**IRON SALTS AND OXIDES IN THE HISTORY OF THE SURFACE-ATMOSPHERE-CLOUD SYSTEM ON VENUS.**

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Introduction: Although the phase composition and oxidation state of Fe in Venus' materials are unknown, they could inform about physical-chemical processes and constrain fate of water on the Earth's sister planet. Iron is reported in three Venera and Vega landing sites in chemically altered basaltic materials [1,2] and in the cloud aerosol [3]. The near infrared absorption of surface materials at Venera landing sites suggests a presence of hematite, α-Fe_2O_3 [4]; and the near UV and blue absorption in the upper clouds do not exclude $FeCl_3$ grains and acidic solutions [5-7]. The oxidation state (fO_2) of the near-surface atmosphere is indistinguishable from conditions of the hematite-magnetite (HM) equilibrium [8] and implies oxidation of Fe(II) in exposed minerals and glasses. Formation of Fe oxides through gas-solid type oxidation of Venus' pyroxenes, olivine and glasses is anticipated based on chemical equilibrium calculations and experiments [9,10]. However, a slow diffusion of Fe^{2+} to surfaces of minerals and glasses may limit formation of surface Fe oxides on Venus [10,11]. Here we constrain speciation, sources and sinks of Fe halides, sulfates and oxides in the gas-solid (+water) systems and discuss origins of secondary Fe phases in surface fines.

Methods: Speciation of Fe and other elements is evaluated through calculations of gas-gas (atmospheric and volcanic gases), gas-solid (surface weathering, condensation from gases) and gas-solid-water (putative early Venus) type chemical equilibria. Both individual chemical reactions (gas-gas, gas-solid) and multicomponent systems (aqueous systems, volcanic gases, near-surface atmosphere) are considered. Thermodynamic data for substances are mainly from [12].

An Early Aqueous History: Chlorites and Fe-Mg smectites are modeled as major aqueously-formed Fe phases. A fast H escape and accumulation of O_2 could cause deposition of Fe(III) hydroxides/oxyhydroxides from surface water. Magnetite and Fe(III) silicates form through oxidation of Fe(II) by water in ultramafic and mafic rocks. Formation of Fe carbonates is modeled in warm reservoirs at elevated atmospheric fCO_2. However, precipitation of abundant Fe chlorides and sulfates from both reduced (Na-Ca-Cl-carbonate) and oxidized (Na-Cl-sulfate-carbonate) surface water reservoirs is not observed in models. After subsequent dehydration of H-bearing phases, magnetite, hematite (e.g. in Fe-rich sedimentary formations) and Fe-rich carbonates could be preserved in a shallow subsurface.

Fig. 1. Stability of solid phases in the Fe-O-S system at the Venus' modal radius (6051.4 km).
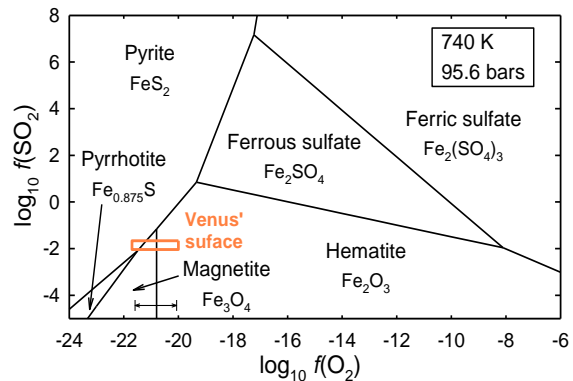
Volcanic Processes: Both suppressed degassing and a dominance of H-free Cl-bearing compounds in Venus' magmatic gases [13, this work] do not favor formation of metal chlorides (e.g. $FeCl_2$) through HCl,g-melt/mineral reactions. As on other bodies [e.g. 14,15] formation Fe chlorides in magmatic/fumarole gases environments is possible on Venus, though an elevated surface temperature limits condensation of $FeCl_2$,g, and Fe(III) chlorides may condense only in the clouds [6,7, this work]. Speciation models for Venus' volcanic gases suggest FeF_3, $FeCl_2$ and $FeCl_3$ as major Fe gases (at 1400 K, 95.6 bars, $\log_{10} fO_2$ = QFM+2 – IW-3, Fe/C (atomic) = 10^{-6}–10^{-15}, H/C at. = 6×10^{-5}). Condensation of $FeCl_2$ (at mole fraction, x, of $FeCl_2$,g > 10^{-7}, 740 K, 95.6 bars) limits supply of Fe to the atmosphere. Formation of Fe sulfates is not expected in anoxic volcanic/fumarole processes on Venus. As in oceanic basalts [15], a suppressed degassing of water from Venus' lavas ~100 bars could cause formation of magnetite through oxidation of Fe(II) by dissolved magmatic water at late stages of crystallization.

Current Surface, Atmosphere and Clouds: Magnetite, hematite, Fe-poor Mg-silicates and pyrite are likely stable phases at Venus' plains and could form through gas-solid type alterations of ferrous silicates and glasses, pyrrhotite and Fe carbonates, if they are exposed to the atmosphere [e.g. 9]. Iron sulfates are unstable and likely alter to Fe oxides and/or pyrite (Fig. 1). The atmospheric xHCl = ~4×10^{-7} and xHF = ~5×10^{-9} are insufficient to form solid Fe halides via alteration of Fe-bearing phases [9, this work].

