

clouds seen in the IR, such as cold collar, hot dipole, and polar cap, are not observed in UV. The IR data show  $H = 3-5$  km on the average for high latitudes outside the cold collar, and the mixing ratio varies from 100–200 ppb in hot dipole to 1000 ppb in inhomogeneous regions with retrieved high diffuse clouds. We find inside the cold collar  $f \sim 1-10$  ppb and  $H \sim 1$  km. The comparison of IR and UV data shows that the vertical profile of  $SO_2$  may be more complex than our two-parametric model, and  $H$  decreases with height at  $h > 69$  km. In this case the differences in  $H$  are explained by viewing angle differences between the observations and the differential opacity at UV and IR. Temporal variations may also contribute.

Latitudinal averaged column density at 62 km (near observed upper boundary of clouds at high latitudes) obtained from the IR is about  $10^{19}$   $cm^{-2}$  at low latitudes and it increases to  $10^{20}$   $cm^{-2}$  at high latitudes.

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#### OUTGASSING HISTORY OF VENUS AND THE ABSENCE OF WATER ON VENUS.

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Similarities in the size and mean density of Earth and Venus encourage the use of Earth-analogue models for the evolution of Venus. However, the amount of water in the present Venus atmosphere is miniscule compared to Earth's oceans [e.g., 1–3]. The "missing" water is thus one of the most significant problems related to the origin and evolution of Venus and has been discussed extensively [e.g., 2–14]. Lewis [4] proposed that Venus accreted with less water, but this has been challenged [10,13]. The high D/H ratio in Venus' atmosphere is consistent with an earlier water mass more than 100 times higher than at present conditions and is often cited to support a "wet" Venus, but this amounts to only 0.01 to 0.1% of the water in terrestrial oceans [5,12,15, and Table 1] and the high D/H ratio on Venus could easily reflect cometary injection [14]. Nevertheless, many authors begin with the premise that Venus once had an oceanlike water mass on its surface, and investigate the many possible mechanisms that might account for its loss [e.g., 2,6–12]. In this paper we propose that Venus degassed to a lower

degree than the Earth and never had an oceanlike surface water mass.

#### Lower degree of outgassing for Venus and its consequences:

1.  $^{40}Ar$  in the atmosphere of Venus and Earth.  $^{40}Ar$  in Venus' atmosphere is  $\sim 1/4$  of that in Earth's atmosphere, when normalized by planetary mass and ignoring  $^{40}Ar$  stored in Earth's continental crust [2,16]. Since K/U and Th/U ratios and K contents in venusian crustal rocks are similar to those in terrestrial rocks [17,18], less  $^{40}Ar$  in Venus' atmosphere implies a lower degree of outgassing for  $^{40}Ar$  [16].  $^{40}Ar$  in Earth's atmosphere represents 62% degassing of the time-integrated  $^{40}Ar$  budget of DM (degassed mantle), but  $^{40}Ar$  in Venus' atmosphere represents only 15% degassing of its DM, if the relative masses of DM in Venus and Earth are similar.

2. Comparison of  $N_2$ ,  $CO_2$ , and  $H_2O$  on Earth and Venus. Previous workers noted that the  $CO_2/N_2$  ratio of surface reservoirs on Venus and Earth are nearly identical when  $CO_2$  stored in Earth's continental crust is included [2,9]. However, such comparisons did not take into account the effect of recycling  $CO_2$  back to Earth's DM, which may be a significant part of the Earth's  $CO_2$  budget [19]. The present venusian crust is hot (surface temperature 740 K) and the formation of carbonates requires liquid water, at least on the Earth, hence the venusian crust is probably a poor repository of volatiles. Most of the outgassed volatiles from Venus' DM are, therefore, likely to reside in the atmosphere. Hence, subduction on Venus, if it occurs, should have little effect on surface  $CO_2$  budget, analogous to the case for  $N_2$  on Earth. In this context, the atmospheric composition of Venus can be used to estimate total outgassing from the interior.

