High-sulfur magma, a product of fluid discharge from underlying mafic magma: Evidence from Mount Pinatubo, Philippines

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ABSTRACT

Beneath Mount Pinatubo in the Philippines, a hot mafic melt ascended, releasing supercritical fluids rich in SO_2 into an overlying semisolidified dacitic magma. The SO_2 was reduced to H_2S in the cool, wet dacite, causing oxidation of this magma. H_2S thus formed was initially precipitated in the dacite as sulfides, which were high in Cu, Cd, Zn, and Se/S, elements also introduced by the fluids. Continued influx of SO_2 and oxidation of the dacite led to an increase in the S solubility of the melt, causing partial resorption of sulfide minerals. Further addition of SO_2 then led to excess S, which, in part, was precipitated as anhydrite. High S contents and the oxidized nature of the eruption products were due to the conjunction of an overlying, cool dacitic magma and ascending hot mafic melt. The 1982 eruption products of El Chichón (Mexico) and those from the 1985 eruption of Nevado del Ruiz (Colombia) have features similar to Pinatubo, suggesting that these high-S magmas may have formed by a similar process.

INTRODUCTION

The Plinian eruption on June 15, 1991, from Mount Pinatubo (Luzon, Philippines) ejected 6000 to 10 000 Mt (megatonne = 10^{12} g) of pyroclastic material (Scott et al., 1991) and discharged 20 Mt of SO_2 into the stratosphere (Bluth et al., 1992); the SO_2 produced a significant impact on Earth's climate. High S content for the erupted dacitic magma is indicated by the presence of anhydrite phenocrysts, similar to the El Chichón rocks, which was erupted along with >8 Mt of SO_2 in 1982. The rare preservation of anhydrite in older volcanic rocks has prompted the suggestion that high-S magmas may be common (Luhr et al., 1984), even occurring in the reduced Archean environment (Hattori and Cameron, 1986). This paper reports on sulfides from the eruption products and shows that supercritical fluids from underlying mafic magma had an essential role in the enrichment of S and oxidation of the dacitic magma.

SAMPLES

The eruption products of June 15, 1991, are porphyritic, well-vesiculated pumice (white pumice) and poorly vesiculated, fine-grained pumice (gray pumice) with minor banded pumice (bands of the two pumices). Dome-forming andesite and minor andesitic scoria were discharged during the eruption of June 7–12, 1991. Compelling evidence indicates that the eruption was triggered by an injection of mafic melt into a semisolidified dacitic magma (e.g., Pallister et al., 1992). This is supported by compositions of olivine (Fo = 85–88) and chromite in dacitic pumices (Knittel et al., 1992), similar to those in the basalt, and abundant basalt fragments (<2 m) in andesite. Basalt contains phenocrysts of hornblende-rimmed olivine, euhedral hornblende, plagioclase, and microphenocrysts of augite, ilmenite-hematite solid solution (Rss), and ulvospinel-magnetite solid solution (Css). All samples for this study (six white pumices, six gray pumices, three banded pumices, nine dome andesites, and four basalts) were collected ~4 km west of the crater wall along Maraunot River and near Clark Air Base along Sacobia River. Their angular shape and the lack of alteration and devitrification in the glass indicate that they are products of the June 1991 eruption.

Analytical Procedures

Major compositions of minerals were determined using a JEOL 6400 digital SEM equipped with a 40° take-off angle and a Link X-ray analyzer. Analytical conditions were 20 kV accelerating potential, 0.8 nA current, and a counting time of 140 to 200 s. Standards for sulfides were pyrite (Fe, S), chalcopyrite (Cu), Ni metal (Ni), Co metal (Co), and ZnS (Zn), and those for oxides were Al_2O_3 (Al), MgO (Mg), $MnTiO_3$ (Mn, Ti), V metal (V), and hematite (Fe). Analyses are believed to be accurate to ±2% of the amount present, and detection limits are 0.1%.

Trace elements in sulfides were determined using a proton-induced X-ray microprobe. Operating conditions were 3 meV of proton energy, ~8 nA of specimen current, 600 to 900 s counting time, a 4 × 5 μm beam, and a 352-μm-thick Al absorber. Detection limits are three times the errors obtained from the background. Details of operation and accuracies appear in Cabri et al. (1984).

