silica glass tubing was used for collecting most of the fumarolic gas samples. At Ohachi-oku (877°C) a Ti tube was connected to a silica tube inserted into the vent. At Arayama, where the site precluded the
### Table 1. Chemical and isotopic composition of volcanic gases from Satsuma-Iwojima

<table>
<thead>
<tr>
<th>No.</th>
<th>Locality</th>
<th>Analyst</th>
<th>Date</th>
<th>Temp. (°C)</th>
<th>δD (%)</th>
<th>δ18O (%)</th>
<th>δ34S (%)</th>
<th>H2O</th>
<th>CO2</th>
<th>S</th>
<th>n2</th>
<th>HCl</th>
<th>HF</th>
<th>NH3</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>H2</th>
<th>O2</th>
<th>N2</th>
<th>CH4</th>
<th>CO</th>
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<td>WFG</td>
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<td>877 n.a.</td>
<td>n.a.</td>
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<td>7922</td>
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<td>n.s.</td>
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<td>n.s.</td>
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<tr>
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<td>n.s.</td>
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<td>n.s.</td>
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<td>WFG</td>
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Chemical composition is given in units of (μmol/mol).
The same sample number refers to duplicate or repeat samples collected from same vents.
All samples collected through silica glass tube except for those noted by (*), which were collected with Ti tube.
HF in GSJ sample was analyzed in the separate water condensate.
WFG: W. F. Giggenbach, GSJ: Aoki M., Shinohara H., and J. W. Hedenquist
n.a.: not analyzed; n.s.: Ne was not separated from He peak. nS: Oxidation state of sulfur (equation 1).
use of short silica tubes, and at the low temperature fumaroles of Monogusa and Kitabirashita, only Ti tubes were used, as indicated in Table 1.

RESULTS

The chemical and isotopic composition of the fumarolic gases and hot spring waters are listed in Tables 1 and 2. The average oxidation state of S species is given by \( n_s \) (Giggenbach 1987). Assuming \( \text{SO}_2 \) (\( n_s = +4 \)) and \( \text{H}_2\text{S} \) (\( n_s = -2 \)) to be the predominant S species in fumarolic gases, \( n_s \) values are converted to an \( X_{\text{SO}_2}/X_{\text{H}_2\text{S}} \) ratio according to

\[
(X_{\text{SO}_2}/X_{\text{H}_2\text{S}}) = (2 + n_s)/(4 - n_s),
\]

where \( X_i \) denotes the mole fraction of the species \( i \).

Most of the volcanic gas samples were taken in duplicate and were chemically analyzed at the Geological Survey of Japan (GSJ) by SH, JWH and Dr. Aoki, M., and by WFG at the Institute of Geological and Nuclear Sciences (Table 1). Matsuo et al. (1974) collected 12 volcanic gas samples in series at Kuromoe and found relatively small variations, up to 17% for major components, except \( \text{H}_2\text{S} \) (100%). The agreement between the two sets of data of the present study (GSJ and WFG in Table 1) is fairly good considering the temporal variations found by Matsuo et al. (1974), but large systematic disagreements can be seen for \( \text{CO}_2 \) and the halogens (\( \text{HCl} \) and \( \text{HF} \)); GSJ report lower \( \text{CO}_2 \) and higher halogen concentrations than those of WFG. Large errors in \( \text{CO}_2 \) and halogen concentrations can occur by loss or gain of condensate during sampling (Giggenbach and Matsuo, 1991). Since the duplicate samples were collected by the use of the same sampling line with similar sampling rates, the disagreement, however, is not likely to be due to the loss of condensate. The analytical methods are also essentially the same, and the reason for the disagreement is not clear. Although these disagreements are not insignificant, the following evaluation is largely based on much larger variations in composition between fumaroles than between duplicates. The large difference in total S concentrations and oxidation states of S of duplicate Kitabirashita samples will be discussed later.

Analyses of more than 70 fumarolic gas samples and more than 20 hot spring waters have

Table 2. Chemical and isotopic composition of water samples from Satsuma-Iwojima

<table>
<thead>
<tr>
<th>No.</th>
<th>Locality</th>
<th>Date</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>( \delta D ) (%)</th>
<th>( \delta^{18}O ) (%)</th>
<th>( \delta^{34}S ) (%)</th>
<th>( \text{SO}_4 ) (mg/kg)</th>
<th>Cl (mg/kg)</th>
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n.a.: not analyzed; n.m.: not measured.
Volcanic gases & hot springs, Satsuma-Iwojima, Japan

previously been reported for Satsuma-Iwojima by Kamada (1964), Kamada et al. (1974), Matsuo et al. (1974) and Matsubaya et al. (1975). Comparison of these data with the present sets shows that the composition of the fumarolic gases and hot spring waters have basically remained unchanged over the last thirty years.

