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# Massive atmospheric sulfur loading of the AD 1600 Huaynaputina eruption and implications for petrologic sulfur estimates

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[1] We combine petrological, analytical, and thermodynamical data to constrain the sulfur yield of the AD 1600 Huaynaputina eruption which has been associated with the largest Earth's temperature shift in the last 600 years. The calculated amount of S (26–55 Tg), partly overlaps, but ranges to almost twice the amount estimated from ice-core data (16–32 Tg), the higher values of our estimate probably reflect that not all S released by the eruption reached the stratosphere. Our study also shows that it is possible to estimate the atmospheric sulfur loading from the volcanic products themselves, which opens the possibility to explore volcano-climate links beyond the time period covered by ice-core archives. **INDEX TERMS:** 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 1620 Global Change: Climate dynamics (3309); 8439 Volcanology: Physics and chemistry of magma bodies. **Citation:** Costa, F., B. Scaillet, and A. Gourgaud, Massive atmospheric sulfur loading of the AD 1600 Huaynaputina eruption and implications for petrologic sulfur estimates, *Geophys. Res. Lett.*, 30(2), 1068, doi:10.1029/2002GL016402, 2003.

## 1. Introduction

[2] The sulfur yield of volcanic eruptions is widely recognized as the main factor that controls the magnitude and longevity of volcanic forcing of Earth's climate [Robock, 2000]. Undisputable examples include the Tambora (1815), El Chichón (1982), and Pinatubo (1991) events. The eruption of Huaynaputina (1600 AD) is perhaps emblematic of the link between climate change and volcanic activity, as tree-ring density chronological studies have associated the eruption with a temperature shift on the average northern hemisphere summer surface of  $-0.8^{\circ}\text{C}$ , the largest in the last 600 years [Briffa *et al.*, 1998]. Notwithstanding, the amount of S released by the Huaynaputina eruption estimated by ice-core data [De Silva and Zielinski, 1998] seems too low to produce such temperature change [Briffa *et al.*, 1998], and clearly illustrates the need of complementary approaches to better quantify the amounts of volcanic S released to the atmosphere. In this manuscript we take an alternative view to constrain the S yield associated with volcanic events (mainly Huaynapu-

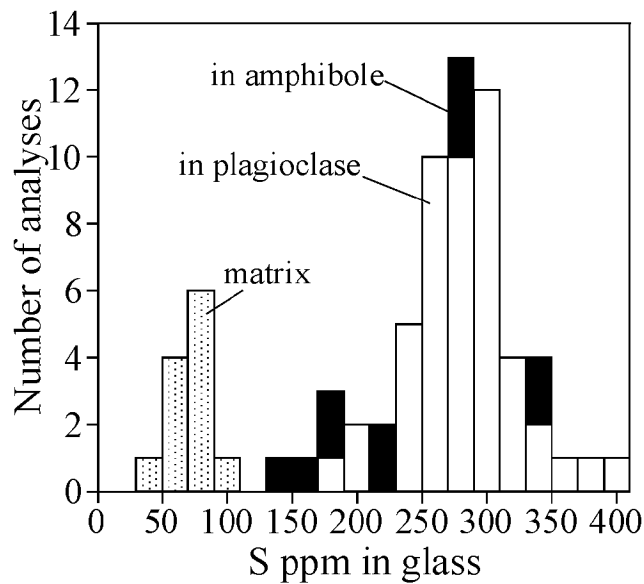
tina, but also Pinatubo and El Chichón) by combining petrological, analytical, and thermodynamical data.

[3] The explosive eruptions of Volcán Huaynaputina (peruvian Andes;  $16^{\circ}36'\text{S}$ ,  $70^{\circ}51'\text{W}$ ) occurred at AD 1600 and lasted a couple of weeks during which between  $12\text{--}25 \times 10^3$  Tg of magma were ejected [De Silva and Zielinski, 1998; Thouret *et al.*, 1999 and 2002; Adams *et al.*, 2001]. The bulk composition of the magma is similar to the 1991 Pinatubo dacite, differing only by slightly higher potassium and lower calcium contents (Table 1). Dacite pumices contain 17–20% (vol) phenocrysts of plagioclase, hornblende, biotite, magnetite, ilmenite, and chalcopyrite set in a rhyolitic matrix glass [Adams *et al.*, 2001]. New electron microprobe analyses of glass inclusions trapped in plagioclase and hornblende contain about 6 wt%  $\text{H}_2\text{O}$  and  $264 \pm 50$  ppm S, (Figure 1 and Table 1), whereas the matrix glass is almost completely outgassed, with low water (<1 wt%) and S contents (<100 ppm). The petrologic method to estimate the S yield from eruptions consists of using the difference between the S content of undegassed glass inclusions and that of the matrix glass, scaled to the amount of glass and of erupted magma [Devine *et al.*, 1984]. For the Huaynaputina eruption, this method allows us to calculate that between 2–4 Tg of S were degassed to the atmosphere. This value is much lower than the estimate from ice-core data [De Silva and Zielinski, 1998] (16–32 Tg) and illustrates the classical problem of calculating the S yield without taking into account the presence of a coexisting S-rich fluid phase [Westrich and Gerlach, 1992].

