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

Introduction: On Earth, the oxygen fugacity (f\textsubscript{O\textsubscript{2}}) of outgassed magmatic volatiles reflects the oxidation state of their respective magmas and magmatic source regions in the lithosphere and asthenosphere \cite{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 \cite{3,4}. The intensive volcanic outgassing is primarily responsible for the composition of Io’s low-pressure patchy atmosphere, plasma torus and surface \cite{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 f\textsubscript{O\textsubscript{2}} values likely reflect the oxidation state of Ionian magmas and Io’s interior.

Model: By analogy with terrestrial volcanic gases \cite{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\textsuperscript{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\textsubscript{2} abundance and SO\textsubscript{3} upper limit (SO\textsubscript{2}/SO\textsubscript{3} < 2×10\textsuperscript{-4}) for the Loki volcanic plume \cite{6} to calculate f\textsubscript{O\textsubscript{2}} from the net thermochemical reaction

\begin{equation}
2 \text{SO}_2 = 2 \text{SO}_3 + \text{O}_2.
\end{equation}

In the second set, we used the atmospheric SO/SO\textsubscript{2} ratio of 3-10\textsuperscript{4} \cite{7} to calculate f\textsubscript{O\textsubscript{2}} from

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2 \text{SO}_2 = 2 \text{SO} + \text{O}_2.
\end{equation}

Our prior work shows that atmospheric SO can be at least partially due to volcanic degassing \cite{8}.

In the third set, we used the free energy minimization method to calculate f\textsubscript{O\textsubscript{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 \cite{9,10}) to ~2 (for SO\textsubscript{2}-rich gases, as in Loki \cite{6}). This range covers the bulk composition of Io’s atmosphere, plasma torus and surface volcanic condensates. An average O/S ratio of 1(±0.4) in torus \cite{11,12} is used as an approximation for average composition of outgassed volatiles. Thermodynamic data for gases are taken from \cite{13}.

Results: The calculated f\textsubscript{O\textsubscript{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 f\textsubscript{O\textsubscript{2}} of Loki gases (Fig. 1). These f\textsubscript{O\textsubscript{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 f\textsubscript{O\textsubscript{2}} calculated from eq. (2) is shown on Fig. 1. If all atmospheric SO is produced volcanically, the calculations give the f\textsubscript{O\textsubscript{2}} of the volcanic gases. If part of atmospheric SO is produced photochemically \cite{7} the calculated f\textsubscript{O\textsubscript{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\textsubscript{2} generates oxidizing conditions, but f\textsubscript{O\textsubscript{2}} does not exceed that for the HM buffer for high temperature (>~1150 K). Small deviations from SO\textsubscript{2} stoichiometry lead to large changes of f\textsubscript{O\textsubscript{2}} (Fig. 2). At lower O/S ratios, f\textsubscript{O\textsubscript{2}} decreases at constant total pressure, and changes gradually at O/S of ~1.8-0.2. The f\textsubscript{O\textsubscript{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 f\textsubscript{O\textsubscript{2}} ~ -9(±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 f\textsubscript{O\textsubscript{2}} values for the NNO and QFM buffers. An O/S ratio of 0.3-0.5 appropriate for possible S\textsubscript{2}O-bearing deposits around Pele \cite{14,15}, provides an f\textsubscript{O\textsubscript{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\textsubscript{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\textsubscript{2}, S\textsubscript{3}, and S\textsubscript{2}O. Sulfur dioxide-S\textsubscript{2} mixtures, which plausibly represent an average volcanic gas on Io, are formed in a narrow f\textsubscript{O\textsubscript{2}} interval from QFM to an about 1.5 log unit lower than QFM. This narrow f\textsubscript{O\textsubscript{2}} range also provides the maximum abundances for SO and S\textsubscript{2}O, which are expected constituents of volcanic gases.
gases on Io [8,14].

Summary and discussion: The oxygen fugacities inferred for Ioan volcanic gases generally match the values for terrestrial volcanic gases [1] and igneous rocks that are roughly around QFM [2,16]. The calculated fO2 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 H2) 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 H2 escape resulting in early oxidation of I0’s interior.

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