Magmatic Vapor Source for Sulfur Dioxide Released During Volcanic Eruptions: Evidence from Mount Pinatubo

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Sulfur dioxide (SO_2) released by the explosive eruption of Mount Pinatubo on 15 June 1991 had an impact on climate and stratospheric ozone. The total mass of SO_2 released was much greater than the amount dissolved in the magma before the eruption, and thus an additional source for the excess SO_2 is required. Infrared spectroscopic analyses of dissolved water and carbon dioxide in glass inclusions from quartz phenocrysts demonstrate that before eruption the magma contained a separate, SO_2-bearing vapor phase. Data for gas emissions from other volcanoes in subduction-related arcs suggest that preeruptive magmatic vapor is a major source of the SO_2 that is released during many volcanic eruptions.

Explosive volcanic eruptions can inject large quantities of SO_2 into the stratosphere, where it is converted into H_2SO_4 aerosols that can affect both climate and atmospheric chemistry (*1, 2*). Emissions of SO_2 from recent eruptions of Mount Pinatubo in the Philippines (1991) and El Chichón in Mexico (1982) were relatively large (*1*), and in both cases pumice ejected during the eruptions contained anhydrite ($CaSO_4$) (*3, 4*). Studies of the preeruptive concentrations of dissolved volatile (C-O-H-S) species in lavas from these and other volcanoes have led to a conundrum concerning sulfur mass balance during volcanic eruptions. Inclusions of melt that were trapped inside of growing phenocrysts in magma before eruption, and subsequently quenched to glass, commonly have sulfur contents that are far too low (by one to two orders of magnitude) to account for the large mass of SO_2 released simply by exsolution of sulfur from melt during eruption (*3, 5–7*). Several potential sources of excess SO_2 considered for Mount Pinatubo (*8*) include the following: (i) a separate C-O-H-S vapor phase present as bubbles in the magma before eruption (*3, 5, 7*); (ii) rapid degassing of a large volume of unerupted magma in the subvolcanic reservoir (*9*); (iii) decomposition of anhydrite during eruption (*10*); and (iv) flash vaporization of sulfate-rich hydrothermal fluids. In this report we present data from the 1991 eruption of Mount Pinatubo that support the first hypothesis and discuss processes through which the vapor phase may have formed.

The hypothesis that SO_2 was contained in a separate magmatic vapor phase can be evaluated by determining the concentrations of the major volatile species that were dissolved in the melt before eruption. Glass inclusions in quartz phenocrysts (Fig. 1) provide a record of preeruptive conditions because the glass represents trapped magmatic liquid that has retained its original dissolved volatile contents. Infrared spectroscopic analyses of these inclusions indicate that concentrations of H_2O (6.1 to 6.6% by weight) and CO_2 (280 to 415 ppm) (Table 1) are relatively high. Silicic melts containing the analyzed H_2O and CO_2 contents at the experimentally determined preeruptive temperature of 780°C (*11*) would be saturated with H_2O-CO_2 vapor at pressures of 250 to 290 MPa (Fig. 2). Independent evidence for the preeruptive pressure of the magma reservoir comes from seismicity associated with the 1991 Mount Pinatubo eruptions, which indicates that a large (~40 to 90 km^3) reservoir of magma resided at depths of 6 to 11 km beneath the volcanic edifice (*12*). These depths correspond to pressures of 160 to 300 MPa, with an assumed average crustal density of 2700 kg/m^3, and agree with preeruptive magma pressure estimates of 220 ± 50 MPa based on measured Al_2O_3 contents of hornblende phenocrysts (*11*) and hornblende inclusions in quartz (*13*) and estimates of 200 to 300 MPa determined from experimental phase equilibrium studies of the Pinatubo phenocryst-melt assemblage (*11*). The excellent correspondence between independent pressure estimates and vapor-saturation pressures based on inclusion H_2O-CO_2 data provides strong evidence confirming suggestions (*5, 8*) that the magma that erupted on 15 June 1991 was saturated with a multicomponent C-O-H-S vapor before eruption.