The SO₂ flux from the volcano was measured by COSPEC in the panning mode using a tripod, giving a result of 470 ± 60 tons/day (Hedenquist et al., 1992; Kazahaya et al., 1992). Okita et al. (1977) determined the SO₂ flux from the volcano to be 470–680 tons/day in 1975 with the traverse method. The relatively constant chemical and isotopic compositions and SO₂ flux indicate that the volcano has been in a stable state of quiet degassing over at least the past thirty years.

**CHEMICAL COMPOSITION OF VOLCANIC GAS**

The widely varying compositions of fumarolic gases discharging from Iwodake are likely to be the result of near-surface differentiation processes, such as addition or condensation of water vapor, reactions among gas species, and addition or loss of sulfur-containing species, such as elemental S or sulfate. The effects of these processes are discussed on the basis of variations in gas compositions as a function of outlet temperatures and location of the vents, with the aim to derive the composition of a possible common parent gas feeding the system.

*Hydrogen and Sulfur Species*

In combination with H₂O, H₂ represents a useful indicator of the redox state of a volcanic gas. As shown by Giggenbach (1987), the redox potential in volcanic systems is controlled mainly by the competition between the SO₂–H₂S gas buffer and a rock buffer involving Fe in its two oxidation states. Under magmatic conditions, the predominant rock buffer appears to be best represented by that involving fayalite and magnetite, while in hydrothermal systems the buffer also involves Fe(II) and Fe(III) of the rock, but in the less specific forms, (FeO) and (FeO₁·₅) (Giggenbach, 1987).

![Fig. 2. Variation of H₂/H₂O ratio of the volcanic gases with outlet temperature. Symbols are as follows: □ Ohachi-oku (877°C); ○ Ohachi-oku (505°C), □ Ohachi-oku (165°C), □ Arayama (760°C), □ Kuromoe (702°C), © Kamanokuchi (330°C), ○ Kamanokuchi (104°C), △ Monogusa (102°C), A Kitabirashita (99°C), and A Shin-Iwojima (34°C). Data from Kamada (1964), Matsuo et al. (1974) and Matsubaya et al. (1975) are also plotted as small circles. Fayalite-magnetite line is the FMQ buffer, and the (FeO)–(FeO₁·₅) rock buffer line is for an unit activity ratio of (FeO) and (FeO₁·₅) components in rocks. The H₂S–SO₂ gas buffer line is given by equation (3). All chemical data are plotted on a molal basis here and in subsequent diagrams.](image)

The positions of data points for the high temperature gases between the two rock buffer lines (Fig. 2) suggest that redox conditions for these gases are more reducing than those of the (FeO)–(FeO₁·₅) rock buffer. The H₂ contents, however, may not be directly reflecting the equilibrium condition with rocks, but could be the result of a change in the X₃H₂/X₃H₂O ratio in response to decreasing temperature and pressure due to internal re-equilibration of the gases according to the reaction

$$2\text{H}_2\text{O} + \text{H}_2\text{S} = \text{SO}_2 + 3\text{H}_2.$$  (2)

Variations in the $X_{\text{H}_2}/X_{\text{H}_2\text{O}}$ ratio as a function of temperature and pressure (fugacity of water) correspond to

$$\log \left( \frac{X_{\text{H}_2}}{X_{\text{H}_2\text{O}}} \right) = 1/3 \log K_2 - 1/3 \log \left( \frac{X_{\text{SO}_2}}{X_{\text{H}_2\text{S}}} \right) - 1/3 \log f_{\text{H}_2\text{O}},$$  (3)
where $K_2$ is the temperature dependent equilibrium constant of reaction (2). Equation (3) shows that the $X_{H_2}/X_{H_2O}$ ratio can be expected to increase by one log unit for a drop in pressure by 1000 bars at a given temperature and a constant $SO_2/H_2S$ ratio. Temperature decrease from 1100° to 900°C will cause a decrease in the $X_{H_2}/X_{H_2O}$ ratio by one log unit at constant pressure and $SO_2/H_2S$ ratio (Fig. 2).

