

COMPARISON OF THERMODYNAMIC CONDITIONS OF EARLY VENUSIAN ATMOSPHERE WITH THOSE OF THE EARLY EARTH AND MARS ATMOSPHERES. A. Pilchin^{1,*}, ¹ Universal Geoscience & Environmental Consulting, 205 Hilda Ave., #1402, North York, Ontario, Canada, M2M 4B1. (*arkadypilchin@yahoo.ca).

Introduction: Previous research shows that: temperature in the Solar Nebula at the distance of Venus, Earth and Mars before accretion was about 750-850 K, 600-700 K and 450-500 K, respectively, and at present is about 740 K, 290 K and 240 K, respectively [1,2,3]; ratio of real solar radiation to planetary radiation for Venus, Earth and Mars is now 0.011, 0.445, and 0.597, respectively (with all planets continuing to cool) [3]; early Earth atmosphere was composed of many layers stratified by density, primarily layers of H₂O, SO₂ and CO in supercritical conditions during accretion and formation of the magma ocean, and mostly layers of H₂O, SO₃ (at <873 K and H₂SO₄ at <700 K) and CO₂ (at <947 K) [3] during cooling of the atmosphere; the main components of the early Venusian atmosphere were similar to those of early Earth [4];

Methods: Thermodynamic methods used to estimate and analyze the composition of the early Earth [1,2,3] and Venusian atmospheres [4] were applied. The methods involve determining the densities of the primary atmospheric compounds under different P-T-conditions, their concentration, comparing them, and determining the different layers and their positions within the atmosphere.

Thermodynamic conditions and content of main components in the early Earth atmosphere: Due to significant content of crustal felsic and intermediate rocks, surface temperatures of Earth's magma-ocean were ≥ 1173 -1373 K, and could have been as high as 1200-1700 K [5]. Estimated partial pressure for main components of the early Earth atmosphere gave minimal values of [1,3]: 4.35 MPa (1MPa \approx 10 bars) for elemental F₂, 2.72 MPa for elemental Cl₂, 2.72 MPa for elemental sulfur, 5.44 MPa for sulfur as SO₂, 2.99 MPa for carbon as CO, 4.35 MPa for carbon as CO₂ and \sim 26-27 MPa for H₂O. The minimal atmospheric pressure was estimated as \sim 35 MPa [1,2,3].

Thermodynamic conditions and content of main components in the early Venus atmosphere: The mostly basaltic composition of crustal rocks of Venus and Mars requires surface temperatures of their magma-oceans ≥ 1273 -1473 K, but they could be considerably higher (e.g. 1773 K [6]). Different estimates of the water content on Venus gave: 4-525 m of global

equivalent layer (GEL) [7] (exerting a pressure of \sim 0.04-4.67 MPa); $\sim 2 \times 10^{20}$ kg (\sim 3.87 MPa) [8]; <10 MPa [9]; \sim 10 MPa [10]; 1-9 MPa [11]. There was definite presence of sulfur in early Venusian atmosphere, but its amount is difficult to determine. Much greater concentrations of SO₂ in the Venusian atmosphere than in the early Earth atmosphere means that the content of sulfur in Venus could be greater than on Earth, and the magmatic activity is much more intensive. Partial pressure of CO₂ on Venus at present was estimated at 9.1 MPa [6], which should be accepted as the minimal pressure of carbon oxides within the early Venusian atmosphere. Given all the facts and estimations, it appears reasonable to accept the value of \sim 15-20 MPa as minimal pressure of the early Venusian atmosphere above its magma-ocean, which is not high.

Thermodynamic conditions and content of main components in the early Mars atmosphere: Different estimates of H₂O content on Mars give: a GEL of 500 m or 300-1030 m [12] (\sim 1.87 MPa or 1.12-3.85 MPa); 600-2700 m GEL [13] (\sim 2.24-10.07 MPa); 540-2430 m GEL [14] (\sim 2.01-9.06 MPa); and >2000 m GEL [15] ($>$ 7.46 MPa); and the absolute minimum (present surface content of H₂O) is 137 m GEL [15] (\sim 0.51 MPa). Estimates of the SO₂ content in the sedimentary reservoir on Mars gave 2.3×10^{19} kg [16] (\sim 0.59 MPa). Estimates of partial pressure of the CO₂ content on Mars came to: 0.2-1.0 MPa [17]; \leq 1.0 MPa [18]; amount of magmatic carbon in Mars' crust plus mantle as 2×10^{18} - 2.5×10^{19} kg [19] exerting a partial pressure of \sim 0.12-1.51 MPa as CO or 0.19-2.37 MPa as CO₂; \sim 1.1-5.4 MPa as lost outgassed CO₂ [20]. The minimum atmospheric pressure above the Martian magma-ocean could then be within the range of \sim 3 and \sim 11 MPa (most likely greater than 5MPa).