The composition of the preeruptive magmatic vapor can be estimated from the dissolved H_2O, CO_2, and sulfur contents of glass inclusions in conjunction with experimental constraints on the vapor pressures of these species. The partial pressure of water (P_{H_2O}) is taken as 220 MPa to be consistent with experimental P_{H_2O} values that reproduce the compositions of the melt in equilibrium with the phenocryst assemblage in the Pinatubo dacite (*11*). At this value of P_{H_2O} the melt would contain 6.3% dissolved H_2O by weight (*14*), consistent with the measured H_2O contents of glass inclusions (Table 1). The partial pressure of SO_2 (P_{SO_2}) is constrained to be 11 MPa; this value is based on experimental data for anhydrite stability in melts containing dissolved sulfur contents of ~60 ppm (*11, 15*). The partial pressure of CO_2 (P_{CO_2}) is calculated to be 40 MPa; this value is based on dissolved CO_2 contents of the glass inclusions and experimental solubility measurements for rhyolitic liquids (*16*). These

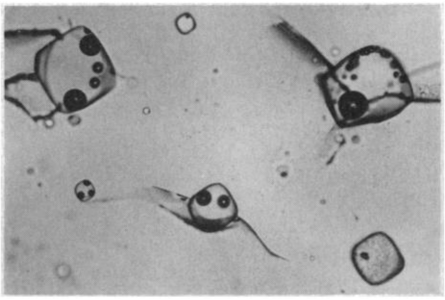

Fig. 1. Glass inclusions in a quartz phenocryst from pumice ejected during the 15 June 1991 eruption of Mount Pinatubo. The width of the photograph is 650 μm. Typical glass inclusions contain one or more relatively large vapor bubbles (round, black spots inside inclusions) and are commonly intersected by small cracks that extend into the surrounding quartz host. The presence of these bubbles complicates interpretations regarding the dissolved volatile contents of the trapped melt (glass) because it is not clear if the bubbles existed at the time of inclusion formation or formed subsequent to entrapment. In either case, mass transfer of dissolved volatile species from liquid to a vapor bubble or bubbles during decompression and cooling drastically reduces the original dissolved CO_2 contents, and to a lesser extent the H_2O contents, of the glass inclusions. To minimize this problem, we analyzed glass inclusions that are bubble-free or contain only a single small bubble (see inclusion in lower right). These inclusions have a speckled appearance because of slight devitrification of the glass. Electron microprobe analyses of these inclusions indicate that they are high-silica rhyolites similar to those reported for bubble-bearing inclusions (*5, 11*). The inclusion compositions overlap with that of degassed matrix glass (*5, 11*) and glass-filled reentrants (embayments) in quartz (*27*), indicating a comagmatic origin for all glasses. However, some of the inclusions have slightly lower CaO, MgO, and total FeO than the matrix glass. These differences are not significant, as the entire compositional range of the inclusion glasses corresponds to a small amount of crystallization (~1% by weight) of the observed phenocryst assemblage.

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constraints indicate a vapor composition of 81 mol% H_2O, 15 mol% CO_2, and 4 mol% SO_2 (*17*) and indicate that the vapor was not excessively rich in SO_2.

Using this composition, we can estimate the total mass of vapor needed to account for the 17-megaton (Mt) SO_2 emission (*18*) from the eruption on 15 June 1991. If all of the SO_2 was contained in the vapor before the eruption, then the bulk magma (silicate melt + crystals + exsolved vapor) would have contained 0.7 to 1.3% vapor by weight. The range of values is a result of uncertainty in the volume of magma erupted (5 to 10 km^3, recalculated to the dense rock equivalent) (*19*). This amount of vapor would lower the bulk density of the magma by only 2 to 4% relative to a vapor-free magma, because at the preeruptive conditions of 780°C and 260 MPa the density of the vapor is 600 kg/m^3 (*20*).