Accepting the increase in $H_2/H_2O$ ratios above those of the (FeO)-(FeO$_{1.5}$) rock buffer line to be due to the pressure decrease along constant temperature, the original pressure of these gases are calculated to be close to 300 bars with a $SO_2/H_2S$ ratio of 3. Once exsolved from the magma, the gases remain in internal equilibrium and $H_2/H_2O$ ratios increase at the expense of $H_2S$ to form $SO_2$ according to reaction (2). The high average oxidation state ($n_s$) of the gases of about 3.4 then may largely be due to this internal re-equilibration process in response to decreasing pressures. If the gases cooled by about 100°C due to isenthalpic expansion, the gases need to have been equilibrated with the rock buffer either at a pressure greater than 300 bars or under conditions more reducing than the (FeO)-(FeO$_{1.5}$) rock buffer.

The data points for high temperature gases (>700°C) lie along the $SO_2$-$H_2S$ buffer line at values for $(X_{SO_2}/X_{H_2S}) \times f_{H_2O}$ of close to 10. According to equation (1), $n_s$ values of 3.4 correspond to an $X_{SO_2}/X_{H_2S}$ ratio of close to 10 and therefore to an $f_{H_2O}$ value of about 1 bar. The redox potential of these gases, as represented by the $X_{H_2}/X_{H_2O}$ ratio, therefore suggests attainment of internal equilibrium of reaction (2) at close to atmospheric pressures. The large scatter in $H_2/H_2O$ ratios of lower temperature gases may reflect varying degrees of attainment of equilibrium and quenching of higher temperature compositions. Effective quenching is likely to preserve such high ratios, reflecting high temperature conditions, while slow cooling allows further readjustments, resulting in low ratios. This interpretation agrees with the observation that gases from low temperature fumaroles on the flanks of the volcano show lower $H_2/H_2O$ ratios than those of the summit area, indicating the summit gases are more effectively quenched than the flank gases.

As pointed out above, the high $SO_2/H_2S$ ratios are likely to be due to the formation of $H_2$ during the rise of the gases to the surface in response to decreasing pressure. Since this effect of pressure decrease is expected to be common for all the gas samples, other secondary processes must be responsible for their varying composition. The possible effects of these processes on the concentration and oxidation state of $S$ are evaluated by means of Fig. 3. Internal re-equilibration of the gases in response to changing redox conditions (and also pressure and temperature), without addition or loss of $S$, is represented by a straight line marked "reduction-oxidation". The general pattern of data points suggests that variations in $S$ content and average oxidation state of the Iwodake gases are not due to this process.

The general trend of the high temperature gases, however, follows closely a line representing addition or loss of elemental $S$. Formation of elemental $S$ most likely occurs through the reaction

![Fig. 3. SO2 versus H2S concentration in the volcanic gases. SO2 and H2S concentrations are calculated by equation (1) with the assumption that SO2 and H2S are the only S species. A negative H2S concentration is calculated for one of the Monogusa samples, due to the presence of sulfate. The composition of the parent gas is plotted as a star. Symbols as in Fig. 2. The possible original compositions of Monogusa samples before sulfur oxidation by air are also indicated by small triangles.](image-url)
2H₂S + SO₂ = 3S₈ + 2H₂O.  \hspace{1cm} (4)

Re-evaporation of previously deposited S, the reverse of reaction (4), will shift data points to higher H₂S and SO₂ contents along a line with a slope of 2 (Fig. 3). Deposition of sulfur is common over the summit area of Iwodake, so much so that mining was conducted there. Migration of fumaroles, frequently observed at Iwodake (Yoshida, M., pers. commun.), results in re-heating of the earlier deposits and readily explains the trends shown by the data in Fig. 3.

There is a large discrepancy between the duplicate samples from Kitabirashita, with trends suggesting sulfate loss and addition (Fig. 3). Sulfuric acid may form from the volcanic gases on contact with liquid water by the disproportionation of SO₂,

\[ 4\text{SO}_2 + 4\text{H}_2\text{O} = \text{H}_2\text{S} + 3\text{H}_2\text{SO}_4 \] \hspace{1cm} (5)

or

\[ 3\text{SO}_2 + 2\text{H}_2\text{O} = \text{S}_8 + 2\text{H}_2\text{SO}_4. \] \hspace{1cm} (6)

This fumarole discharges on a steep slope and its gas flux is low. Therefore, a sulfate-rich condensate may have entered the sampling train and variably contaminated the samples, possibly accounting for the widely diverging S contents and average oxidation states of the two Kitabirashita samples.

