Flux of volatiles and ore-forming metals from the magmatic-hydrothermal system of Satsuma Iwojima volcano

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ABSTRACT

The Satsuma Iwojima volcano, southwest Japan, degasses 5 x 10^6 t/yr H_2O, 9 x 10^6 t/yr S, and 6 x 10^6 t/yr CI from high-temperature (>880 °C) fumaroles atop a now-eroded rhyolite dome that erupted 1200 yr ago. Acidic hot springs (pH 1.1–1.8) discharge ~20 x 10^4 t/yr H_2O to the sea; this water is composed of ~1 part magmatic vapor flux, absorbed by ~6 parts meteoric ground water. The CI and SO_4 fluxes in solution originate from the vapor, whereas cation components are derived largely by dissolution of the rhyolite. The flux of Pb, Zn, Cu, and Mo in the vapor and acidic springs ranges from 0.1 to 10 t/yr each, whereas the Au flux is 10^{–3} and 10^{–2} t/yr, respectively. The low concentrations of NaCl and metals in the vapor arise largely from degassing magma bodies in the subsurface; such mineralization requires the subsequent ascent of a metal-rich fluid.

INTRODUCTION

The isotopic composition of water discharged from high-temperature fumaroles (300 to 900 °C) of arc volcanoes indicates that the water vapor is largely derived from degassing magma bodies (Giggenbach, 1992). Analysis of gas and trace metal concentrations in these low-density vapors, combined with the measurement of the SO_2 flux, allows the flux of each component to be estimated (Buat-Menard and Arnold, 1978; Symonds et al., 1992). However, such calculations of surface flux will underestimate the total flux of components degassed from the magma if a portion of the aqueous fluid remains at depth, owing to the separation of a dense, hypersaline liquid at subcritical pressures (Henley and McNabb, 1978), and forms a hydrothermal system over the magma body. In addition, the ascending gas-rich vapor may be absorbed by shallow ground water within the volcano, forming highly acidic waters. The surface expressions of these magmatic-hydrothermal systems include high-temperature fumaroles, acidic to neutral pH hot springs, and acidic crater lakes (Giggenbach et al., 1990; Sturchio et al., 1993). However, because the springs are commonly dispersed over large areas, determination of the flux of magmatic components absorbed by the hydrothermal system is difficult.

We measured the component fluxes associated with high-temperature fumaroles and acidic springs on the volcanic island of Satsuma Iwojima, southwest Japan (Fig. 1, inset). Because the subsurface outflow of ground water is contained by the hydrologic head of the surrounding seawater, most acidic springs discharge near sea level, allowing them to be sampled and their flux estimated. The fumaroles discharge from a rhyolite dome that is strongly altered and leached. The silica-rich rock remaining is typical of that hostig high-sulfidation Cu-Au ore deposits deduced to have formed in this acidic magmatic-hydrothermal environment.

SATSUMA IWOJIMA MAGMATIC-HYDROTHERMAL SYSTEM

The composition of the Satsuma Iwojima high-temperature fumaroles (Shinohara et al., 1993) is broadly similar to fumaroles of other calc-alkaline arc volcanoes such as those at White Island, New Zealand, where acidic springs also flow into the sea (Giggenbach and Sheppard, 1989). However, the vast majority of the high metal flux from White Island is associated with aerosols entrained with the volcanic eruption of ash (Hedenquist et al., 1993). In contrast, the fumarolic activity on Satsuma Iwojima is related to passive degassing of the underlying magma, where the most recent eruption occurred ~1200 yrs ago (Ono et al., 1982), associated with extrusion of the rhyolitic dome of Iwodake (Fig. 1). The western part of the island is composed of andesitic to rhyolitic lavas that erupted prior to the formation of the Kikai caldera 6300 yr ago.

High-temperature fumaroles (up to 880 °C) discharge within the summit crater at an elevation of ~600 m (Fig. 1). Low-temperature fumaroles (<110 °C) are also found on the outer flanks of the volcano. Acidic hot springs (pH 1.1–1.8, 70–42 °C) discharge along the eastern half of the island, mainly at elevations <5 m above high tide, from Heikenojo eastward to Ketsunohama and around to the south shore westward as far as Higashi. Along this part of the coast are almost continuous, sharply defined white to green patches of water that are due to hydrated oxides formed when the Al- and Fe-rich acidic waters mix with seawater (Nogami et al., 1993). These patches indicate a subsea-level outflow of acidic water around most of the eastern half of the island. Bright red seawater is present at Akaya and in Nagahama harbor and is due to the outflow of neutral pH, iron-bicarbonate water, related to the basaltic cone of Inamuradake (Kamada, 1964). Near-neutral pH springs are also present on

Figure 1. Map of Satsuma Iwojima. Large symbols—hot springs, same as in Figures 2 and 3. Some sites have more than one spring. Contour interval = 100 m.