The exsolved vapor may have formed through a number of magmatic processes. At the time of eruption, the Pinatubo dacitic magma was relatively crystal-rich (~45% phenocrysts) (*21*), suggesting that all of the preeruptive vapor may have been dissolved at an earlier stage when the magma was entirely molten. However, because of the low solubility of CO_2 in silicate melts, it is not possible for all of the preeruptive vapor to be dissolved in 5 to 10 km^3 of dacitic liquid at 260 MPa. The decompression of an ascending magma is another potential mechanism by which magmatic vapor may form, because the solubilities of H_2O and CO_2 strongly depend on pressure. We modeled the exsolution of vapor during decompression and crystallization of a dacitic melt behaving as a closed system (Fig. 2). The results suggest that, for closed system processes to be effective in generating ~1.0% vapor by weight, the initial dacitic melt must have contained high concentrations of dissolved CO_2 (4000 ppm). This model can simultaneously explain the mass and composition of vapor erupted, the H_2O and CO_2 contents of glass inclusions, and the observed phenocryst abundances. The estimated pressure (500 MPa) needed to dissolve 4000 ppm CO_2 requires that the initial magma be at a depth of at least 18 km beneath the volcano.

An additional constraint that must be considered is the sulfur content of the initial liquid. Sulfur is present in the Pinatubo dacite as sulfate because of high magmatic oxygen fugacity (*5, 11*). Because sulfate solubility in silicate melts is strongly temperature-dependent (*22*), the initial liquid at a pressure of 500 MPa in the combined decompression and crystallization model must be at a temperature greater than 830°C, so that there is sufficient dissolved sulfate to account for both the mass of SO_2 in the preeruptive vapor and the amount of anhydrite that precipitated (Fig. 3). However, as with the high CO_2 contents required by the model in Fig. 2, the hypothesis of high initial sulfur contents (≥2000 ppm) is difficult to test and seems unlikely, given that virtually all of the glass inclusions that have been analyzed (~100 inclusions from many pumice clasts) from all major phenocryst phases contain less than 100 ppm sulfur on average (*5, 11*).

An alternative to closed-system decompression and crystallization is that silicic magma that erupted from Mount Pinatubo came from the upper regions of a large magmatic system and was enriched in exsolved vapor as a result of the long-term flux of volatiles from underlying, less differenti-

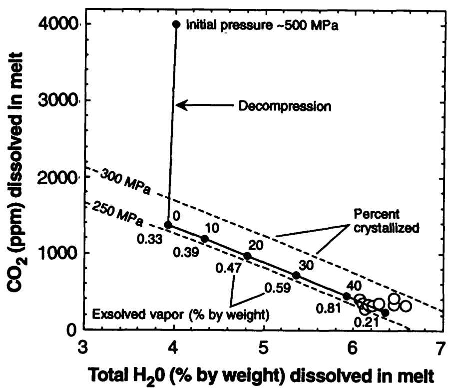

Fig. 2. Total H_2O and CO_2 contents dissolved in glass inclusions from quartz phenocrysts (open circles). Dashed lines indicate the H_2O and CO_2 contents of silicic melts saturated with H_2O-CO_2 vapor at 250 and 300 MPa. The solid line shows variations in dissolved H_2O and CO_2 for an initial, crystal-free magma with 4.0% dissolved H_2O by weight and 4000 ppm of CO_2 undergoing closed system decompression followed by 50% crystallization by weight at 260 MPa. Values for the total mass (in percentage by weight) of vapor exsolved and the amount of crystallization (in percentage by weight) are indicated. The initial H_2O and CO_2 contents were chosen so that, after decompression and crystallization, the data for the residual liquids in the model calculation match the glass inclusion data. The mass of vapor exsolved during these processes (~1% by weight) agrees well with the estimated range of vapor contents (0.7 to 1.3% by weight) needed to explain the 17-Mt SO_2 emission.

