

Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia

ROBERT B. SYMONDS¹, WILLIAM I. ROSE¹, MARK H. REED², FREDERICK E. LICHTER³
and DAVID L. FINNEGAN⁴

¹Department of Geology and Geological Engineering, Michigan Technological University, Houghton, MI 49931, U.S.A.

²Department of Geology, University of Oregon, Eugene, OR 97403, U.S.A.

³U.S. Geological Survey, Box 25046, M.S. 928, Denver Federal Center, Denver, CO 80225, U.S.A.

⁴Los Alamos Scientific Laboratory, M.S. J514, Los Alamos, NM 87545, U.S.A.

(Received January 2, 1986; accepted in revised form April 30, 1987)

Abstract—Condensates, silica tube sublimates and incrustations were sampled from 500–800°C fumaroles and lava samples were collected at Merapi Volcano, Indonesia in Jan.–Feb., 1984. With respect to the magma, Merapi gases are enriched by factors greater than 10^5 in Se, Re, Bi and Cd; 10^4 – 10^5 in Au, Br, In, Pb and W; 10^3 – 10^4 in Mo, Cl, Cs, S, Sn and Ag; 10^2 – 10^3 in As, Zn, F and Rb; and 1 – 10^2 in Cu, K, Na, Sb, Ni, Ga, V, Fe, Mn and Li. The fumaroles are transporting more than 10^6 grams/day (g/d) of S, Cl and F; 10^4 – 10^6 g/d of Al, Br, Zn, Fe, K and Mg; 10^3 – 10^4 g/d of Pb, As, Mo, Mn, V, W and Sr; and less than 10^3 g/d of Ni, Cu, Cr, Ga, Sb, Bi, Cd, Li, Co and U.

With decreasing temperature (800–500°C) there were five sublimate zones found in silica tubes: 1) cristobalite and magnetite (first deposition of Si, Fe and Al); 2) K-Ca sulfate, acmite, halite, sylvite and pyrite (maximum deposition of Cl, Na, K, Si, S, Fe, Mo, Br, Al, Rb, Cs, Mn, W, P, Ca, Re, Ag, Au and Co); 3) apthitalite (K-Na sulfate), sphalerite, galena and Cs-K sulfate (maximum deposition of Zn, Bi, Cd, Se and In; higher deposition of Pb and Sn); 4) Pb-K chloride and Na-K-Fe sulfate (maximum deposition of Pb, Sn and Cu); and 5) Zn, Cu and K-Pb sulfates (maximum deposition of Pb, Sn, Ti, As and Sb).

The incrustations surrounding the fumaroles are also chemically zoned. Bi, Cd, Pb, W, Mo, Zn, Cu, K, Na, V, Fe and Mn are concentrated most in or very close to the vent as expected with cooling, atmospheric contamination and dispersion. The highly volatile elements Br, Cl, As and Sb are transported primarily away from high temperature vents. Ba, Si, P, Al, Ca and Cr are derived from wall rock reactions.

Incomplete degassing of shallow magma at 915°C is the origin of most of the elements in the Merapi volcanic gas, although it is partly contaminated by particles or wall rock reactions. The metals are transported predominantly as chloride species. As the gas cools in the fumarolic environment, it becomes saturated with sublimate phases that fractionate from the gas in the order of their equilibrium saturation temperatures. Devolatilization of a cooling batholith could transport enough acids and metals to a hydrothermal system to play a significant role in forming an ore deposit. However, sublimation from a high temperature, high velocity carrier gas is not efficient enough to form a large ore deposit. Re, Se, Cd and Bi could be used as supporting evidence for magmatic fluid transport in an ore deposit.

INTRODUCTION

VOLCANIC FUMARoles are sites of complex interactions of cooling volcanic gases with the atmosphere and surrounding wall rock. Around fumaroles, some volatile species are deposited as brightly colored incrustations, whereas others are transported into the atmosphere. Understanding of the volatilization, transport and deposition of volatile elements and compounds provides insight into volcanic contributions to the atmosphere, the role of magmatic fluids in ore-forming processes and the effect of volatile transport of trace metals on the trace element composition of igneous rocks. Furthermore, volatiles may be an indicator of the intensive parameters of shallow magma bodies and thus, may be useful in sensing changes in magma chambers.

This study of volcanic emanations focuses on the trace components of volcanic gases and relates those elements emitted in the gas with those forming sublimates to understand the fumarolic environment. The purposes of this work are to understand the origin, transport and sublimation of trace elements in volcanic gases and to evaluate the degassing of magma as an

ore-forming process. To accomplish these objectives, 1) condensates, sublimates, incrustations and lava samples have been collected and analyzed; 2) sublimate mineralogy was studied; 3) enrichment factors and fluxes for volatile elements were calculated; and 4) thermodynamics was used to predict the stable gas species, calculate volatilities and model sublimate zoning.

Merapi, an andesitic stratovolcano, was chosen because of its high temperature (up to 900°C) fumaroles, which have been the site of several gas and sublimate studies (e.g., LE GUERN and BERNARD, 1982; LE GUERN *et al.*, 1982; BERNARD, 1985). Furthermore, a better understanding of the Merapi volcanic system will help forecast future eruptions of this dangerous volcano.

PREVIOUS WORK

Analyses of volcanic gases have shown that they are dominated by H₂O, CO₂, SO₂, H₂, H₂S, HCl, CO, HF and S₂ (GREENLAND, 1984; GERLACH, 1980). Changes in the relative abundances of these major gas species have been shown to correlate with changing volcanic activity (GREENLAND, 1984; CASADEVALL *et al.*, 1983).

Fifty trace elements have been described in studies of incrustations, sublimates, condensates and particles from volcanic fumaroles and particles from volcanic plumes, which demonstrates that many additional volatile species are transported by volcanic gases. Some of the more unusual trace elements in volcanic gases include V, Se, Ag, I, Ir and Au. (*e.g.*, STOIBER and ROSE, 1974; ZOLLER *et al.*, 1983).

Condensates are liquids (mostly H₂O) collected by condensing volcanic gas. These liquids trap most of the trace elements in the volcanic gas. The most complete work on condensates is by STOIBER and ROSE (1970) who studied condensate samples from Central American volcanoes.

Incrustations are colored deposits that are formed around volcanic fumaroles. STOIBER and ROSE (1974) have described 47 minerals which occur as incrustations at Central American volcanoes. Other studies have described the mineralogy of incrustations at Mount St. Helens (KEITH *et al.*, 1981), Icelandic volcanoes (OSKARSSON, 1981) and Kamchatka-Kurile volcanoes (NABOKO, 1959, 1964).

Sublimates are solids deposited directly from the gas phase. Incrustations include both sublimates and minerals formed by a liquid or gas phase reacting with the wall rock (STOIBER and ROSE, 1974). This makes it difficult to interpret whether the elements in incrustations were derived from the volcanic gas or the wall rock. Several methods have been used to isolate sublimates from incrustations that are derived by liquid-rock or gas-rock reactions. NAUGHTON *et al.* (1974) collected sublimates from Kilauea by suspending quartz tubes filled with quartz wool above vents of fountaining lava. LE GUERN and BERNARD (1982) inserted silica tubes into fumaroles to collect sublimates at Merapi Volcano, Indonesia. The most complete work on quartz tube sublimate sampling is by BERNARD (1985).

GEOLOGIC SETTING

Merapi is an andesitic stratovolcano located 25 km north of Yogyakarta, in central Java Indonesia. It is on the volcanically active Sunda arc at the intersection of transverse and longitudinal faults (NEUMAN VAN PADANG, 1951). Merapi is one of the world's most active and dangerous volcanoes with over 60 eruptions since 1500 A.D. (KUSUMADINATA, 1979).

From 1977 to Jan. 1984 activity at Merapi was relatively constant and characterized by the continuous extrusion of an andesitic dome. Active dome growth was indicated by glowing rockfalls that spalled off the dome every 15–20 minutes. The 1977–1979 rate of lava production from these rockfalls has been estimated at 10,000–20,000 m³ per day (LE GUERN *et al.*, 1982). Dome growth was accompanied by the emission of gases from high temperature summit fumaroles (up to 900°C as measured in 1979 by LE GUERN *et al.*, 1982). These fumaroles have been named Belvedere, Gendol and Woro (LE GUERN *et al.*, 1982). The relatively constant dome growth has been accompanied by consistent SO₂ emission rates from 250–450 metric tonnes/day from February, 1983 to January, 1984 (BADRUDIN, unpublished data).

FIELD AND ANALYTICAL METHODS

All the field work was done during Jan.–Feb. 1984. This was during the rainy season in Java when it rained almost every afternoon.

Condensates

Condensates were collected from the Gendol (796°C) and Woro (576°C) fumaroles. A tube of a silica, stainless steel or aluminum was inserted in the vent. This was connected to a polyethylene or pyrex flask by a series of tygon, Na-lime glass and rubber tubing. As the gas was pumped through this apparatus, condensate accumulated in the flask. To test the efficiency of sublimation, one condensate sample was collected from the end of a sublimate sampling tube.

Seven samples were collected on four days. In general, 125 ml of sample were collected, although one sample (Gendol-1) contained only 40 ml. All samples contained a cloudy white precipitate. Three samples (Gendol-3, Gendol-4 and Woro-2) were green due to contamination from the stainless steel tube.

The anions (SO₄²⁻, F⁻, Cl⁻ and Br⁻) were analyzed using ion chromatography (SMALL, 1983). Cations (except U) were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (SCOTT and KOKOT, 1975). U was analyzed by the fission track method.

Since a variety of materials were used to collect the condensates, the samples were carefully evaluated (SYMONDS, 1985) for contamination. All analytical data on elements that constitute part of the apparatus used to collect a particular sample were discarded.

Sublimates

Using the silica tube method (LE GUERN and BERNARD, 1982) sublimates were collected from the Gendol and Woro fumaroles. Three silica tubes (1 m long and 3 cm inner diameter) were inserted into these fumaroles. Volcanic gas vented freely through the tubes and gradually deposited sublimates on the tube walls. After a period of four days, the tubes were removed and sealed with plastic tape.

In the lab, the tubes were cut into 10 sections (approximately 10 cm long). Each tube section was weighed prior to removing the sublimates. Finally, the sections of tube were reweighed to determine the mass of sublimate by difference.

One fraction of sublimate from each tube section was analyzed by X-ray fluorescence spectrometry (XRF) (SYMONDS, 1985). A variety of rock (ROSE *et al.*, 1986), geochemical (GLADNEY *et al.*, 1984; MYERS *et al.*, 1976) and synthetic (SYMONDS, 1985) standards were used. Since the rock and geochemical standards did not match the Pb-rich matrix of most samples, a mass absorption correction was made using a Compton scattering technique modified (SYMONDS, 1985) from REYNOLDS (1963). The Gendol G-1 sublimates were also analyzed by instrumental neutron activation (INAA) (GERMANI *et al.*, 1980). A third fraction of sublimate was dissolved ultrasonically in distilled water and analyzed by a specific ion electrode for NH₄⁺. A fourth fraction was studied by scanning electron microscopy (SEM) to look at sublimate morphology and to constrain the elemental proportions of the sublimate phases by energy dispersive spectroscopy (EDS) using a ZAF correction (deconvolution routines were used when peak overlap was a problem). Because light elements (F, O, N and C) are undetectable by these methods, their presence (notably O in sulfates) was inferred from crystal forms (SYMONDS, 1985). Finally, X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to confirm the presence of some of the minerals.

When available, the INAA data were used as they are probably more accurate than the corresponding XRF data reported by SYMONDS (1985) because of the lack of matrix effects associated with this method. Because the two methods agree generally within ±15%, the accuracy of these data is normally at least that good for elements analyzed by both methods (Na, Al, Cl, K, Mn, Fe, Zn, Br, Rb, Mo, Cd, Sn, Cs and W).

