

OXIDATION STATE OF VOLCANIC GASES ON IO. M. Yu. Zolotov^{1,2} and B. Fegley¹, ¹Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mails: zolotov@zonvark.wustl.edu, bfegley@levee.wustl.edu, ²Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin str. 19, Moscow 117975, Russia.

Introduction: On Earth, the oxygen fugacity (fO_2) of outgassed magmatic volatiles reflects the oxidation state of their respective magmas and magmatic source regions in the lithosphere and asthenosphere [1,2]. These relationships could be also valid for Jupiter's moon Io which is the most volcanically active body of the solar system. Io's volcanism is caused by tidal heating and silicate magmas with temperatures up to 1700-2000 K are observed [e.g., 3]. The intensive volcanic outgassing is primarily responsible for the composition of Io's low-pressure patchy atmosphere, plasma torus and surface [4,5]. Here we use available data on the composition of a volcanic plume, the atmosphere, torus and surface, as well as observed temperatures of hot spots, to infer the fO_2 of volcanic gases by thermochemical equilibrium calculations. These fO_2 values likely reflect the oxidation state of Ionian magmas and Io's interior.

Model: By analogy with terrestrial volcanic gases [1], we assume thermochemical equilibrium in volcanic conduits on Io and quenching of the gas chemistry in the vicinity of volcanic vents. Thermodynamic equilibrium calculations were done from 1000-2000 K and 10^4 -100 bars covering the plausible range of temperatures and pressures for volcanic gases on Io. Vent pressures of ~1-100 bars seem to be more likely to provide the observed explosive activity.

Three sets of calculations were done. In the first set, we used the SO_2 abundance and SO_3 upper limit ($SO_3/SO_2 < 2 \times 10^{-4}$) for the Loki volcanic plume [6] to calculate fO_2 from the net thermochemical reaction



In the second set, we used the atmospheric SO/SO_2 ratio of 3-10% [7] to calculate fO_2 from



Our prior work shows that atmospheric SO can be at least partially due to volcanic degassing [8].

In the third set, we used the free energy minimization method to calculate fO_2 for the S-O system as a function of elemental bulk composition, temperature and total pressure that are appropriate for Ionian volcanic gases. We varied the O/S atomic ratio from ~0 (for S-gases, as in Ra patera [9,10]) to ~2 (for SO_2 -rich gases, as in Loki [6]). This range covers the bulk composition of Io's atmosphere, plasma torus and surface volcanic condensates. An average O/S ratio of $1(\pm 0.4)$ in torus [11,12] is used as an approximation for average composition of outgassed volatiles. Thermodynamic data for gases are taken from [13].

Results: The calculated fO_2 values are consistent

and indicate a relatively oxidized, terrestrial-like redox state for volcanic gases on Io.

Loki volcanic gas. Reaction (1) gives upper limits for the fO_2 of Loki gases (Fig. 1). These fO_2 values are less oxidizing than the hematite-magnetite (HM) buffer above 1300 K, but are several orders of magnitude more oxidizing than the Ni-NiO (NNO) and quartz-fayalite-magnetite (QFM) buffers.

Volcanic atmosphere. The fO_2 calculated from eq. (2) is shown on Fig. 1. If all atmospheric SO is produced volcanically, the calculations give the fO_2 of the volcanic gases. If part of atmospheric SO is produced photochemically [7] the calculated fO_2 values are only lower limits, as shown in the graph. Both lower limits for 3% and 10% SO lie above the iron-wüstite (IW) buffer and about 2-4 log units below the NNO buffer. Even if all atmospheric SO is of volcanic origin, the average redox conditions of volcanic gases are more oxidized than the IW buffer.

Oxygen fugacity in the S-O system on Io. Thermodynamic calculations at O/S = 2 show that thermal dissociation of pure SO_2 generates oxidizing conditions, but fO_2 does not exceed that for the HM buffer for high temperature ($> \sim 1150$ K). Small deviations from SO_2 stoichiometry lead to large changes of fO_2 (Fig. 2). At lower O/S ratios, fO_2 decreases at constant total pressure, and changes gradually at O/S of ~1.8-0.2. The fO_2 values decrease gradually with decreasing total pressure at constant bulk composition. At vent pressures of 1-100 bars, 1400 K and O/S ~0.3-1.7, the calculated $\log fO_2 \sim -9(\pm 1)$ is in the range of the NNO and QFM buffers (see Fig. 2). Other calculations show that bulk compositions of O/S ~1-1.9 and magma temperatures (of ~1500 K and lower) also match the fO_2 values for the NNO and QFM buffers. An O/S ratio of 0.3-0.5 appropriate for possible S_2O -bearing deposits around Pele [14,15], provides an fO_2 value about one log unit lower than the QFM buffer at ~1 bar.