SULFUR MINERALS

Anhydrite is common in dacitic pumices (Bernard et al., 1991, and others), andesitic scoria, and dome rocks. Smooth contacts with glass show that anhydrite was stable in the dacitic magma immediately before eruption.

Sulfide minerals are volumetrically minor (<0.01 vol%) and generally small (<10 μm), but they are present in all samples: >100 grains per section of basalts and andesites and >30 grains per section in most dacitic pumice. The sulfides occur as (1) sulfide grains included in phenocrysts (hornblende, oxides) and (2) late sulfide enclosed in glass, quartz, and plagioclase. The former are globular, consisting of Ni pyrrhotite ($Fe_{1-x}S$; Table 1) and Cu-Fe sulfides (cubanite, $CuFe_2S_3$; chalcopyrite, Cp; $CuFeS_2$). Some grains in plagioclase are globular, but high in Cu (Fig. 1A). Late-formed sulfides enclosed in glass have irregular shapes and are Cu-rich (Table 1): Cp intergrown with bornite (Bo; Cu_5FeS_4). Some are so high in Cu that Cp has exsolved from a Bo matrix. Other characteristic features of the sulfides in glass are high Zn (<1.4 wt%), Cd (<40 ppm), Ag (<240 ppm), and Mo (<150 ppm) and Se/S weight ratios of 80 to 100 × 10^{-5} (Tables 2, 3). Se/S ratios are significantly higher than those of mid-oceanic ridge basalts and mantle-derived sulfides, ~20 to 30 × 10^{-5} (Hattori et al., 1992). Sulfides in glass commonly display evidence of desulfurization (Fig. 1B).

TABLE 1. REPRESENTATIVE COMPOSITIONS OF SULFIDES IN PINATUBO ERUPTION PRODUCTS

Rocks:	White Pumice			And		Basalt	
Host:	Plag	Glass	Glass	Ol-Hbl	Glass	Rss	Glass
S	31.67	35.54	26.55	39.65	30.51	39.05	36.67
Fe	30.43	41.74	14.83	54.34	14.69	58.96	46.37
Ni	0.28	0.00	0.00	4.34	0.00	1.33	0.00
Cu	34.24	21.69	55.84	0.00	56.86	0.00	19.48
Zn	0.00	1.30	0.00	0.00	0.00	0.00	0.00
Total	96.62	100.27	97.22	98.33	102.06	99.33	102.75

Note: And=andesite, Plag=plagioclase, Ol=olivine, Hbl=hornblende, Rss=unexsolved ilmenite-hematite solid solution. Values are weight percent.

Figure 1. Backscattered electron image of Cu-Fe sulfide in white pumice. Bornite (brighter) exsolved from chalcopyrite matrix (dark). A: Sulfide in plagioclase (Pl) phenocrysts. B: Sulfide attached to magnetite (Mag) in glass (Gl). Note desulfidation reaction rim.
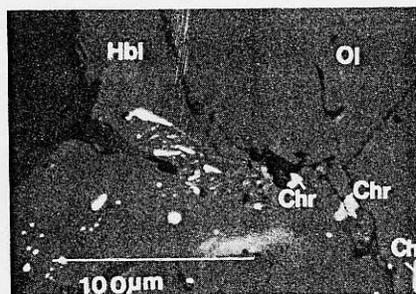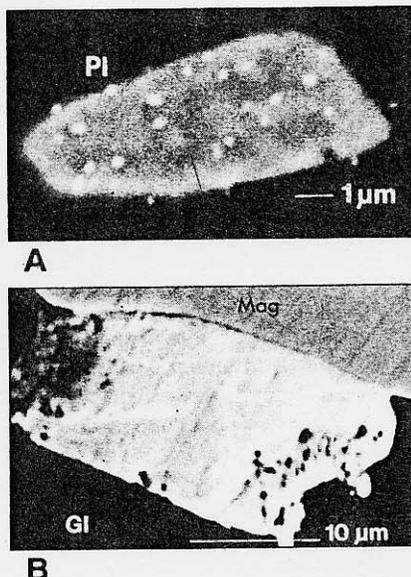