Incrustations

Incrustation samples were collected from the Gendol (GHT, GMZ, GLT) and Woro (WS91, WS92, WS93, WS94) fumaroles at 0 to several m from each vent. The samples were analyzed by XRF (and specific ion electrode for NH₄⁺) using a similar method as described for the sublimates (SYMONDS, 1985). With the exception of GHT and WS91, mass absorption corrections were not used because the samples had a similar matrix to the geochemical reference standards.

Rocks

Four rock samples were collected for XRF analysis. These included a fresh sample of the 1983 lava (M-6C), a 1940 lava sample (MS-40) and a prehistoric lava sample (M-13). Rocks were analyzed by quantitative XRF analysis using the technique described by ROSE *et al.* (1986). Precision is generally better than $\pm 1\%$ for the major elements and less than $\pm 5\%$ for the trace elements (ROSE *et al.*, 1986).

ANALYTICAL RESULTS AND CHEMICAL TRENDS

Condensates

Analytical results and lognormal statistics for 26 anions and cations for seven condensate samples are reported in Table 1. STOIBER and ROSE (1970) have shown that the anions and cations in Central American volcanic gas condensates are lognormally distributed. This also applies to the Merapi condensates, especially the cations.

The condensates also contain 42–240 ppm Ca, 1.6–180 ppm Na and 4.7–19 ppm B, but these data are unreliable because of possible contamination from sampling materials. Averages for atomic Cl/S = 12.3 (Cl/SO₄²⁻ = 4.5), atomic Cl/F = 11.0 and atomic Cl/Br = 494. The pH of the condensates is about 1.0.

The Gendol-1 condensate sample collected from the end of a sublimate sampling tube (Gendol G-1) is not greatly different from the other condensate samples. This is evidence that the sublimation in the silica tubes is not very efficient and a significant proportion of most volatile elements do not deposit in the tubes.

Sublimates

The sublimates were black and covered the inner walls of the tubes except for that part submerged below the vent. The temperature gradient in the tubes ranged from 796 to 525°C in Gendol G-2, from 767 to 530°C in Gendol G-1 and from 576 to 458°C in Woro W-1. The greatest mass of sublimate

was deposited 10–40 cm from the hottest end of the tubes after which, the mass was relatively constant at $\frac{2}{3}$ – $\frac{1}{2}$ of the maximum mass. The total mass of sublimate deposited was 3.99 g in Gendol G-1, 3.92 g in Gendol G-2 and .90 g in Woro W-1 in about 96 hours of sampling.

Analytical results for the Gendol G-1 tube are reported in Table 2. Additional XRF data are reported elsewhere (SYMONDS, 1985).

Chemical variations (micromoles/cm²) in the Gendol G-1 sublimates are shown in Fig. 1. These are similar to the trends reported for the Gendol G-2 tube (SYMONDS, 1985) except that Ca, Mn, S and P have maximum depositions at lower temperature zones than inferred here and NH₄⁺ has a maximum deposition at the cooler end of the tube. In general, the trends agree well with the observed mineralogy (see "Sublimate Mineralogy") of the Gendol sublimates. However, the occurrence of major amounts of cristobalite and Al-bearing magnetite at the high temperature end of the hotter Gendol G-2 tube suggests that Si, Fe and Al should also be grouped together as a higher temperature zone, above the zone of maximum deposition. Furthermore, since BERNARD (1985) found NH₄⁺-bearing sublimates at temperatures less than 450°C at Merapi, NH₄⁺ is probably best interpreted as observed in the Gendol G-2 tube.

The combined chemical zonation for the Gendol sublimates is divided into seven inferred groups (from 800 to 500°C): 1) first deposition of Si, Fe and Al; 2) maximum deposition of Cl, Na, K, Si, S, Fe, Mo, Br, Al, Rb, Cs, P, Mn, W, Ca, Re, Ag, Au, and Co; 3) maximum deposition of Zn, Bi, Cd, Se and In; high deposition of Pb, Sn and all elements in group 2; 4) beginning of maximum deposition of Pb and Sn; 5) maximum deposition of Pb, Sn, and Cu; 6) maximum deposition of Pb, Sn and Ti; and 7) maximum deposition of As and Sb; continued deposition of all elements (except Ca) in groups 2–6.

Selected variation diagrams are shown in Fig. 2. The alkali metals Na, K, Rb and to a lesser extent Cs have similar depositional patterns (Fig. 1) and tend to covary. The group VIB elements Mo and W have similar depositional patterns (Fig. 1) and covary (Fig. 2). Re also correlates strongly with Mo

Table 1. Analyses of gas condensates from Merapi fumaroles. All data in ppm.

Methods	Gendol-1	Gendol-2	Gendol-3	Gendol-4	Woro-1	Woro-2	Woro-3	Antilog
	1-13-84	1-19-84	1-27-84	2-13-84	1-19-84	1-27-84	2-13-84	Mean
	1	1,3	1,2,3	1,2	1,3	1,2,3	1,2	
Cl ⁻	3600.	3200.	3800.	3100.	3500.	3700.	3300.	3500.
SO ₄ ²⁻	520.	820.	2500.	540.	490.	1000.	590.	770.
F ⁻	310.	110.	230.	130.	120.	140.	220.	170.
Al	25.	---	---	120.	---	---	23.	41.
Br ⁻	8.	240.	8.	1t 4.	22.	1t 4.	40.	16.
Zn	10.	11.	10.	5.3	82.	3.6	6.2	10.
Fe	11.	7.1	---	---	8.	---	---	9.
K	20.	6.8	9.6	14.	6.2	2.6	2.9	7.
Mg	2.3	5.0	17.	24.	6.7	3.9	3.9	6.
Pb	1.6	1.5	1.0	1.0	.83	.32	.35	.8
As	.96	.28	.84	.63	.72	.35	.34	.53
Mo	.12	.11	.15	2.8	.08	.16	.18	.20
Mn	.22	.16	---	---	.16	---	---	.18
V	.022	.10	.80	1.1	.029	.98	.083	.17
W	.07	.07	1t .05	1.1	.38	1t .05	.13	1t .13
Sr	.19	.046	.098	.21	.20	.095	.089	.12
Ni	.05	.26	---	---	.07	---	---	.10
Cu	.042	.013	.24	1.0	.034	.37	.021	.09
Ga	.01	.09	.58	.43	.02	.49	.01	.08
Cr	.05	.08	---	---	.12	---	---	.08
Bi	.13	1t .01	.23	.17	.03	.17	1t .01	1t .06
Sb	1t .05	1t .05	1t .05	.16	1t .05	1t .05	1t .05	1t .06
Cd	.04	.08	.02	.01	.05	.01	1t .01	1t .02
Li	.024	.011	.010	.088	.007	.002	.006	.011
Co	.002	1t .002	---	---	.003	---	---	1t .002
U [*]	.001	1t .0005	.0007	.0085	1t .0005	.0008	.0005	1t .0009

* Analyzed by R. Zielinski

--- No data or data deleted because of contamination

1t less than the reported detection limit

1 Na-line glass, tygon and rubber tubing, pyrex flask

2 Stainless steel tubing

3 Aluminum tubing

Table 2. Major and trace element composition of the sublimates collected in the Gendol G-1 tube. The samples (G1-S2 through G1-S9) were taken at increasing distances from the hot end of the tube, temperatures ranged from 767–530°C. All chemical data are in wt. %. Mg, V, Cr and Ba are below detection in all samples. Listed in order of decreasing maximum concentration.

	G1-S1	G1-S2	G1-S3	G1-S4	G1-S5	G1-S6	G1-S7	G1-S8	G1-S9	G1-S10
D ¹	4.3	14.1	24.8	35.4	46.1	56.9	67.7	78.5	89.2	97.3
M/A ²	0.88	9.08	6.54	6.00	5.86	4.27	5.25	4.93	4.05	2.90
Cl ¹	38.1	32.2	28.6	29.5	29.3	23.3	26.9	29.6	31.1	20.1
Pb	N.D.	.28	12.34	18.62	19.08	22.02	20.01	22.20	22.03	N.D.
Na ¹	17.7	21.7	14.9	15.5	14.5	14.6	14.2	14.5	13.5	11.2
K ¹	17.9	17.1	17.4	17.5	17.2	16.8	16.3	16.2	14.5	14.7
S	N.D.	4.65	5.59	5.55	6.42	6.55	5.62	5.29	5.72	N.D.
Si	N.D.	4.97	2.15	1.46	2.34	1.14	1.93	1.76	.97	N.D.
Fe ¹	1.4	2.5	2.0	1.9	1.7	1.9	1.7	1.6	1.7	2.0
Zn ¹	.35	.36	1.9	1.8	1.7	1.9	1.7	1.5	1.2	1.3
Bi	N.D.	.012	1.44	1.22	.98	.98	.96	1.00	1.28	N.D.
Mo ¹	.32	.68	.51	.52	.50	.54	.53	.56	.69	.84
Sn	---	.0038	.26 [*]	.42 [*]	.32 [*]	.53 [*]	.48 [*]	.48 [*]	.60 [*]	.61 [*]
Cs ¹	.15	.30	.31	.28	.37	.11	.14	.17	.11	.10
Br ¹	.21	.33	.23	.22	.20	.23	.22	.22	.25	.36
Rb ¹	.12	.23	.23	.23	.20	.24	.22	.19	.23	.29
Cd ¹	.08	.08	.28	.24	.23	.25	.26	.23	.23	.27
Al ¹	.170	.091	.066	.049	.030	.030	.027	.020	.021	.054
Ti	N.D.	.050	.089	.073	.089	.14	.16	.12	.10	N.D.
W ¹	.076	.146	.123	.126	.127	.139	.128	.129	.137	.157
As ¹	.0034	.0024	.0023	.0042	.0086	.017	.028	.038	.063	.097
Cu	N.D.	.029	.043	.044	.066	.073	.050	.052	.053	N.D.
Mn	.028 [*]	.042 [*]	.039 [*]	.030	.042 [*]	.040	.030	.024	.031 [*]	.039 [*]
Se ¹	.0029	---	.0330	.0355	.0281	.0256	.0176	.0175	.0075	.0086
In ¹	.0058	.0047	.0312	.0234	.0213	.0224	.0296	.0234	.0270	.0273
Ca	N.D.	.026	.012	.0078	.012	---	---	---	---	N.D.
P	N.D.	.025	.016	.015	.021	.024	.018	.017	.022	N.D.
Re ¹	.0096	.0160	.0126	.0132	.0126	.0148	.0139	.0154	.0169	.0238
Ag ¹	.0026	.0031	.0045	.0042	.0043	.0043	.0040	.0040	.0042	.0051
Sb ¹	.00045	.00005	.00134	.00139	.00149	.00043	.0027	.0030	.0039	.0043
NH ₄ ⁺	N.D.	.0022	.0012	.0010	.0013	.0013	.0009	.0014	.0021	N.D.
Au ¹	.0006	.0013	.0011	.0010	.0009	.0010	.0009	.0009	.0010	.0013
Co ¹	.00052	.00028	.00018	.00025	.00018	.00026	.00025	.00019	.00022	.0004
Sc ¹	.000011	.000011	.000002	---	---	---	---	---	---	.000002
Sum ³	76.63	85.84	88.62	95.39	95.51	91.93	91.68	95.97	94.60	52.19

--- = Below detection limit. Approximate detection limits are 13 ppm for Mg, 27 ppm for Ca, .02 ppm for Sc, 5 ppm for V, 2 ppm for Cr, 15 ppm for Se, .05% for Sn (INAA) and 16 ppm for Ba.

¹ INAA data. All other data, except NH₄⁺, is by XRF.

² Represents the median distance in cm of that section from the 767°C end of the tube.

³ Represents the average mass of sublimate per unit area in that section of the tube. Units are milligrams/cm².

⁴ Totals do not include B, O, F and other elements below atomic number 11.

