

Eruption conditions of Pele volcano on Io inferred from chemistry of its volcanic plume

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Abstract. We use thermodynamic models and published 1996 Hubble Space Telescope (HST) observations of SO₂, SO, and monatomic sulfur gas in the Pele volcanic plume on Jupiter's moon Io to evaluate the temperature (1440 K) and oxidation state (3.3 log *f*O₂ units below the Ni-NiO buffer) of Pele's magma and exsolved volcanic gas. Combination of these results with 1999 HST data on the SO₂/S₂ ratio in the Pele plume allows us to calculate pressures (10^{-4.7}-10^{-5.4} bar) in the vicinity of volcanic vent and to present a detailed chemical model for the plume. Our model indicates that the Pele plume represents volcanic gas, which last equilibrated at magmatic temperature and was not significantly altered in the plume. Finally, the redox state of Pele plume indicates that Io is differentiated and has an oxidized, Fe-metal free mantle.

Introduction

Pele is one of the most active volcanoes on Io [Spencer and Schneider, 1996; McEwen *et al.*, 1998a]. Its eruptive plumes are up to 460 km high and have been observed periodically by *Voyager* spacecrafts in 1979 [Strom *et al.*, 1981], by the HST in 1995-1999 [Spencer *et al.*, 1997b, 2000; McGrath *et al.*, 2000], and by the *Galileo* spacecraft since 1996 [McEwen *et al.*, 1998a]. The eruptions of Pele lead to the formation of sulfur-bearing [Spencer *et al.*, 1997a; Kargel *et al.*, 2000] pyroclastic red deposits of ~1200 km in diameter in contrast to the white SO₂ frost observed around other volcanoes. Pele is an intense high-temperature hot spot with temperatures up to 1475 K as evaluated from *Voyager*, *Galileo*, and ground-based spectra at near infrared wavelengths [Pearl and Sinton, 1982; Spencer and Schneider, 1996; McEwen *et al.*, 1998b; Davies *et al.*, 1999].

On Earth, magma temperature and oxidation state are commonly evaluated from the chemical composition of emitted volcanic gases [Gerlach, 1980; Symonds *et al.*, 1994]. On Io, evaluations of this type were impossible until now. Only SO₂ gas was detected in Io's volcanic plumes or local volcanic atmospheres by the *Voyager* spacecraft [Pearl *et al.*, 1979] and by the HST [Sartoretti *et al.* 1994; Spencer, 1997b]. However recent analysis of 1996 HST observations led to the detection of SO₂, monatomic sulfur vapor, and SO gas in the plume or volcanic atmosphere of Pele [McGrath *et al.*, 2000]. The 1999 HST observations allowed Spencer *et al.* [2000] to detect both S₂ and SO₂ in the plume of Pele. Here we use these HST observations and thermodynamic calculations to model the eruption conditions and chemistry of Pele's volcanic gases. Preliminary results are published in [Zolotov and Fegley, 2000].

Model

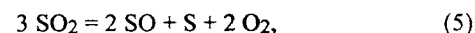
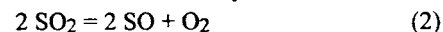
Our computations of magma temperature, oxidation state, vent pressure, and gas chemistry for Pele's eruptions are based on the assumption that ionian volcanic gases are in thermochemical equilibrium in a high-temperature volcanic conduit and/or lava lake and that gas chemistry quenches in the vicinity of volcanic vent(s) [Zolotov and Fegley, 1998a, 1998b, 1999]. This assumption implies that gas in the plume reflects the chemistry and oxidation state of the volcanic gas and associated magma.

Three sets of thermodynamic calculations were used to model volcanic gas chemistry at Pele in order to evaluate the temperature and oxidation state of magma and exsolved volcanic gas, and vent pressure. First, we used the nominal molecular abundances of gases in the Pele plume (S/SO = 0.04, SO/SO₂ = 0.077, S/SO₂ = 0.003 [McGrath *et al.*, 2000]) to evaluate the temperature of the volcanic gas (that usually equals the temperature of the magma from which it exsolves), at which these abundance ratios correspond to chemical equilibrium. For this purpose, we calculated the equilibrium conditions for the net thermochemical reaction



as a function of temperature. These and other calculations were done using thermodynamic data for S-O gases from Gurvich *et al.* [1989-1994]. Reaction (1) is pressure-independent and thus allows us to estimate the equilibrium temperature for coexisting S, SO, and SO₂ without any additional assumptions. This is a common procedure used in terrestrial volcanology [Gerlach, 1980; Symonds *et al.*, 1994], although reaction (1) is unique to Io.

