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# Comparison of carbon, nitrogen and water budgets on Venus and the Earth

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## Abstract

Carbon, nitrogen and water abundances at the surfaces of Earth and Venus are compared in order to investigate the distributions of these elements between fluid and solid envelopes in both planets. The atmosphere of Venus contains about twice more carbon ( $1.25 \times 10^{20}$  kg of C) and nitrogen ( $4.8 \times 10^{18}$  kg of N) than the atmosphere, hydrosphere and sediments of the Earth ( $5.4 \times 10^{19}$  kg of C and  $3 \times 10^{18}$  kg of N). After scaling to the planetary masses, surface excesses of  $1 \times 10^{20}$  kg of C and  $2.7 \times 10^{18}$  kg of N are calculated for Venus relatively to the Earth. The simplest proposed explanation is the storage of 25 ppm of C and 0.7 ppm of N in the Earth mantle due to lithospheric subduction, a mechanism not operating on Venus. Following the same line of arguments, the Earth has an excess surface water of about  $1.2 \times 10^{21}$  kg of H<sub>2</sub>O, when compared to Venus. Under the hypothesis of a primordial sizable water mass on Venus, thermodynamic modeling of mineral stabilities reveals that hydrous minerals are stable at the  $P$ – $T$  conditions of both the surface and the deep crust of Venus, and thus could be the carriers of the missing Venusian water. A combination of crustal hydration and hydrogen escape processes may explain the present-day low amount and high deuterium/hydrogen (D/H) ratio ( $2.5 \times 10^{-2}$ ) of water in the Venusian atmosphere relatively to the Earth's hydrosphere ( $1.55 \times 10^{-4}$ ). Alternatively, if the high D/H ratio of Venus only resulted from hydrogen escape, the reservoir of remaining oxygen must have been involved in the oxidation of a rock layer of about 50 km in depth. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Venus; Earth; water balance; D/H; carbon; nitrogen; mass balance

## 1. Introduction

The abundance and distribution of light ele-

ments such as H, C, N and O during the early evolution of terrestrial planets is critical for the emergence of stable atmosphere and hydrosphere that will generate climatic conditions propitious to the birth and development of life. Among the three terrestrial planets of our solar system having an atmosphere, the Earth is unique in possessing a thick layer of water averaging to 3700 m in depth that covers 70% of the surface and a CO<sub>2</sub>-poor atmosphere (370 ppmv) that contrib-

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utes to maintain cool and stable climatic conditions with an average surface temperature of 288 K. Venus with a size comparable to the Earth is commonly considered as its ‘twin sister’. However, the average surface temperature is maintained at 735 K as the consequence of strong greenhouse conditions generated by a thick atmosphere composed of 96.5% of CO<sub>2</sub> and about 30 ppmv of water. According to Wetherill [1], in the 0.5–1.5 AU belt of the solar system, volatile mixing and homogenization likely occurred during collisions among planetesimals. Except if Earth and Venus were formed with different parent bodies or in very different proportions, we may question why the compositions of fluid reservoirs appear to be so different of each other?

This study explores plausible mass distributions of carbon, nitrogen, and water between the surface and the deep layers of the Earth and Venus by using well constrained elemental abundances measured in superficial reservoirs of both planets. The aim of the mass balance approach is to provide boundary conditions for the early chemical evolution of planetary atmospheres that lead on one hand to a CO<sub>2</sub>-poor Earth atmosphere and on the other hand to an apparently ‘dry Venus’.

## 2. Carbon and nitrogen

The atmosphere of Venus contains  $1.25 \times 10^{20}$  kg of carbon and  $4.8 \times 10^{18}$  kg of N ([2] and references therein; Table 1). At the surface of the

Table 1  
Inventory of carbon, nitrogen, oxygen and water abundances in Venus and Earth surface reservoirs

Mass of reservoirs	Earth	Venus
Bulk planet (kg)	$5.97 \times 10^{24}$	$4.87 \times 10^{24}$
Superficial C (kg)	$5.4 \times 10^{19a}$	$1.25 \times 10^{20}$
Superficial H <sub>2</sub> O (kg)	$1.41 \times 10^{21b}$	$6 \times 10^{15}$
Atmospheric N (kg)	$2 \times 10^{18}$	$4.8 \times 10^{18}$
Superficial N (kg)	$3 \times 10^{18a}$	$\geq 4.8 \times 10^{18}$
C/N mass ratio	18	26
C/H mass ratio	0.69	$\approx 10^5$

Data sources from Taylor and McLennan [42], Pepin [43] and Taylor [2].