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the northwest coast near Sakamoto; their isotopic and chemical compositions indicate that they are a mixture of heated seawater and meteoric ground water (Fig. 2).

The isotopic and major element composition of the fumaroles and hot springs has been reported by Shinohara et al. (1993), and we briefly review their results here. Coupled with the isotopic composition of the high-temperature fumaroles (Fig. 2), the Cl (essentially HCl) and S (largely SO₂) concentrations allow the end-member parent composition to be estimated for the shallow, low-pressure vapor (star; Figs. 2 and 3), just before discharge at the surface. Near-surface processes such as S deposition and condensation of Cl-rich liquid account for the range in the S/Cl ratio of the fumaroles. Absorption of the high-temperature vapors (or those having undergone some Cl or S depletion) by meteoric ground water accounts for both the isotopic (Fig. 2A) and major anion (Cl and S; Figs. 2B, 3) composition of the acidic springs. Near-surface boiling causes some isotopic enrichment of the hot-spring waters compared to that expected for simple mixing (dashed line, Fig. 2A), consistent with the depleted isotopic composition of the fumaroles on the lower flanks (e.g., at Kitabirashita). Assuming that the Cl and S content of the acidic springs is derived from absorption of the high-temperature vapor, the magmatic to meteoric water ratio varies from ~1:2 for the most acidic springs at Ketsunohama and Heikenojo to ~1:7 for the Yunotaki springs (Fig. 3); these estimates are generally consistent with the isotopic compositions of the springs (Fig. 2A).

MAJOR AND TRACE ELEMENT CONCENTRATIONS AND FLUXES

The average concentrations of cations in the most acidic springs (Table A) ¹ parallel the composition of fresh Iwodake rhyolite (Fig. 4), indicating isochemochemical dissolution of the rock by the acidic waters. By contrast, the concentrations of the rock-forming elements in the high-temperature (>700 °C) vapors are orders of magnitude lower than those in the most acidic waters, though the Cl and S concentrations are higher (Fig. 4). Trace metal concentrations and trends are variable; the vapors usually have slightly higher base metal, but lower Au, concentrations than the acidic waters.

The SO₂ flux from the summit of the volcano was measured by correlation spectrometry over 4 d in October 1990 (Kazahaya et al., 1992), corresponding to the period of fumarole sampling. The results indicate 470 ±60 t/d SO₂ flux, similar to the 470–680 t/d measured in 1975 (Okita et al., 1977). The average H₂O/SO₂ mole ratio in the high-temperature fumaroles is ~108 (Shinohara et al., 1993), indicating the total water discharged from the fumaroles is ~5.2 × 10⁶ t/yr (a power output of ~540 MW).

The flow of acidic hot-spring water is less accurately known. Kamada (1964) estimated the flow to be ~20 × 10⁶ t/yr by measuring both the flow of Higashi spring and the size of the related discolored zone in the ocean. By using this relation and the total area of discolored water around the island (from aerial photographs), the flow of acidic water to the ocean was estimated, assuming that all acidic springs were of similar composition and would result in similar-sized areas of discoloration after mixing with seawater. Although approximate, this method has an advantage in that it accounts for the large proportion of acidic water runoff that occurs below low tide. Sup-

Figures 2–4 are shown in the layout as follows:

Figure 2. Compositions of (A) δD-δ¹⁸O and (B) Cl for fumarole vapors and hot-spring waters. Symbols same as in Figure 1; dashed line and dotted line—mixing of parent vapor (star; Shinohara et al., 1993) and Cl-depleted vapor with meteoric ground water, respectively; dot-dashed line—mixing of ground water and seawater (diamond).

Figure 3. Relative proportion of H₂O, Cl, and S (total S) for fumarole vapors and hot-spring waters. Acidic waters form by absorption of magmatic vapor. Symbols and lines same as in Figures 1 and 2.

