

**ERUPTION CONDITIONS OF PELE VOLCANO ON IO INFERRED FROM CHEMISTRY OF ITS VOLCANIC PLUME.** M. Yu. Zolotov and B. Fegley, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mails: zolotov@zonvark.wustl.edu, bfegley@levee.wustl.edu

**Introduction:** Modeling of Earth-based and *Galileo* spectra of hot spots gives estimates for magma temperatures on Io [1,2]. Magma temperatures could also be evaluated independently from the chemical composition of emitted volcanic gases, as commonly done in terrestrial volcanology [3,4]. However, until now evaluations of this type on Io were impossible. Only SO<sub>2</sub> gas was detected in a volcanic plume by *Voyager* in 1979 [5]. In 1992, Hubble Space Telescope (HST) observations indicated volcanic outgassing of SO<sub>2</sub> in the local atmosphere over Pele [6], which is one of the most active volcanoes on Io [7,8]. Subsequent HST observations in 1996 led to the detection of SO<sub>2</sub>, monatomic sulfur vapor, and SO gas in local atmospheres over several active volcanoes, including Pele [9]. October 1999 HST observations of Io by McGrath and colleagues led to the detection of S<sub>2</sub> vapor over Pele [10]. The detection these gases in volcanic plumes is consistent with our published models for the chemistry of ionian volcanic gases [11-14]. Here we use thermodynamic models and observations of SO<sub>2</sub>, SO, and S in the Pele plume to evaluate the temperature and oxidation state of magma for the 1996 eruption. We also estimate the range of vent pressures that are consistent with the observations for an assumed bulk composition of the volcanic gas [12], and provide a detailed chemical model for the Pele plume. Finally, we argue that the observed gas abundances in the Pele plume represent a quenched volcanic gas and that the plume chemistry has not been significantly altered by subsequent disequilibrium processes (e.g., photochemistry, charged particle chemistry, or condensation).

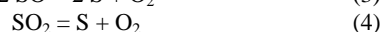
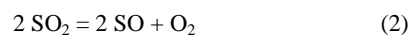
**Model:** We assume that ionian volcanic gases are in thermochemical equilibrium in a high-temperature volcanic conduit and/or lava lake and that gas chemistry quenches in the vicinity of volcanic vents, as we did in [11-14]. This implies that the gas in the plume reflects the chemistry and oxidation state of the volcanic gas and associated magma.

Three sets of thermodynamic calculations were done. First, we used the relative abundances of gases in the Pele plume (S/SO = 0.04, SO/SO<sub>2</sub> = 0.077, S/SO<sub>2</sub> = 0.003 [9]) to evaluate the equilibrium temperature of the volcanic gas (that usually equals the temperature of the magma from which it exsolves). For this purpose, we calculated the equilibrium conditions for the net reaction



as a function of temperature. Reaction (1) is pressure-independent and thus allows us to estimate the equilibrium temperature for coexisting S, SO, and SO<sub>2</sub> without any additional constraints. This is a common procedure used in terrestrial volcanology [3,4], and the calculated equilibrium temperature is called the correspondence temperature.

Second, the oxidation state of Pele volcanic gases and their parent magmas were evaluated from the following net reactions:



by solving for the oxygen fugacity. These calculations are made from 1000-2000 K, that is an appropriate range for magma temperatures on Io [1,2,7].

Total pressure in the volcanic vent(s) cannot be inferred from the relative abundances of SO<sub>2</sub>, SO, and S without additional information. Here we make an assumption about the bulk composition of volcanic gases from Pele. For this third set of calculations we used the free energy minimization method to calculate chemical equilibrium in the S-O system [see 11-13] at the magma temperature of 1430 K inferred for reaction (1). The bulk O/S atomic ratio was varied from 0.1 to 1.9, which is a good proxy for Io's volcanic gases [11-13]. This range of O/S ratios covers the nominal value of O/S=1 which we used in [12,13] for most volcanic gases on Io and the value of O/S=0.5, which we suggested specifically for Pele's volcanic gases [12]. Thermodynamic data for the calculations are taken from [15].

**Results: Temperature of magma.** The calculated equilibrium temperature for reaction (1) is 1430 K. This is illustrated in Fig. 1, where the log K<sub>1</sub> is plotted and compared to the reaction quotient (log Q<sub>1</sub>), which is computed from the observed abundance ratios (x) of S, SO, and SO<sub>2</sub>. The intersection of these two curves gives the equilibrium temperature. The calculated equilibrium temperature is in the range of temperatures (1200-1470 K) for Pele magmas that are independently derived from *Galileo* NIMS and SSI spectra [1,2]. Our calculated equilibrium temperature is typical for Mg-rich terrestrial hot spot basalts and their corresponding volcanic gases (e.g., in Kilauea [4].) This is in agreement with the presence of Mg-rich minerals (orthopyroxene) in Io's lavas, as inferred from *Galileo* spectra in 0.8-1 mkm [17].

