MARTIAN VOLCANIC GASES: ARE THEY TERRESTRIAL-LIKE?

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Introduction: Volcanism was a major geological process in the geologic history of Mars [1-3]. Associated volcanic degassing [4,5] should have affected the composition of the atmosphere, contributed to the greenhouse effect [6,7], and influenced the chemistry and mineralogy of crustal materials through condensation of volcanic aerosols and chemical weathering [8]. Despite the importance of volcanic degassing, the chemical composition of martian volcanic emanations is weakly constrained. The presence of H_2O, CO_2, oxidized sulfur, and Cl compounds in the atmosphere and surface materials implies that typical martian volcanic gases contain water, carbon oxides, and S-, Cl-bearing species. Even with tentative detection of magmatic H_2O and CO_2 in tiny fluid-gas inclusions in pyroxene in the ALH84001 meteorite [9] and the presence of a magmatic amphibole in several martian rocks, martian meteorites generally reveal volatile-depleted magmatic environments [e.g., 10]. Although terrestrial volcanic gases are often used as analogs in martian climatic and geochemical models [4-7], several factors could affect bulk composition, speciation, and the amount of martian volcanic gases compared to their terrestrial counterparts. Here I briefly review those factors and then evaluate the effects of pressure, temperature, oxidation state, and the Cl/S ratio on speciation of modeled martian volcanic gases.

Why is Mars' volcanic degassing different from the Earth's? The lack of plate tectonics, low gravity, and low atmospheric pressure on Mars, as well as discrepancies in bulk planetary compositions could account for differences in the composition and abundance of terrestrial and martian volcanic gases. The lack of subduction of lithospheric plates may cause a sharp contrast in the oxidation states [11,12] and volatile contents between the mantle and crust. It could also account for higher liquidus temperatures of H_2O-depleted mantle magmas. Deep mantle plumes, which could have been responsible for the formation of major volcanic structures (Alba Patera, Syrtis Major, and major Tharsis volcanoes), could have supplied reduced high-temperature and volatile-depleted magmas, consistent with mostly effusive eruptions in those areas. A high percentage of ultramafic rocks among the martian meteorites [10] and the detection of abundant olivine in surface materials [13] imply a broad occurrence of high-temperature magmas that could be characterized by specific degassing products. Nevertheless, morphologic evidence of explosive activity, especially in earlier periods of martian history, indicate degassing of volatile-rich magmas [3]. The majority of the volatiles degassed from those and many other martian volcanoes could represent recycled crustal volatiles (H_2O, CO_2, and S-, Cl-bearing species). Indeed, slow magma ascent in low gravity [14] and high liquidus temperatures of H_2O-depleted mantle magmas favor assimilation of crustal materials. In particular, interaction of magma with low-temperature Cl-rich crustal brines could have led to saturation of magmas with respect to both H_2O and Cl. Significant assimilation of crustal volatiles is consistent with the high oxidation state of the majority of shergottites [11,12] and with ubiquitous Cl-apatites in martian meteorites. Both low gravity and low atmospheric pressure on Mars should produce greater depths of gas nucleation resulting in thorough degassing of ascending magmas [3, 14]. Low atmospheric pressure, which could have characterized the majority of geological history, should affect bulk composition of volcanic gases by favoring degassing of volatiles with higher solubility (H_2O, Cl). In contrast to Earth and Venus, degassing of H_2O would not be suppressed compared to less-soluble CO_2. In other words, martian conditions could be more favorable for recycling of volatiles in the crust because of profound assimilation and subsequent efficient degassing. The degree of assimilation of crustal material could be a major factor that affected temperature, composition, and the oxidation state of erupting magmas, as well as the amount, bulk composition and speciation of volcanic gases. Evolution of volcanism styles from explosive to effusive eruptions [3] could reflect changes in the degree of assimilation.

Speciation modeling: Ideal gas equilibrium calculations were performed to evaluate speciation in the H-C-O-S-Cl-F-N system using thermodynamic data for 123 gases from [15]. Calculations were done for temperatures of 1400 K and 1700 K, which represent basaltic and ultramafic melts, respectively. Nominal vent pressure of 0.006 bar was chosen to model pressure-balanced eruptions at the present epoch. Calculations at higher pressures were performed to explore an influence of higher atmospheric pressure, as well as effects of over-pressured eruptions ($P_{vent} > P_{atm}$) that should have occurred on Mars [16]. For the nominal atomic composition I used Kilauea summit lava lake 1918-1919 "*J*" gases [17] (H:C:S:Cl:F:N = 7.14:2.13:1 :0.0094:0.0094:0.0016). The Cl/S atomic ratio was varied to explore the speciation of Cl-rich compositions. Nitrogen balance was also changed to explore its effect on the speciation. The oxygen balance was set according to the chosen oxidation state (fO_2), which was normalized to the Ni-NiO (NNO) buffer. The oxidation state of the iron-wüstite (IW) buffer was used to model uncontaminated mantle magmas (see [11]).