## 2. Estimation of the Pre-Eruptive Conditions of the Huaynaputina Magma

[4] To better estimate the amount of pre-eruptive sulfur of the Huaynaputina magma one needs a good knowledge of the conditions at which it was stored. Given the nearly identical bulk-rock chemistry of the Huaynaputina and Pinatubo dacites, we have used the phase equilibria data obtained experimentally on the latter [Scaillet and Evans, 1999] to constrain the pre-eruptive pressure (P), temperature (T), and oxygen fugacity ( $f\text{O}_2$ ) of the Huaynaputina magma. The pressure can be estimated by the aluminium content of hornblende to be in the range 200–250 MPa, whereas the similarity between the compositions of experimental glasses and those of Huaynaputina suggests that the magma was stored at 833 to 866 $^{\circ}\text{C}$ , and close to or at water-saturated conditions (Table 1). The slightly higher CaO and lower  $\text{K}_2\text{O}$  contents of the experimental glasses reflect the

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**Figure 1.** Histogram of sulfur contents in glass inclusions and matrix glass. The total number of analyses is 72.

small difference in bulk-rock chemistries between the Pinatubo and Huaynaputina dacites. The composition of coexisting iron-titanium oxides and solutions models [Andersen and Lindsley, 1988; Ghiorsso and Sack, 1991] can be used to calculate the T- $f_{O_2}$  conditions, but the values depend on which solution model is used, and the temperature varies between 910 and 839°C. This is due to inaccurate calibration of existing thermodynamic models in the T- $f_{O_2}$  range appropriate to silicic arc magmas [Evans and Scaillet, 1997; Scaillet and Evans, 1999]. Comparison between the compositions of experimental [Scaillet and Evans, 1999] and natural Fe-Ti oxides and amphiboles shows that  $f_{O_2}$  was close to NNO + 1.2 (1.2 log unit above the Ni-NiO solid buffer), at a temperature of ~850°C. The sulfur fugacity

**Table 2.** Calculated Composition of the Pre-Eruptive Fluid Phase for the 1600 AD Huaynaputina Dacite Magma

$f_{O_2}$	NNO + 1.2	
<i>fugacities in bar</i>		
$f_{H_2O}$		1887
$f_{H_2}$		2.5
$f_{CO_2}$		104
$f_{H_2S}$		89
$f_{SO_2}$		29
$f_{S_2}$		0.64
<i>Mole fractions</i>		
$X_{H_2O}$		0.943
$X_{CO_2}$		0.031
$X_{H_2S}$		0.022
$X_{SO_2}$		0.004
S in fluid (wt%)		4.2
CO <sub>2</sub> in melt (ppm)		33

The calculation is for 240 MPa and 850°C. Total pressures lower than 240 MPa result in fluid pressures higher than total pressure. The CO<sub>2</sub> in melt is the carbon dioxide dissolved in the rhyolitic melt at the calculated  $f_{CO_2}$ , following Holloway and Blank [1994]. The fugacity of water ( $f_{H_2O}$ ) was calculated using the pre-eruptive melt H<sub>2</sub>O content and the thermodynamic model of Zhang [1999], whereas the sulfur fugacity ( $f_{S_2}$ ) was determined using an empirical model of sulfur solubility in silicate melts [Scaillet et al., 2002].

( $f_{S_2}$ ), calculated using an empirical solubility model [Scaillet et al., 2002] is 0.64 bar. In summary, combining experimental and petrological data, we infer that the Huaynaputina magma was stored at 220–250 MPa, at about 850°C, with an  $f_{O_2}$  at NNO + 1.2, with melt H<sub>2</sub>O contents of ~6 wt% and coexisted with a fluid phase.