Table 1. Analytical data for glass inclusions in quartz phenocrysts from the 15 June 1991 eruption of Mount Pinatubo. Inclusions are from six individual quartz crystals from a pumice clast collected in the Sacobia River valley located northeast of Mount Pinatubo. This clast is a sample of phenocryst-rich dacite that is similar to those studied by other investigators (*5, 8, 11*). Values for H_2O molecular (H_2O mol) (5200 cm^{-1}), OH^- (4500 cm^{-1}), and CO_2 (2350 cm^{-1}) were determined by infrared spectroscopy (*16, 25*). The sum of H_2O mol and OH^- is H_2O tot. Analytical uncertainties are ±0.4% for total H_2O and ±20 ppm for CO_2. Sulfur contents were measured by electron microprobe and have an uncertainty of ±20 ppm. We calculated bubble volumes assuming spherical geometry for both bubble and inclusion. We calculated pressures (P_{sat}) at which silicic melt would be saturated with a vapor phase containing H_2O and CO_2 using experimental solubility data (*14, 16*) and methods modified from Dixon (*26*).

Inclusion	H_2O mol (% by weight)	OH^- (% by weight)	H_2O tot (% by weight)	CO_2 (ppm)	S (ppm)	Bubble (% by volume)	P_{sat} (MPa)
1.2	4.94	1.22	6.16	336	80	0.07	260
1.3	4.89	1.22	6.11	356	–	0.32	260
2.1	5.45	1.13	6.58	325	–	0.07	280
3.2	5.05	1.23	6.28	348	60	None	270
3.3	5.05	1.08	6.13	278	–	None	250
4.1	5.04	1.17	6.21	328	70	0.07	260
4.2	5.22	1.23	6.45	339	70	0.14	280
5.1	5.13	1.32	6.45	416	80	0.31	290
6.1	4.95	1.12	6.07	403	90	0.04	260

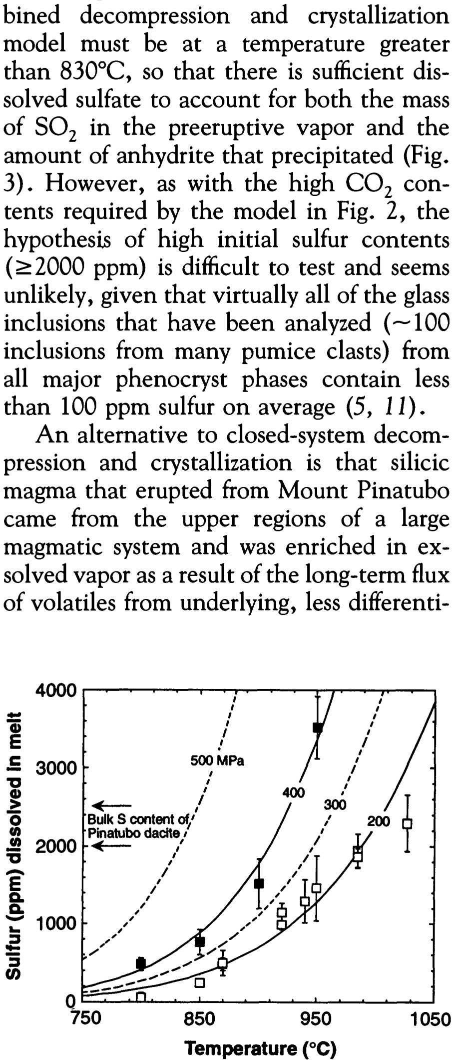

Fig. 3. Sulfur solubility in anhydrite-saturated melts equilibrated at the MnO-Mn_3O_4 oxygen buffer. Open and solid squares indicate experimental measurements at 200 and 400 MPa, respectively (*11, 22*). Solid lines are best fit values to the experimental data determined by regression analysis with the expression ln S (ppm) = *a*/*T* + *b*, where *T* is the temperature and *a* and *b* are constants. Dashed lines are estimated solubilities at 300 and 500 MPa. Arrows indicate the range of bulk sulfur contents for the Pinatubo dacite and include sulfur contributions from anhydrite (*4*) and preeruptive magmatic vapor.