The oxidation state of Io's magmas should reflect the degree of differentiation of the satellite [Consolmagno, 1981; Lewis, 1982; Zolotov and Fegley, 1999]. We evaluated the oxidation state of Pele's volcanic gases and their parental magmas from the net thermochemical equilibria:



which depend upon the fugacity (*f*) of O₂. These calculations of *f*O₂, that are independent of total pressure, were made from 1000-2000 K covering the temperatures of magma at Pele and many other silicate volcanoes on Io.

Total pressure in the volcanic vent(s) of Pele cannot be inferred from the observed abundances of SO₂, SO, and S without additional information. We made an assumption about the bulk composition (O/S ratio) of volcanic gases from Pele. We used the Gibbs free energy minimization method to calculate pressure-dependent chemical equilibria

in the S-O system with variable bulk composition (see *Zolotov and Fegley* [1998a, 1998b, 1999]) at the temperature inferred for equilibrium (1). These calculations lead to a range of pressures at which the observed abundances of S, SO, and SO₂ are in equilibrium for different bulk compositions. In order to narrow the range of calculated vent pressures, we assumed that chemical composition of Pele's plume and eruption conditions did not change from the 1996 to the 1999 HST observations and combined the 1996 HST data for SO₂, SO, and S [*McGrath et al.*, 2000] with 1999 HST data for the molecular SO₂/S₂ ratio (3-12) reported by *Spencer et al.* [2000]. As we show below, SO₂ and S₂ are the most abundant species and the SO₂/S₂ ratio roughly defines the bulk composition of Pele's volcanic gases.

Results and Discussion

Temperature of Magma and Exsolved Gas

The evaluation of magma temperature is illustrated in Figure 1, where the logarithm of the equilibrium constant ($\log K_1$) for reaction (1) is plotted as a function of temperature. The reaction quotient ($\log Q_1$), which is computed from the observed molecular abundance (X) ratios of S, SO, and SO₂ is also shown. The intersection of these two curves gives the equilibrium temperature of 1440 K for the nominal abundances reported by *McGrath et al.* [2000]. The uncertainty in thermodynamic data leads to the error bar of 40 degrees. The uncertainty in the observed abundance of S (gas) also contributes to the uncertainty of the calculated temperature. Although this is not specified by *McGrath et al.* [2000], a 10-30 % uncertainty results in error bars of 60-150 degrees, respectively. The calculated temperature (1440 K) is within the range of temperatures (~1200-1475 K) for Pele's magmas that are independently derived from *Galileo* NIMS and SSI near infrared spectra [*McEwen et al.*, 1998b; *Davies et al.*, 1999]. Our calculated equilibrium temperature is typical for magnesium-rich terrestrial hot spot basalts and their corresponding volcanic gases (e.g., at Kilauea [*Gerlach, 1980; Symonds et al.*, 1994]), and also agrees with the presence of magnesium-rich silicates (orthopyroxene) in Pele's pyroclastic deposits, inferred from *Galileo* SSI spectra at 0.8-1 microns [*Geissler et al.*, 2000].

Oxidation State of Magma and Exsolved Gas

The temperature dependent equilibrium fO_2 values for reactions (2)-(5) are plotted in Figure 2 and are compared to the fO_2 values for several petrologically important oxygen

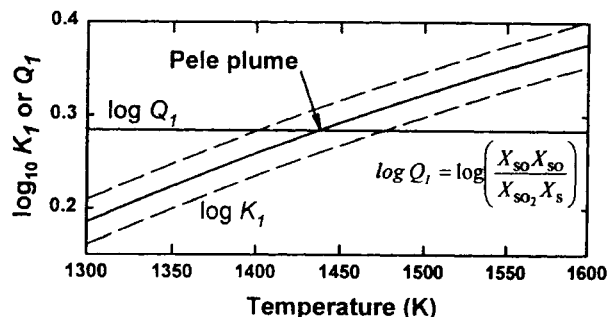


Figure 1. The equilibrium temperature for volcanic gases at Pele. Intersection of the two lines gives an equilibrium temperature of 1440 K. Dashed lines show the uncertainty range for $\log K_1$.