The oxidation state of the host magma is the important factor in controlling the speciation in the volcanic gas. Fig. 3 shows that at typical temperature of basaltic magma (1400 K) SO_2 -rich gases are produced under conditions more oxidizing than QFM and NNO. The reduced conditions around the IW buffer yield gases that are enriched in S_2 , S_3 and S_2O . Sulfur dioxide- S_2 mixtures, which plausibly represent an average volcanic gas on Io, are formed in a narrow fO_2 interval from QFM to an about 1.5 log unit lower than QFM. This narrow fO_2 range also provides the maximum abundances for SO and S_2O , which are expected constituents of volcanic

gases on Io [8,14].

Summary and discussion: The oxygen fugacities inferred for Ionian volcanic gases generally match the values for terrestrial volcanic gases [1] and igneous rocks that are roughly around QFM [2,16]. The calculated fO_2 of the outgassed volatiles and implied oxidation state of the host magmas indicate that iron metal and elemental carbon are absent from the magma source regions on Io. That is consistent with differentiation of Io's interior and the concentration of Fe metal in the large core discovered by *Galileo* [17].

In analogy with the Earth, Mars and Venus [e.g., 16,18,19], the silicate part of Io could have been oxidized by water in magmatic/volcanic, impact and hydrothermal processes followed by escape of reduced gases (predominantly H_2) to space. The water could have come from hydrous silicates formed in the Jovian subnebula [20] or from ice-bearing planetesimals. The oxygen released from water oxidized Fe metal and FeS to FeO-bearing silicates and magnetite. The presence of water in accreting material is probably the main reason for the difference in oxidation state between the Moon and lunar-sized Io. In contrast to Earth, which was gradually oxidized in subduction-related processes [16,18], an oxidized silicate part on Io was probably formed during the early stages of Io's evolution. Low gravity should have led to faster H_2 escape resulting in early oxidation of Io's interior.

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Fig 1. Calculated fO_2 on Io in comparison with oxygen fugacities of mineral buffers. Dotted line shows upper limits for the Loki plume obtained from the SO_3/SO_2 ratio. Solid lines show fO_2 calculated from atmospheric SO/SO_2 ratios of 3% and 10%. Dashed lines represent oxygen buffers.

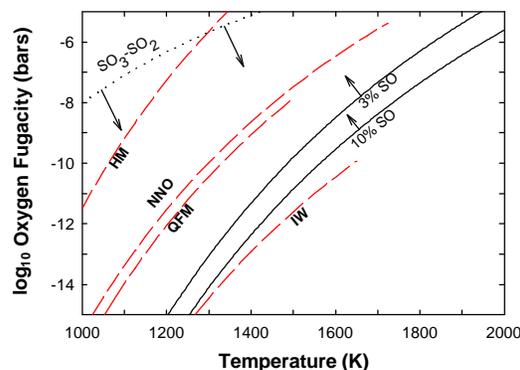


Fig. 2. The oxygen fugacity in Ionian volcanic gases as a function of bulk composition and total pressure at 1400 K.

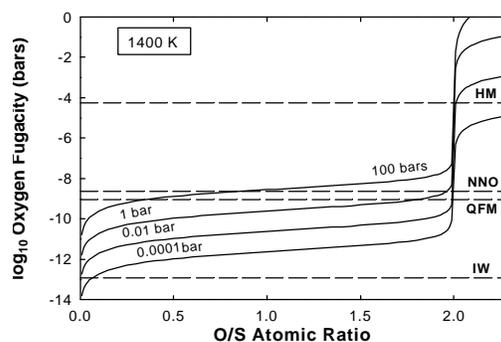


Fig. 3. Chemical equilibrium abundances in Ionian volcanic gas as a function of fO_2 at 1400 K and 1 bar.