<sup>a</sup>Sediments+atmospheric gases+dissolved aqueous species.

<sup>b</sup>Ocean water.

Table 2

Inventory of carbon and hydrogen isotopic compositions of Venus and Earth reservoirs

Reservoirs	D/H	<sup>13</sup> C/ <sup>12</sup> C
Venus (atmosphere)	$2.5 \times 10^{-2}$	0.01120
Bulk Earth	$1.49(\pm 0.03) \times 10^{-4}$	0.01118
Earth (carbonates)	–	0.01124
Earth (organic matter)	–	0.01096
Earth (hydrosphere)	$1.55 \times 10^{-4}$	0.01123

Data sources from Galimov et al. [44], Hoefs [45], Donahue et al. [46], Schidlowski [4], Taylor [2], Lécuyer et al. [47] and Donahue [21].

Earth, carbon is stored in two main reservoirs that are carbonates (80 wt%) and organic matter (20 wt%). Various estimates of the total amount of carbon contained in these two reservoirs range from  $5.4 \times 10^{19}$  [3,4] to  $8.7 \times 10^{19}$  kg [5–7]. A recent estimate of  $7.5 \times 10^{19}$  kg by Berner [8] indicates that the Earth’s surface carbon inventory is known with an uncertainty of about 30%. This should be kept in mind for the meaning of further calculations, indeed we used the low estimate of  $5.4 \times 10^{19}$  kg which implies maximum differences between the carbon budgets of the two planets.

The main reservoir of nitrogen is the atmosphere ( $2 \times 10^{18}$  kg of N) whereas seawater nitrates constitute only a minor contribution ( $3.7 \times 10^{16}$  kg of N) which can be ignored for mass balance considerations (Table 1). We consider that there are no significant crustal Venusian reservoirs of C and N, and consequently that their atmospheric abundances may be used to estimate primordial abundances at the Earth surface. It is indeed remarkable that the carbon isotope ratio of the Venusian atmosphere is similar to the Earth surface ratio (Table 2) when combining the weighted  $\delta^{13}\text{C}$  values of carbonates and organic matter [9]. A linear mass scaling law is used to compare the elemental abundances (Table 1) since the mass of Venus is 82% of the Earth’s mass. Apparent surface excesses of  $1 \times 10^{20}$  kg of C and  $2.7 \times 10^{18}$  kg of N are derived for Venus relatively to the Earth. The simplest hypothesis is to consider that these missing light elements have been buried in the deep Earth by lithospheric subduction.

On Earth, carbon is mainly recycled into the mantle as hydrothermal carbonates veining the

oceanic basaltic crust and its flux is estimated close to  $10^{11}$  kg a<sup>-1</sup> [10,11] in the same order of magnitude as the carbon flux at oceanic ridges [10–12]. The difference between superficial reservoirs of Venus and the Earth could indeed be achieved by a carbon flux toward the mantle 30% higher than the carbon flux extracted from the mantle at mid-ocean ridges, i.e. an average flux of  $3 \times 10^{10}$  kg a<sup>-1</sup> into the mantle integrated over 3.5 Gyr. In this way, the subducted component of superficial mostly inorganic carbon would represent a mean concentration of  $25 \pm 5$  ppm of carbon in the Earth's mantle which corresponds to about 10 or 30 wt% of the carbon reservoir in the primitive mantle depending on estimates provided by Javoy [13] and Canil et al. [14], respectively. One direct consequence of this mass balance calculation concerns the  $\delta^{13}\text{C}$  of the primordial mantle that should be close to  $-15\%$  compared to the present-day  $\delta^{13}\text{C}$  of upper mantle carbon estimated at  $-4\%$  [10,15] and that became progressively <sup>13</sup>C-enriched by mixing with carbon derived from marine carbonates ( $\delta^{13}\text{C} \approx 0$ ; Table 2). The mixing of primordial and surface carbon at a Gyr time scale could be a component of the observed spectrum of carbon isotope ratios of diamonds [16,17].