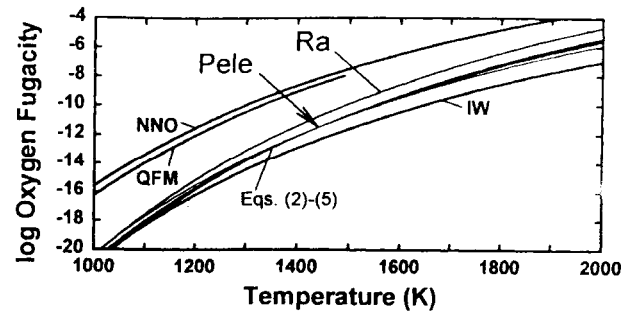


Figure 2. Oxidation state for volcanic gases at Pele and Ra. The equilibrium fO_2 values for reactions (2) to (5) for Pele intersect at ~1440 K (indicated by the arrow). The curves for petrologically important oxygen buffers (see text) are also shown.

buffers (QFM = quartz - fayalite - magnetite, NNO = nickel - nickel oxide, IW = iron - wüstite). The fO_2 values for reactions (2)-(5) are very close together but intersect at about 1440 K, indicating equilibrium among SO₂, SO, S, and O₂ at this temperature. The inferred $\log fO_2$ (bar) value of -11.5 ± 0.1 at 1440 K corresponds to an oxidation state of 3.3 log units below NNO. For Ra, another volcano on Io, we obtained slightly more oxidizing conditions based on the SO₂/SO = 30 in its plume, which was observed with HST in 1996 by *McGrath et al.*, [2000]. At 1400-1500 K, the oxygen fugacity for Ra calculated from reaction (2) is 2.4-2.8 log units below NNO (see Figure 2). The less reddish color of deposits around Ra [*McEwen et al.*, 1998a] compared to those at Pele is consistent with the more oxidizing (SO₂-rich) character of Ra's plume. Equilibrium calculations show that more oxidizing conditions lead to higher SO₂/S₂ ratios in the volcanic gas [*Zolotov and Fegley*, 1999] which should whiten the plume deposits.

Redox conditions at Pele and Ra are more oxidized than for the IW buffer, and native iron is probably absent from magmas of these volcanoes. This is consistent with inferences from *Galileo* gravity data [*Anderson et al.*, 1996] that Io is differentiated and has a Fe-rich core. However, the *Galileo* gravity data do not constrain the oxidation state of Io's silicate mantle. The oxidation state calculated for magma and gas at Pele and Ra is consistent with that of terrestrial middle oceanic ridge basalts [*Carmichael*, 1991]. The presence of sulfur deposits around Pele [e.g., *Spencer et al.*, 1997a, 2000; *Kargel et al.*, 2000] and sulfur lava flows at Ra [*Pieri et al.*, 1984; *McEwen et al.*, 1998a] indicates relatively reduced conditions compared to other volcanoes. Therefore, volcanic gases erupted by many of Io's other volcanoes are probably more oxidized than those at Pele and Ra. This indicates a general correspondence of oxidation conditions in ionian and terrestrial volcanic systems, as we proposed earlier [*Zolotov and Fegley*, 1999].

The consistency of thermodynamic calculations for equilibria (1) to (5) with *Galileo's* temperatures of magma indicates that Pele's plume can represent a quenched volcanic gas and disequilibrium processes (e.g., photochemistry, charged particle chemistry, and condensation) have not altered the plume chemistry. In particular, the SO at Pele seems to be volcanic, as proposed by *Zolotov and Fegley* [1998a] for ionian high-temperature and/or low-pressure volcanic gases. This does not necessarily mean that all SO on Io is volcanic, but indicates that at Pele the plume gas is replenished by volcanic activity at a rate faster than that at