Considerable air contamination is suggested for the Monogusa samples, based on the high O₂ content and also high N₂ and Ar contents relative to that of He, as discussed later. The O₂/N₂ ratio in these samples is about 1/3 that of air. If all the N₂ in the samples originated from air, the 2/3 depletion of O₂ may be due to reactions such as the oxidation of sulfur species to H₂SO₄. Symonds et al. (1992) showed that H₂SO₄ containing liquids may form even at temperature well above 100°C under highly oxidizing conditions. Loss and addition of such H₂SO₄ may also be the reason for the variability in the composition of the Monogusa samples.

The H₂S and SO₂ data of the present study generally agree well with those previously reported by Kamada (1964), Matsuo et al. (1974) and Matsubaya et al. (1975). Many of the earlier data for low temperature gases, however, show a distinct trend to low SO₂ and low H₂S values. Although the data can simply be interpreted as the result of dilution of the volcanic gases by low S gas, such as evaporated ground water (Fig. 3), the CO₂/H₂O ratios of most of these gases are similar to those of high temperature gases, indicating that the effect of the dilution is not significant. Furthermore, δ¹⁸O data of some of these gases (Matsubaya et al., 1975) suggest that the volcanic gases are little diluted with meteoric water. Since most S-poor gases have high SO₂/H₂S ratios (up to 40) and show very low HCl contents (Kamada, 1964; Matsubaya, 1975), the S-poor gases are likely to be the result of elemental S deposition with decreasing temperature during their ascent.

**Carbon Monoxide**

A species equilibrating with rates similar to H₂ is CO (Giggenbach, 1987). The redox reaction controlling CO contents in the gases is

\[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}. \] \hspace{1cm} (7)

The CO/CO₂ ratio under equilibrium condition is given as a function of temperature and X_{H₂}/X_{H₂O} ratio by

\[ \log \left( \frac{X_{\text{CO}}}{X_{\text{CO}_2}} \right) = \log K_7 + \log \left( \frac{X_{\text{H}_2}}{X_{\text{H}_2\text{O}}} \right), \] \hspace{1cm} (8)
where $K_7$ is temperature-dependent equilibrium constant of reaction (7). In combination with equation (3), an expression is obtained describing the variation in the CO/CO$_2$ ratio as a function of SO$_2$/H$_2$S ratios:

$$\log \left( \frac{X_{CO}}{X_{CO}} \right) = \log K_7 + \frac{1}{3} \log K_2 - \frac{1}{3} \log \left( \frac{X_{SO_2}}{X_{H_2S}} \right) - \frac{1}{3} \log f_{H_2O}. \quad (9)$$

The CO/CO$_2$ ratios of most of the Iwodake gases decrease with decreasing fumarolic temperature (Fig. 4), similar to the behavior of the H$_2$/H$_2$O ratios (Fig. 3). The positions of the highest temperature samples (Ohachi-oku at 877°C), however, lie on the SO$_2$-H$_2$S gas buffer line with ($X_{SO_2}/X_{H_2S}$) $\times f_{H_2O}$ values of 1000. With an SO$_2$/H$_2$S ratio of 10, these values indicate an equilibration pressure of about 100 bars, considerably higher than that of 1 bar suggested by H$_2$/H$_2$O ratios (Fig. 2). The difference in equilibration pressures for the two systems is likely to be due to different rates of response of the CO/CO$_2$ ratio to changes in pressure during the ascent of the gases.

**Methane and Ammonia**

Based on a study of the White Island volcanic system, Giggenbach (1987) showed that CH$_4$ and NH$_3$ are essentially hydrothermal components. Their contents in the volcanic gas are mainly controlled by the (FeO)-(FeO$_{1.5}$) rock buffer through reaction at relatively deep levels in the two-phase, saline brine-vapor envelope which surrounds the magma. Since reaction rates involving these components are low, attainment of equilibrium is limited to hydrothermal conditions, where not only the high pressure but also the existence of a liquid phase accelerates the reactions. The reaction rates become progressively slower for species in the order H$_2$ > CO > CH$_4$ > NH$_3$ (Giggenbach, 1987).