Fig. 2. Mole fractions (x) of $FeCl_2$ and $FeCl_3$ gases in the near-surface atmosphere of Venus constrained by gas-solid type equilibria. The arrows show Venus' fO_2 conditions and the error bars are for the HM equilibrium [8].
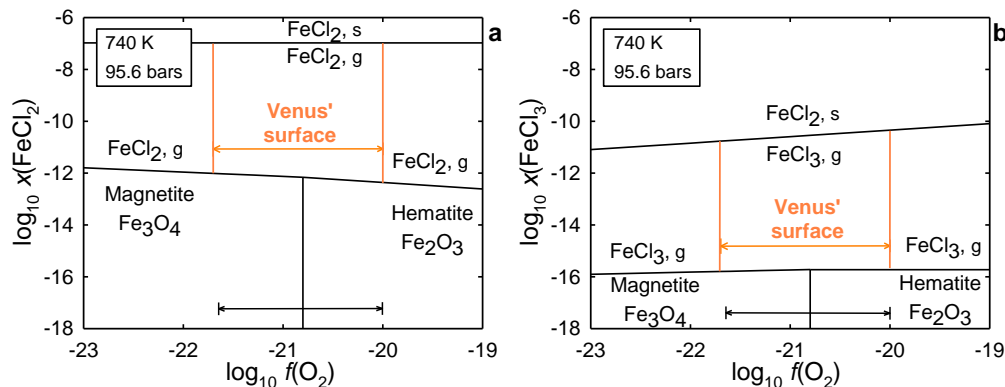
For the conditions of the modal radius (740 K, 95.6 bars), C-O-N-S-H-Cl-F-Fe gas speciation models for the atmosphere suggest $FeCl_2$ as the major Fe gas. At Fe/C (atomic) = 10^{-13}–10^{-9}, $FeCl_2 > FeCl_3 > Fe_2Cl_4$, at Fe/C = 10^{-9}–10^{-7}, $FeCl_2 > Fe_2Cl_4 > FeCl_3$. At Fe/C = 10^{-13}–10^{-7}, FeF_3, FeF_2, Fe_2Cl_6, $FeCl$ and $Fe(CO)_5$ are less abundant. An upper limit for $xFeCl_2,g$ of 10^{-7} is set by the $FeCl_2$ gas-solid equilibrium (Fig. 2a). A HM-$FeCl_2$,g-HCl,g-H_2O,g equilibrium gives $xFeCl_2,g = 6.7×10^{-13}$ (Fig. 2a). At the supposed $FeCl_2$-$FeCl_3$ gas equilibrium, the assessed range of $xFeCl_2,g$ corresponds to $xFeCl_3,g = 1.3×10^{-11}$–$1.9×10^{-16}$ (Fig. 2b).

The lesser $xFeCl_2,g$ value allows condensation at > 28.5 km. If $FeCl_2$ grains reach the clouds, the $FeCl_2$,s-H_2SO_4-H_2O(l) interaction causes Fe^{2+} oxidation. The range of $xFeCl_3,g$ allows condensation at 48–58 km, though possible $FeCl_3$,g to Fe_2Cl_6,g conversion at altitudes may not allow condensation to $FeCl_3$,s [c.f. 7].

Dehydration of sulfuric acid aerosols below the main clouds likely produces $Fe_2(SO_4)_3$ grains that may account for a sub-cloud haze material [6]. Settling of the grains and their conversion to hematite and/or magnetite and pyrite (Fig. 1) provides the sink of Fe.

Cosmic Fe in Clouds and Surface Fines: A low-scale current volcanism (if any) and suppressed magma degassing do not imply volcanic sources of Fe halides. It is unclear if Fe oxide-HCl,g equilibria (Fig. 2) control near-surface abundances of $FeCl_2$,g and $FeCl_3$,g. As in the Earth's stratospheric H_2SO_4-rich clouds [17], cosmic dust and meteoric smoke [18] could be a major source of atmospheric Fe in the current epoch. Denser Venus' atmosphere implies stronger ablation and contribution of meteoroids to the atmosphere composition.

The accumulation of cosmic Fe on Venus during the last 0.3–0.7 Ga estimated from [19,20] corresponds to (1.4–16) kg Fe m^{-2}, (2–23) kg Fe_2O_3 m^{-2} and 0.4–4 vol.% Fe_2O_3 in a 0.1 m thick surface layer. The exogenic Fe_2O_3 in surface fines formed from $Fe_2(SO_4)_3$ could contribute to the near infrared absorption [4] and agrees with a relatively slow surface oxidation of Fe(II) in silicates and glasses [10,11]. The surface would be 'red' in the near infrared even without oxidation of surface materials. A measurement of siderophile elements (e.g. Ni, Ir, Os) in surface fines will constrain the cosmic contribution.

Summary: Putative aqueous environments on early Venus did not produce abundant Fe chlorides and sulfates. Volcanic degassing and gas-solid reactions could have supplied Fe halide gases in history of Venus. Without current volcanism, cosmic Fe could be the major and only source of atmospheric Fe. Fe irreversibly sinks from the clouds in sulfates and contributes to the oxide-sulfide mineralogy of surface fines.

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