(Fig. 2). The group IIB metals Zn and Cd correlate with each other (Fig. 2) and have quite similar depositional patterns (Fig. 1). Indium also correlates with Zn (Fig. 2) and Cd, and has similar depositional patterns to both (Fig. 1). The group IVA elements Sn and Pb have similar depositional patterns (Fig. 1) and covary (Fig. 2). The VA elements Sb and As correlate with each other (Fig. 2).

Thus, there is a general correlation of elements in similar periodic groups and the chemical trends in the sublimates, as one would expect. These trends are not surprising as elements that covary chemically generally coexist in the same phase or form similar phases (see "Sublimate Mineralogy"). For instance, Zn and Cd coexist in sphalerite and K and Na reside in chloride and sulfate minerals.

Since the closest correlations of chemical elements relate to substitutions in the same phase, these can be explained by similarity of bonding properties (e.g., ionic radii and electronegativity). For instance, Re and Mo probably coexist in molybdenite. This is to be expected since Re⁺⁴ and Mo⁺⁴ have ionic radii (coordination number, C.N. = 6) of 77 and 79 pm, respectively (SHANNON, 1976). Zn⁺², Cd⁺² and probably In⁺³ coexist in sphalerite and have ionic radii (C.N. = 6) of 74, 92 and 76 pm, respectively (SHANNON, 1976), and Pauling electronegativities of 1.65, 1.69 and 1.78 (ALLRED, 1961). Alter-

natively, In⁺³ may substitute for Bi⁺³ in galena. Se⁻² probably substitutes for S⁻², possibly in sphalerite, can be explained by similar ionic radii (C.N. = 6) of 184 and 170 pm (SHANNON, 1976), and electronegativities of 2.55 and 2.58 (ALLRED, 1961). Sn substitutes for Pb in galena. This can be explained as the electronegativities of Sn⁺² and Pb⁺² are 1.80 and 1.87 (ALLRED, 1961). Ionic radii for the +2 oxidation state are not available, but Sn⁺⁴ and Pb⁺⁴ have radii (C.N. = 4) of 69 and 79 pm (SHANNON, 1976).

Incrustations

The Woro incrustations are characterized by an inner black zone surrounded by a brownish-orange zone. Analytical results for the WS91, WS92, WS93 and WS94 samples taken at 0 to several meters (decreasing temperature) from a 576°C vent are shown in Table 3.

Chemical variations for the Woro incrustations are shown in Fig. 3. There are three trends: 1) Pb, Al, Fe, K, Ca, Na, Cl, Bi, Sn, P, Cs, Zn, Cd, Mn, Mo, Rb and V decrease drastically away from the vent. Mg, NH₄⁺ and Cu show a similar, but less dramatic decrease. 2) Si, Ti, Ba and Cr are most concentrated away from the vent. 3) Br and S remain relatively unchanged.

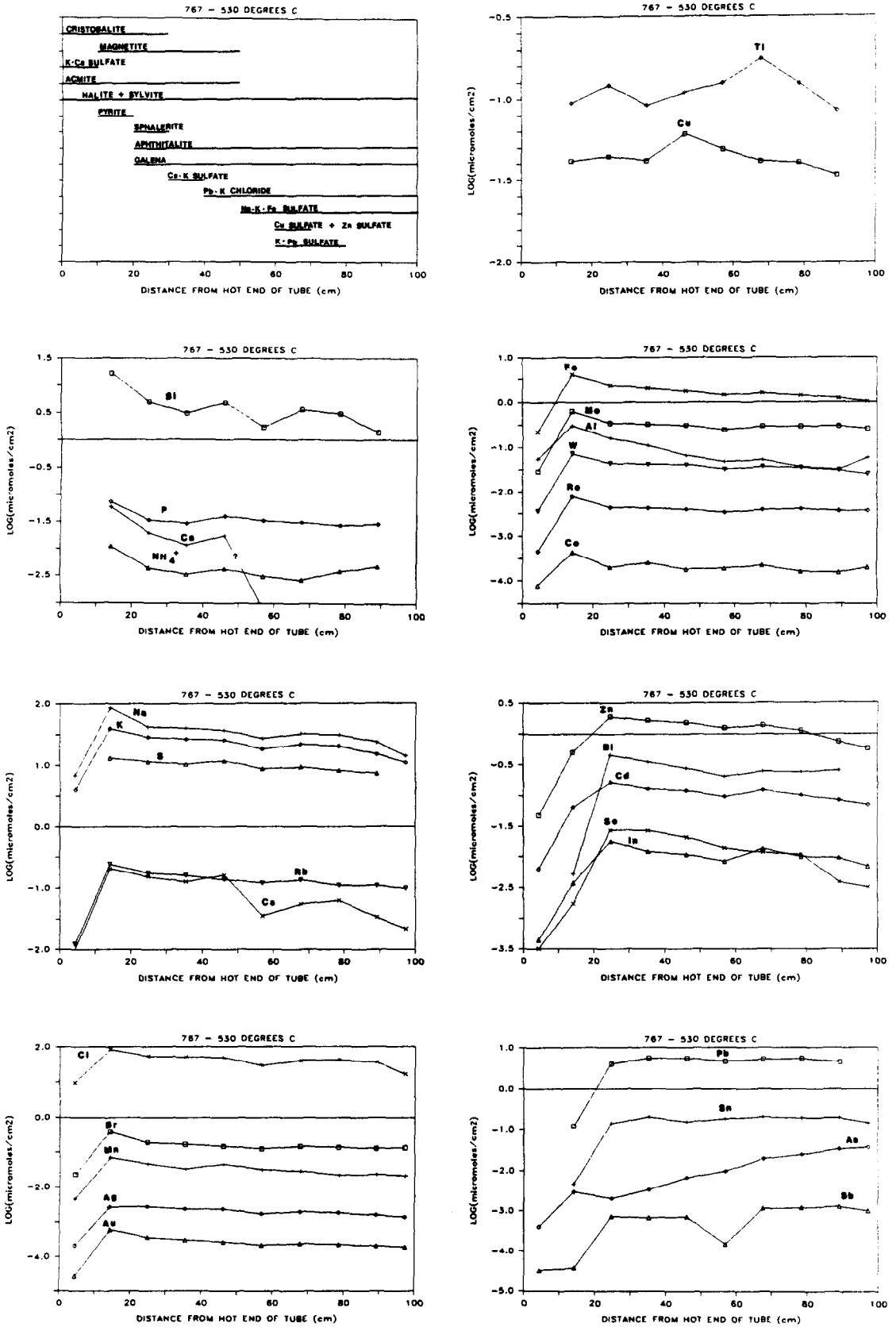


FIG. 1. Chemical variation in the sublimates collected in the Gendol G-1 quartz tube. All data in micromoles/cm².

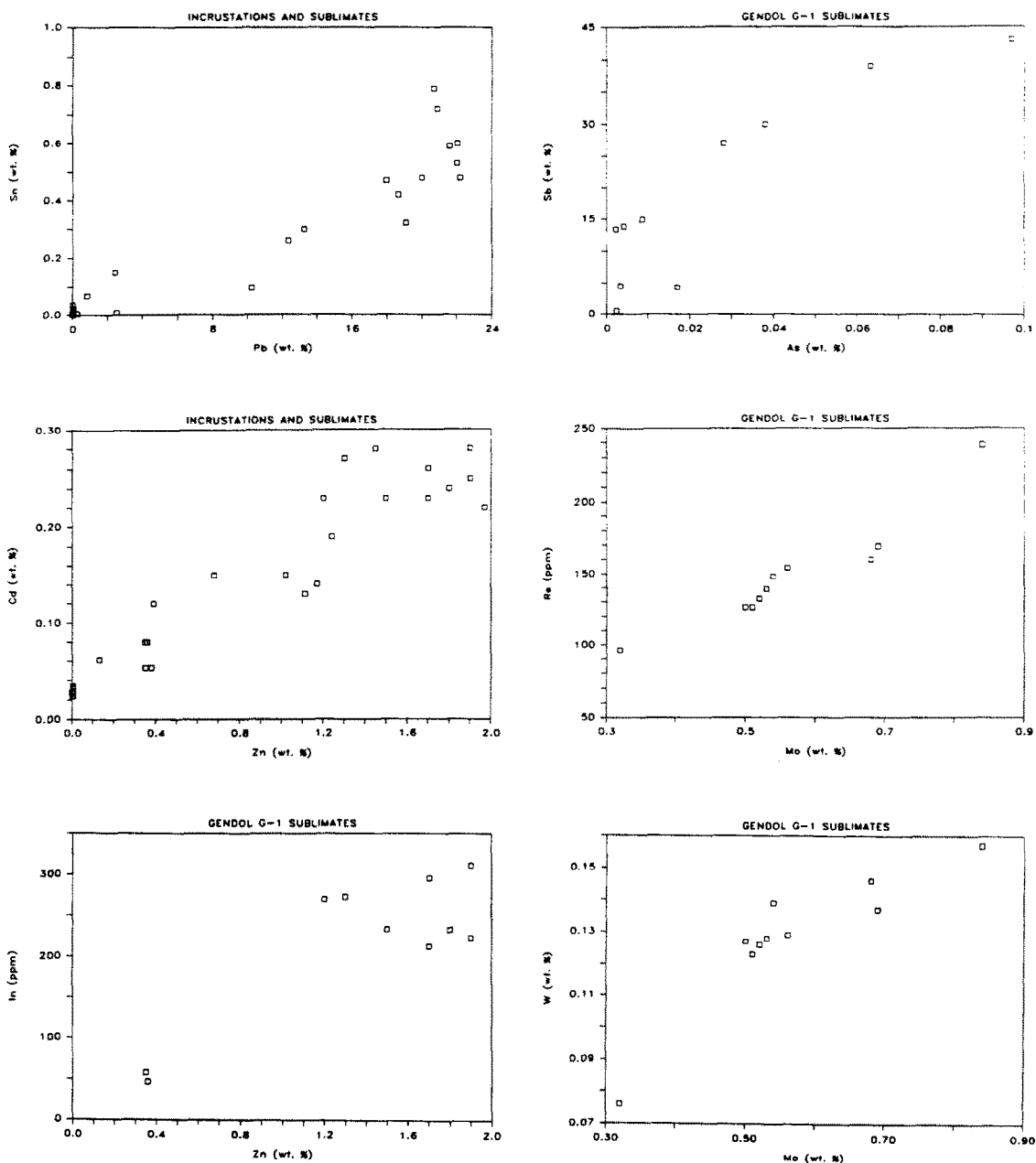


FIG. 2. Selected variation diagrams showing correlations of elements in the sublimates and incrustation samples.

The incrustations surrounding the Gendol fumaroles are characterized by three zones: 1) an inner black zone; 2) a middle, greenish-yellow zone; and 3) an outer brownish-orange zone. Analytical results for the GHT, GMZ and GLT samples at 0 to several meters (decreasing temperature) from a 767°C vent are shown in Table 3. Many elements that have anomalous concentrations (compared to the 1983 lava) in the sublimates are most abundant in the incrustation sample collected closest to the vent and then decrease in concentration away from the vent. These elements include Fe, Al, Na, K, Pb, Ca, Cl, Mg, Zn, Cs, Mo, W, P, Sn, Mn, Bi, Cd, Rb and V. S and Cu show a similar but less dramatic decrease. Si, Ba, NH_4^+ and Br increase away from the vent. Ti remains relatively constant.

In both the Woro and Gendol incrustation samples, most of the volatile elements show a large decrease in concentration

at increasing distance away from the vent as expected with decreasing temperature, increasing atmospheric contamination and dispersion. S, Br and NH_4^+ are exceptions to the rule and generally remain relatively constant or increase away from the vent. The less volatile elements Si, Ba, Cr and Ti generally increase in concentration away from the vent, probably due to wall rock contamination.