The fumarolic gases of Iwodake fall into two groups based on their CH$_4$ contents, regardless of temperature, locality and chemical composition. The CH$_4$/CO$_2$ ratio of the high CH$_4$ group is around $10^{-3}$, and that of the low CH$_4$ group is $<10^{-8}$, which is near or below our analytical detection limit. If the CH$_4$ contents reflect equilibrium with the (FeO)-(FeO$_{1.5}$) rock buffer at 877°C and 100 bars, as indicated by the CO contents, the CH$_4$/CO$_2$ ratio should be about $10^{-8}$, similar to those of the low CH$_4$ group of samples. The CH$_4$/CO$_2$ ratio of the high CH$_4$ group can either be explained by equilibrium with the rock buffer at 877°C and 30 kbars, or at 350°C and 100 bars (Giggenbach, 1987, his Fig. 11). The CH$_4$/CO$_2$ ratios of the high CH$_4$ group of Iwodake fumaroles are comparable to those at White Island (Giggenbach, 1987), where the high CH$_4$ content in the high-temperature fumarolic gases was explained by admixture of a CH$_4$-rich hydrothermal gas, forming under lower temperature conditions. Since the CH$_4$ contents do not correlate with temperature or locality of the fumaroles at Iwodake, they may be affected by near-surface contamination and reaction with sampling materials, or may reflect variable addition of hydrothermal CH$_4$ in response to variations in local permeability conditions.

The NH$_3$ content in the fumarolic gases is nearly constant (about 1 μmol/mol), except for Kamanokuchi (104°C) and Kitabirashita, where NH$_3$ concentrations are ten times less than those at the other locations, probably due to absorption as NH$_4^+$ into acid condensate formed in the fumaroles. The equilibrium pressure for the high NH$_3$ samples at 877°C is 3000 bars, or 300 bars at 500°C, assuming a redox state controlled by the (FeO)-(FeO$_{1.5}$) buffer (Giggenbach, 1987, his Fig. 14). If the redox potential is controlled by a reaction involving fayalite-magnetite instead of (FeO)-(FeO$_{1.5}$), the equilibrium pressure obtained for 877°C is 100 bars. Considering the uncertainty of the dominant rock buffer, it is difficult to decide whether the NH$_3$ formed under high temperature magmatic conditions, or is due to contamination from the low temperature hydrothermal system.

**HCl and HF**

The concentrations of HCl show the largest variability in Iwodake fumarolic gases, along
with H₂. They are nearly constant at high temperature, but show a scatter to low contents in fumaroles of around 100°C. Since the solubility of HCl in liquid water is very high, the sudden decrease in HCl concentrations near the boiling point of water is most likely due to absorption into a liquid phase at shallow depths.

The Arayama samples contain less HCl and more H₂ than the other high temperature samples, possibly due to reaction of HCl with the 2 m long Ti sampling tube. Such a very long sampling train, inserted directly into the fumarole without a silica glass adaptor, was required because of the difficult sampling conditions.

The HF/HCl ratio of the fumarolic gases decreases with decreasing temperature, but there is a subsequent scatter to higher values near 100°C. Yoshida (1975) demonstrated, based on his laboratory experiments, that a decrease in the F/Cl ratio in gases with decreasing temperature is due to fluoride fixation during reaction with volcanic rocks. The high-temperature fumarolic gases (>700°C) have a relatively constant F/Cl ratio of 0.05, and are least affected by the fluoride fixation reaction. The large scatter in F/Cl ratio at lower temperature, near 100°C, is probably due to the HCl loss to condensed water.

**Chemical Composition of Parent Gas**

The composition of the parent gas from Iwodake can be estimated by considering the differentiation processes discussed above. The effects of these processes were deduced by use of the composition of samples collected at atmospheric pressure; as a consequence, the parent gas composition derived here may be more representative of the volcanic gases reaching the surface, rather than the composition of the gas phase at depth in the vicinity of the magma. Furthermore, the gas phase reaching the surface may be only a fraction of the fluid exsolving from the magma, as part of this fluid may separate to a dense liquid that coexists with the gas phase at depth (Pitzer and Pabalan, 1986; Giggenbach, 1987).

**Reactive Gases**

The relative contents of H₂O, CO₂ and S, for Iwodake gases show only a minor scatter (Fig. 5). The previous data by Kamada (1964), Matsuo et al. (1974) and Matsubaya et al. (1975) also agree well with the present set, suggesting that the high-temperature gas compositions were relatively constant over the past thirty years, with variations due largely to near-surface processes. Comparison with other island arc volcanic gases (Giggenbach and Matsuo, 1991) shows that Iwodake fumarolic gases are characterized by a relatively CO₂-poor composition. Degassing at Iwodake has continued for at least the last 800 years (Kamada, 1964). Therefore, if the degassing of the volcano occurs from a single magma body, such long-term degassing may have depleted the magma in CO₂ because of its low solubility, resulting in the present CO₂-poor volcanic gas discharges.