### 3. Estimation of the S Release From the Huaynaputina Eruption

[5] The composition of the fluid phase can be constrained by using S partition coefficients between fluid and melt [e.g., Scaillet et al., 1998]. Hydrothermal experiments in the

**Table 1.** Bulk-Rock and Glass Compositions of the Huaynaputina Dacite and Comparison With Pinatubo Data

	Pin bulk-rock	Hua bulk-rock	Hua matrix glass	Hua glass inclusions	Pin exp 866°C	Pin exp 866°C	Pin exp 834°C	Pin exp 834°C
n wt%			12	60	4	4	5	6
SiO <sub>2</sub>	65.5	65.5	73.3(4)	72.5(6)	73.3(2)	74.2(7)	73.6(5)	75.0(9)
TiO <sub>2</sub>	0.45	0.57	0.34(1)	0.33(6)	0.26(3)	0.38(7)	0.33(8)	0.32(8)
Al <sub>2</sub> O <sub>3</sub>	16.25	16.78	14.84(8)	15.11(23)	15.72(62)	14.67(23)	15.61(13)	14.07(17)
FeO <sub>tot</sub>	4.13	3.68	1.47(4)	1.60(25)	1.81(13)	1.95(43)	1.60(16)	1.68(7)
MgO	2.11	1.82	0.32(1)	0.46(10)	0.27(11)	0.28(9)	0.41(10)	0.08(6)
CaO	4.82	4.16	1.45(7)	1.61(14)	2.26(5)	2.03(11)	2.15(13)	1.78(13)
Na <sub>2</sub> O	4.56	4.54	4.36(33)	4.52(45)	3.88(15)	3.78(13)	3.84(18)	3.80(50)
K <sub>2</sub> O	1.58	2.74	3.82(13)	3.86(30)	2.49(5)	2.66(8)	2.41(8)	2.86(6)
H <sub>2</sub> O	-	-	0.6	6.1(1.4)	7.0	5.0	7.0	5.8
S (ppm)	-	-	<100	264(50)	-	-	-	-
phenocryst (vol%)	45–50	17–20	-	-	16	38	17	38

Hua = Huaynaputina. Pinatubo (= Pin) bulk-rock and experimental data (exp) are from Scaillet and Evans [1999]. The experiments were performed at 220 MPa in the  $f_{O_2}$  range NNO + 1–NNO + 2.5. Water contents of natural and experimental glasses determined with the summation deficit method in which the difference to 100 of the electron microprobe analysis (EMPA) is calibrated against a set of hydrous glass standards of known water contents [Scaillet and Evans, 1999]. The S content was determined via EMPA using wavelength dispersive spectrometers with the following analytical conditions: accelerating voltage 15 kV, sample current 50 nA, a focused beam of ~2 μm, and a counting time of 60 s on both peak and background. The detection limit is 50 ppm. The proportion of phenocrysts of the Huaynaputina dacite is from Adams et al. [2001]. For the experimental data, the weight proportions have been converted into vol% using average glass and crystal densities of 2300 and 3000 kgm<sup>-3</sup>, respectively. n = number of analyses. Numbers within brackets are the 2 σ in terms of the last significant digits. All analyses normalized to 100% anhydrous.

dacite-H<sub>2</sub>O-S system have shown that above NNO + 1, the S partition coefficient dramatically increases in favor of the fluid phase with values up to  $\sim 10^3$ . This suggests that the fluid phase coexisting with Huaynaputina magma had *ca.* 3 wt% sulfur. A second approach relies on equilibrium thermodynamic calculations of the fluid phase [Scaillet and Pichavant, in press]. For this, we have considered the C-O-H-S system at the pre-eruptive P, T,  $f_{S_2}$ , and  $f_{O_2}$  of the Huaynaputina magma and a modified Redlich-Kwong equation of state [Holloway, 1977]. The results of the calculations (Table 2) show that the fluid phase was water-rich, with 4.2 wt% of S (value used in the following calculations).

[6] To estimate the S yield, one needs also to know the amount of fluid phase coexisting with the magma. Although there is no direct evidence for such a parameter, it can be reasonably constrained by comparison with other studies. Inversion of trace element behavior in evolved arc magmas gives fluid amounts in the range 1–6 wt% [Wallace et al., 1995]. Eruptions that had their sulfur yield monitored either via satellite or ground-based spectroscopic methods give similar values [Gerlach et al., 1996; Scaillet et al., 1998]. Theoretical considerations based on the three dimensional interconnectivity of a fluid phase, also suggest that magmas stored at pressures of about 200 MPa cannot hold much more than 5 wt% fluid [Wallace, 2001]. We therefore adopt a value of 5 wt% for the amount of fluid coexisting with the Huaynaputina dacite. Considering the mass of magma erupted and the sulfur content of the fluid phase obtained from thermodynamic calculations, we calculate that 26–55 Tg of S were injected into the atmosphere (Table 3). This is  $\sim 5$ –10 times the amount associated with the Pinatubo eruption [6.5 Tg S; Bluth et al., 1993], but similar to that estimated for the Tambora eruption [65 Tg S; Rampino et al., 1988].