Rocks

Selected analytical results (from over 20 samples) for a prehistoric lava sample (M-13), 1940 lava sample (MS-40) and a 1983 lava sample (M-6C) are shown in Table 4. Chemically, the Merapi lavas are high-K, tholeiitic, basic andesites (GILL, 1981). Additional unpublished data suggest that the prehistoric lavas are more mafic than the historic lavas. Many of the most

Table 3. Major and trace element composition of incrustation samples collected from the Gendol and Woro fumaroles. WS91, WS92, WS93 and WS94 were collected at 0 to several m (decreasing temperature) from a 576°C vent at the Woro fumaroles. GHT, GMZ and GLT were collected at 0 to several m (decreasing temperature) from a 767°C fumarole at Gendol. All chemical data are in wt. %. Listed in order of decreasing maximum concentration.

	WS91	WS92	WS93	WS94	GHT	GMZ	GLT
Dist. (m)	0			several	0		several
Si	8.55	33.24	37.93	41.69	17.12	34.70	32.14
Pb	13.25	.087	.026	.012	2.42	.014	.076
Al	11.49	4.66	2.05	1.43	5.93	3.45	3.43
S	7.66	4.08	4.55	7.28	8.80	4.95	7.26
Fe	7.18	2.30	.54	.40	6.40	1.16	.85
K	6.25	1.34	.53	.42	3.85	1.37	1.06
Na	2.15	1.05	.32	.29	5.1	.93	.67
Ca	3.31	1.63	.52	.18	2.03	.61	.73
Cl	1.74	.33	.22	.21	.90	.23	.28
Ti	.43	.33	.85	.082	.26	.20	.35
Mg	.32	.19	.10	---	.47	---	---
Bi	.44	.0057	---	---	.10	.016	---
Zn	.13	.0070	.0037	.0023	.38	.0064	.0043
Sn	.30	.022	.013	.0032	.15	.035	.020
P	.27	.087	.036	.0002	.16	.0083	.020
Ba	.031	.084	.20	.019	.024	.068	.080
Cs	.16	---	---	---	.18	---	---
Mo	.023	---	---	---	.18	.0014	.0044
W	---	---	---	---	.17	---	.0024
Mn	.059	.046	.016	.011	.14	.036	.029
Cd	.061	.024	.034	.024	.053	.028	.027
Rb	.022	.010	.0078	.0055	.045	.012	.0086
NH ₄ ⁺	.037	.032	.027	.0053	.0017	.037	.027
Br	.025	.019	.023	.020	.0090	---	.0360
Cu	.030	.015	.016	.017	.024	.022	.018
V	.014	---	---	---	.015	---	---
Cr	---	.0048	.0002	---	---	---	---
Sum ¹	63.93	49.59	48.02	52.11	54.90	47.89	47.13

--- = Below detection limit. Approximate detection limits are 13 ppm for Mg, 5 ppm for V, 2 ppm for Cr, 40 ppm for Br, 8 ppm for Mo, 120 ppm for Cs, 16 ppm for W and 17 ppm for Bi.

¹Totals do not include B, O, F and other elements below atomic number 11.

abundant elements in the condensates, sublimates and incrustations (e.g., Cl, Pb, S, Zn) are among the least abundant elements in the 1983 lava.

SUBLIMATE MINERALOGY

Eighteen sublimate phases have been tentatively identified (Table 5) by SEM and EDS analyses (SYMONDS, 1985). Of the 18 phases, only halite, sylvite, cristobalite, and sphalerite, pyrite and magnetite could be confirmed by XRD or TEM.

The sublimates consist of a complex intergrowth of minerals in a matrix of halite and sylvite. Phases are generally euhedral, but the largest and most perfect crystals of each species occur at the highest temperature where that phase precipitates. At lower temperatures, the sublimates are characterized by more numerous, smaller crystals, which are subhedral to euhedral. There are several examples of skeletal or elongate mineral textures including acicular grains of acmite and wolastonite; elongate grains of magnetite; and halite crystals with holes in them. These textures and the steep temperature gradient (up to 271°C/m) suggest that the sublimates started precipitating in equilibrium with the volcanic gas with increasing disequilibrium at lower temperatures.

In general, the mineral zoning of the Gendol G-1 tube corresponds with the chemical zoning (Fig. 1).

Zoning in other quartz tubes is similar (SYMONDS, 1985). With decreasing temperature from 800 to 500°C there are five inferred zones: 1) cristobalite and magnetite (first deposition of Si, Fe and Al); 2) K-Ca sulfate, acmite, halite, sylvite, and pyrite (maximum deposition of Cl, Na, K, Si, S, Fe, Mo, Br, Al, Rb, Cs, Mn, W, P, Ca, Re, Ag, Au and Co); 3) apthitalite (K-Na sulfate), sphalerite, galena and Cs-K sulfate (maximum deposition of Zn, Bi, Cd, Se and In; higher deposition of Pb and Sn); 4) Pb-K chloride and Na-K-Fe sulfate (maximum deposition of Pb, Sn and Cu); and 5) Zn, Cu and K-Pb sulfates (maximum deposition of Pb, Sn, Ti, As and Sb).

The sublimate phases and mineral zoning are very similar to the 1978-80 results at Merapi by LE GUERN and BERNARD (1982) and BERNARD (1985), but there are some differences. BERNARD (1985) reports the following mineral sequence (from 900 to 100°C): 1) magnetite, hercynite (with Mn and Zn) and cristobalite at temperatures above 600°C, 2) acmite (650-600°C), Re-bearing molybdenite (650-550°C), Mn-bearing wolframite (630-600°C), halite (630-300°C) and sylvite (630-300°C), 3) pyrite and sphalerite (with Cd and Fe) at 550-300°C, 4) galena (with Bi and Sn) and Pb-Bi sulfide (with Sn) at 450-150°C, 5) Pb-ammonium chloride (with Br and Tl) at 300-150°C and sal-ammoniac (with Br) at 250-150°C, and 6) native S

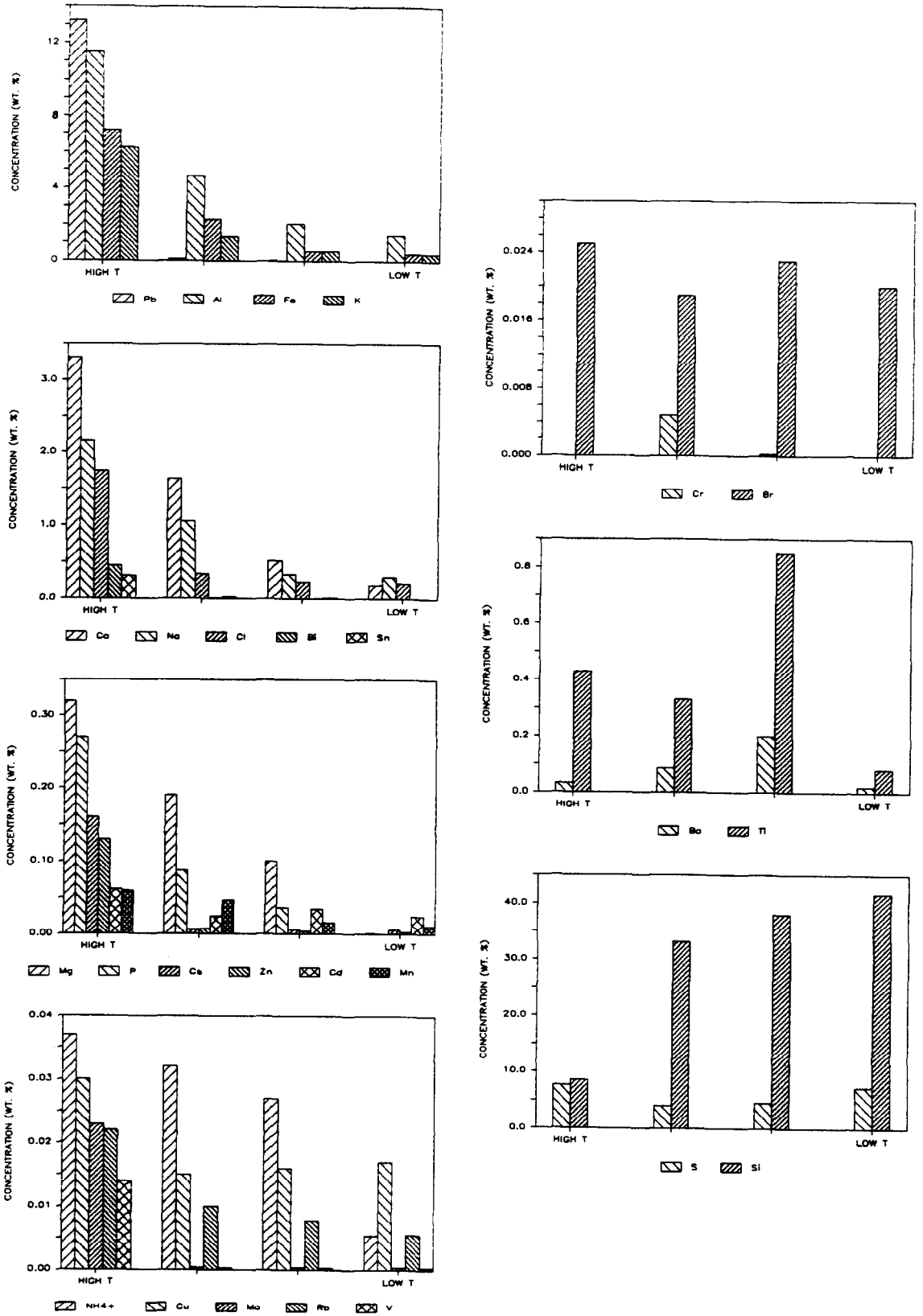


FIG. 3. Typical variation in incrustations from Merapi fumaroles. Samples WS91, WS92, WS93 and WS94 collected at 0 to several meters from a 576°C vent in the Woro fumaroles. All data in wt. %.

Table 4. Major and trace element composition of representative Merapi lavas. Major element data recalculated to 100 % using FeO as total Fe. Listed in order of decreasing maximum concentration.

Date:	Prehistoric	1940	1983
Rock type:	lava	lava	lava
Sample #	M-13	MS-40	M-6C
MAJOR ELEMENTS (wt. %)			
SiO ₂	55.36	57.36	57.65
Al ₂ O ₃	19.15	19.33	19.97
CaO	8.17	7.54	7.70
FeO	7.83	5.91	5.44
Na ₂ O	3.64	4.29	4.06
K ₂ O	2.17	2.71	2.56
MgO	1.94	1.37	1.27
TiO ₂	1.09	.86	.71
P ₂ O ₅	.47	.45	.45
MnO	.18	.18	.19
BaO	.0559	.0564	.0567
TRACE ELEMENTS (ppm)¹			
Cl	429	134	561
Sr	490	538	533
Zr	133	144	149
V	118	81	77
S	87	94	104
Cu	92	35	51
Zn	64	69	69
Ce	63	52	40
Rb	35	49	50
Cr	26	29	13
Pb	19	17	29
Y	17	21	21
Sc	21	14	12
La	13	16	17
Nb	7	6	6
Ni	---	5	---

--- = Below detection limit.

Approximate detection limit is 3 ppm for Ni.

¹Some elements were below detection in all samples. Approximate detection limits are 50 ppm for As, 40 ppm for Br, 9 ppm for Mo, 110 ppm for Cd, 15 ppm for Sn, 30 ppm for Sb, 50 ppm for Cs, 9 ppm for Ta, 8 ppm for Tl and 7 ppm for Bi.

(with As, I, Tl and Se) at 150–100°C. The most significant difference is the absence of sulfates in the 1978–80 sublimates and their presence in 1984.