The dry gas composition is plotted in terms of CO₂–S–Cl (Fig. 6), also emphasizing that the
Iwodake fumarolic gas is CO₂-poor compared with Vulcano, Usu and White Island. As discussed previously, the Sₓ and HCl concentration of the Ohachi-oku fumarolic gases has been least affected by near-surface processes, and is regarded as the best estimate (Table 1) for the Sₓ and HCl concentration of the parent gas, after depressurization to near-surface conditions but before significant differentiation processes have occurred. Much of the variability in the composition of the Iwodake data appears to be due to variations in relative HCl contents at constant C/S ratios of 0.4.

**Inert Gases**

Helium, Ar and N₂ are useful as tracers in discussing the origin of volcanic gases. The variation in the relative amounts of these three components in Iwodake samples indicate mixing of air or air-saturated water with another end-member marked by a star in Fig. 7. Giggenbach (1992b) proposed four major sources for these components: meteoric (air and ASW; air-saturated water), andesitic subducted (AS), andesitic thermogenic (AT) and basaltic mantle (BM). Since the endmember for Iwodake gas has a relatively low N₂/He ratio, it is not consistent with the andesitic endmember.

Similarly low N₂/He ratios have also been reported from Vulcano and Campi Flegrei, both in Italy (Giggenbach, 1992b), and were interpreted to indicate that the tectonic conditions specific to that area promote a larger contribution of mantle components (He) to the volcanic gas. Kita et al. (1993) also found similar low N₂/He ratios in volcanic and geothermal gases from the southeast Japan arc of northern Kyushu (Unzen, Kuju, and Beppu). They inferred that the low N₂/He ratio in the southeast Japan arc volcanoes is due to smaller contributions of subducted sediments to arc magmas compared with other areas, possibly related to the efficiency or age of sediment subduction beneath the arc.

**ISOTOPIC COMPOSITIONS OF WATER AND SULFUR**

Most isotopic data for water in high-temperature fumarolic gases show a trend towards an endmember with δD = -20 ± 10%o and
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\[ \delta^{18}O = +10 \pm 2\%o \] (Giggenbach, 1992a), which is distinct in \( \delta D \) from the composition for "primary magmatic water" (Taylor, 1979). Recently, Giggenbach (1992a) demonstrated that these values represent the composition of waters associated with subduction-related magmatism, and the "primary" values may largely reflect those of degassed magma (Taylor, 1986).

The isotopic composition of water in the high-temperature (>700°C) fumarolic gases of Iwodake is \( \delta D = -23 \) to \(-26\%o \) and \( \delta^{18}O = +6.6 \) to \(+7.1\%o \). The \( \delta^{18}O \) values of the water coincide with those of fresh lavas and tufts (+6.6 to +7.0\%o; Matsubaya et al., 1975). The low temperature gases from the summit area tend to have higher \( \delta D \) and \( \delta^{18}O \) values (Fig. 8a). Although there is no ready explanation for these high \( \delta D \) and \( \delta^{18}O \) values of the low-temperature fumarolic gases, they agree well with previous results by Matsuo et al. (1974) and Matsubaya et al. (1975). In contrast to the fumaroles in the summit area, the \( \delta D \) and \( \delta^{18}O \) values of the Monogusa fumarolic gas indicate mixing of local meteoric water with the high-temperature fumarolic gas, in a ratio of 2 to 1. The low \( \delta D \) and \( \delta^{18}O \) values of the Kitabirashita fumarolic condensates suggest that these vapors are derived from the boiling of a volcanic gas-meteoritic water mixture, consistent with the isotopic composition of Kitabirashita hot springs (Fig. 8a). The constant isotopic composition of the high temperature fumaroles is most likely representative of the parent gas of Iwodake, averaging \( \delta D = -25\%o \) and \( \delta^{18}O = +7\%o \). This agrees closely with the values determined for subduction-related magmatism (Giggenbach, 1992a).

The sulfur isotope ratios of total S in the summit fumarolic gases, except for Kamanokuchi (104°C), have a very narrow range of +9.7 to +10.9\%o (CDT) (Table 1). This range generally agrees with the \( \delta^{34}S \) values of unaltered post-caldera lavas (from Iwodake, Inamuradake and Shin-Iwojima) of +11.3 to +12.1\%o (Ueda, 1983). Matsubaya et al. (1975) reported the average \( \delta^{34}S \) values of total S in the high-temperature fumarolic gases of Iwodake to be 12\%o, which is 1 to 2\%o higher than the present results. We have no clear account for this small difference in the \( \delta^{34}S \) values, whether it reflects a change in the \( \delta^{34}S \) value with time or it is due to some sampling and analytical errors. In any case, the representative \( \delta^{34}S \) value of total S in the parent gas is believed to be close to +10\%o.