Table 1 compares the volatile inventory of Earth, which is corrected for recycling, with that of Venus. Although the atmosphere of Venus has twice as much  $N_2$  as the AC\* of Earth, it has only about half as much  $CO_2$ , and orders of magnitude less water. This sequence is the inverse of the solubilities of these volatile components in basaltic melts (Table 1). In the context of a solubility-controlled degassing model, the relative difference in  $N_2$ ,  $CO_2$ , and  $H_2O$  on Earth and Venus can perhaps be explained by a lower degree of outgassing of Venus compared to Earth.

For solubility-controlled equilibrium outgassing we can write the following equation [20]

$$c_i M + \frac{P_i V_g}{RT_m} = c_i^0 M_0 \Rightarrow \frac{c_i^0}{c_i} = 1 + \frac{V_g}{K_i RT_m M} \Rightarrow$$

$$K_i \left( \frac{1}{1-F_i} - 1 \right) = K_j \left( \frac{1}{1-F_j} - 1 \right)$$

where  $c_i^0$  and  $c_i$  are the initial and final concentrations of gas species  $i$  in the magma,  $M_0$  and  $M$  are the initial and final mass of the magma

TABLE 1. Comparison of volatile inventory of Earth and Venus.

	$H_2O$	$CO_2$	$N_2$
Solubility (in mol $g^{-1}$ bar $^{-1}$ )	$1.8 \times 10^{-6}$	$1.8 \times 10^{-8}$	$\sim 3.6 \times 10^{-9}$
AC* of Earth (in moles)	$8 \times 10^{22}$	$(2.4^{+0.9}_{-0.6}) \times 10^{22}$	$(2.0 \pm 0.2) \times 10^{20}$
Atm of Venus (in moles)	$10^{16}$ to $10^{17}$	$(1.1 \pm 0.1) \times 10^{22}$	$(4.3 \pm 0.5) \times 10^{20}$

Solubility data are those in basaltic magma at 1 kbar partial vapor pressure and 1200°C. Source of data: water [21];  $CO_2$  [22,23]; and  $N_2$  [24], atm of Venus [1–3]. AC\* (atm + crust) plus a correction for recycling (recycling of water is ignored since the comparison is not affected by augmenting water on Earth's surface).

( $M=M_0$ ),  $P_i$  is the partial pressure and  $V_g$  is the total volume of the gas phase,  $R$  is the universal gas constant and  $T_m$  is the magma temperature,  $K_i = c_i/P_i$  where  $K_i$  is the solubility of  $i$  in the melt, and  $F_i (=1-c_i/c_i^0)$  is the degree of degassing.

If we assume that the outgassing of Venus can be approximately described by this equilibrium degassing formulation as is the case for Earth [20], then we can estimate the degree of outgassing for different volatile components in Venus by reproducing the present atmospheric  $\text{CO}_2/\text{N}_2$  ratio from the initial ratio, assumed to be the same as the initial ratio of the Earth. We note that the  $\text{H}_2\text{O}/\text{N}_2$  ratio cannot be reproduced exactly due to loss of water from Venus' atmosphere. Uncertainties in the initial  $\text{CO}_2/\text{N}_2$  ratio for Earth and the present  $\text{CO}_2/\text{N}_2$  ratio in Venus' atmosphere (and in the degassing species), combine to permit large ranges in the degrees of outgassing for each of the components. All possible solutions, however, suggest very low degrees of degassing for water (less than 1%), if  $\text{H}_2\text{O}$  is the major degassing species for water. A "best" solution is shown in Table 2 with 0.2% outgassing for  $\text{H}_2\text{O}$  from the DM of Venus. (The total amount of  $^{40}\text{Ar}$  in Venus' atmosphere also provides, in principle, a constraint on the degree of degassing, but it is difficult to utilize the constraint in a quantitative way due to the contribution of continental degassing to  $^{40}\text{Ar}$  in Venus' atmosphere [16] and the fact that the degree of degassing for  $^{40}\text{Ar}$  is not equivalent to that for  $^{36}\text{Ar}$ .)

