

VOLCANIC DEGASSING OF HYDROGEN COMPOUNDS 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: On Earth, hydrogen-bearing species (H_2O , H_2 , H_2S , HCl , and HF) are abundant constituents of volcanic gases and H_2O is usually the most abundant gas [1]. In contrast, products of volcanic degassing on Jupiter's satellite Io seem to consist mainly of S-, and O-bearing compounds (SO_2 , S_1 to S_8 , S_2O , and SO) [2-5] with smaller amounts of Na-, K-, Cl-bearing gases in form of alkali chlorides, monatomic gases, or sulfur chlorides [6,7]. Nevertheless, recent observations of iogenic hydrogen in Io's ionosphere by the *Galileo* spacecraft [8,9] at H/Na ratios of a few percent [8] indicate the presence of hydrogen species in Io's volcanic products that form its volcanic atmosphere and surface deposits. These *Galileo* observations agree with the tentative identification of H_2S and H_2O in surface frosts [10,11]. Here we assume that the reported H is outgassed (instead of originating from micrometeorite impacts or other sources) and use thermodynamic calculations along with elemental abundances in Io's plasma torus to infer the speciation and abundances of H-bearing species that may degas from high-temperature silicate magmas on Io.

Model: We used the free energy minimization method to calculate the equilibrium speciation in the O-S-Na-K-Cl-H system, which models the chemistry of Io's volcanic vents. Calculations for volcanic vents were done at 1 bar total pressure and 1500 K, which represents a typical temperature of Io's magmas [2,12]. The nominal atomic abundances (O:S:Na:K:Cl = 1:1:0.05:0.0033:0.01) are taken from atomic ratios observed in Io's plasma torus and extended atmosphere (see [2-7]). The Na/K ratio corresponds to the solar value. The H/S atomic ratio was varied from 10^{-10} to 0.1 to cover the range of H elemental abundances that might occur in volcanic gases. The calculations included the following hydrogen gases: H_2O , H_2 , H, H_2S , HS, HCl, OH, NaH, NaOH, and KOH. Thermodynamic data for gases are taken from [13] and [14] (for HS).

Results: Figure 1 shows how the presence of hydrogen affects the chemistry of ionian volcanic gases. Each plot in Fig. 1 shows trends in the abundances of hydrogen-bearing compounds in comparison with abundances of other species containing the elements S, Na, K, and Cl.

Hydrogen chemistry is displayed in Fig. 1a. At H/S ratios less than $\sim 10^{-6}$, the major hydrogen gases in order of decreasing importance are HS, NaOH, KOH, and HCl. As the hydrogen abundance continues to increase, H_2O becomes more important until it becomes the major hydrogen bearing gas at an H/S ratio of

$\sim 10^{-5}$. The abundances of H_2S and H_2 increase more sharply than do the abundances of HS, NaOH, KOH, and HCl and the former two gases become the second and third most abundant species at H/S ratios above ~ 0.006 . The H/S ratios of about 10^{-3} corresponding to the composition of Io's torus imply hydrogen degassing in the form of H_2O , which is the major gas, followed by H_2S , HS, H_2 , NaOH, KOH, and HCl, which have similar concentrations within one order of magnitude. Monatomic hydrogen is a trace species under the conditions studied and is not shown because its volume fraction is less than or about equal to 10^{-10} for the range of H/S ratios plotted. However, larger amounts of H may be produced by photochemical and/or charged particle destruction of H_2O and H_2S outgassed from ionian volcanoes.

Fig. 1b shows that the major effect of hydrogen on sulfur chemistry is to dramatically increase the abundance of H_2S . However, even at H/S ~ 0.1 , the largest ratio considered, less than 1% of all sulfur is present as H_2S . At this H/S ratio H_2S is only as important as SO and remains less abundant than SO_2 , S_2 , and S_2O .

Sodium chemistry is displayed in Fig. 1c. The abundances of NaOH and NaH, which is a trace species, increase with the hydrogen abundance. Sodium chemistry is unaffected otherwise. Sodium chloride remains the most abundant sodium gas, while monatomic Na and $(\text{NaCl})_2$, which have almost identical abundances, are the next most important gases. The potassium chemistry in Fig. 1d is similar to sodium chemistry, although KOH becomes the second most abundant potassium gas at H/S ratios above ~ 0.01 .

Chlorine chemistry shown in Fig. 1e is relatively unaltered except an increase in HCl abundance as the hydrogen abundance increases. Even at H/S as high as 0.001-0.01, HCl is much less abundant than alkali chlorides. This is in dramatic contrast to terrestrial volcanic gases where HCl is the major chlorine gas.

Summary and Discussion: The speciation of hydrogen in magma degassing products on Io depends on the H/S ratio in volcanic gas. Hydrogen/sulfur ratios below $\sim 10^{-5}$ favor hydrogen degassing in form of HS, NaOH, KOH, and HCl. At H/S ratios higher than $\sim 10^{-5}$ corresponding to observations in the plasma, H_2O is the major hydrogen gas. Hydrogen sulfide, H_2 , and NaOH are the next abundant gases at the high H/S ratios. Further data on composition of H-bearing surface deposits may provide constraints on the H/S ratio in products of magma degassing. The chemistry of major S, Na, K, and Cl gases remains unchanged at H/S ratios less than $\sim 1\%$. Therefore, our prior conclusions about

degassing for S [3-5] and for Cl, Na, and K [6,7] remain valid.

The low hydrogen abundance in Io's plasma indicates that at present, the volatiles outgassed from Io are depleted in hydrogen. The low abundance of hydrogen in the plasma is consistent with the upper limits for mole fractions for H_2O , H_2S , and HCl (0.023, 0.35, and 0.01, respectively) determined for the Loki plume by the *Voyager 1* IRIS experiment [15]. These data indicate that ionian magmas are significantly dryer compared to terrestrial counterparts. The deficiency of water in Io's magmas should lead to higher melting temperature of mantle/lithospheric materials and higher liquidus temperatures of magmas. This water deficiency can, in part, account for the observed high-temperature magmas [12] and the absence of plate tectonic processes. It is also consistent with the *Galileo* SSI data [16] indicates mafic/ultramafic rather than silicic character of solidified lava flows.

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Figure 1. Chemical equilibrium concentrations of hydrogen-bearing gases in a modeled volcanic vent on Io as a function of H/S atomic ratio at 1500 K, 1 bar total pressure, and nominal values for the O, S, Na, K, and Cl abundances. The vertical dotted lines at $\log H/S = -3$ indicates an H abundance consistent with the recent reports.