The lower \( \delta^{34}S \) value (+6.0\%o) of Kamanokuchi (104°C) gas may be due to the addition of \( ^{34}S \)-poor sulfur, previously formed by the deposition of elemental S from volcanic gas, in agreement with the chemical composition of the gas (Fig. 3). This is also consistent with the values of +3 ± 5\%o reported for elemental S of Iwodake (Ueda et al., 1981). The flank fumarolic gases contain sulfur with relatively high \( \delta^{34}S \) (+13.2 and 13.5\%o). The high \( \delta^{34}S \) of Kitabirashita gas may be the result of subsurface deposition of elemental S. This is consistent with the low sulfur content of the gas. In contrast, the
relatively high S content in Monogusa gas does not agree with the elemental S deposition process to explain the high $\delta^{34}$S values. The high $\delta^{34}$S values of Monogusa gas may rather reflect addition of isotopically heavy H$_2$SO$_4$, as suggested by its high values for $S_t$ and $n_5$ (Fig. 3).

**CHEMICAL AND ISOTOPIC COMPOSITIONS OF HOT SPRING DISCHARGES**

Kamada (1964) classified the hot springs of Satsuma-Iwojima into the following three types: 1) very low pH (<2) waters, discharged around Iwodake at Heikenojo, Higashi, Kitabirashita, Yunotaki, and others, 2) low pH (4–6), CO$_2$-rich chloride waters, issuing around Inamuradake basaltic cone at Nagahama and Akayu, and 3) neutral pH, chloride water, located outside the caldera rim, e.g., at Sakamoto (Fig. 1). The origin of these hot spring waters is discussed here on the basis of the results of isotopic analyses of water and S, and the Cl and SO$_4$ concentrations. More detailed discussion of the major element and trace metal contents of the springs is given elsewhere (Hedenquist et al., in prep.).

The relative amounts of S and Cl in water samples and fumarolic gases define a mixing relationship between volcanic gas, meteoric water, and seawater (Fig. 9). The compositions of the very acid hot springs, which are shown by large circles and squares in Fig. 9, lie between meteoric water and the fumarolic gases, indicating that they are a mixture of these components. In contrast, the Sakamoto neutral pH hot spring has a composition indicating mixing of meteoric water and seawater. The Nagahama weakly acidic CO$_2$-rich chloride hot spring also plots close to the seawater-meteoric water mixing line but has a higher sulfate content, indicating addition of a S-rich third component, probably low temperature volcanic gases.

The sulfate in the hot spring waters is most likely produced through the disproportionation of SO$_2$ (reaction 5 and 6). Oxidation of H$_2$S or elemental S by biochemical processes or atmospheric O$_2$ are other possibilities. These latter processes are believed to be relatively unimportant due to the very acid conditions and high sulfate concentrations of the hot springs.

The disproportionation reaction (5) produces 3 moles of sulfate and 1 mole of H$_2$S for every 4 moles of SO$_2$, and 2 moles of sulfate and 1 mole of elemental S are produced from 3 moles of SO$_2$ through reaction (6). Therefore, at most only 3/4 of the amount of SO$_2$ sulfur will be converted to hot spring sulfate, while the rest is deposited as elemental S or released as H$_2$S. Consequently the mixing line between volcanic gas and meteoric water should shift along a S-depletion trend (Fig. 9).

The compositions of the very acid hot springs lie between meteoric water and the fumarolic gases; but tend to have lower Cl/S ratios than that of the mixing line from meteoric water to the S-depleted parent gas endmember (dashed line in Fig. 9). This Cl-depletion is most likely due to the subsurface absorption of volcanic HCl into a deep brine before the vapor is condensed by meteoric water.

The relationship between the $\delta^D$ and $\delta^{18}$O values of hot spring waters of Satsuma-Iwojima is shown in Fig. 8a. The isotopic compositions of
most hot springs lie parallel to a simple mixing line between meteoric water and volcanic gas, but appear to be enriched in D by up to 10%. This D enrichment may be due to mixing with seawater, which accounts for the isotopic composition of Sakamoto and Nagahama hot springs and is consistent with the chemical trends of these two springs (Figs. 8b and 9). However, the major anion composition of the highly acid hot spring waters does not indicate any entrainment of seawater (Figs. 8b and 9). Rather, the D enrichment is most likely due to loss of vapor through subsurface boiling. If the vapor-liquid phase separation occurs at 100°C as a batch process, evaporation of one third of the water will result in a D enrichment by approximately 10‰ in the residual liquid. The isotopic composition of Kitabirashita fumarolic gas (Fig. 8a) supports such an evaporation process of the volcanic gas-meteoric water mixture.