The fractionation effects on volatile-element ratios during outgassing can be likened to that on incompatible and compatible elements during the partial melting process, although we hasten to emphasize that such a comparison should not be taken to imply that inferred low degrees of degassing for Venus are equivalent to, or a result of, lower degrees of melting. At low degrees of partial melting, large proportions of incompatible elements (such as K), and only very small proportions of the compatible elements (such as Ni), partition into the melt. At high degrees of melting, large proportions of both compatible and incompatible elements go into the melt. Similar effects are produced during different degrees of degassing. The degree of outgassing for Earth is very high, so that even water has been outgassed to ~50%. The degree of outgassing for Venus is low, hence only incompatible volatiles have outgassed significantly, while  $\text{H}_2\text{O}$ , a very compatible volatile in silicate melts (100 times more soluble than  $\text{CO}_2$  and ~500 times more soluble than  $\text{N}_2$  [21-24]), remains predominantly within the mantle.

To illustrate the implication of the solubility-controlled outgassing model for Venus, we first assume that Venus accreted the same amount of water as the Earth although lower or higher amounts of initial water are possible and consistent with the model. Taking the "best" solution shown in Table 2, only ~0.2% of this water has been outgassed from the Venus' mantle to its atmosphere. The total amount of outgassed water is  $\sim 3 \times 10^{20}$  mol or ~0.4% of the water mass now present in terrestrial oceans, enough to generate 13 m of water on the surface of Venus if it were all present at the same time. This estimate is similar to an independent estimate of 8 m of water [15]. There is now  $10^{16}$  to  $10^{17}$  mol of water in Venus' atmosphere, which requires a time-integrated escaping rate of  $7 \times 10^{10}$  mol/yr, ~30 times the present loss rate [7,14]. Such losses are capable of generating a 100-fold enrichment in the D/H ratio over Venus' history [5]. The important point is that Venus never had much water at its surface, and the absence of a globe-encircling ocean on Venus must have had profound effects on its geological evolution, making it very different from that of Earth.

**Discussion:** It is difficult to explain why Venus outgassed to a lower degree than the Earth. One possibility is that a lower degree of degassing reflects the lack of plate tectonics on Venus [16]. It is

TABLE 2. Calculated degree of outgassing from DM of Earth (corrected for recycling) and Venus.

	$\text{H}_2\text{O}$	$\text{CO}_2$	$\text{N}_2$
Earth	0.45	0.98	0.997
Venus	0.002	0.15	0.50

often suggested that present heat losses on Venus are mostly via hot spots [e.g., 25,26], as opposed to spreading ridges. The degree of melting at hot spots may be higher on average than that at normal ocean ridges, at least for the Earth [27]. The elevated surface temperatures on Venus, if it is more than a very recent phenomenon, also serves to elevate the geotherm and hence increase the degrees of melting. If so, the average degree of melting on Venus may be higher than on Earth, leading to lower volatile concentrations in the undegassed magma. If the rates of magma production or heat dissipation on Venus and the Earth are the same, the lower initial concentration of volatiles results in a decreased level of degassing on average because a column of magmas must ascend closer to the surface before it reaches saturation and begins to degas.

The slow outgassing is probably a positive-feedback process. If the initial outgassing is slow, very little water is outgassed. The deposition of carbonates requires water as a medium, so  $\text{CO}_2$  quickly accumulates in the atmosphere. The surface temperature then rises due to the greenhouse effect, which then impedes subduction by increasing the buoyancy of the lithosphere [25,26,28-30]. This results in even slower outgassing, and hence higher surface temperatures.

In summary, there are two major lines of evidence to support our contention that Venus outgassed to a lower degree than did the Earth. (1) There is less  $^{40}\text{Ar}$  in Venus' atmosphere than in the terrestrial atmosphere. This implies that the time-integrated degree of degassing for Venus is lower than that for Earth. (2) When recycling effects are corrected for, the major volatiles of both planets show a relationship between solubility and mass on the surface. This relationship is consistent with outgassing on both planets being controlled by melt-vapor partitioning, provided that Venus outgassed to a lower degree. In the context of this scenario, the absence of water on Venus' surface is just the most conspicuous expression of a lower degree of outgassing than Earth. We note that our model can be tested in the future for other volatile components that have solubilities between those of  $\text{CO}_2$  and water, or higher than that of water. Venus probably never had much water on its surface, even if Venus and Earth accreted the same amount of water. Therefore, there is no compelling need to explain the loss of massive water quantities from Venus' atmosphere.

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