Enriched minor and trace elements

EDS analyses confirm that major elements in the phases described include Bi, Ca, Cl, Cs, Cu, Fe, K, Na, S, Si, Pb and Zn (Table 5). Analytical results (Table 5) show that the sublimate phases also contain minor elements (between 8 and .2 atomic%, the detection limit of EDS). Al and Ti are found in magnetite and Al is also found in wollastonite. Cd and Fe are minor constituents of sphalerite. The correlation of Cd and Zn in 27 Merapi Sublimate and Incrustation samples (Fig. 2) and the fact that Cd was below detection in other Zn-bearing phases suggests that most of the Cd occurs in sphalerite. Cu is present in acmite and like Zn, in many of the sulfate phases. K, Cu, Zn and Pb are minor constituents of acmite. Sn is a minor element in galena.

The correlations of In with Zn (Fig. 2) and Cd, and similar chemical trends for these elements in the Gendol G-1 sublimates (Fig. 1), suggests that In might substitute for Zn in sphalerite. Alternatively, In may substitute for Bi in galena as Bi and In have similar chem-

ical trends (Fig. 1). The correlation between Re and Mo (Fig. 2) and similar chemical trends for the two elements (Fig. 1), suggests that Re and Mo coexist, probably in Re-bearing MoS₂ as reported by BERNARD (1985).

ENRICHMENT FACTORS

By definition (ZOLLER *et al.*, 1983) the enrichment factor is

$$EF_{\text{sample}} = (X/R)_{\text{sample}} / (X/R)_{\text{magma}}$$

where EF_{sample} is the enrichment of the element in the sample (condensate, sublimate or incrustation); $(X/R)_{\text{sample}}$ is the ratio of the element to a reference element R in the sample; and $(X/R)_{\text{magma}}$ is the ratio of the element to the reference element in the magma. When data were available, the magma composition was assumed to be the partly degassed 1983 lava (sample M-6C, Table 5). Literature values (GOVINDARAJU, 1984) for the AGV-1 andesite standard (for Ag, As, Au, Bi, Br, Cd, Co, Cs, Ga, In, Li, Mo, Ni, Sb, Sn, U and W) or the BCR-1 basalt standard (for Re and Se) were used when data for M-6C were lacking. Ti was used as the reference element for the sublimates and incrustations, since it is considered one of the least reactive elements in acid gases—Ti tubing is often used for gas sampling (GIGGENBACH, 1975). (Ti values of .05 and .10 wt.% were assumed for the Gendol G1-S1 and G1-S10 samples, respectively, since Ti data were not available.) Mg was used for the condensates since Ti data were not available and it was considered much better than all other choices (SO₄²⁻, Cl, Cu, K, Pb, Sr,

Table 5. Tentative summary of the sublimate phases collected in silica tubes at Merapi Volcano in Jan. 1984 (see text). Listed in the order observed in the silica tubes (from highest to lowest temperature).

PHASE	COMPOSITION	ENRICHED MINOR ELEMENTS
(AROUND 800° C)		
Cristobalite [*]	SiO ₂	
Magnetite [*]	Fe ₃ O ₄	Al, Ti
K-Ca Sulfate ¹	K ₂ Ca(SO ₄) ₂	Cu, Zn, Cl
Acmite	NaFeSi ₃ O ₈	Cl, K, Cu, Zn, Pb
Halite ²	NaCl	
Sylvite ²	KCl	
Pyrite ²	FeS ₂	
Wollastonite	CaSiO ₃	Cl, Al
Sphalerite ²	ZnS	Cd, Fe
Aphthitalite	(K,Na),Na(SO ₄) ₂	Cu, Zn, Cl
Galena ³	Pb/Bi = 1.3-1.5	Sn
Cs-K Sulfate	?	
Pb-K Chloride	PbKCl ₂	
Na-K-Fe Sulfate ⁴	(Na,K),Fe(SO ₄)(Cl) ₂	Cu, Zn
Chalcocyanite	Cu ₂ SO	
Zn Sulfate ⁵	Zn ₂ (SO ₄)(Cl,OH) ₂	
K-Pb Sulfate ⁶	K ₂ Pb(SO ₄) ₂	
K-Zn Sulfate ⁶	K ₂ Zn(SO ₄)(Cl) ₂	
(AROUND 450° C)		

* = Confirmed by X-ray diffraction.

- Crystal forms similar to glauberite (Na₂Ca(SO₄)₂), but may be syngenite K₂Ca(SO₄)₂ · H₂O.
- Confirmed by N. Long using TEM.
- XRD data by J. Hughes and TEM work by N. Long match a cubic (galena) structure, and Pb/Bi = 1.3-1.5. This is consistent with bismuthian galena (ASTM card 22-652) or a multilayer structure with alternating layers of galena and Bi sulfide.
- The composition of this phase is variable and does not match any Na-K-Fe sulfates.
- Known Zn-bearing sulfates do not match the stoichiometry of these phases.
- TEM work by N. Long suggests it might be tetragonal. Composition is somewhat variable.

V) for which data were available for all the condensate samples and the 1983 lava sample M-6C. Mg was not used throughout because it is below detection in the Gendol G-1 sublimates.

Enrichment factors (E.F.) for the condensates, sublimates and incrustations as compared to the assumed magma composition are reported in Table 6. Only the maximum E.F. was reported for the incrustations since the mean E.F. is partly controlled by sampling density and sampling distance away from the vent. With the exceptions of Si, S, Cu, Br, Cd, Ba and Cr the maximum E.F. for the Gendol and Woro incrustations was from the sample collected closest to the vent. Thus, most volatile elements in the gas decrease in concentration away from the vent as expected with the decrease in temperature, mixing with atmospheric gases and dispersion.

A comparison between the mean E.F. for the condensates and sublimates, and the maximum E.F. for the incrustation samples is shown in Fig. 4. In general, the sublimates have higher E.F. for volatile elements than the condensate and incrustation samples. Clear exceptions to the above rule are as follows: 1) Br, Cl, As, Sb and Cr have higher enrichments in the condensates than in the sublimates or incrustations; and 2) S,

Table 6. Enrichment factors for condensate, sublimate and incrustation data (see text). Detection limits were used to calculate an upper limits for E.F. when some or all (Ba and Cr in the sublimates) of the data were below detection.

	CONDENSATES	SUBLIMATES	INCRUSTATIONS	
	(Antilog Mean)	(Antilog Mean)	Woro (Maximum)	Gendol (Maximum)
Se	---	5.8×10^4	---	---
Re	---	8.5×10^3	---	---
Bi	1300.	4.9×10^3	7.6×10^4	2.9×10^4
Cd	430.	1.5×10^3	2.1×10^4	1.4×10^4
Au	---	7.6×10^2	---	---
Br	6.0×10^3	3.3×10^3	3000.	1300.
In	---	2.1×10^3	---	---
Pb	35.	1.7×10^3	4600.	1400.
W	310.	1.1×10^3	---	5200.
Mo	85.	8700.	76.	980.
Cl	8000.	2400.	31.	26.
Ce	---	6600.	1200.	2200.
S	3200.	2400.	3600.	1400.
Sn	---	2900.	830.	680.
Ag	---	1700.	---	---
As	810.	680.	---	---
Zn	190.	810.	19.	91.
F	540.	---	---	---
Rb	---	200.	4.4	15.
Cu	2.3	43.	6.	9.
K	---.4	36.	2.9	3.0
Na	---	23.	.7	2.8
Sb	17.	12.	---	---
Cr	11.	1.t. .7	4.8	---
Ni	8.	---	---	---
Ga	5.	---	---	---
Ba	---	1.t. .1	2.1	2.9
V	2.8	4.0^*	1.	3.2
Si	---	.3	1.6	2.8
Fe	.4	2.0	1.7	2.5
Mn	.2	1.1	.4	1.6
P	---	.4	1.3	1.3
Al	.5	.02	1.1	.9
Li	1.	---	---	---
Mg	---	1.0^*	.4	1.0
Co	.2	.8	---	---
U	.6	---	---	---
Ca	---	.005	.6	.6
Sr	.3	---	---	---
Sc	---	.01	---	---

--- = No data or below detection.

* = From Gendol G-2 sublimate data. All other sublimate E.F. values from the Gendol G-1 data.

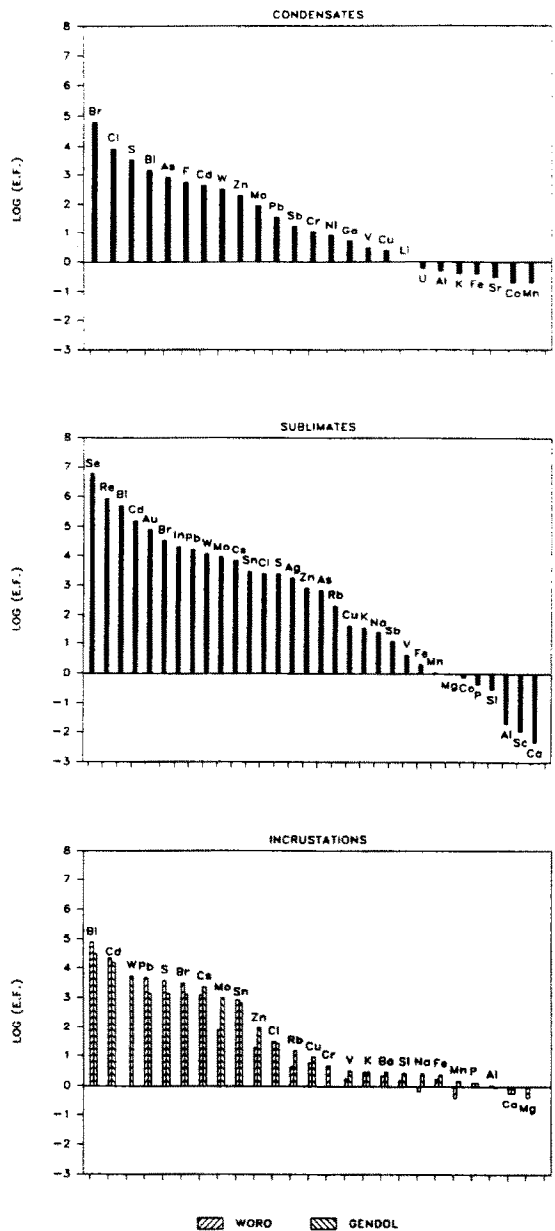


FIG. 4. Mean enrichment factors for elements in the condensates and sublimates, and maximum enrichment factors for the incrustations. Mg was used as the reference element for the condensates and Ti was used for the sublimates and incrustations. The sublimate enrichment factors were from the Gendol G-1 tube, except Mg and V, which were from the Gendol G-2 tube.

Cr, Ba, Si, P, Al and Ca have higher E.F. in the incrustations than in the sublimates.

Differences in the maximum enrichment factors for the condensates, sublimates and incrustations suggest that the highly volatile elements Br, Cl, As and Sb are transported mostly away from high temperature vents; whereas Bi, Cd, Pb, W, Mo, Zn, Cu, K, Na, V, Fe and Mn are concentrated more as high temperature sublimates in or very close to the vent. Since Cr has a low volatility (see "Volatility Modelling") it may be enriched in the condensates because of contamination

from particles or wall rock in the vent. The higher enrichment of S in the incrustations suggests that it is primarily deposited as lower temperature incrustations rather than high temperature sublimates, although most of the S probably reaches the atmosphere (the condensate E.F. for S is probably low as some gaseous S species probably pass through the condensate collection apparatus). The higher enrichments of Ba, Si, P, Al, Cr and Ca in the incrustations are probably due to wallrock contamination. STOIBER and ROSE (1970, 1974) suggested that Si, Al and Ca could be derived from wall rock reactions and BERNARD (pers. commun.) has observed barite crystals in deeply altered rock in fumarolic areas at Usu and Momotombo volcanoes.