Figure 2. Photomicrograph of symplectic arrays of Ni pyrrhotite (bright spot) and chromite (Chr) in hornblende (Hbl) rimming olivine (Ol) in basalt.
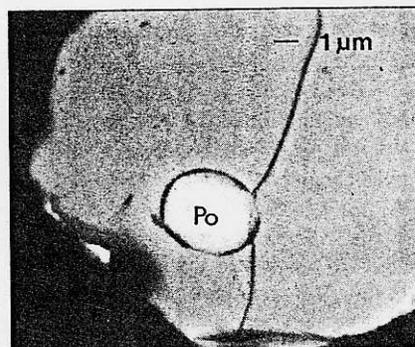

Figure 3. Backscattered electron image of typical globular Ni-pyrrhotite (Po) inclusion in magnetite in dome andesite.

TABLE 2. TRACE ELEMENTS IN SULFIDES IN PINATUBO WHITE PUMICE

Sample	Host·	Zn	As	Se	Mo	Ag	Cd	Sb	Te	Se/S (x10⁻⁵)
UK29-3	Gl	2233	24	314	<6	36	20	<15	35	93.1
PP1BB	Gl	2569	<8	299	<6	32	24	<16	<22	83.9
PP1BB	Gl	2884	<9	266	8	10	14	<15	<23	80.4
PP1BA	Gl	212	<3	170	<4	242	42	<22	<34	49.2
PP1C,F†	Hbl	1247	12	61	<5	21	<10	<17	74	36.5
PP1A1A†	Gl	2209	8	276	44	91	22	<18	39	66.6
PPA1A†	Gl	2184	22	333	149	173	16	36	43	87.3

Note: Values (ppm) determined by proton-induced X-ray microprobe.
* Phase containing sulfides; Gl=glass, Hbl=hornblende.
† Grains were too small, and totals of Cu, Fe, and S are in the range of 50 -90%. Trace element concentrations are normalized accordingly.

TABLE 3. TEMPERATURE AND f_{O_2} ESTIMATES FROM Fe-Ti OXIDES

Sample	Rock	Usp	Ilm	$T(°C)$	Δ_{FMQ}*
UK29AX	white pumice	0.127	0.557	825	+3.1
812-3A	gray pumice	0.121	0.547	817	+3.2
813-17E	banded	0.129	0.542	821	+3.1
	pumice	0.230	0.552	841	+3.1
814-3C	andesite	0.153	0.550	856	+2.9

Note: Fe₂O₃ and components of ulvospinel (Usp) and ilmenite (Ilm) calculated using QUILF program (Andersen et al., 1993).
* Difference between the f_{O_2} and FMQ buffer, in log units.

In basalt and andesite, symplectic arrays and globular inclusions of Ni-bearing pyrrhotite (Po) are common in augite, hornblende rimming olivine, and euhedral hornblende phenocysts (Figs. 2, 3). None of the sulfide grains in basalt display desulfurization rims; this suggests that they were stable in the melt and that the f_{O_2} of the melt remained below the sulfate/sulfide redox boundary (Fig. 4). This is consistent with low abundances of Css and an absence of anhydrite in basalts. The oxide compositions could not be used to estimate melt temperature and f_{O_2} because of subsolidus reequilibration (e.g., Hammond and Taylor, 1982) during cooling of the andesite and the enclosed fragments of basalts.

DISCUSSION
Sulfur in Melts and Fluids

The solubility of S in silicate melts is controlled by temperature, pressure, f_{O_2}, and melt composition. Sulfur in reduced melts is present as S^{2-} with minor HS^-; saturation causes separation of an immiscible sulfide melt (Fig. 4). The solubility of S increases with increasing Fe (Nagashima and Katsura, 1973); thus, S is generally higher in mafic melts. Sulfur in oxidized melt is present as SO_4^{2-}. Solubility of S is at a minimum near the redox boundary between SO_4^{2-} and S^{2-}, approximately one log f_{O_2} unit above the Ni-NiO (NNO) buffer (Nagashima and Katsura, 1973; Carroll and Rutherford, 1987), but increases as f_{O_2} increases above this boundary (Fig. 4).

