CHEMISTRY AND VENT PRESSURE OF VERY HIGH-TEMPERATURE GASES EMITTED FROM PELE VOLCANO ON IO. M. Yu. Zolotov and B. Fegley, Jr., Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mails: zolotov@zonvark.wustl.edu, bfegley@levee.wustl.edu

Introduction: Pele is one of the most active volcanoes on Jupiter's moon Io [1,2]. Modeling of *Galileo* infrared spectra of the Pele hot spot gave estimates of 1260-1510 K for magma temperatures [3,4]. Previously, we calculated a magma temperature of 1440±150 K [5] from Hubble Space Telescope (HST) observations of the abundances of SO_2, S_2, SO, and S in the Pele volcanic plumes [6,7]. The calculated magma temperature is based on the thermochemical reaction $SO_2 + S = 2\ SO$. The 150 degree uncertainty is from an assumed uncertainty of 30% in the S (gas) abundance [5]. The reported abundance of S (gas) is more uncertain than the abundances of the other sulfur gases and may represent only a lower limit [6,8]. In addition, photochemical modeling of a Pele-type volcanic atmosphere shows that S (gas) has a photochemical time constant of ~2 minutes and is rapidly produced photochemically from S_2 [8]. The photochemical time constants of SO_2, S_2, and SO are longer and are about 50 hours, 4 hours, and 4 hours, respectively, in the model described by [8]. It follows that use of S (gas) for calculations of magma temperatures is subject to uncertainties.

A recent interpretation of *Galileo* (I27 orbit, February 2000) infrared data suggests that Pele magma temperatures are as high as 1760±210 K [9]. Here we use these temperatures together with HST chemical data (SO_2, SO, S_2) for Pele plumes [6,7] to calculate pressure near the volcanic vent(s), the oxidation state of volcanic gases, and mole fractions of detected and undetected O-S gases at Pele. These calculations do not use the observed S (gas) abundance [6] as a constraint. We compare the results with those we have previously published [5].

Model: We assume that volcanic gases at Pele 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 [5,10-13]. This implies that the gas in the plume reflects the chemistry of the volcanic gas and associated magma. We used molecular ratios of gases in the Pele 1996 and 1999 eruptions (SO_2/SO = 13 [6], SO_2/S_2 = 3-12 [7]) in order to evaluate bulk composition and pressure at which these gases were at chemical equilibrium. We used the free energy minimization method to calculate chemical equilibrium in the S-O system [see 5, 10-13] at temperatures of 1760±210 K. The bulk O/S ratio and total pressure were varied in order to fit the observed SO_2/S_2 and SO_2/SO ratios. In addition to the O/S atomic ratio and total pressure, these calculations give equilibrium concentrations of SO_2, SO, S_2O, SO_3, O, O_2, O_3, S, and S_2 to S_8. Thermodynamic data are taken from [14].

Results: Fig. 1 shows the calculated vent pressure, the oxidation state, the O/S atomic ratio, and chemistry of volcanic gases at Pele as functions of temperature. Gas mole fractions are given for three distinct SO_2/S_2 ratios: 3, 7, and 12 (Figs. 1d-f). Table 1 shows our results for Pele volcanic gases at 1760 K for the three SO_2/S_2 ratios studied.

Vent pressure. At temperatures of 1550 K to 1970 K, the calculated vent pressure varies from $10^{-4.2}$ bar to 1.6 bar, respectively. Higher SO_2/S_2 ratios correspond to slightly lower pressures. At 1760 K and SO_2/S_2 = 3-12, calculated pressures are $10^{-1.53}$ bar to $10^{-2.21}$ bar, respectively. These pressures are higher than we calculated for a magma temperature of 1440 K [5], but they are consistent with values inferred from physical models of volcanic eruptions in a vacuum on Moon [15] and Vesta [16].

Table 1. Pele volcanic gas at 1760 K (mole fraction)

	A	B	C
SO_2/S_2	3	7	12
O/S	1.183	1.518	1.665
log P (bar)	-1.53	-1.96	-2.21
SO_2	0.704	0.816	0.859
S_2	0.235	0.116	0.0712
SO	0.0541	0.0627	0.0659
S_2O	5.66(-3)	2.81(-3)	1.72(-3)
S	1.47(-3)	1.70(-3)	1.78(-3)
S_3	2.13(-4)	4.53(-5)	1.62(-5)
SO_3	1.55(-6)	1.80(-6)	1.90(-6)
O_2	1.02(-6)	2.76(-6)	4.97(-6)
O	4.82(-7)	1.30(-6)	2.34(-6)
S_4	3.66(-8)	3.33(-9)	7.0(-10)

The SO_2/S_2 ratio represents minimum (A), nominal (B), and maximum (C) values reported for the 1999 Pele Plume [7]. For all three models, the SO_2/SO ratio is 13 and represents the 1996 Pele plume [6]. Calculated log fO_2 for all models is -7.52 (2.46 log units below the Ni-NiO buffer).

The oxidation state. At temperatures of 1550-1970 K, the oxygen fugacity (fO_2) is 2 to 3 log units below the Ni-NiO (NNO) buffer. Volcanic gases become more oxidizing relative to NNO as temperature increases, as shown in Fig. 1b. The oxygen fugacity fO_2 in Pele volcanic gases is determined by the net thermochemical equilibrium

$$SO_2 = SO + 0.5\ O_2,$$

so the SO_2/SO ratio constrains oxygen fugacity at a given temperature. We previously calculated that Pele volcanic gases are 3.3 log units below the NNO buffer for a magma temperature of 1440 K [5].