#### 4. Discussion

[7] The calculated S yield (26–55 Tg) is higher than the estimated from peak acidity in ice cores of 16–32 Tg S [Table 3; De Silva and Zielinski, 1998]. This is what one would expect if the petrological S estimates and those derived from ice-cores worked perfectly, since the petrological approach estimates the total sulfur release to the atmosphere, whereas ice-core method relates only to the stratospheric sulfur load. Other possibilities to explain the discrepancy between the two estimates are that: (i) a smaller amount of fluid was present in the magma reservoir; for example, if we use a value of 2.5 wt% of fluid (in the lower end of the reported values by other studies- see above) the amount of degassed S (14–26 Tg) fully overlaps with ice core data, and (ii) the ice core data underestimates the actual sulfur loading; as noted by Briffa et al. [1998] the cooling associated with the Huaynaputina eruption recorded by tree-ring density chronology ( $-0.8^\circ\text{C}$ ) is greater than suggested by the acidity peaks in ice core records. Given the uncertainties associated with each method it is difficult to assess how significant are the differences between the two estimates, and thus, taking a conservative approach, we consider them to be roughly the same. If we perform the same calculations for El Chichón (1982) and Pinatubo (1991) eruptions and we compare to the S yield estimated by total ozone mapping spectrometer, it is apparent that

**Table 3.** Comparison of S Release Estimates by the Petrologic Method and Those by TOMS and Ice Core Data for Three Well Characterized Eruptions

Eruption	AD 1600 Huaynaputina	1982 El Chichón	1991 Pinatubo
mass of magma (Tg)	12000–25000	2800	13000
	Petrologic estimate of S (Tg)		
melt degassing	2–4	0.3	0.0
fluid release	24–51	2–9	9
total	26–55	2.3–9.3	9
	TOMS* or ice core estimates of S (Tg)		
S	16–32	3*	8*
T <sup>o</sup> C	–0.8	<–0.4	–0.4

For calculations the fluid phase has 1.8–7 wt% S for El Chichón and 1.4 wt% S for Pinatubo [Scaillet and Pichavant, in press]. All magmas coexist with 5 wt% fluid. Melt degassing for El Chichón from Devine et al. [1984], and for Pinatubo from Westrich and Gerlach [1992]. Estimate from ice-core data of Huaynaputina from De Silva and Zielinski [1998]. TOMS (total ozone mapping spectrometer) data for El Chichón and Pinatubo from Bluth et al. [1993]. Masses of erupted magma for Huaynaputina from De Silva and Zielinski [1998] and Thouret et al. [2002], El Chichón from Luhr et al. [1984], and Pinatubo from Holasek et al. [1996]. T<sup>o</sup>C is the temperature shift caused by each eruption, for Huaynaputina from Briffa et al. [1998], El Chichón from Rampino et al. [1988], and for Pinatubo from Hansen et al. [1996]. Rock density for dacite and trachyandesite is 2600 kgm<sup>-3</sup>.

there is an overall good correspondence between both methods although the petrologic estimates are in general higher (Table 3).

#### 5. Implications and Conclusions

[8] The eruption of Huaynaputina provides an additional example of the effectiveness of explosive silicic arc magmas in producing short term but abrupt climate changes. However, in contrast with the Pinatubo and El Chichón eruptions, which were oxidized and contained the anhydrite mineral, the Huaynaputina dacite has a common oxidation state for silicic arc magmas and lacks anhydrite. Although this could be due to readiness of which anhydrite dissolves during the weathering [Luhr et al., 1984], it could also be that it was not stable, since our estimated redox state lies on limit of the lower stability of this mineral [NNO + 1.2, Carroll and Rutherford, 1987; Scaillet and Evans, 1999]. More generally, dacitic magmas are widespread in modern convergent zones and the Huaynaputina and Pinatubo examples suggest that they are often sulfur-rich. An accurate definition of pre-eruption conditions does not demand exceptional conditions of rock preservation but only a good level of petrological understanding of volcanic ejecta. It can thus be applied to as many eruptive events as required or at least to those that are suspected to have had a worldwide climatic effect.

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