Results: Some results of speciation calculations are presented in Figures 1-3. Reduced gases are rich in CO and H_2, but CH_4 and NH_3 are not abundant. The methane volume ratio does not exceed 10^{-4}. N_2 is the major N-bearing gas at all conditions considered (see also [18]). Emanations from reduced ultramafic magmas (Figs. 1b, 2b) are enriched in H_2, CO, S_2, H_2S, HS, H, S, COS, and S_2O compared to oxidized basaltic magmas. Oxidized gases emanating from magmas that assimilated crustal volatiles mainly consist of H_2O, CO_2, SO_2, HCl and HF. These results generally complement earlier models for martian degassing performed for 1 bar [19]. Emanations from low-pressure vents, which should be typical throughout the geologic history, are characterized by higher concentrations of SO_2, S_2, SO, HS, H, S and lower concentrations of H_2S and COS compared to high-pressure gases. Chorine and F degas as HCl and HF, and the speciation of Cl and F is not strongly affected by fO_2, temperature, and pressure. In contrast to lunar [20] and Venus' [21] volcanic gases, martian Cl-rich gases are rich in HCl. Although degassing of both mantle and recycled crustal volatiles on Mars should differ from their terrestrial counterparts, martian gases are closer to Earth's than other volcanic emanations in the solar system.

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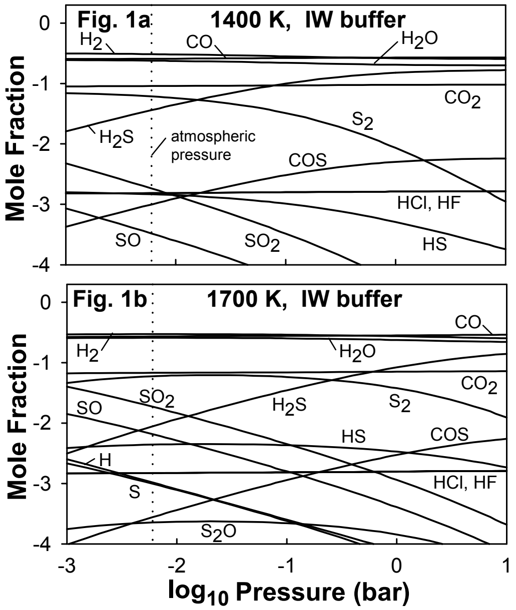

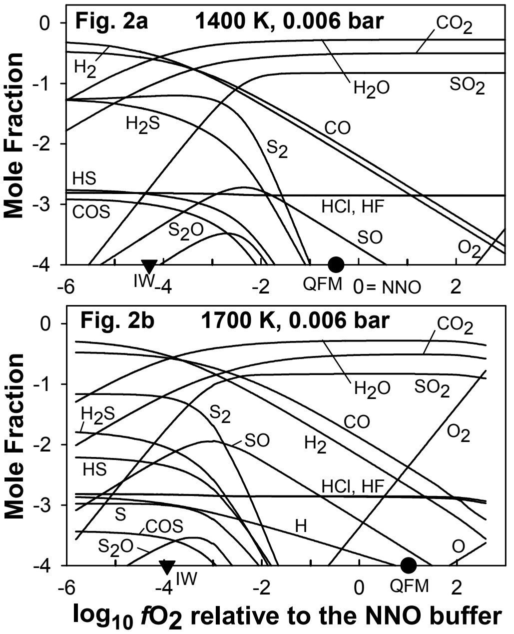

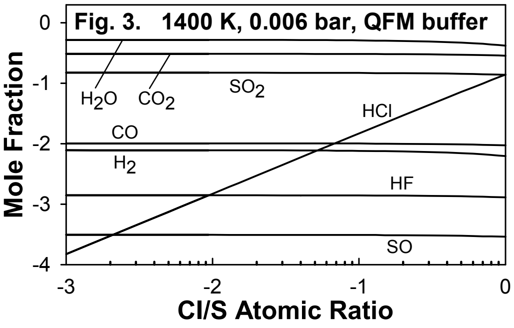

Figures 1-3. Equilibrium speciation of martian volcanic gases as functions of pressure, temperature, the oxidation state, and the Cl/S atomic ratio. The vertical dashed lines in Fig. 1 represent pressure in the present martian atmosphere. Bold symbols in Fig. 2 represent fO_2 buffers. Note that the oxidation states of basaltic martian meteorites vary from ~IW to about one fO_2 log unit below QFM [e.g., 11, 12].