CHEMICAL MODELS FOR VOLCANIC GASES ON VENUS M. Yu. Zolotov[1] and T. Matsui[2], [1]Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, e-mail: zolotov@zonvark.wustl.edu. [2]Department of Complexity Science and Engineering, Graduate School of Frontier Science, Univ. of Tokyo, Japan.

Introduction: The morphology of Venus' surface reveals widespread volcanic features [1] that could have formed during a short period of volcanic emplacement [2,3]. It has been realized that corresponding volcanic degassing must have affected composition of the atmosphere and clouds, temperature of the atmosphere and lithosphere through the greenhouse effect, as well as mineralogy of the surface [4-9]. The influence of volcanic degassing on atmospheric and lithospheric processes depended on timing, the amount, bulk composition, and speciation of released volcanic gases. Despite of a prediction of unusual forms of degassing for S, Cl, and F (*e.g.*, Cl_2, SF_4, CS_2) from Venus' anhydrous magmas [10], the bulk composition and speciation of volcanic gases remain unexplored. Here we model speciation of volcanic gases at bulk compositions, vent pressures, temperatures and oxidation states of magma determined to be plausible for Venus.

Models for volcanic gases: Ideal gas equilibrium calculations are used to evaluate speciation of the H-C-O-S-Cl-F system using thermodynamic data for 106 gases from [11].

Magma temperature and vent pressure. Morphology of volcanic features [1] and Soviet XRF analyses [12,13] suggest mostly basaltic composition of Venus' lavas. Our calculations are done at temperature 1500 K, which corresponds to an anhydrous basaltic magma. Vent pressure of 92.1 bar is chosen to model pressure-balanced eruptions.

Bulk composition. The atmospheric composition implies that Venus' volcanic gases could be depleted in H and contain C, S, Cl, and F species. Low (S+Cl+F)/C ratios in the Venus' atmosphere compared to typical Earth's volcanic gases and meteoritic abundances suggest that volcanically degassed S, Cl, and F are stored in the lithosphere [14,15]. Unusually high S content (0.6-1.9 wt.%) in Venus' surface materials [12,13] is consistent with consumption of volcanic sulfur from the atmosphere [14,15,16]. In contrast to S, Cl, and F, chemical consumption of atmospheric carbon into surface minerals (carbonates) is highly questionable [6,16,17]. It follows that recycling of lithospheric S, Cl, and F could account for elevated (S,Cl,F)/C ratios in some volcanic gases. For example, gases emitted from Venus' alkaline magmas could be rich in S, Cl, and F. In addition, Cl could have preferentially accumulated in the lithosphere throughout the history, while S and F could in part have been consumed into mantle minerals. High Cl/S ratios could represent degassing products of non-silicate magmas (molten salts) and silicate magmas that contaminated crustal materials.

High atmospheric pressure should affect bulk composition of volcanic gases by favoring degassing of volatiles with relatively low solubilities. For example, degassing of H_2O (if any) could be suppressed compared to less-soluble CO_2 [18].

For the nominal bulk composition we use Kilauea summit 1918-1919 "*J*" gas samples [19] (H : C : S : Cl : F = 1.34 $\times 10^{-4}$: 2.13 : 1 : 9.4×10^{-3} : 9.4×10^{-3}), in which the H/C atomic ratio is set to match the Venus' atmospheric value (6.3×10^{-5}). The oxygen balance is set according to the chosen oxidation state (fO_2). In order to explore compositional variations, we vary H/C, (Cl+S)/C, and Cl/C ratios.

Oxidation state. Evaluation of the oxidation state of Venus' magmas depends on the amount of water that has been accreted. The high D/H ratio in the Venus' atmosphere indicates that some amount of water has been lost through preferential hydrogen escape and oxidation of the lithosphere and the atmosphere [e.g., 20]. Although periodic submerging [21,22] of an oxidized lithosphere may contribute to oxidation of the Venus' mantle, it is hard to believe that it has been oxidized as thoroughly as the Earth's counterpart.

The oxidation state of Venus' volcanic gases and parental magmas could vary with geologic setting and time. Although mantle magmas are likely to be reduced, contamination of the surface-formed magnetite-hematite-anhydrite material in crustal magmatic chambers could cause oxidation of magmas. Flood-type volcanic eruptions that form Venus' plains during the global resurfacing event could have been

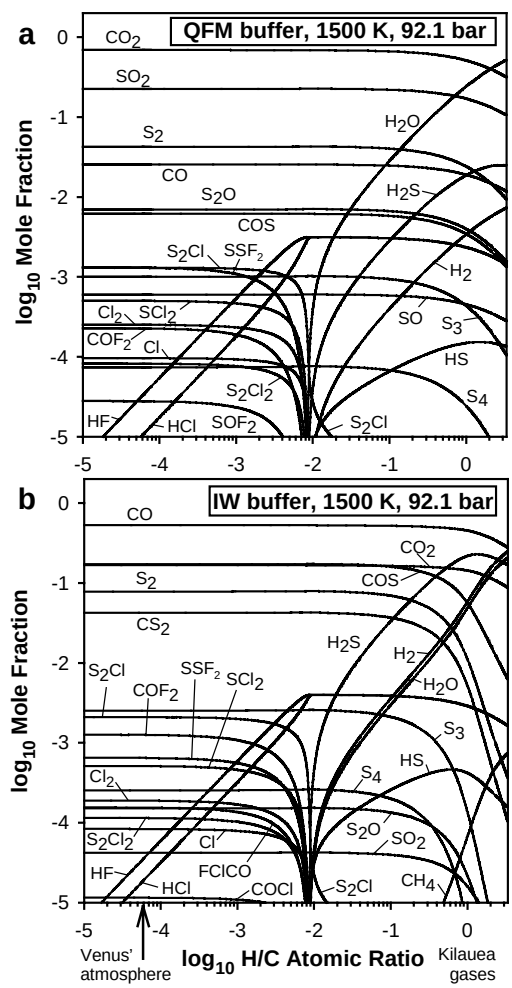

Fig. 1. Speciation of volcanic gases as a function of the H/C ratio at the oxidation state of the QFM (a) and the IW buffer (b). Venus' gases are likely to have H/C < 0.01.