The O/S atomic ratio. Sulfur dioxide and S_2 are the two major species in volcanic gases at Pele and their ratio roughly defines the bulk O/S ratio of the volcanic gases. However, at a fixed SO_2/S_2 ratio, the O/S ratio slightly varies with temperature (Fig. 1c).

Chemistry of volcanic gases. Sulfur dioxide, S_2, and SO are the three most abundant gases at all temperatures considered in our modeling. The SO_2/S_2/SO ratios are taken from the HST observations and are an input to this modeling. The concentrations of these three gases do not change with temperature and they are the same as we evaluated for 1440 K [5]. However, the abundances of other O-S gases vary with temperature, and our present results differ from those in [5].

Monatomic sulfur is the fourth most abundant gas at lower temperatures and higher SO_2/S_2 ratios. The equilibrium mole fraction of S varies from ~2.3×10^{-3} to ~1.2×10^{-3} at 1550-1970 K, respectively. The SO_2/S ratios are 380 to 570 for all cases considered. The *calculated* ratios do not differ significantly from the *observed* ratio of SO_2/S = 330 for the 1996 Pele plume [6]. The similarity of the calculated and observed ratios could be accidental or could indicate that photochemical processes in the plume affect the S gas abundance less than calculated in [8].

Disulfur monoxide (S_2O) is the fourth most abundant gas at higher temperatures and lower SO_2/S_2 ratios. The mole fraction of S_2O gas increases as temperature increases and can reach ~1% at 1970 K. The calculated photochemical time constant for S_2O gas is 10 minutes in the model described by [8]. This is less than the ballistic lifetime of 20 minutes for a plume, but it would nevertheless be interesting to search for S_2O in volcanic plumes on Io.

Summary: We combined Pele magma temperatures obtained from *Galileo* infrared data and HST chemical data ($SO_2/S_2/SO$) Pele plumes in order to evaluate vent pressures (~0.01-2 bar), the oxidation state (2 to 3 log units below the NNO buffer) and chemistry of S-O volcanic gases. We show that eruption conditions could be evaluated from chemical data (see also [5]), but chemical data for monatomic sulfur gas may not be useful for this purpose. We encourage simultaneous observations of SO_2, S_2, SO, and S_2O in Io's plumes. It may be possible to use these data to evaluate magma temperature, vent pressure, and oxidation state of volcanic gases. However, the short photochemical time constant of S_2O may be a problem for doing this. In addition, simultaneous observations of plume chemistry and the infrared emission from venting areas would be useful for independent evaluations of magma temperature and for analysis of chemical transformations of volcanic gases in the plume.

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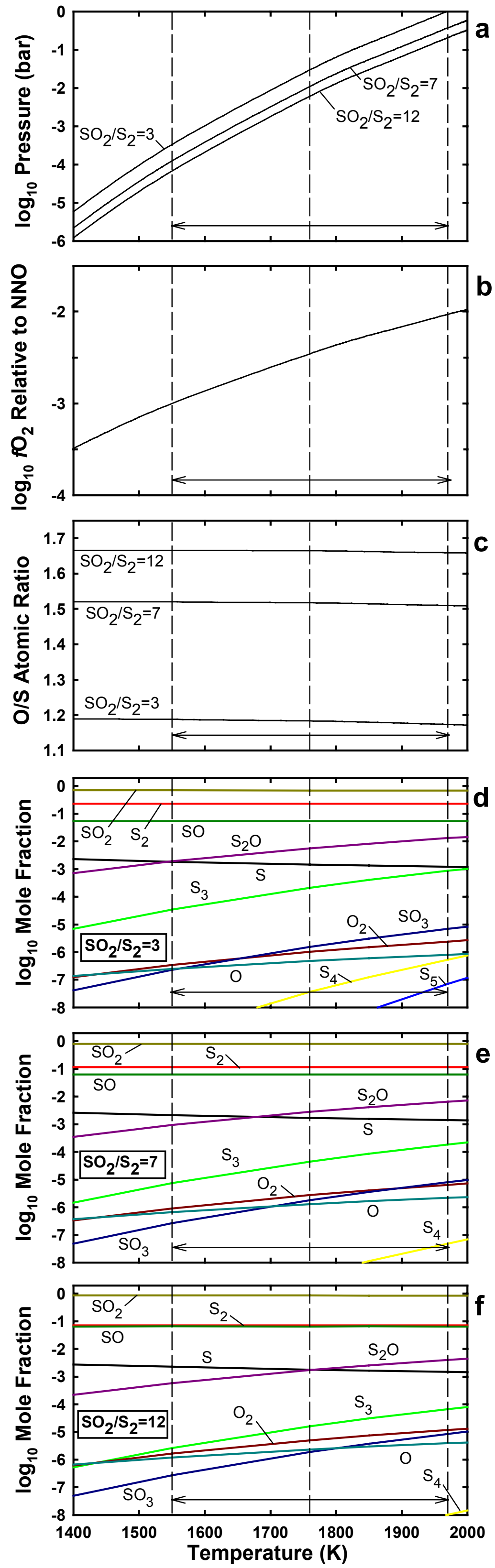

Fig 1. Equilibrium vent pressure and chemistry of Pele volcanic gases. The double arrows show the range of magma temperature at Pele [9]. The vertical dashed lines represent minimum (1550 K), nominal (1760 K) and maximum (1970 K) magma temperatures.