The Cl and 18O contents of the very acid hot springs lie below a mixing line between meteoric water and the volcanic gas (Fig. 8b). The deviation from the mixing line may be due to mixing with a Cl-depleted volcanic gas, also suggested from the chemical trends of hot springs (Fig. 9). Reaction of the highly acid hot spring waters with fresh volcanic rocks may also result in a small oxygen shift of the hot spring waters.

For the very acid hot springs, the mixing ratio of meteoric water to volcanic gases is estimated to range from 1:1 (Kitabirashita) to 7:1 (Higashi) based on their chemical composition (Fig. 9). These estimates are generally consistent with those based on Cl-δ18O constraints (Fig. 8b), though the latter show more scatter. The mixing ratio of meteoric water to seawater for the Sakamoto and Nagahama hot springs is estimated to be 2:1 and 1:1, respectively, consistent with their isotopic composition.

The sulfur isotopic composition of sulfate in the very acid hot spring waters range from +15.2 to +17.6‰, higher than the δ34S of the fumarolic gases. Since the sulfate is produced through disproportionation of SO2, sulfur isotope fractionation between the sulfate and H2S or elemental sulfur results in the high δ34S values of sulfate (Kusakabe and Komoda, 1991). The high δ34S may also be due to the addition of seawater sulfate (of +20‰), though this is inconsistent with the chemical and other isotopic constraints on the origin of the very acid hot spring waters. In contrast, a seawater sulfate source is the most likely explanation for the high δ34S value of the Nagahama hot spring. There is no obvious explanation for the very high δ34S value of the sulfate of the Sakamoto hot springs (+26‰), which is likely to be derived originally from seawater.

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**Fig. 10. Schematic NW-SE cross-section through the Iwodake magmatic-hydrothermal system. Location of the cross-section is shown in Fig. 1. The geological cross-section is modified from Ono et al. (1982). The short dashed curves show the inferred depth of the 100°C isotherm.**
GENERAL DISCUSSION

The genetic relationship of the fumaroles and hot springs is summarized in a schematic cross-section of the island (Fig. 10). The diagram is based on the following conclusions from our study: 1) fumarolic discharges from the summit and the flank are derived from a common parent gas, 2) the compositional variations of the summit fumarolic gases are largely due to reactions occurring during temperature decrease and the entrainment of elemental S, 3) the very acid hot springs around Iwodake volcano are formed by condensation of volcanic gases into local meteoric water, and 4) the flank fumarolic gases, comprising a volcanic gas-meteoric water mixture, have separated from a liquid phase, similar in composition to that discharged from the acid springs.

Iwodake volcano is likely to have been heated during the long period of continuous degassing. Underground temperatures at 1 m depth were measured in 1975 at 71 points in the summit area (Geological Survey of Japan, 1976). The minimum temperature at the 20 points within the 200 m diameter crater bottom is 98°C, the boiling point at this elevation (560 m), while a temperature greater than 90°C was recorded at 70% of the points over the whole summit area (500 x 500 m). The thermal study indicates that Iwodake has been heated by vapor discharges over its life. Iwodake volcano consists mainly of thick lava flows and resulting talus deposits (Ono et al., 1982), and the flank fumaroles are found only in deep gullies. The topographic distribution of the gas outlets on the flanks of the volcano lacks any deep structural control, also suggesting that Iwodake is quite hot to its margins (Fig. 10).

There is no trace of seawater entrainment in the Iwodake fumarole-hot spring system based on our study of the chemical and isotopic composition of the very acid hot spring waters. The distribution of hot springs along the coast indicates that the flow of the thermal waters is influenced by the seallevel-controlled hydraulic pressure gradient. The penetration of seawater, however, is likely to be impeded by the high thermal and pressure gradient from the volcano to the surroundings. Anhydrite precipitation during heating of invading seawater will also provide an effective physical barrier against seawater penetration, similar to the suggestion for White Island (Giggenbach and Sheppard, 1989).

Formation of an HCl-rich liquid phase at depth is inferred based on the composition of the HCl-poor, low-temperature fumarolic gases, and is also required to account for the Cl-depleted composition of the deduced volcanic gas endmember responsible for forming the hot springs (Fig. 8). However, there is no direct evidence for this inferred Cl-rich condensed phase, probably due to retention at depth because of its high density.

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REFERENCES