Sulfur released from a silicate melt is mostly SO_2 and H_2S, and the two are controlled by the reaction $SO_2 + H_2O = H_2S + 1.5\ O_2$. Higher temperature and lower f_{H_2O} ("dry" melts) promote higher SO_2/H_2S (Fig. 5). Mafic melts are generally dry, and the predominant S gas released from the melts is SO_2, as documented by study of many volcanic gases. Felsic magmas, which are cool and hydrated, generally release gases with low SO_2/H_2S.
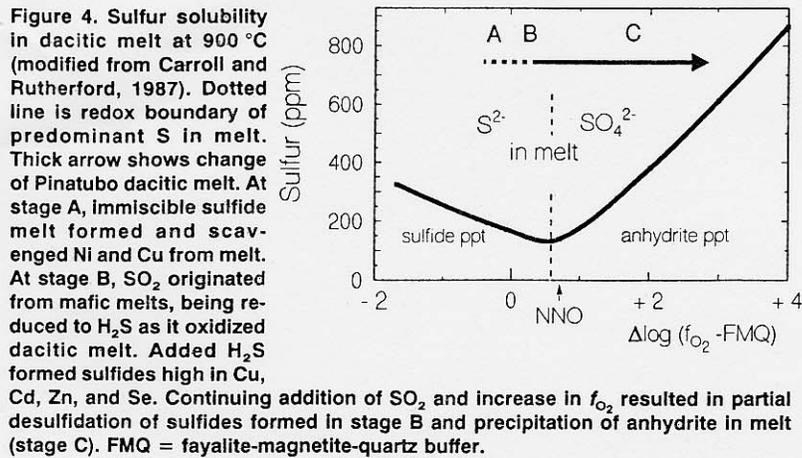
Chalcophile and Siderophile Elements in Melt

Upon separation of immiscible sulfide melt from silicate melts, chalcophile and siderophile elements are preferentially enriched in the sulfide melt ($D_{sul-sil} > 250$ for Ni and Cu and 50 for Co at 1200 °C; Rajamani and Naldrett, 1978). Copper is scavenged from a silicate melt as a sulfide melt separates. A fluid released from silicate melts is enriched in volatile elements and hydrophyllic metals. These include Cu (Candela and Holland, 1984), Se (e.g., Greenland and Aruscavage, 1986), Cd, Zn, Ag, and Mo (Symonds et al., 1990).

Sulfur in the Pinatubo Magma

Globular sulfide in phenocrysts of dacitic pumices and basalt fragments indicates that an immiscible sulfide melt initially formed in both melts, and at this stage f_{O_2} values of both silicate melts were below the redox boundary of S. The dacitic magma became oxidized, because the occurrence of anhydrite requires f_{O_2} higher than the redox boundary. High f_{O_2} values are confirmed by the estimates from Fe-Ti oxides in white pumices (Rutherford and Devine, 1991; this study), gray pumices, banded pumices, and andesites (Table 3).

The solubility of S as SO_4^{2-} is much higher than that of S^{2-} (Nagashima and Katsura, 1973; Fig. 4). Thus, progressive oxidation of a melt does not result in crystallization of anhydrite; it requires

Figure 4. Sulfur solubility in dacitic melt at 900 °C (modified from Carroll and Rutherford, 1987). Dotted line is redox boundary of predominant S in melt. Thick arrow shows change of Pinatubo dacitic melt. At stage A, immiscible sulfide melt formed and scavenged Ni and Cu from melt. At stage B, SO_2 originated from mafic melts, being reduced to H_2S as it oxidized dacitic melt. Added H_2S formed sulfides high in Cu, Cd, Zn, and Se. Continuing addition of SO_2 and increase in f_{O_2} resulted in partial desulfidation of sulfides formed in stage B and precipitation of anhydrite in melt (stage C). FMQ = fayalite-magnetite-quartz buffer.

Figure 5. Equal concentrations of SO_2 and H_2S at 200 atm (dashed curve), 2 kbar (dash-dot curve). "Dry" and "wet" fluids have X_{H_2O} of 0.01 and 1, respectively. Heavy-line curves are fayalite-magnetite-quartz (FMQ) and magnetite-hematite (MH) buffers. Dotted area indicates oxidation condition (Wallace and Carmichael, 1992). Vertical-ruled area labeled Dac indicates condition of Pinatubo dacitic melt prior to eruption. Thick arrow shows evolution of Pinatubo dacitic magma. Note that fluid released from dryer and hotter melt has high SO_2/H_2S ratio.

addition of S from an external source. The high Se/S of sulfides present in Pinatubo glass appears to suggest that the external source of S had high Se/S.