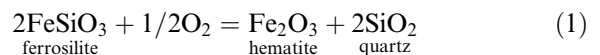
The observed deficit of nitrogen in the Earth's atmosphere compared to Venus is partly explained by the growth of the continental crust that contains from 50 to 60 ppm of nitrogen [18], thus constituting a reservoir of  $10^{18}$  kg. Another sink could be the subduction of about  $1.4 \times 10^{12}$  kg a<sup>-1</sup> of marine sediments [19] that contains 0.015% of organic nitrogen in average [20]. This would result in another  $7.4 \times 10^{17}$  kg of nitrogen that could be injected over a period of 3.5 Gyr into the mantle. A total amount of about  $2 \times 10^{18}$  kg of N removed from the terrestrial atmosphere is thus estimated, and constitutes two thirds of the calculated surface deficit relatively to Venus. The apparent remaining missing nitrogen could be due to uncertainties in the amount of N stored in the continental crust or to varying sizes in the fluxes of subducted N through time. The  $3 \times 10^{18}$  kg of nitrogen, potentially subducted into the mantle, correspond to an average concentration of 0.7 ppm in the mantle

which represents no more than 3 wt% of the primitive mantle nitrogen abundance according to Javoy [13]. Consequently, the difference between the C/N ratios for the superficial reservoirs of the Earth and Venus (Table 1) could be more likely attributed to fractionation processes occurring during subduction of lithospheric plates with relatively more injection of C than N in the deep Earth.

### 3. Water

The total mass of water at the surface of the Earth can be identified to the oceanic reservoir which is  $1.41 \times 10^{21}$  kg. Using the same scaling law as above, the initial amount of water on Venus should be close to  $1.2 \times 10^{21}$  kg. The present-day mass of water at the surface of Venus is only of  $6 \times 10^{15}$  kg ([21]; Table 1). Does this low amount of water require that the two planets had initially very different bulk H contents? This is rather unlikely because collisions among planetesimals would have produced volatile mixing and homogenization in the region from 0.5–1.5 AU, leading to similar volatile contents in both Earth and Venus [1].

The high deuterium/hydrogen (D/H) ratio of  $2.5 \times 10^{-2}$  measured in the atmosphere of Venus [22,23] suggests that the planet may have sheltered at its surface more than 100 times as much water as it has in its present atmosphere [24]. A common hypothesis is to consider that primordial water has been lost by photodissociation followed by hydrodynamic escape of hydrogen [21,25–28]. If this surface water disappeared through photodissociation and escape of hydrogen towards the interplanetary space, a water mass of  $1.2 \times 10^{21}$  kg would have left  $1.07 \times 10^{21}$  kg of molecular oxygen in the Venusian atmosphere. At the temperatures of Venus' surface, oxidation of basaltic rocks can be modeled as:



the ferrosilite, hematite and quartz constituents being dissolved in relevant minerals (e.g. pyroxenes, spinel). Thermodynamic modeling of Eq. 1

using a free-energy minimization procedure [29] indeed predicts the stability of hematite at  $P$ - $T$  conditions of the Venusian surface (Fig. 1). The stoichiometry of this reaction implies the oxidation of  $5.3 \times 10^{22}$  to  $6.9 \times 10^{22}$  kg of basalt assuming an average concentration of 7–9% of FeO in Venusian basalts [30] which represents an equivalent crustal thickness of  $50 \pm 10$  km. Lewis and Prinn [31] reached a similar conclusion on the basis of mass balance calculations also involving oxidation of ferrous iron into ferric iron. Oxidation of Venusian surface rocks with the presence of ferric minerals has already been proposed by Pieters et al. [32] on the basis of their analysis of multispectral images obtained by Venera 13.