ated magma in the roots of the system. Basaltic magma undoubtedly provides heat and mass to sustain the silicic magma reservoir at Mount Pinatubo, as indicated by the mingling and mixing of basalt and dacite in eruptive products from the volcano during the last 30,000 years (*21*). In this context, mantle-derived basaltic magma must be viewed as the ultimate source of both sulfur and CO_2 in the silicic magma reservoir (*23*). Vapor accumulation in the roof zone of the system is consistent with chemical and stable isotopic data for hydrothermal fluids and gases that indicate the introduction of a magmatic component into the overlying hydrothermal system (*8*). Upward concentrations of exsolved vapor could form through various processes such as (i) sidewall crystallization and buoyant rise of derivative silicic liquids with entrained vapor bubbles and (ii) diapiric rise of bubble-rich foams (*24*).

The vapor accumulation hypothesis can be tested by monitoring both CO_2 and SO_2 emissions from volcanoes during eruptive and noneruptive degassing. Many volcanoes in subduction-related arcs are similar to Mount Pinatubo in emitting quantities of SO_2 that greatly exceed preeruptive dissolved SO_2 contents (*3*, *6*, *7*), and there is only a weak correlation between the magnitude of an eruption (measured by tephra volume and eruption column height) and the mass of SO_2 emitted (*1*). In some cases, direct measurements of CO_2 in coerupted volcanic gases indicate that bulk magmatic CO_2 contents exceed the amounts that could be dissolved at crustal pressures (*7*). Magmas in crustal reservoirs probably range from those that are undersaturated, to those that are saturated with C-O-H-S vapor, to those that have accumulations of vapor. Within this continuum, magmatic systems with the highest fluxes of hydrous, SO_2-bearing vapor from underlying mafic magma have the greatest potential for injecting climate-altering quantities of SO_2 into the stratosphere during explosive volcanic eruptions.

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Evidence from Paleosols for the Geological Antiquity of Rain Forest

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Kaolinitic claystones in Paleozoic paleokarst underlying the Middle Pennsylvanian Fort Scott Limestone near Drake, Missouri, contain abundant fossil root traces. These include a surficial root mat as well as stout, woody, deeply penetrating root traces: a rooting pattern similar to that under rain forest. Also similar to soils of rain forest is the deeply weathered clay of the paleosol, in which minimal amounts of nutrient bases remain. Forest communities adapted to oligotrophic clayey substrates in humid climates existed at least 305 million years ago.

Fossil evidence of rain forest is sparse, because most rain forests colonize sites too well drained to favor the preservation of fossil plants and soils insufficiently calcareous to preserve bone and shell (*1*). Exceptional fossil biotas of well-drained wet forest as old as the Eocene are known from paleokarst (*2*). Fossil fruits, seeds, and leaves similar to those of Indo-Malesian rain forest also are known no further back in time than the Eocene (*3*). Fossil plants of Carboniferous coal measures have been interpreted as the remains of rain forest, but despite the discovery of a great diversity of Carboniferous plants including vines (*4*) and epiphytes (*5*), no Carboniferous plant assemblages are physiognomically comparable to Guineo-Congolian, Amazonian, or Indo-Malesian rain forest (*6*). Given this sparse fossil record and preservational biases, rain forests of the past may be better recognized from fossil soils than from fossil plants. Rain forests have high productivity and stature despite their oxidized oligotrophic clayey soils (*7*).

An ancient example of a deeply weathered and oxidized paleosol containing large woody root traces is in the Farnberg pit, 5 km southwest of Drake, Missouri (*8*). The pit is an excavation for refractory clay in the Cheltenham Formation. These clays and sandstones fill paleokarst with 46 m of relief into the Ordovician Jefferson City Dolomite (*9*). Elsewhere in this region this paleokarst is incised into Burlington Limestone, and so is younger than the Mississippian (*9*). The Farnberg clay paleosol is only 15 cm below the top of the Cheltenham Formation, which is overlain by the Fort Scott Limestone of Middle Pennsylvanian age [middle Desmoinesian (*10*)], correlative with the European Moscovian and Westphalian D some 305 million years old (*11*).

The Farnberg clay paleosol is overlain abruptly by gray clayey siltstone containing

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