

ON THE COMPOSITION OF PUTATIVE OCEANS ON EARLY VENUS. M. Yu. Zolotov¹ and M. V. Mironenko², ¹School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, e-mail: zolotov@asu.edu. ²Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, e-mail: mironenko@geokhi.ru.

Introduction: Venus once had substantially more water and possibly even oceans early in its history. Given the close proximity of Venus and Earth, the planets could have accreted comparable amounts of volatiles. The high D/H ratio in the atmosphere of Venus implies an elevated water abundance earlier in the history of Venus [1,2]. This water was lost by mechanisms that may have involved evaporation under runaway greenhouse conditions, photo-dissociation of H₂O, and water-rock reactions [1]. Preferential hydrodynamic escape of hydrogen released through H₂O dissociation [3] could have caused net oxidation of rocks and atmospheric gases, and accumulation of deuterium in the atmosphere [1-3].

The existence of early oceans should have affected the subsequent evolution of the atmosphere and lithosphere. The involvement of aqueously altered and oxidized rocks, and oceanic sediments (e.g., salts) in lithospheric processes could have influenced rock deformations, melting and degassing patterns, the composition of igneous rocks, and distribution of volatiles in the lithosphere-atmosphere system. In addition to the D/H ratio, signatures of ancient aqueous processes could be manifested in the chemical and isotopic composition of the current atmosphere and lithosphere, in geological features, and in lithospheric geophysical data. These signatures could vary depending on formation scenarios, composition, and loss mechanisms of the early hydrosphere. Here we discuss and roughly evaluate chemical scenarios of early aqueous evolution.

Evolution of Venus' hydrosphere: Outer solar system planetesimals containing water ice and/or hydrated minerals could have delivered Venus' water. The same planetesimals probably supplied Cl (as HCl clathrates and/or secondary phases). These and local planetesimals delivered C, N, and S (in organic matter, troilite, and secondary carbonates, sulfides, and sulfates). Impacts during late stages of accretion led to degassing of H₂O, HCl, and some other volatiles. The low luminosity of the young sun and limited amounts of atmospheric greenhouse gases may have allowed condensation of water. Dissolution of HCl and CO₂ in the aqueous phase led to acidic solutions that reacted with rocks. These reactions caused some neutralization of solutions and precipitation of secondary phases. The primordial surface waters could have been mostly metal (Na, Ca, K, Mg) chloride solutions.

Intensifying high-temperature (*T*) processes in the interior led to differentiation and development of igneous

activity in the upper mantle. High *T* also favored dehydration of the interior and oxidation of C and N in organic compounds. Some H₂O was consumed through oxidation of Fe⁰-metal, and S, C, and N species leading to the production of H₂. Early magmatic gases delivered H₂, CO, H₂O, CO₂, H₂S, S₂, HCl, and N₂ into the atmosphere and hydrosphere.

Below are several possible scenarios of oceanic evolution. I) The formation of abundant H₂ through oxidation by H₂O of the interior led to the production of CH₄, which accumulated in the atmosphere. Corresponding strong greenhouse heating caused evaporation of fluids and precipitation of chlorides. Hydrogen was then lost through hydrodynamic escape [3] and CH₄ was oxidized to CO₂. II) An intense supply of acidic species (HCl, H₂S, CO₂, CO) toward the surface and a limited exposure of silicate rocks led to low-pH oceans and the accumulation of CO₂ in the atmosphere, which increased greenhouse heating and atmospheric pressure (*P*). This pathway may have caused rapid evaporation of fluids and precipitation of chlorides. III) A limited supply of acidic species, large continental areas, and permeable suboceanic rocks would have favored neutralization of solutions and trapping of a substantial CO₂ mass in carbonates. Corresponding water reservoirs survived longer and were oxidized through hydrogen escape. Evaporation of these reservoirs led to salt deposits containing chlorides and carbonates. IV) If not abundant, surface aqueous solutions could have been consumed through hydration and oxidation of rocks followed by dehydration due to the greenhouse effect. Formation of chlorides is also likely in this scenario.

Modeling approach: We developed chemical equilibrium models to explore the above scenarios, though calculations of atmospheric *P* and *T* have yet to be coupled with these models. It is assumed that the majority of C, N, and Cl was extracted/degassed into the atmosphere-ocean system on early Venus, and the speciation of all of the elements was controlled by thermochemical equilibria among gases, solids, and aqueous species. These equilibria were calculated in the O-H-C-S-Cl-N-Na-K-Mg-Fe-Ca-Si-Al system with the GEOCHEQ code [4]. Achaean basalt was used to exemplify the rock composition. We explored effects of the water/rock mass ratio (*W/R*), *T*, *P*, and *f*O₂ (with open system calculations) on the composition of aqueous and gas phases, and secondary mineralogy. Basic calculations were performed for *T* = 50°C to 350°C, *P* = 7 bar to 180 bar, and *W/R* = 0.3 (~1 km deep global ocean interacts with ~1 km thick rock layer). Mass balances of CO₂ and N₂ corresponded to today's atmos-

phere of Venus; and Cl (as HCl) and S abundances were represented by the Earth's ocean and crustal reservoirs scaled to Venus' mass [5].