Discussion and conclusions: Under temperature conditions of the magma-oceans on Earth, Venus and Mars, all of the most common carbonates, sulfides, sulfates, halides, hydrates, hydroxides, and many other compounds [1,2,3,] were unstable and decomposed forming the thick early atmosphere on each of the planets, mostly composed of S⁰, SO₂, SO₃, CO, CO₂ and

H₂O layers. The order of layers at the start of the solidifying magma-ocean on each of these three planets (excluding virtual layers of F₂, HF, Cl₂ and HCl; as being extremely active, they were re-distributed into the solid Earth very quickly) was from the bottom up as S⁰, CO, SO₃, SO₂, CO₂ and H₂O. The order of layers, as well as their thickness, would continue to change with atmospheric cooling on each planet.

Taking into consideration that the region of Venus's accretion within the solar nebula was relatively hot (750-850K); Venus was most likely able to collect more heat energy during accretion than Earth or Mars. Venus was under heavy bombardment during its early evolution, as any other planet, and it receives much more heat energy from the Sun than Earth or Mars. It is then likely that Venus never had a surface temperature lower than it currently has (~740K). This means that the Venusian surface never cooled below the temperature of water-ocean formation, which prevented the redistribution of carbon oxides from the atmosphere into solid rocks, as it takes place on Earth. This could also explain why Venus has the highest loss of water through hydrogen escape.

The real early atmospheric pressure on all three planets could be from a few times to orders of magnitude higher than the minimal estimates. For example, partial pressures of different atmospheric components depending on their estimated abundances could be as high as: up to 6 MPa or 21.5 MPa for carbon content on Earth; from ~1-3 to ~5-6 current water oceans on earth with ~24-25 MPa for each extra ocean [1]; 0.99-179.61 MPa for CO₂, 0.63-114.03 MPa for CO, and 22.0-734.0 MPa for SO₂ on Mars (for abundances by [21]); the maximum content of water on Mars could have been as great as 7.2×10^{21} kg [22] (~185.5 MPa) or 1.4×10^{22} kg [23] (~360.64 MPa); >20 MPa for CO₂ in early atmosphere on Venus [9]; 102.8 MPa as CO and 161.6 MPa as CO₂, and 1523.3 MPa for S⁰, 3046.6 MPa for SO₂, and 3808.25 MPa for SO₃ on Venus (for abundances by [24]).

Vast decreases of atmospheric pressure could have been caused by outgassing, in particular with the escape of hydrogen. The amount of outgassed H₂O and CO₂ from Mars was estimated [20] to be ~5.2–25.7 MPa and ~1.1–5.4 MPa, respectively; and ~1300 m of GEL (~11.57 MPa) of H₂O is estimated to have been lost from Venus through hydrogen escape [12].

To analyze the hydrogen escape, deuterium-to-hydrogen (D/H) ratio pairs W₀ and W_R, H₀ and H_R, and D₀ and D_R were accepted as initial and remaining values of water, hydrogen and deuterium on a planet.

Based on analysis of published estimated values of D/H ratios, the ratio of $16-20 \times 10^{-6}$ within the protoplanetary nebula before accretion was accepted as D₀/H₀; and values of $(1.49-1.56) \times 10^{-4}$, $(1.6-2.5) \times 10^{-2}$, and $(7.8 - 8.1) \times 10^{-4}$ were accepted as D_R/H_R ratios for Earth, Venus, and Mars, respectively. If we accept that change in deuterium content was negligible (D₀ ≈ D_R; any escape of deuterium would only increase the amount of escaped hydrogen), relative change of the ratio over any specific period of time would be (D₀/H₀)/(D_R/H_R) = H_R/H₀. Substitution of accepted values for D/H ratios shows that only 10.2-13.4 %, 0.060-0.125 %, and 1.98-2.56 % of hydrogen remains on Earth, Venus, and Mars, respectively. Assuming that all escaped hydrogen was previously contained in water (maximum loss of water), there should be a relation W_R/W₀ ≈ H_R/H₀. This allows to estimate the maximum loss of water as 86.6-89.8 %, 99.875-99.94 %, and 97.44-98.02 % from the initial water content on Earth, Venus, and Mars, respectively. This also demonstrates how pressure within the atmospheres of early Earth, Venus and Mars was much greater than estimated minimal values.

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