**Oxidation states.** The calculation of fO<sub>2</sub> from reactions (2)-(4) leads to surprisingly consistent results that are shown in Fig. 2. The intersection of fO<sub>2</sub> values for these reactions occurs at ~1430 K and indicates equilibrium among SO<sub>2</sub>, SO and S. The log fO<sub>2</sub> value (at 1430 K) of -11.7 corresponds to a magma oxidation state about 3 orders of magnitude below the Ni-NiO oxygen buffer. The inferred oxidation state of Pele magma represents more reduced conditions than we modeled for the Loki plume [13]. Perhaps this is not surprising because S<sub>2</sub> has been detected at Pele but not at Loki. As shown in [13], more reducing conditions lead to more S<sub>2</sub> in the volcanic gas. However, redox conditions at Pele are more oxidized than for the iron-wüstite buffer, and native iron is probably absent from Pele's magmas. The oxidation state calculated for Pele magmas is consistent with that of terrestrial MORB basalts [16].

**Vent total pressure.** The pressures calculated in our third set of computations are depicted in Fig. 3 as a function of the atomic O/S ratio. The O/S ratios of 0.1 to 1.9 correspond to pressures of 10<sup>-2.4</sup> to 10<sup>-6.7</sup> bar, respectively. Despite the uncertainty, these results are the first quantitative constraints on the total pressure of erupted volcanic gases at Pele. Higher and lower pressures are incompatible with the observed gas

abundances in the plume. At O/S from 0.5 to 1, which are our nominal cases [12,13], the vent pressure is between  $10^{-3.9}$  and  $10^{-4.6}$  bar.

**Models for vent chemistry.** Our modeling predicts equilibrium compositions for Pele volcanic gases at 1430 K. Model A represents volcanic gas at  $10^{-3.9}$  bars and O/S=0.5, model B is for  $10^{-4.6}$  bars and O/S=1. Both models predict comparable abundances for  $S_2$  and  $SO_2$ .

Pele volcanic gas at 1430 K (mole ratios)		
	A	B
O/S	0.5	1.0
Log P, bar	-3.9	-4.6
$SO_2$	0.38	0.63
$S_2$	0.59	0.32
SO	0.029	0.048
$S_2O$	2.3(-3)	1.2(-3)
S	1.1(-3)	1.9(-3)
$S_3$	1.2(-4)	2.0(-5)
$SO_3$	3.3(-8)	5.5(-8)
$O_2$	1.8(-8)	9.1(-8)
o	1.7(-8)	9.0(-8)
$S_4$	6.1(-9)	3.4(-10)

**Other plumes.** The values of  $fO_2$  calculated for Ra volcanic gases based on the value of  $SO_2/SO=30$  in the plume [9] are consistent with  $fO_2$  values for Pele. At 1400-1500 K, the value of  $\log fO_2$  for Ra is about 2.5 log units below NNO (see Fig. 2). For the T3 plume [9], the  $fO_2$  values obtained from abundances of  $SO_2$ , S, and S indicate a reduced gas (3-4 log units below NNO at 1400-1500 K). However, calculations with eq. (1) show that the composition of the T3 plume [9] can only be matched at an unreasonably high equilibrium

temperature ( $>3000$  K). Therefore, the observed  $SO/SO_2$  ratio either includes a contribution from disequilibrium processes (e.g., photochemical formation of SO) or is incorrect.

**Summary:** The consistency of thermodynamic calculations obtained for eqs. (1)-(4) demonstrates that the composition of Pele plume represents a quenched volcanic gas. The plume chemistry has not been altered by disequilibrium processes. The observed SO at Pele is a volcanic product as proposed by us in [11] and is not a photochemical product. This does not necessarily mean that all SO on Io is volcanic, but does show that at Pele the plume gas is replenished by volcanic activity at a rate faster than that at which photochemistry and other disequilibrium processes occur.

Although Pele volcanic gases probably have lower pressures compared to terrestrial counterparts, they appear to be overpressured and are able to form plumes of several hundreds of kilometers high. The pressure range inferred for Pele vents is consistent with fire fountaining from the fissure on the lava lake in Pele's caldera [18], rather than with direct degassing of upwelling magma, as we assumed earlier ([12], Fig. 1 in [13]). The relatively low pressures of Pele vent(s) do not favor the volcanic production of any significant amount of  $S_2O$  gas and condensate (see Fig. 2 in [12]). Low pressures in Pele gases reinforce the suggestion [12] that that red deposits around Pele are caused by sulfur compounds rather than by solid  $S_2O$ . In addition, low pressures favor SO production and are consistent with the hypothesis of the volcanic source for atmospheric SO [11].

We can make more accurate evaluations of pressure for vents at Pele using the abundance of  $S_2$  (or the  $S_2/SO_2$  ratio) when these values are obtained from data analysis of the October 1999 HST observations of the Pele plume. However,

we note that the eruption conditions and volcanic gas chemistry differ with time for terrestrial volcanoes [4], and by analogy the plume chemistry at Pele may differ in 1996 and 1999. Thus we encourage simultaneous observations of S,  $S_2$ , SO, and  $SO_2$  in order for obtaining the best estimates for P, T, and  $fO_2$ .

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