The hypothesis of a primordial sizable water mass on Venus also led to the investigation of possible hydration reactions of basaltic rocks by analogy with hydrothermal seawater–rock interactions occurring on Earth. Thermodynamic calculations have been therefore performed in  $P$ - $T$  ranges that satisfy both surface ( $T = 660$ – $760$  K;  $P = 48$ – $100$  bar; [33]) and subsurface (thermal gradient =  $10$ – $30$  K km<sup>-1</sup> down to 40 km; [34,35]) Venusian conditions. For example, serpentines, talc and chlorites, that contain from 10 to 15 wt% of H<sub>2</sub>O, are stable under an atmosphere of

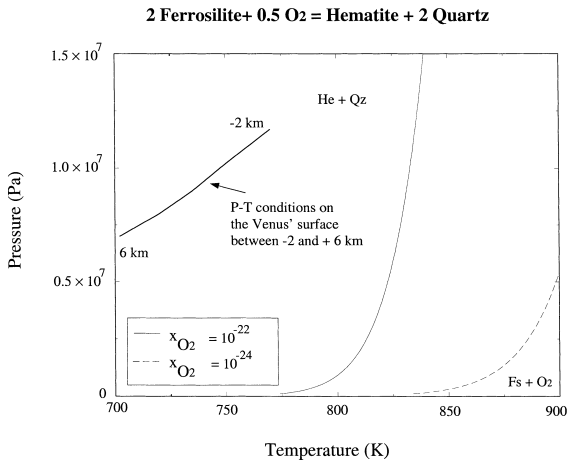


Fig. 1. Stability curves of hematite and the  $P$ - $T$  conditions at the surface of Venus for different mol fractions of molecular oxygen in the atmosphere. Thermodynamic data used to compute these curves are from Robie et al. [48]. Equation of the state for molecular oxygen is taken from Holland and Powell [49].

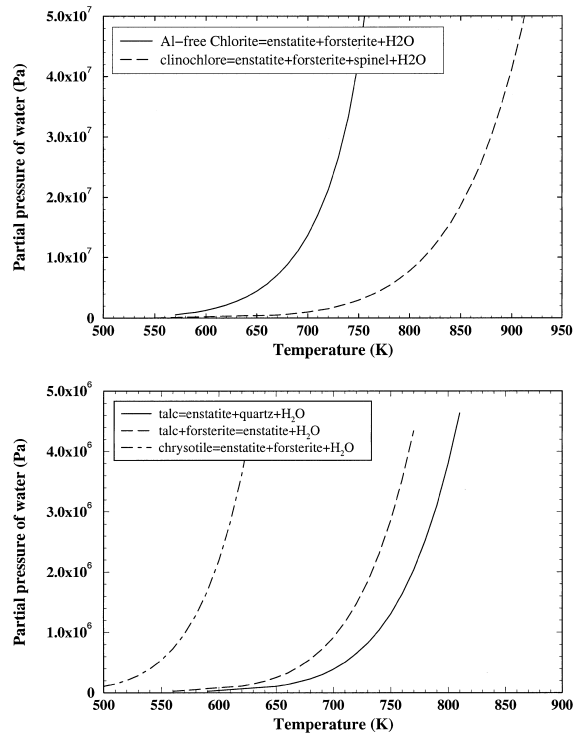


Fig. 2. Stability curves of chlorite, serpentine and talc considering various phase reactions that are compatible with the  $P$ - $T$  conditions at the surface of Venus. Thermodynamic data used to compute these curves are from Holland and Powell [50].

100 bar of CO<sub>2</sub> when water is abundant (Fig. 2). Mg-amphibole (tremolite) and phlogopite, that contain about 4 wt% of H<sub>2</sub>O, are also stable even when water represents no more than a few percent of the fluid envelope (Fig. 3). Hydration of 10–30 km of Venusian crust is required for trapping  $1.2 \times 10^{21}$  kg of water in these metamorphic hydrous minerals depending on their proportions. Phlogopite may be considered only as a minor phase according to the low-K basaltic compositions [30]. Tremolite could be the last hydrous mineral to crystallize at the surface of Venus leaving a residual atmospheric water mass that ranges between 1 and  $2 \times 10^{18}$  kg. MacDonald and Fyfe [36] have shown that 1 Myr is required for the serpentinization of a 1 km thick basaltic layer at 300°C. At surface Venusian temperatures, the rate of serpentinization is expected to be enhanced by at least one order in magnitude, thus likely result-