RATES OF TRANSPORT

The basic equation to calculate the rate of transport is as follows:

$$\text{Flux}_Z = C \times G \times \text{Flux}_S \times A$$

where Flux_Z is the flux in grams/day of element Z; C is the mole ratio of $Z/\text{H}_2\text{O}$ in the condensate; G is the mole% ratio of $\text{H}_2\text{O}/\text{SO}_2$ in a 1979 gas sample (number 79-2 reported by LE GUERN *et al.*, 1982); Flux_S is the SO_2 flux (moles/day) assuming an SO_2 emission rate of 400 metric tonnes/day from ground-based correlation spectrometry (COSPEC) 5–10 km from the plume (BADRUDIN, unpublished data); and A is the atomic mass of element Z. These estimates are subject to large errors because the $\text{H}_2\text{O}/\text{SO}_2$ ratio may have changed since 1979 and COSPEC measurements have errors as high as $\pm 40\%$ (CASADEVALL *et al.*, 1983). Despite these errors, the relative fluxes hold regardless of the assumed $\text{H}_2\text{O}/\text{SO}_2$ ratio and SO_2 flux. These fluxes are a minimum estimate of the transport rate from the magma chamber because a fraction of most elements is deposited as sublimates or incrustations and other elements (*e.g.* Hg) may pass through the condensate collection apparatus. Furthermore, these calculations do not imply anything about the distance of transport away from the vent.

Rates of transport of elements from Merapi Volcano are reported in Table 7. These fluxes are not unusual for active volcanoes and are similar or lower than those estimated (assuming higher SO_2 fluxes) for quiescent plumes from Mount Etna (BUAT-MÉNARD and ARNOLD, 1978) and Mount St. Helens (PHELAN *et al.*, 1982) (Table 7).

The rates of transport of Pb and Zn along with the concentrations of these elements in the magma can be used to estimate the magma required to account for the degassing rate. Assuming that Pb and Zn are transported at a rate of 7000 and 8.9×10^4 g/day, respectively, and that a metric tonne of magma degasses 29 g of Pb and 69 g of Zn (from the partly degassed 1983 lava sample M-6C in Table 4), this corresponds to a magma production rate of 2×10^5 to 1×10^6 kg/day for Pb and Zn, respectively. These calculations are an order of magnitude less than the estimated Merapi ef-

Table 7. Estimates of elemental fluxes from Merapi fumaroles (see text). For comparison, fluxes are shown for Mt. Etna and Mt. St. Helens. All fluxes in grams/day.

Year:	Merapi ¹	Mt. Etna ²	Mt. St. Helens ³
	1984	1976	1980
S	2.0×10^5	4.2×10^5	5.0×10^5
Cl	3.0×10^7	3.0×10^6	3.5×10^6
F	1.5×10^6	---	---
Al	3.6×10^5	6.0×10^6	---
Br	1.4×10^5	6.3×10^6	---
Zn	8.9×10^4	3.0×10^6	1.0×10^6
Fe	7.9×10^4	3.0×10^6	---
K	6.2×10^4	2.8×10^7	---
Mg	5.2×10^4	---	---
Pb	7000	3.6×10^5	---
As	4600	1.1×10^4	8.0×10^5
Mo	1700	---	---
Mn	1600	3.9×10^5	---
V	1500	2.4×10^4	---
W	1100	---	---
Sr	1000	---	---
Ni	860	1.0×10^5	---
Cu	790	1.0×10^5	---
Cr	710	2.0×10^6	---
Ga	680	---	---
Sb	520	1.0×10^4	3.0×10^4
Bi	520	---	---
Cd	180	2.8×10^4	5000
Li	100	---	---
Co	20	8000	---
U	8	---	---

--- = No data.

¹S flux from COSPEC data (see text)

²Buat-Menard and Arnold (1978)

³Phelan *et al.* (1982)

fusion rate for 1977–1979 of $10\text{--}20 \times 10^3$ m³/day (LE GUERN *et al.*, 1982), which corresponds to $3\text{--}5 \times 10^7$ kg/day assuming a density of 2.6 g/cm³. Thus, only small fractions of the Pb and Zn in the magma are actually degassed. Because the erupted amount of lava can easily account for the transport rates of Pb and Zn, it is reasonable that all the Pb, Zn and probably many other elements in the Merapi volcanic gas are volatilized directly from shallow magma.

THERMODYNAMIC MODELLING

Previous workers (*e.g.* NAUGHTON *et al.*, 1974; OSKARSSON, 1981) have speculated on the species transporting trace components, such as Na, K and Cu, in magmatic gases. A study by MURATA (1960) actually confirmed that Cu is transported as $\text{CuCl}(\text{g})$ in the Kilauea volcanic gas, by spectroscopic measurements. Short of spectroscopic measurements, the next best approach is to determine the probable stable gas species using thermodynamic modelling. KRAUSKOPF (1964) and NAUGHTON *et al.* (1974) used this approach and concluded that metals were stable as halide species in magmatic gases.

Past studies have also applied thermodynamics to explain the zoning of fumarolic incrustations (STOIBER and ROSE, 1974) and the formation of sublimates

(NAUGHTON *et al.*, 1974). KRAUSKOPF (1964) used thermodynamics to calculate the volatilities of metals from magma. Since these studies were completed, the quality and quantity of thermochemical data have greatly improved, making reevaluation necessary. Furthermore, it is now possible to do much more sophisticated calculations as has been done for aqueous geothermal or epithermal systems (*e.g.*, REED, 1982).

Method of calculation

All calculations were done with SOLVGAS (SYMONDS and REED, in prep.), a computer program for calculating homogeneous equilibrium in gases. SOLVGAS calculates the distribution of over 350 gas species as a function of temperature and pressure using the basic formulations of equilibrium calculations for aqueous system of REED (1982) modified (SYMONDS and REED, in prep.) for gases. The calculations consist of solving simultaneously a series of mass balance and mass action equations using a Newton-Raphson method.

Assumptions and thermochemical data

The calculations were done using the following assumptions: 1) The volcanic gases behave ideally. 2) The equilibrium temperature and major gas data (H_2O , H_2 , CO_2 , CO , SO_2 , H_2S , HCl , HF) from 1979–80 (LE GUERN *et al.*, 1982; BERNARD, 1985) could be combined with the 1984 condensates to approximate the actual 1984 magmatic temperature and gas composition. 3) Activities of solid components for volatility modelling can be calculated using ideal mixing.

Thermochemical data for gases and minerals were obtained from PANKRATZ (1982, 1984); PANKRATZ *et al.* (1984), STULL and PROPHET (1971), CHASE *et al.* (1974, 1975, 1978, 1982), BARIN and KNACK (1973), BARIN *et al.* (1977), HELGESON *et al.* (1978) and BERMAN *et al.* (1985).

Two principal uncertainties in these calculations concern the extent to which equilibrium thermodynamics applies and the question of whether the thermochemical data are of sufficient quality and quantity. The applicability of equilibrium thermodynamics and the quality of data can be evaluated by combining numerical calculations with studies of volcanic condensates and sublimates. Even if the calculations do not exactly reproduce the observed sublimate sequence or trace gas composition, they provide insight into natural processes, as illustrated below.

Speciation of trace components

The distribution of gas species upon cooling was calculated for more than 350 gas species in the 27 analyzed components in the Merapi volcanic gas. The most stable gas species from 900 to 100°C for each component are shown in Fig. 5. The calculations show that most of the trace components are transported as simple chloride species. Exceptions to this trend are as

follows: 1) At higher temperatures, As, Bi and Pb are transported as sulfide species. 2) At temperatures below 200°C, bromide species become more abundant (or dominant) for Cu, Mn, Pb and Zn. 3) Oxychloride species of Cr, Mo, V and W are most abundant over much of the temperature range. At higher temperatures, though, Mo and W are transported as molybdic and tungstic acid and V is transported as an oxide species. At temperatures below 475°C, Cr is most stable as a simple chloride species. 4) Aluminum is transported as an oxyfluoride, or at lower temperatures, a fluoride species. 5) At magmatic temperatures, elemental species of Zn and Cd are more abundant (thermochemical data are not available to test if Cd chlorides are most stable).

Another significant trend is that dimeric species are more stable than monomers at lower temperatures. At very low temperatures, trimeric species become more stable than dimeric species. For example, Li is most stable as $LiCl(g)$ above 430°C, $(LiCl)_2(g)$ between 430 and 135°C and $(LiCl)_3(g)$ below 135°C. This trend results in part from the lower entropy of a gas of dimers and trimers than a gas of monomers. With decreasing temperature, the contribution of the entropy term to the Gibbs free energy of a monomer to dimer (or trimer) reaction decreases so the enthalpy term favoring the dimers and trimers dominates.

The zoning of sublimates

SOLVGAS can also be used to model the zoning of sublimates collected in the quartz tubes. The basic technique is to calculate the temperature at which the volcanic gas saturates with a particular phase by using a plot of a saturation index, $\log(Q/K)$, against temperature as has been applied to geothermal waters by REED and SPYCHER (1984). For the sublimation reaction, $NaCl(\text{halite}) = NaCl(g)$, K is the thermodynamic equilibrium constant at a given temperature and pressure and Q is the calculated activity quotient (in this case Q equals the fugacity of $NaCl(g)$ if the activity of halite is unity). When $\log(Q/K)$ for a particular solid or liquid phase is zero, the gas is saturated with the phase. When $\log(Q/K)$ is greater or less than zero, the gas is oversaturated or undersaturated with that phase, respectively.

In general, the calculations (Fig. 6) agree well with the highest temperature occurrence of each sublimate phase in 1978–80 (LE GUERN and BERNARD, 1982; BERNARD, 1985) and in 1984 (Table 5, Fig. 1). The calculations also explain the 1978–1984 sublimate zoning: 1) a magnetite zone at the hottest end of the tubes, 2) a Fe-Mo-S-K-Cl zone with molybdenite, sylvite and pyrite at lower temperatures, 3) maximum deposition of Bi and Cd with Cd-bearing sphalerite, K-Na sulfate and Bi-bearing sulfides at still lower temperatures, and 4) deposition of As-bearing native S at the coolest end of the tube. The agreement of these calculations with the highest temperature occurrence of each phase is evidence that sublimation in this zone

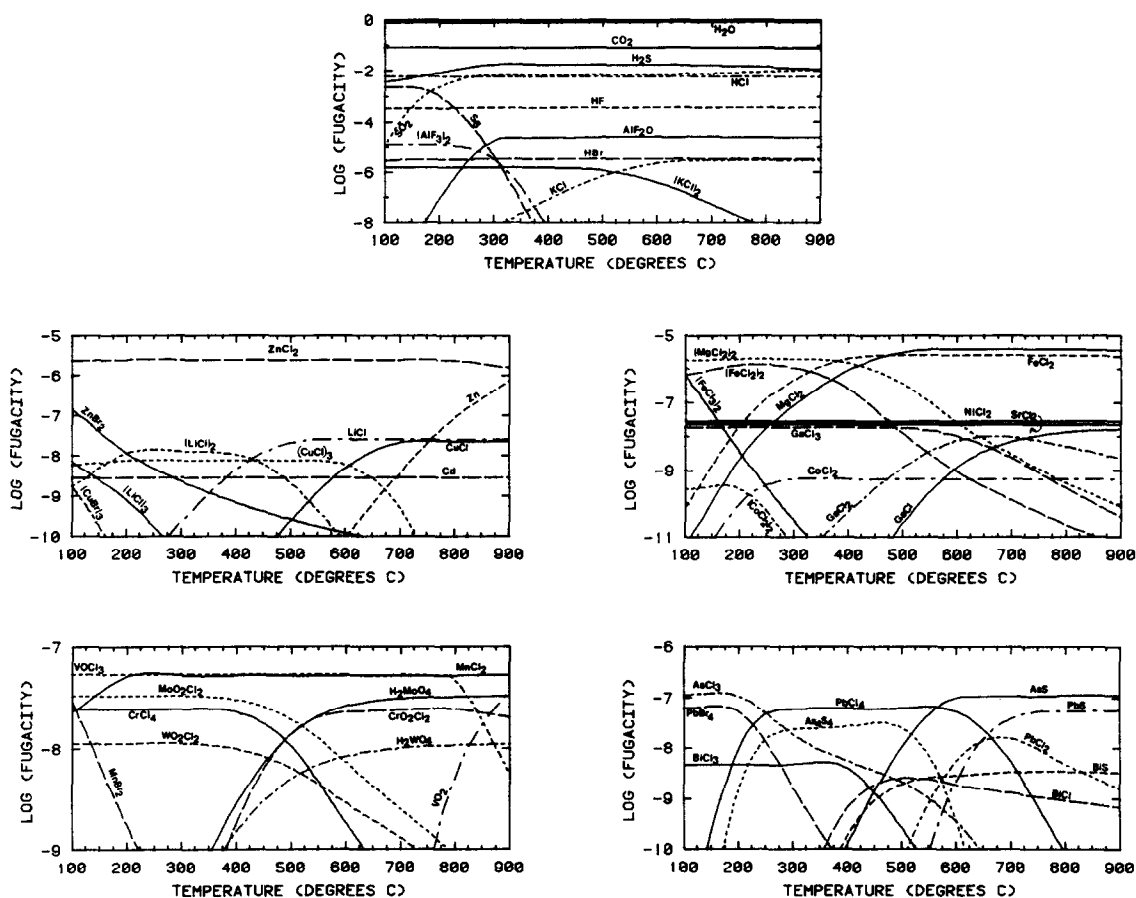


FIG. 5. Most stable gas species for the 27 analyzed components in the Merapi volcanic gas from 900–100 degrees C and 1 bar pressure.

is close to equilibrium as inferred from euhedral crystal forms (SYMONDS, 1985). Because the condensate data suggest that sublimation is inefficient (see "Analytical Results . . ."), increasing disequilibrium must occur at lower temperatures.