Figure 4. Logarithmic plot of composition of fresh Iwodake rhyolite (Ono et al., 1982), acidic hot springs (Heikenojo, Yunotaki, and Higashi spring averages), and high-temperature (>700 °C) vapors (Kuromoe and average of two Ohachi-oku samples).
porting this estimate, the yearly rainfall on the island varies from $25 \times 10^3$ to $40 \times 10^3$ t/yr (Yoshida and Ozawa, 1981), an amount only slightly greater than the calculated acidic water runoff. There are no perennial streams on the island, so most of the runoff must occur as ground water, which absorbs the ascending vapors to form the acidic waters.

On the basis of the water flux from the high-temperature fumaroles and acidic springs, the flux of all other components in the vapors and springs may be estimated (Table B; see footnote 1). The flux of Pb, Zn, Mo, and Sn in the high-temperature vapor and acidic spring water ranges from $\sim 1$ to 10 t/yr each, whereas the Cu flux is slightly lower (Fig. 5). By contrast, the Au flux is very low, $\sim 10^{-3}$ t/yr in the acidic waters and $\sim 10^{-5}$ t/yr in the vapors.

The average vapor and acidic spring compositions (Table B; see footnote 1) indicate that the acidic water discharging from the volcano consists of $\sim 1$ part magmatic vapor condensate to 6 parts meteoric water, assuming that the Cl and S in the acidic water is derived from absorption of vapor similar in composition to that discharging from the summit. This average value corresponds to $\sim 3.0 \times 10^5$ t/yr of vapor being absorbed, compared with $5.2 \times 10^6$ t/yr of fumarole water; i.e., about one third of the magmatic vapor ascending to a shallow depth is absorbed by and heats ground water. The amount of reaction between the resulting acidic waters and rock may be estimated from the acidic spring flux data and the composition of the rhyolite, indicating that $\sim 0.4 \times 10^6$ t/yr of rock is totally leached of its major cations, leaving a silica-rich residue.

**MAGMATIC-HYDROTHERMAL SYSTEM AT DEPTH**

If the magma beneath Satsuma Iwojima is degassing at a pressure of at least several hundred bars, an aqueous fluid rich in NaCl (1-10 wt%) will exsolve upon saturation (Burnham, 1979). This fluid will form an immiscible hypersaline liquid and low-density vapor below the critical pressure (Sourirajan and Kennedy, 1962; Fig. 6, inset), with chloride-complexed metals tend and dividing portion into the hypersaline liquid, adjacent to the intrusion. This hypersaline liquid is commonly observed in fluid inclusions associated with intrusion-hosted porphyry Cu deposits. Recent evidence (Lowenstein, 1994) also substantiates the existence of hypersaline liquids in volcanic systems. However, at high pressure (>500 bar), a significant fraction of the metals may also be contained by the coexisting vapor (Hemley et al., 1992). The density contrast will promote separation of the buoyant vapor from the hypersaline liquid (Fig. 6), and as the high-pressure vapor ascends and depressurizes, most of the remaining NaCl (and chloride-complexed metals) will partition into a continuously condensing hypersaline liquid (or salt), further depleting the evolving vapor phase in metal chlorides. The low-pressure vapor that finally discharges from the volcano will contain only a small fraction of the NaCl and metals initially exsolved from the magma, even though a large fraction of the volatile species ($H_2O$ plus $SO_2$, $CO_2$, $HCl$, etc.) reaches the surface. Thus, the composition of vapor discharged from such passively degassing volcanoes does not reflect the metal concentrations of aqueous fluids exsolving from magmas.

The low metal flux from Satsuma Iwojima and other passively degassing volcanoes contrasts with that of similar arc volcanoes during eruption. Although the flux of $SO_2$, $H_2O$, and other volatiles is similar (470 t/d $SO_2$ at Satsuma Iwojima vs., e.g., 300–1000 t/d at White Island), the flux of NaCl and metals such as Cu and Au contained by aerosols erupted with ash from White Island (Hedenquist et al., 1993) is about three orders of magnitude greater than that associated with the similarly high temperature but passive degassing of Satsuma Iwojima (Fig. 5). This difference is due to discharge of a high-pressure vapor during eruption at White Island that is much richer in NaCl and metals compared with the distilled low-pressure vapor associated with quiescent discharge (Fig. 6, inset). Even if a dense hypersaline liquid (or salt) forms because of rapid pressure decrease accompanying eruption, it will be entrained by the energetic eruption of aerosol. Therefore, if we consider the phase relations in the NaCl-$H_2O$ system during depressurization (Fig. 6, inset), and combine these constraints with the observation of low NaCl and