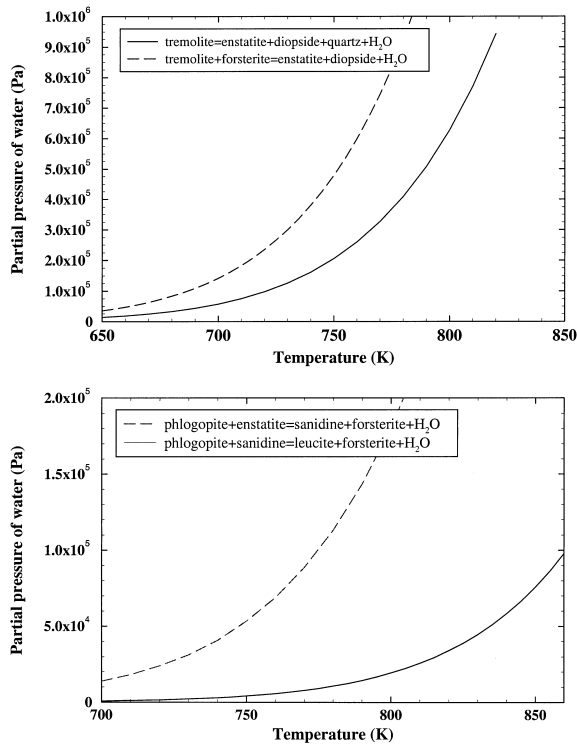


Fig. 3. Stability curves of tremolite and phlogopite considering various phase reactions that are compatible with the  $P$ – $T$  conditions at the surface of Venus. Thermodynamic data used to compute these curves are from Holland and Powell [50].

ing in a characteristic time of 1 Myr for the hydration of 10 km of Venusian basaltic crust. Extensive resurfacing of the planet by volcanic activity during the last 400 Myr [37–39] could also enhance deep crustal hydration, possibly generating silica-rich magmas in some locations instead of basalts.

During hydrothermal reactions in the temperature range from 500 to 800 K, residual water is deuterium-enriched at the expense of the initial reservoir of free-water, the fractionation factor,  $\alpha$ , between OH-bearing minerals (amphiboles) and water is [40]:

$$\alpha_{r-w} = \frac{R_r^f}{R_w^f} = 0.935 \quad (2)$$

The effect of a D/H fractionation occurring between water and hydrated basalts on the D/H

ratio of the residual water may be readily tested with the following mass balance equation that describes a batch equilibrium mechanism of both hydration and isotopic fractionation between given masses of rock and water:

$$M_w^i \cdot X_w \cdot R_w^i + M_r^i \cdot X_r^i \cdot R_r^i = M_w^f \cdot X_w \cdot R_w^f + M_r^f \cdot X_r^f \cdot R_r^f \quad (3)$$

where  $M$  is the mass,  $X$  the molar fractions of hydrogen in water (w) or rock (r),  $R$  the D/H ratios before hydration reaction (i) and at batch equilibrium (f). The following data have been selected considering that tremolite is the dominant mineral that replaced 30 km of basalts equivalent to  $3 \times 10^{22}$  kg:  $M_w^i = 1.2 \times 10^{21}$  kg,  $M_w^f = 1-2 \times 10^{18}$  kg,  $M_r^i = M_r^f = 3 \times 10^{22}$  kg,  $R_w^i = 0.000155$ ,  $X_w = 1/9$ ,  $X_r^f = 2/812$ , and if we neglect the amount of water, likely very small, in primordial Venusian basalts ( $X_r^i = 0$ ), Eq. 3 is reduced to:

$$R_w^f = \frac{M_w^i \cdot X_w \cdot R_w^i}{M_w^f \cdot X_w + M_r^f \cdot X_r^f \cdot \alpha} \quad (4)$$

Solving Eq. 4 leads to a D/H ratio of residual water of  $3.0 \times 10^{-4}$ , which is about twice the initial ratio (SMOW hypothesis). Even if the hydration mechanism could be more complex than a simple batch equilibrium process, it cannot explain the 160-fold enrichment observed in the present-day Venusian atmosphere. However, hydrogen escape of residual water from the atmosphere may be associated with hydration processes to produce the D-rich atmosphere. The remaining 80-fold enrichment may be tested using the equations given by Gurwell [41] and Donahue [21] that describe D and H behaviors during hydrogen escape. We emphasize that the thermodynamic calculations of crust hydration provide an independent constraint for models of hydrogen escape. Using our calculated amount of initial remaining water in the range  $1-2 \times 10^{18}$  kg, computation of the equations (see Fig. 4 for detailed explanations) reveals that photodissociation and escape processes over 2 Gyr may explain the present-day mass of  $6 \times 10^{15}$  kg of atmospheric water with a D/H ratio of  $2.5 \times 10^{-2}$ . It is noteworthy that the calculated initial water mass of about