In detail, however, there are some differences, especially with sphalerite, galena (not plotted) and Pb-

chloride (not plotted). The calculations indicate that the sublimation of sphalerite should occur in the same zone as molybdenite, but it is observed first in a lower temperature zone with pyrite (in 1978–80) or galena (in 1984). The problem with galena and Pb chloride is that the calculations indicate that, upon cooling, the volcanic gas should never be saturated with these

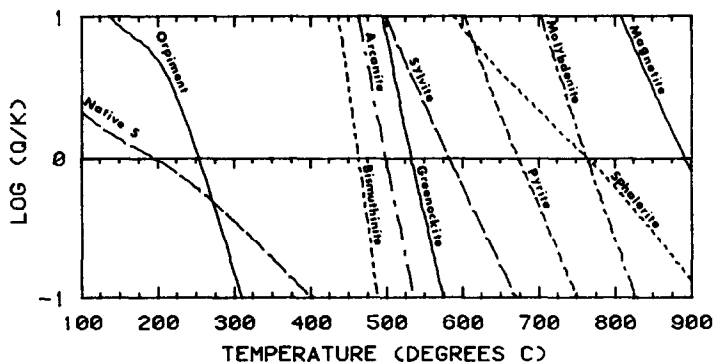


FIG. 6. Log (Q/K) versus temperature plot showing the calculated sublimation zoning upon numerical cooling of the analyzed composition of the Merapi volcanic gas. Greenockite (CdS) is used to model the Cd component in Sphalerite. Arcanite (K sulfate) is used to represent the K component of Aphthitalite (K-Na sulfate). Bismuthinite (a Bi sulfide) is used to approximate the Bi component of galena. Orpiment (an As sulfide) is used to represent the As component in native S. S liquid is the stable phase of native S at 200 degrees C.

phases, although they are major minerals in the sublimates. Possible explanations for why the calculations depart from the observed results are as follows: 1) The analyzed gas composition may not be correct. 2) Sublimate phases may actually exist in higher temperature zones than reported, but have not been found because of their low concentrations in these zones. 3) The system is not in equilibrium. 4) The thermodynamic data are not correct.

Figure 1 shows that some Zn was deposited at the highest temperature zone of the Gendol G-1 tube and that throughout the tube, Zn covaries with Cd (Figs. 1–2). This is evidence that trace amounts of Cd-bearing sphalerite may exist in higher temperature zones than reported (Fig. 1) from SEM observations. Thus, the apparent discrepancy may be a result of analytical limitations, although other hypotheses can not be discounted.

The problem with galena and Pb chloride is difficult to explain. It is unlikely that enough Pb is lost from sublimation (in the vent or condensation apparatus) to account for this discrepancy because about 1000 times more Pb (800–1000 ppm in the condensates) is required for saturation with galena. Another explanation is that the thermochemical data for Pb halide gases are incorrect. This is supported by the ± 20 kcal/mole uncertainties associated with the enthalpies of formation of $\text{PbCl}_4(\text{g})$ and $\text{PbBr}_4(\text{g})$ (CHASE *et al.*, 1975). Alternatively, $\text{PbS}(\text{g})$ may be the dominant species at lower temperatures because of kinetics. The last two hypotheses are supported by calculations which suppress all Pb halide species (except $\text{PbCl}_2(\text{g})$) and for which galena and PbCl_2 (cotunnite) saturate in the gas below 500°C.

Volatility modelling

Program SOLVGAS can also be used to calculate volatilities (fugacities) of the metals (or other trace components) in the volcanic gas in equilibrium with the magma. Such calculations can be used to: 1) compute a hypothetical gas composition in equilibrium with the magma to compare with the analyzed gas composition, 2) determine whether the trace components in the gas are in equilibrium with the magma, 3) understand the origin, abundance and enrichment of trace components in volcanic gas, and 4) predict the concentration of trace components for which there are not any analytical data.

To calculate volatilities, we assumed a composition of the major gas species as described above. Then we made some assumptions about what thermodynamic activity the metals have in the magma by estimating the activity of metal-bearing components in minerals that actually exist in the magma. The 1983 lava (sample M-6C) has plagioclase, augite, Fe-Ti oxides and normative quartz. GILL (1981) has shown that the composition of augite in high-K andesites is close to pure

diopside and that ilmenite occurs in most andesites. so the activities of these species and clinoenstatite were assumed to be unity and .5, respectively. The activities of Ni, Cr, Co, Mn and Zn spinels in magnetite were estimated by assuming a composition of a typical andesitic (EWART *et al.*, 1973; DUNCAN and TAYLOR, 1969) or, for Zn, basaltic (HAGGERTY, 1976) magnetites. The calculated feldspar norm was used to estimate the activities of Ca, Na and K feldspars in plagioclase. Finally, for lack of a better assumption, we assumed that chalcopyrite was present in the magma because chalcopyrite has been observed in basaltic lava lakes (SKINNER and PECK, 1969). The preceding approximations were adopted because microprobe analyses of these phases have not been collected. However, most of the estimated activities (Table 8) are probably within an order of magnitude of the actual values, which is close enough to test the volatility model. Having estimated the activities of components in the solid phases (Table 8) and using the assumed major gas composition, the concentration of each trace element was adjusted until the gas was saturated ($\log(Q/K) = 0$) with the various solid phases at magmatic temperature.

The results of these calculations are shown in Table 8. In general, the calculated volatilities agree closely with the analyzed gas composition (Table 8). One way to check the volatility calculations is to cool the calculated volcanic gas numerically and calculate the temperature at which the gas saturates with various sublimate phases. The calculated sequence and temperature of sublimate saturation (Fig. 7) are in good agreement with those calculated using the analyzed gas composition (Fig. 6) and the observed sublimate zoning in 1984 (Table 5, Fig. 1) and in 1978–1980 (LE GUERN and BERNARD, 1982; BERNARD, 1985). Thus, the quantities of most trace components in the Merapi volcanic gas can be explained by volatilization from shallow magma at 915°C. This provides strong evidence that the gas is in equilibrium with the magma.

This modelling shows that the relatively large enrichments and fluxes of alkali (K, Na) and transition (Zn, Fe, Cu and Mn) metals result from their high volatilities. Low calculated volatilities explain the low concentrations of Ca, Si, Al and Ti in the sublimates and support previous conclusions that Ca, Al and Si are derived from wall rock or particle contamination.

The amounts of Al, Mg and Cr in the condensates are too large to be explained by the volatility calculations. There are three possibilities: 1) particle (ash or aerosol) contamination in the condensates, 2) contamination from wall rock, and 3) incorrect thermodynamic data. Because the calculated volatility of Al predicts (Fig. 7) the observed (BERNARD, 1985) saturation temperature of hercynite (above 600°C), contamination from the wall rock or particles is the likely origin of Al, and probably Mg and Cr as well. If Cr is enriched in the condensates because of contamination, then it is likely that acid-rock reactions are the source of Cr in the incrustations.

Table 8. Dominant gas species, solid magmatic phases and calculated volatilities for elements at 1 atm. Assumed gas composition from 1979 - 1980 Merapi gas data (Le Guern et al., 1982; Bernard, 1985). All calculations at 915°C assuming that the log of the O₂ fugacity = -12.49.

DOMINANT GAS SPECIES		SOLID ¹ PHASE	ASSUMED ² ACTIVITY	CALCULATED VOLATILITY LOG (atm.)	OBSERVED COMPOSITION LOG (atm.)
Silicates					
Si	SiF ₄	Quartz	1.0	-13.71	—
Mg	MgCl ₂	Clinoenstatite	0.5	-9.63	-5.8 - -4.8
Ca	CaCl ₂	Diopside	1.0	-10.22	—
Al	AlF ₃ O	Anorthite	0.37	-9.56	-4.9 - -4.2
K	KCl	K-feldspar	0.19	-5.17	-6.0 - -5.1
Na	NaCl	Albite	0.44	-4.81	—
Oxides					
Fe	FeCl ₂	Magnetite	0.44	-5.61	-5.7 - -5.5
Co	CoCl ₂	CoFe ₂ O ₄	0.00027	-9.35	-9.3 - -9.1
Cr	CrO ₂ Cl ₂	Chromite	0.0000017	-18.69	-7.8 - -7.4
Mn	MnCl ₂	Jacobsite	0.0047	-6.76	-7.3 - -7.2
Ni	NiCl ₂	Trevorite	0.00012	-9.44	-7.9 - -7.2
Ti	TiF ₄	Ilmenite	1.0	-14.46	—
Zn	ZnCl ₂	Franklinite	0.0013	-5.11	-6.1 - -4.7
Sulfides					
Cu	CuCl	Chalcopyrite	1.0	-6.15	-8.5 - -6.6

¹It is most convenient to solve the volatility equations in order from the top down so that there is only one unknown at a time to solve for.

²The activities for these components were calculated from the assumed compositions of clinopyroxene, plagioclase and magnetite (see text).

Sublimation reactions

A knowledge of the most stable gas species (Fig. 5, Table 8) can be used to speculate on particular reaction stoichiometries for precipitation of sublimates. One can know if the calculated gas species are valid if the Q/K calculations (Figs. 6-7) reproduce the observed sublimate zoning. Using this criterion, the following sublimation reactions are possible:

1. NaCl(g) = halite
2. KCl(g) = sylvite
3. 3FeCl₂(g) + 4H₂O(g) = magnetite + 6HCl(g) + H₂(g)

4. FeCl₂(g) + 2H₂S(g) = pyrite + 2HCl(g) + H₂(g)
5. ZnCl₂(g) + H₂S(g) = sphalerite + 2HCl(g)
6. H₂MoO₄(g) + 2H₂S(g) + H₂(g) = molybdenite + 4H₂O(g).