Results and discussion: Basic modeling indicates that hot oceanic water could be a CaCl₂-NaCl-rich solution with a salinity of ~70-400 g/kg solution. Major aqueous species are Cl⁻, Na⁺, NaCl⁰, CaCl⁺, Ca²⁺, and CaCl₂. Dissolved CO₂ and aqueous species of K and Mg are less abundant. Neither sulfide (HS⁻, H₂S⁰) nor sulfate (SO₄²⁻) sulfur is abundant. At higher *T*, neutral aqueous complexes become more abundant, and the Ca/Na ratio tends to increase. The pH is typically from 6 to 7. However, the pH is lower if the mass of reacted rocks is smaller (at elevated *W/R* ratios) and/or at higher atmospheric *P*, which corresponds to elevated *PCO*₂.

The dominance of Cl, Ca, and Na in oceanic water is accounted for by the large mass of Cl and its preferential accumulation in the aqueous phase, and by the limited amounts of secondary minerals of Na and Ca. Calcium is abundant in basalts, and precipitations of anhydrite (CaSO₄), Ca-carbonates, and Ca-phyllsilicates still allow accumulation of Ca in solution. Aqueous Mg species are not very abundant because of the formation of dolomite and Mg-phyllsilicates. Concentrations of K species are limited by precipitation of K-feldspar, smectites, and K deficiency in rock. Aqueous concentrations of sulfate and sulfides are limited by precipitation of anhydrite and pyrite, respectively. In contrast to low-*T* oceans of Earth, precipitation of CaSO₄ prevents the formation of sulfate-rich oceanic water even at very oxidized conditions.

The modeling does not reveal conditions that are favorable for the formation of a Na-carbonate "soda" ocean that would trap the majority of atmospheric CO₂. Assumed high abundances of HCl and CO₂, and trapping of Na in albite, play roles in preventing the development of a "soda" ocean. Therefore, formation of Na carbonates was unlikely upon evaporation of early oceans.

Secondary mineralogy. The models reveal significant hydration of suboceanic rocks and some oxidation of S and Fe in minerals. Major secondary minerals are phyllsilicates (chlorite, montmorillonite, saponite, talc, tremolite, kaolinite), quartz, albite, microcline, carbonates (dolomite, ankerite, calcite), pyrite, and anhydrite. Some assemblages contain hematite (especially at high *T*) or magnetite. At elevated *fO*₂ (when much H₂ escapes), hematite and anhydrite compose the majority of Fe and S minerals, respectively. Higher atmospheric *P* leads to lower pH and may prevent formation of carbonates.

At the specified amount of volatilities, the *W/R* ratio is the major parameter that affects the redox state, secondary mineralogy, and speciation of coexisting oceanic water and the gas phase. The *W/R* ratio may represent thickness of the rock layer involved into the water-rock interaction. At lower *W/R* ratios, the mineral assemblage becomes

more reduced. For example, pyrrhotite and magnetite can be present instead of pyrite, anhydrite, and hematite. At high *W/R* ratios, acidic and oxidized (HCl-CO₂) solutions coexist with a quartz-rich rock formation. Note that a decrease in *W/R* ratio may also represent a vertical profile through suboceanic rocks. The uppermost layer would be rich in quartz, intermediate layers contain the assemblage observed in our nominal models (phyllsilicates, quartz, anhydrite, pyrite, carbonates, etc.), and lower layers are only slightly oxidized and hydrated.

Atmospheric composition. Our models produce a near-ocean atmosphere that contains mostly CO₂, H₂O, and N₂. Volume fractions vary as follows, CO₂, ~0.3-0.9; H₂O, ~0.01-0.6; N₂, ~0.02-0.15. Higher *T* leads to higher H₂O/CO₂ and H₂O/N₂ ratios. Higher *P* corresponds to lower H₂O/CO₂ and N₂/CO₂ ratios. In contrast, the formation of abundant carbonates at lower *W/R* ratios increases the N₂/CO₂ ratio. Low *W/R* ratios also favor formation of methane. However, methane becomes abundant only if a significant amount of H₂ is supplied from the interior and the synthesis of hydrocarbons is efficient.

Implications for subsequent history and Venus exploration: The evaporation of Venus' oceans could have caused local precipitation of chlorides atop hydrated rocks that contained quartz, carbonates, anhydrite, pyrite, and Fe(III) oxides. Subsequent greenhouse and/or endogenic heating(s) may have caused major dehydration and decarbonation, while some subsurface calcite could have equilibrated with Ca-silicates and CO₂. Anhydrite, pyrite, and Fe oxides may control abundances of S gases and the atmospheric redox state throughout history [5]. Quartz-rich, partially hydrated, and chloride-bearing rocks could be easily involved in anatexis. CaCl₂ and NaCl could form a eutectic (*T* = ~580°C) melt, which would affect lithospheric viscosity and convective heat transfer. The formation of Venus' channels [6], crater outflows, and alkali-rich rocks (Venera data) could have been related to this low-*T* and chemically active melt. If chlorides are present in channels, this would be an indication of aqueous processes on early Venus. Other indications would be an elevated concentration of Cl in alkaline rocks and the presence of schists, quartzites, or banded iron formations.

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