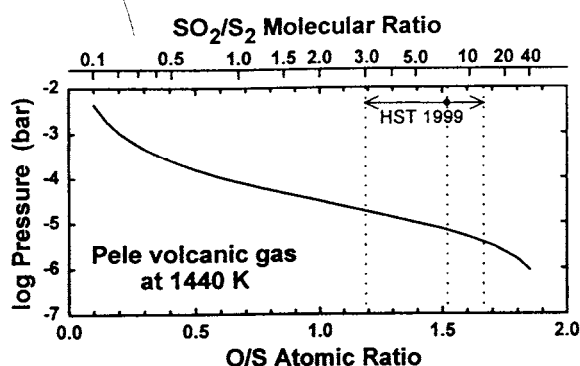


Figure 3. Vent pressure of Pele volcano as a function of bulk composition of its volcanic gases at 1440 K for the relative abundances of SO_2 , S, and SO observed in the Pele plume in 1996 by *McGrath et al.* [2000]. The SO_2/S_2 molecular ratio corresponding to the bulk O/S ratios are also shown. Vertical dotted lines represent minimum (3), nominal (7), and maximum (12) SO_2/S_2 ratios reported by *Spencer et al.* [2000] for their 1999 observations of the Pele plume. The resulting vent pressures are $10^{-4.74}$ to $10^{-5.42}$ bar.

which photochemistry and other disequilibrium processes occur. This conclusion is supported by models of atmospheric photochemistry, which show that S_2 is rapidly destroyed on Io [*Moses et al.*, 2000]. However since S_2 and SO were not observed simultaneously, the S_2 observed in Pele's plume implies, but not prove, that the SO is volcanic.

Vent Pressure

The pressures calculated at 1440 K are depicted in Figure 3 as a function of the bulk O/S atomic ratio. The O/S ratios of 0.1 to 1.9 correspond to pressures of $10^{-2.4}$ to $10^{-6.6}$ bar, respectively. At 1000-2000 K, SO_2 and S_2 are the most abundant gases in the O-S system and to first order the O/S ratio corresponds to the SO_2/S_2 molecular ratio, as shown in Figure 3. This allows us to make more accurate evaluations of pressure for vent(s) at Pele using the S_2/SO_2 ratio obtained from the 1999 HST observations of the Pele plume [*Spencer et al.*, 2000]. These data lead to pressures from $10^{-4.74}$ to $10^{-5.42}$ bar. Although Pele volcanic gases probably have lower pressures compared to terrestrial counterparts, they are overpressured with respect to Io's atmosphere ($\sim 10^{-9}$ bar). The pressure range inferred for Pele vent(s) for the 1996-1999 eruptions is consistent with calm degassing during fire fountaining from the fissure on a lava lake in Pele's caldera [*McEwen et al.*, 1998a, 2000].

Theoretical modeling shows that direct degassing of upwelling magma in a vacuum requires pressures $>10^{-5}$ bar [*Wilson and Head*, 1981; *Wilson and Keil*, 1997], that are higher than our estimates. However, the possibility exists that our calculated pressure of $\sim 10^{-5}$ bar represents an upper part of a fire fountain, where gas was last equilibrated at magmatic temperature (Lionel Wilson, private communication). In this case, direct degassing of upwelling magma can form the plume, and the value of $\sim 10^{-5}$ bar gives a lower limit for vent pressure at Pele. Despite the uncertainty, our calculated pressure in Pele's volcanic vent or fire fountains is the first quantitative constraint on the total pressure of erupted volcanic gases on Io.

Plume Chemistry

Our modeling predicts equilibrium compositions for Pele volcanic gases at 1440 K for the 1996 eruption. Although the