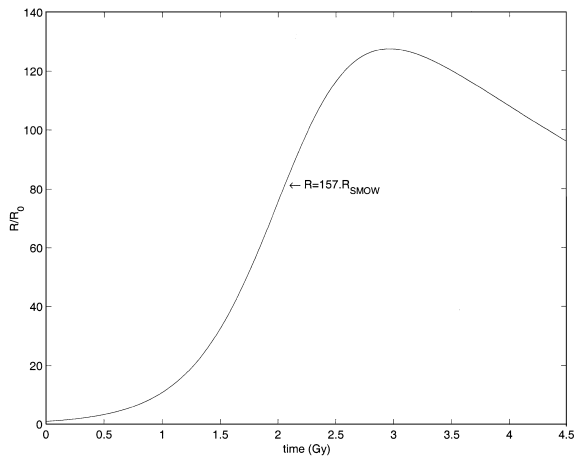


Fig. 4. Time dependence of the D/H ratio during hydrogen escape from Venus calculated from equations 1–8 given in [21]. The D/H ratio before escape,  $R_0 = 3 \times 10^{-2}$ , and the ratio between water masses before and after hydrogen escape,  $H_0/H_1 = 150$ , are fixed by the results of thermodynamic calculations of crust hydration. The computed curve has been obtained using the following parameter values: the escape flux of hydrogen;  $\Phi_1 = 0.7 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ , the source flux;  $P_1 = 0.5\Phi_1$ , and the fractionation factor;  $f = 0.1$ . These parameters are in the ranges of calculated values that are respectively  $0.7\text{--}3.3 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ ,  $0.1\Phi_1\text{--}0.44\Phi_1$ , and 0–1 ([21], and references therein).

$10^{18} \text{ kg}$  corresponds to the lower limit of the range ( $10^{18}\text{--}10^{20} \text{ kg}$ ) defined by Donahue [21] on the basis of various modeling results of hydrogen escape.

Therefore, we consider that the low amount of Venusian water atmosphere and its high D/H ratio are compatible with a combination of crustal hydration and hydrogen escape. In this scenario, oxidation processes are more limited than in the case of a global hydrogen escape without hydration reactions, and the corresponding crustal thickness of oxidized rocks is only a few meters.

#### 4. Conclusions

A comparison of carbon, nitrogen and water abundances at the surface of the Earth and Venus leads to conclude that these two planets likely had similar primitive atmospheres which reacted differently with the solid envelopes. The capability of

the Earth to maintain at its surface a thick layer of liquid water resulted in a major long-term storage of carbon and nitrogen in the continental crust, oceanic platforms and deep mantle. As the result of 3.5 Gyr of lithospheric subduction on Earth, at least 10% of mantle carbon and less than 3% of mantle nitrogen originated from the surface.

Assuming the hypothesis of the early presence of a Venusian reservoir of water comparable in size to that on Earth, thermodynamic modeling of mineral stabilities reveals that chlorites, serpentines, tremolite and phlogopite are stable at the  $P\text{--}T$  conditions of both the surface and the deep crust of Venus, and thus could be the carriers of the missing Venusian water. The low amount of present-day water in the Venusian atmosphere and its high D/H ratio are in fact not incompatible with a combination of crustal hydration and hydrogen escape processes. Alternatively, if the high D/H ratio of  $2.5 \times 10^{-2}$  of Venus atmospheric water only resulted from hydrogen escape after photodissociation of water, the huge reservoir of remaining oxygen must have been involved in the oxidation of a rock layer as deep as 50 km in depth to match the observed present-day very low amounts of molecular oxygen in the atmosphere.

The Venusian crust could thus be either a major reservoir of water or strongly oxidized, and in both cases, these reactions would deeply modify its rheology and seismic properties. Interpretations of spectroscopic data obtained during the Venera and Magellan missions should be viewed keeping in mind that significant volumes of Venusian rocks can be either strongly oxidized or hydrated.