**Figure 5. Flux (t/yr and t/ka) of $H_2O$, S, Cl, and metals of interest for acidic hot springs and passive degassing of high-temperature (700 °C) fumarole vapors from Satsuma Iwojima. Metal flux of White Island volcano, despite similar $H_2O$, Cl, and S flux during eruption, is much greater (Le Cloarec et al., 1992) due to degassing of high-pressure vapor that is relatively NaCl rich (30 x that of Satsuma Iwojima vapor; Table B [see footnote 1]).**

**Figure 6. Schematic north-south cross section through Iwodake dome, showing absorption of part of magmatic vapor into meteoric ground water, forming acidic waters that leach rock and flow to sea. Fumaroles have a heat flow of ~540 MW (for equal proportions of 700 and 100 °C vapor), and $3.0 \times 10^3$ t/yr of 700 °C vapor absorbed by ground water accounts for 370 MW. At depth, degassing magma likely has envelope of hypersaline liquid (solid circles) and low-density vapor (open circles). Inset illustrates immiscibility in NaCl-$H_2O$ system as a function of pressure (modified from Sourirajan and Kennedy, 1962). As high-pressure vapor ascends and depressurizes, its NaCl (and Cl-complexed metal) content decreases owing to condensation of hypersaline liquid. This process continues to atmospheric pressure during passive degassing (Satsuma Iwojima), unless high-pressure vapor (relatively rich in NaCl and metals) accompanies volcanic eruption (White Island).**
metal fluxes during passive degassing at Satsuma Iwojima (in contrast to much higher fluxes associated with eruption of otherwise broadly similar magmas), we conclude that there is likely a dense, hypersaline liquid condensing from high-pressure vapor beneath Satsuma Iwojima (Fig. 6). This brine is a sink for chloride-complexed metals, accounting for the low metal flux here.

**IMPLICATIONS FOR THE FORMATION OF HYDROTHERMAL ORE DEPOSITS**

Iwodake has been passively degassing for $\sim 10^3$ yr, since extrusion of the rhyolite dome, on the basis of old records of fumarolic activity. Over this period, $> 10^5$ t of rock (see above) has likely been leached by the acidic waters formed by ground-water absorption of $SO_2$ and HCl-bearing magmatic vapor. The residual silica-rich rock, commonly containing $>$95% SiO$_2$, is the characteristic host to high-sulfidation Cu-Au ore (Stoffregen, 1987). These bodies of leached rock are typically $10^7$ to $10^8$ t in size and, thus, can easily form over a period of $< 10^5$ yr, on the basis of these results. However, the flux of base metals and Au in the high-temperature vapor, as sampled at the surface (Fig. 5), appears inadequate as a potential ore-forming fluid, even if such degassing continues for $\sim 10^4$ yr, the period over which single intrusions crystallize, because high-sulfidation Cu-Au deposits typically contain $> 10^5$ t Cu and $10^2$ t Au.

The flux of base metals, particularly Cu, derived by reaction of the acidic waters and leaching of the host rhyolite (Fig. 5) is also insufficient by about two orders of magnitude to account for a typical high-sulfidation Cu-Au orebody. The flux of Au leached from the rocks is greater than that in the vapor but over $10^5$ yr will account for only $\sim 1$ t of Au transport in a system such as Satsuma Iwojima. Thus, rock leaching is not a significant source of metals at Satsuma Iwojima, although if leaching takes place at greater depths, and there is a longer reaction path length (i.e., a smaller water/rock ratio), higher metal concentrations in the hydrothermal fluid may result (Reed, 1992).

Although different magmas may exsolve aqueous fluids of varying metal content, it is unlikely that any low-pressure, low-NaCl vapor will be able to transport ore quantities of metals. How then do we explain the apparent paradox that low-pressure, passively degassing magmatic vapors are not a potential source of metals for mineralization, despite the strong evidence that magmatic fluids with similar chemical and isotopic signatures are involved in the formation of high-sulfidation Cu-Au deposits (Stoffregen, 1987; Rye et al., 1992)? One possibility may be that a high-pressure, NaCl- and metal-rich vapor, similar to that discharging from White Island (Fig. 5), is cooled by absorption into deep meteoric water, forming a potential ore fluid. Where this or a similar process (e.g., entrainment of a hypersaline brine; White, 1991) does not occur, only the highly leached but unmineralized cap that is typical of many volcanoes will remain.

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**REFERENCES CITED**


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