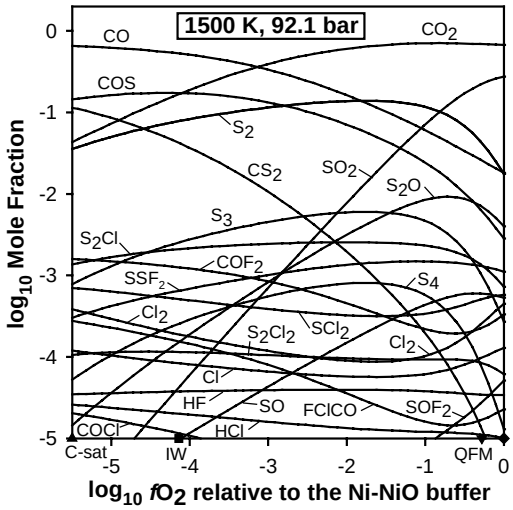

Fig. 2. Venus' volcanic gases as a function of the oxidation state. C-sat, graphite-saturation conditions.

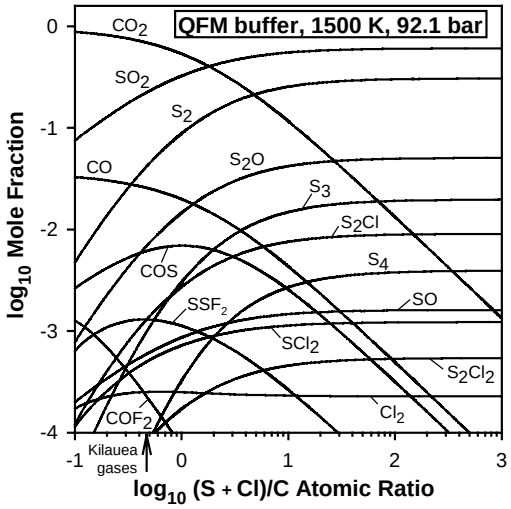

Fig. 3. Speciation of Venus' volcanic gases as a function of the (S + Cl)/C atomic ratio.

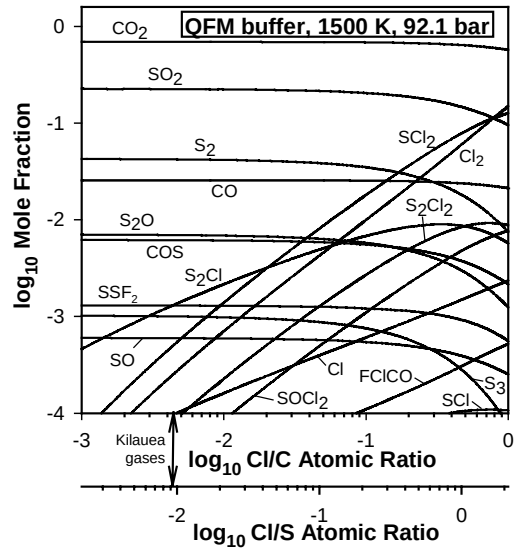

Fig. 4. Speciation of Venus' volcanic gases as a function of the Cl/C and S/C atomic ratios.

more reduced than subsequent low-volume eruptions, which are likely to be affected by crustal contamination. Here we explore volcanic gases with fO_2 varied from graphite saturation conditions to the Ni-NiO buffer.

Results: Fig. 1 shows how volcanic gas speciation is affected by the H/C ratio. At the H/C ratio < ~0.01, which could represent Venus' gases, H degasses in HCl and HF; Cl degasses in sulfur chlorides (S_2Cl, SCl_2, S_2Cl_2), Cl_2, FClCO, Cl, HCl, and COCl; and F degasses in SSF_2, COF_2, FClCO, HF, and SOF_2. Water is not important component in Venus' gases. Effect of fO_2 on speciation of Venus' H-depleted volcanic gases (H/C = 6.3×10^{-5}) is shown in Fig. 2. Reduced gases, which could represent uncontaminated mantle magmas, are rich in CO, COS, S_2, and CS_2. Oxidized gases are rich in CO_2 and SO_2. Speciation of Cl and F is not strongly affected by the oxidation state. Figs. 3 and 4 explore the effect of high bulk abundances of Cl+S and Cl that could represent volcanic gases rich in oxidized crustal volatiles. Sulfur dioxide, S_2, S_2O, and S chlorides dominate in gases rich in S and Cl (Fig. 3). Gases rich in chlorine (Cl≈C, Fig. 4) contain compatible concentrations of SCl_2, Cl_2, and SO_2.

The models show that degassing of both mantle and recycled crustal volatiles on Venus could differ from the terrestrial counterparts. A detection of S halogenides, Cl_2, Cl, or other gases, which are unusual for Earth's volcanoes (e.g., COF_2, SOF_2, FClCO), in Venus' atmosphere could indicate recent volcanic activity. Relative abundances of these and other volcanic gases could be used to evaluate the bulk composition and oxidation state of Venus' volcanic emanations.

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