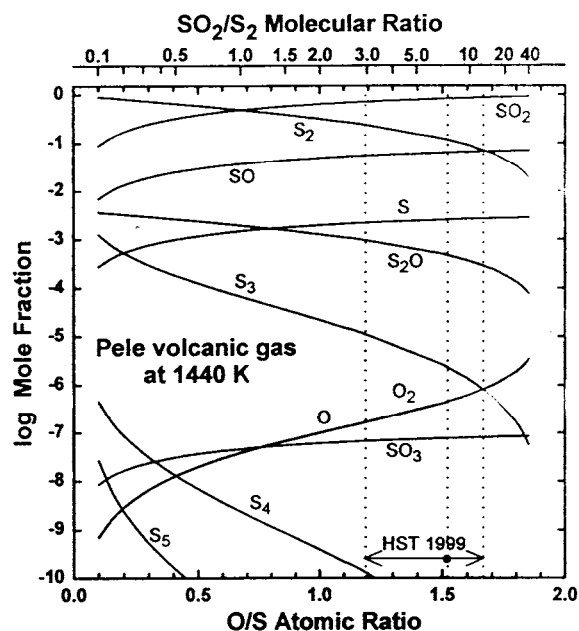


Figure 4. Equilibrium abundances in Pele volcanic gases at 1440 K. Corresponding vent pressures can be found in Figure 3. The relative abundances of SO_2 , S, and SO match the observations in the 1996 plume [*McGrath et al.*, 2000]. Vertical dotted lines represent the range of the SO_2/S_2 molecular ratios in the 1999 Pele plume from *Spencer et al.* [2000]. Molecular and atomic oxygen have very similar abundances, and are shown by one line.

exact vent pressure and bulk composition (O/S ratio) of gases are unknown, the variation of vent pressure with the bulk O/S ratio (see Figure 3) leads to a limited range of abundances for several undetected gases (Figure 4). The combination of data for the 1996 and 1999 eruptions narrows the range of calculated plume chemistry, as shown by dotted vertical lines in Figure 4. Table 1 lists calculated abundances for 3 models of volcanic gas chemistry that correspond to the minimum (model A), nominal (B), and maximum (C) SO_2/S_2 ratio

Table 1. Chemistry of Pele Volcanic Gas at 1440 K (Mole Fractions)

	Model A	Model B	Model C
SO_2/S_2 Mole Ratio	3	7	12
O/S Atomic Ratio	1.190	1.521	1.665
Log Pressure (bar)	-4.74	-5.16	-5.42
SO_2	0.707	0.818	0.859
S_2	0.235	0.116	0.0717
SO	0.0547	0.0629	0.0663
S	2.19×10^{-3}	2.50×10^{-3}	2.65×10^{-3}
S_2O	9.46×10^{-4}	4.72×10^{-4}	2.89×10^{-4}
S_3	1.09×10^{-5}	2.34×10^{-6}	8.37×10^{-7}
O_2	1.71×10^{-7}	4.54×10^{-7}	8.20×10^{-7}
O	1.67×10^{-7}	4.42×10^{-7}	8.02×10^{-7}
SO_3	6.75×10^{-8}	7.84×10^{-8}	8.21×10^{-8}
S_4	1.3×10^{-10}	1.2×10^{-11}	2.5×10^{-12}
S_5	2.5×10^{-13}	1.0×10^{-14}	1.2×10^{-15}

The SO_2/S_2 ratio represents minimum (A), nominal (B), and maximum (C) values reported for the 1999 Pele plume [*Spencer et al.*, 2000]. For all three models, relative mole ratios among SO_2 , SO, and S represent the 1996 observations of the Pele plume [*McGrath et al.*, 2000]. Mole fractions of S_6 , S_7 , S_8 , and O_3 are lower than 10^{-17} . $\text{Log } f_{\text{O}_2}$ for all models is -11.5.

reported by Spencer *et al.* [2000] for the 1999 eruption at Pele. Each model fits all the observations in the plume and predicts abundances of undetected species (e.g., S₂O, S₃, O₂, O, S₄, SO₃) in the volcanic atmosphere around Pele. The presence of S₂ as the second (after SO₂) most abundant volcanic gas is in agreement with the spectral characteristics of red deposits around Pele [Spencer *et al.*, 1997a; Kargel *et al.*, 2000]. The calculations show that S₂O is not an abundant gas reinforcing suggestions [Zolotov and Fegley, 1998b; Spencer *et al.*, 2000] that red ring deposits around Pele are caused by sulfur rather than by solid S₂O volcanic condensate.

The eruption conditions and volcanic gas chemistry differ with time for terrestrial volcanoes [Symonds *et al.*, 1994], and observations show that volcanic activity of Pele is episodic [Strom *et al.*, 1981; McEwen *et al.*, 1998a]. Therefore, the plume chemistry and eruptive conditions at Pele may differ in 1996 and 1999. Thus we encourage simultaneous observations of S, S₂, SO, and SO₂ to get the best estimates for eruption pressures, temperature, and oxidation state of magma and exsolved volcanic gas. Finally, our work demonstrates the use of telescopic observations for studying physics and chemistry of igneous processes on Io.

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