High Cu contents of sulfides, ~30 wt%, in the glass cannot be attained by enrichment of Cu by fractional crystallization. They require >0.15 wt% Cu in the silicate melt using $D_{sul-sil}$ (>250; Rajamani and Naldrett, 1978). Copper was probably added to the dacitic melt along with the introduction of S. Zinc, Cd, Mo, and Ag, which are also high in the sulfides, were likely introduced at this time. The metal assemblage is remarkably similar to enriched elements in a fluid separating from a silicate melt (e.g., Symonds et al., 1990).

Source of Sulfur in the Dacitic Magma

Proposed sources of S in high-S magmas include (1) subducted seafloor sulfide deposits (Whitney, 1984), (2) evaporite beds (Rye et al., 1984), (3) sulfide deposits in underlying ophiolitic rocks (Fournelle, 1991), (4) sulfate minerals from preexisting volcanic rocks (McKibben et al., 1992), and (5) SO_2 released from underlying mafic magma (Pallister et al., 1992). High S in the dacite melt at source (model 1) is inapplicable, because this study shows that the dacitic magma acquired S from an external source during and after crystallization of phenocrysts. Incorporation of evaporite (model 2) proposed at El Chichón (Rye et al., 1984) is not feasible because of the lack of evaporites in the Pinatubo area. Eocene-Pliocene shallow-marine rocks may contain evaporite minerals, but this possibility is discounted for three reasons. First, the assimilation would lower Se/S because of their low Se/S ratios (<0.1 × 10^{-5}; Measures et al., 1980). Second, evaporites generally contain little Cu. Third, it would raise $^{87}Sr/^{86}Sr$, given high $^{87}Sr/^{86}Sr$ (0.70912) of young evaporites. The ratios of anhydrite in pumices (0.70421 ±0.0001; this study) and bulk pumice (0.70422 to 0.70426) are similar to other volcanic rocks in the Bataan arc (Knittel et al., 1992).

Incorporation of ophiolite-derived sulfide (model 3) is also discounted because it would not provide S with high Se/S and an oxidizing agent for the magma. The incorporation of hydrothermal anhydrite (model 4) is appealing because anhydrite is abundant in preexisting volcanic rocks (my examination of PNOC drill chips in 1992). The direct contribution of fluids to the dacitic magma (model 5) is, however, favored. First, there are abundant fluid inclusions in hornblende, plagioclase, and quartz. Second, common presence of anhydrite in the dacitic pumice indicates it was evenly dispersed in semisolidified magma. Third, the dacitic magma was pervasively oxidized as documented from >100 analyses of oxides in dacitic pumice (this study). Loss of S from the mafic melt is also supported by low S contents in the basalts, <200 ppm (this study). Sulfur isotope values, +6‰ to +8‰ (Knittel et al., 1992) with several values outside the range (McKibben et al., 1992), also support the pro-
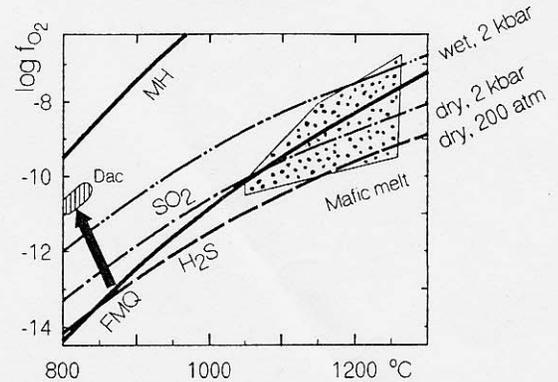
posed model. SO_2 discharged from mafic melts has $\delta^{34}S$, ~+6‰ (Sakai et al., 1984); the value varies depending upon temperature, f_{O_2}, and f_{H_2O} of the melts (e.g., Sakai et al., 1984).