DISCUSSION—IMPLICATIONS FOR ORE FORMATION

The rates of transport of S, Cl, F, Al, Br, Zn, Fe, K, Mg, Pb, As, Mo, Mn, V, W and Sr at Merapi is evidence that volcanic gases can transport significant quantities of elements from a magma body. This suggests that volatile transport may be an important process in the exchange of metallic and non-metallic elements to a

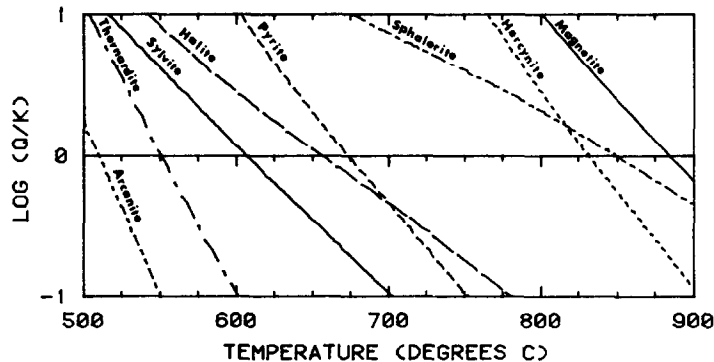


FIG. 7. Log (Q/K) versus temperature plot showing the calculated sublimate zoning upon numerical cooling of a theoretical Merapi volcanic gas derived, in part, from volatility calculations (Table 8). Thernardite (Na Sulfate) and Arcanite (K sulfate) were used to approximate Apthitalite (K-Na Sulfate), observed in the Merapi sublimates.

forming ore deposit. The extreme enrichment of metals in the sublimates and incrustations suggests that in some cases, deposition directly from the vapor phase could form an ore deposit. However, these deposits at Merapi and other volcanoes (*e.g.*, STOIBER and ROSE, 1974) are restricted to the several fumaroles that exist and only occur within several meters of each vent. The severe metal zoning in the Merapi sublimates and incrustations suggests that many metallic sulfides, oxides and sulfates have maximum depositions at temperatures in excess of 500°C at low pressure. At these high temperatures and with the large gas velocities at the Merapi fumaroles, a significant fraction of the metals is carried away from the vent and dispersed into the atmosphere. Such atmospheric dispersal is also indicated by the large metal transport in volcanic plumes (*e.g.*, BUAT-MÉNARD and ARNOLD, 1978). Finally, since many of the phases deposited are water soluble, they are easily remobilized or washed away by leaching.

Mineralization associated with topaz rhyolites is a notable example of the volatile transport and deposition of Be, Mo, W and Sn (BURT *et al.*, 1982). One such occurrence is the Taylor Creek tin district in the Black Range, N.M., which is noted for cassiterite (wood tin) mineralization associated with flows and domes of the miarolitic Taylor Creek rhyolite. The occurrence of hematite, pseudobrookite, bixbyite and some cassiterite in miarolitic cavities and lithophysae of the rhyolite and experimentally determined stabilities of Fe and Mn oxides (MUAN and SOMIYA, 1962; HAGGERTY and LINDSLEY, 1970) led LUFKIN (1976) to suggest that these minerals crystallized from a gas phase at temperatures of at least 500°C. Most of the mineralization, however, is placer wood tin, which LUFKIN (1977) believed to have been remobilized from low temperature veins in the rhyolite. However, trace amounts of the volatile elements As, Cl, Pb, Zn, Ag, In and S in the wood tin (LUFKIN, 1977), which are highly enriched in volcanic gases at Merapi and Kilauea (ZOLLER *et al.*, 1983) is consistent with an initial gas phase transport of Sn. Like most gas-phase mineralization associated with topaz rhyolites (BURT and SHERIDAN, 1981), there is no evidence of a large tin resource in the Taylor Creek district (EGGLESTON and NORMAN, 1983). As concluded by BURT and SHERIDAN (1981), sublimation in the high energy environment of a volcanic fumarole does not remove metals from the gas efficiently enough to form a large orebody.

However, this does not discount the possibility of volatile transport from a magma body to the shell of a hydrothermal ore deposit as proposed by HENLEY and MCNABB (1978) for the origin of porphyry copper deposits. In support of this hypothesis, fluid inclusion homogenization temperatures of 500°C or higher have been reported at porphyry Cu-Mo, Sn-W-Mo greisen and skarn deposits (ROEDDER, 1972). Furthermore, injection of magmatic gases into hydrothermal waters has been observed in Iceland where volcanic gas vents into active geothermal systems (ÁRMANNSSON *et al.*, 1982) and at El Chichón Volcano where volcanic gas

vents through an acid crater lake (CASADEVALL *et al.*, 1984). In such systems, the magmatic gas transports metals and acid gases to the hydrothermal system. The volatile metals would be a source of ore metals. The acids and K (K metasomatism) would contribute to sericitic, potassic and hypogene advanced argillic wall rock alteration, which could in some cases mobilize additional metals for ores. This study suggests the possibility that volatile element transport from a high-K, tholeiitic andesite system like Merapi could contribute significant amounts of chemicals for wall rock alteration (sulfuric acid, hydrochloric acid, hydrofluoric acid and K) and ore-forming metals (Zn, Pb, As, Mo, W, Cu and others) to the hydrothermal shell of a forming ore deposit.

Assuming a 2.65 wt.% loss of water upon eruption (GILL, 1981, lists a post-eruption water content of .35 wt.% for the Merapi lava and argues that hornblende, which occurs in the Merapi lava, requires at least 3 wt.% water in the liquid phase from which it crystallized) and a gas composition inferred from the gas (LE GUERN *et al.*, 1982) and condensate (Table 1) data, the degassing of 300 km³ of andesite (density of 2.6 g/cm³) would produce an estimated: 2.1 × 10¹⁰ t (metric tonnes) of H₂O, 9.7 × 10⁸ t of S, 7.4 × 10⁷ t of Cl, 3.5 × 10⁶ t of F, 3.3 × 10⁵ t of Br, 2.1 × 10⁵ t of Zn, 1.4 × 10⁵ t of K, 1.7 × 10⁴ t of Pb, 1.1 × 10⁴ t of As, 4.1 × 10³ t of Mo, 3.7 × 10³ t of Mn, 3.5 × 10³ t of V, 2.7 × 10³ t of W, 1.9 × 10³ t of Cu and 1.2 × 10³ t of Bi. In general, these estimates are similar to the quantity of metal produced during the period 1880–1964 from the Main Stage veins at Butte, Montana, which are 7.34 × 10⁶ t of Cu, 2.17 × 10⁶ t of Zn, 1.68 × 10⁶ t of Mn, 3.8 × 10⁵ t of Pb, 1.85 × 10⁵ t of Cd, 1.44 × 10⁵ t of As and 1.83 × 10³ t of Bi (MEYER *et al.*, 1967). Allowing for several orders of magnitude error in these estimates, it is still reasonable that the devolatilization of a batholith-sized magma body could make a significant contribution to a forming ore deposit. Perhaps the largest chemical contribution would be the addition of K and the acids of S, Cl and F, for wall rock alteration. Another inference from these estimates is that the degassing of a fairly typical andesitic magma could produce a large quantity of ore-forming elements. Although an enriched magma would probably increase the degassing rates, it is not clear that unusual pre-enrichments are required. On the other hand, unusual enrichments in halides may play an important role by increasing the efficiency of metal scavenging from the magma during degassing.

Direct evidence for a magmatic supply of metals is difficult to demonstrate in most magma-related hydrothermal ore deposits. In light of this study, however, elements that are highly enriched in volcanic gases and have a very small concentration in magmas could be used as supporting evidence for magmatic derivation and volatile transport of metals. Such elements include Re, Se, Bi and Cd. These elements all have concentrations of less than 200 ppb in typical mafic lavas (*e.g.*, AGV-1 andesite or BCR-1 basalt reported by GOV-

INDARAJU, 1984) yet are enriched by factors greater than 10^5 in the Merapi sublimates. These elements may be fairly common in volcanic emanations as Re-bearing molybdenite (or Re sulfide), Cd-bearing sulfides, Bi-bearing sulfides and Se-bearing native S all have been found (BERNARD, 1985; GREENLAND and ARUSCAVAGE, 1986) in sublimates or incrustations collected at Kilauea, Merapi, and Momotombo volcanoes. Thus, these highly volatile elements might be good indicators of magmatic fluid transport in ore deposits. Re-bearing molybdenites have been found at many porphyry copper ore deposits (NEWBERRY, 1979) and minor amounts (relative to Cu, but still significant quantities) of Cd, Bi and Se have been mined from deposits such as Butte (MEYER *et al.*, 1967). Could it be that the Re, Se, Cd and Bi in these deposits came from an exsolved magmatic fluid? Although it is apparent that these elements were deposited from a hydrothermal fluid, the strong fractionation of these elements into a gas phase at active volcanoes and typically low concentrations of these elements in rocks is good evidence that they are magma-derived by volatile transport, as opposed to having been leached from deep country rocks by hydrothermal waters.

One final point concerning ore genesis is that the ore fluids for the acid sulfate-type epithermal ores (HAYBA *et al.*, 1985) may resemble more nearly acidic volcanic gas condensates (with meteoric dilution) than they do the boiling geothermal waters (*e.g.*, REED and SPYCHER, 1985) that may be responsible for generating the adularia-sericite-type epithermal ores. Characteristic features of the acid sulfate ore type (*e.g.*, Summitville, Colorado; STOFFREGEN, 1985; HAYBA *et al.*, 1985) that support this view include: a) the extreme development of hypogene advanced argillic alteration due to acid attack of wall rocks, b) the small separation in age (less than 0.5 m.y.) between the igneous host rock and mineralization relative to the long separation (greater than 1 m.y.) for the adularia-sericite type, c) the anomalous bismuth that is common in the acid sulfate ores and abundant in Merapi sublimates, but which is absent in the adularia-sericite ore type. HAYBA *et al.* (1985) discuss additional evidence favoring a close connection between magmatism and the formation of acid sulfate-type epithermal deposits.

CONCLUSIONS

Most of the complex set of elements (largely metals) in the Merapi volcanic gas are derived from incomplete degassing of shallow magma. Many of the trace components in the gas leave the magma in equilibrium with it at 915°C. In the order of decreasing abundance, they are transported as chloride, sulfide, bromide, oxychloride, acid, oxyfluoride, fluoride, and elemental gas species. As the gas ascends through the fracture system, some of the major rock-forming elements may be added to the gas by contamination from particles or the reactions with wall rock. Upon reaching the fumarolic environment, the gas cools rapidly and sub-

limes form as the gas saturates with various sublimate phases. Sublimates start to fractionate from the gas phase in an order that depends on their equilibrium saturation temperatures, despite increasing disequilibrium at lower temperatures. Once the gas emerges from a fumarole, sublimation continues, but other processes such as acid-rock or gas-atmosphere reactions also contribute to the formation of incrustations around the fumarole.

Because the volcanic gas ascends rapidly from the magma and does not equilibrate fully with the sublimates and wall rock, trace components could be used as sensitive indicators of the intensive parameters of shallow magma. Such uses include geothermometry, such as has been applied successfully to active geothermal systems (REED and SPYCHER, 1984). Because there are so many trace components in the gas, they could be a very powerful tool to unravel the ascent history of volcanic gases.

The metals and acidic gases emitted by volcanoes provide insight into ore deposits formed in part by magmatic fluids. Volatile transport could remove enough metal from a large magma body to form an ore deposit, but direct sublimation from a high temperature, high velocity carrier gas is too inefficient to form a sizeable orebody. Highly volatile elements like Re, Se, Bi and Cd could be used as supporting evidence for magmatic vapor transport in ore deposits.

Acknowledgements—Special thanks goes to the Volcanological Survey of Indonesia for their logistical support of the project. The condensates were analyzed for anions by Analytical Services at Michigan Tech. and for U by R. Zielinski (USGS, Denver, CO). N. Long (Arizona State Univ.) and J. Hughes (Miami Univ.) provided TEM analyses and XRD data, respectively, on some of the sublimate phases. G. Swartz is thanked for helpful comments in the early stages of this project. We also thank A. Bernard, N. Oskarsson, B. Nordlie, D. McDowell, T. Bornhorst and two anonymous reviewers for extensive comments on the manuscript.

Editorial handling: E. B. Watson

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