In summary, I propose that the dacitic melt was enriched in S by a supercritical fluid discharged from underlying mafic melt during its ascent. SO_2/H_2S ratios of fluids released from the hotter mafic melt were high, and the ratios decreased in the cooler and wetter dacitic melt (Fig. 5) as SO_2 was reduced to H_2S. This reduction caused the complementary oxidation of the dacitic melt and the resulting H_2S was initially precipitated as sulfides in the dacite magma. Progressive oxidation of the magma resulted in f_{O_2} above the redox boundary of S, when SO_4^{2-} became stable in the melt and formed anhydrite by the disproportioning reaction $4 SO_2 + 3 (CaO) + H_2O = 3 CaSO_4 + H_2S$, where CaO is a component in the magma. At this stage, sulfide minerals became unstable, resulting in desulfurization of their rims.

The total amount of S released from the volcano during eruption was 18 to 23 Mt (10 Mt in SO_2, 6 to 10 Mt within the 6000 to 10 000 Mt of rock, 2 to 3 Mt adsorbed on ashes). The amount of S adsorbed on ashes was estimated on the basis of S at El Chichón where adsorbed S on ash accounts for 25% of S in the rocks (Varekamp et al., 1984). If all S was derived from mafic magma, it would require 16 000 to 20 000 Mt of mafic magma (6 to 8 km^3 with a density of 2.5 g/cm^3), assuming the total degassing of 1000 ppm S from the melt. The volume is comparable to the ejected dacitic magma. This estimate is a maximum, because 1000 ppm loss of S is conservative; many mafic melts contain much higher S (<2400 ppm; Wallace and Carmichael, 1992) and alkalic basalts contain even higher contents of S. Low S contents in subaerial basalts (<50 ppm; Ueda and Sakai, 1984) indicate that S in the melt is essentially degassed during its shallow emplacement.

Origin of SO_2 Discharged to the Stratosphere from Mount Pinatubo

Proposed origins of SO_2 discharged to the stratosphere during the height of the 1991 eruption include (1) breakdown of anhydrite in the magma (Rutherford and Devine, 1991), (2) breakdown and absorption of sulfides in melts (Whitney, 1992), or (3) release of gas present in a separate vapor phase (Westrich and Gerlach, 1992). Lack of reaction rims around anhydrite argue against the first model. It is also difficult to envisage such a fast reaction even at magmatic temperatures. Thin reaction rims of sulfides in glass in pumice are

not in accord with the second hypothesis. This study supports the proposal by Westrich and Gerlach (1992) that the SO_2 was most likely derived by release of S present in a vapor phase in dacitic melt.

Other High-Sulfur Volcanic Rocks

The products of two recent volcanic eruptions are known to contain anhydrite phenocrysts: El Chichón, Mexico (Luhr et al., 1984), and Nevado del Ruiz, Colombia (Fournelle, 1990). They display features indicative of fluid percolation, suggesting that their S-rich, oxidized nature may also be attributed to the introduction of fluids from an underlying mafic magma. Sulfides at El Chichón contain high Cu (Luhr et al., 1984) and high Zn, As, and Se/S (Hattori and J. F. Luhr, unpublished data). El Chichón rocks also display abundant fluid inclusions in phenocrysts (Luhr et al., 1984) and the $\delta^{34}S$ of magma, +5.8‰ (Rye et al., 1984). Similarly, fluid inclusions are abundant in phenocrysts of the Nevado del Ruiz eruption products (Melson et al., 1990), sulfides are high in Cu (Hattori and J. Stix, unpublished data), and evidence for the presence of an underlying mafic magma has been indicated by Sigurdsson et al. (1990) and Melson et al. (1990).

The 1982 eruption of El Chichón released a total of 10.4 Mt of S, comprising 8 Mt of SO_2, S adsorbed on ash-fall deposits, and S in the eruption products as anhydrite (Varekamp et al., 1984). An estimate similar to the volume calculation for Pinatubo indicates a requirement for 6000 Mt of mafic melt ($\sim$2.3 km^3). Nevado del Ruiz has discharged $\sim$3 Mt of SO_2 since late 1984 (Williams et al., 1990), requiring 1500 Mt of mafic melt (0.6 km^3).

The importance of contemporaneous mafic magmatism to the eruption of felsic magma has been widely documented (e.g., Sigurdsson et al., 1990), but the significance of fluid from the former has not been fully recognized. Chemical and isotopic disequilibrium among phases and enrichment of alkalis in felsic magmas may also be related to fluid infiltration in magmas.

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