If more mineralogical data became available about the Venusian crust, important conclusions could be drawn:

- if superficial rocks are found neither strongly oxidized nor massively hydrated, different accretion histories will have to be invoked for Earth and Venus;
- if massively oxidized rocks are discovered, this will support the important role of photodissociation of water, and hydrogen hydrodynamic

escape for explaining the low water content of Venus atmosphere

- if massively hydrated rocks are observed, it will be consistent with the scenario of extensive high-temperature hydrothermal reactions that took place between the crust and a primordial ocean during the early history of Venus.

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## References

- [1] G.W. Wetherill, Accumulation of the terrestrial planets and implications concerning lunar origin, in: W.K. Hartmann et al. (Eds.), *Origin of the Moon*, Lunar and Planetary Institute (1986) 519–550.
- [2] S.R. Taylor, *Solar System Evolution: A new perspective. An inquiry into the chemical composition, origin, and evolution of the solar system*, Cambridge University Press, Cambridge, 1992, 307 pp.
- [3] J. Hoefs, Isotope geochemistry of carbon, in: H.-L. Schmidt, H. Forstel, et al. (Eds.), *Stable Isotopes*, Elsevier Scientific Publishing Company, Amsterdam (1982) 103–113.
- [4] M. Schidlowski, A 3800-million-year isotopic record of life from carbon in sedimentary rocks, *Nature* 333 (1988) 313–318.
- [5] A.B. Ronov and A.A. Yaroshevsky, Chemical composition of the Earth's crust, in: P.J. Hart (Ed.), *The Earth's crust and upper mantle*, Am. Geophys. Union, Washington (1969) 37–57.
- [6] H.D. Holland, *The chemistry of atmosphere and oceans*, J. Wiley and sons, New York, 1978, 351 pp.
- [7] R.A. Berner, Atmospheric carbon dioxide levels over Phanerozoic time, *Science* 249 (1990) 1382–1386.
- [8] R.A. Berner, The carbon cycle and CO<sub>2</sub> over Phanerozoic time: the role of land plants, *Phil. Trans. R. Soc. Lond. B* 353 (1998) 75–82.
- [9] P. Deines, The isotopic composition of reduced organic carbon, in: P. Fritz and J. C. Fontes (Eds.), *Handbook of environmental isotope geology*, Elsevier, Amsterdam (1980) 329–406.
- [10] M. Javoy, F. Pineau, The volatiles record of a 'popping' rock from the Mid-Atlantic Ridge at 14°N: chemical and isotopic composition of gas trapped in the vesicles, *Earth Planet. Sci. Lett.* 107 (1991) 598–611.
- [11] G.E. Bebout, The impact of subduction-zone metamorphism on mantle-ocean chemical cycling, *Chem. Geol.* 126 (1995) 191–218.
- [12] A.W. Jambon, Earth degassing and large-scale geochemical cycling of volatile elements, in: M.R. Carroll, J.R. Holloway (Eds.), *Volatiles In Magmas*, Min. Soc. Am. (1994) 479–517.
- [13] M. Javoy, The major volatile elements of the Earth: Their origin, behavior, and fate, *Geophys. Res. Lett.* 24 (1997) 177–180.
- [14] D. Canil, H.S.C. O'Neil, D.G. Pearson, R.L. Rudnick, W.F. McDonough, D.A. Carswell, Ferric iron in peridotites and mantle oxidation states, *Earth Planet. Sci. Lett.* 123 (1994) 205–220.
- [15] M. Javoy, F. Pineau, H. Delorme, Carbon and nitrogen isotopes in the mantle, *Chem. Geol.* 57 (1986) 41–62.
- [16] P. Deines, The carbon isotopic composition of diamonds: relationship to diamond shape, color, occurrence and vapor composition, *Geochim. Cosmochim. Acta* 44 (1980) 943–961.
- [17] P. Cartigny, J.W. Harris, D. Phillips, M. Girard, M. Javoy, Subduction-related diamonds?: The evidence for a mantle-derived origin from coupled  $\delta^{13}\text{C}$ – $\delta^{15}\text{N}$  determinations, *Chem. Geol.* 147 (1998) 147–159.
- [18] K.H. Wedepohl, The composition of the continental crust, *Geochim. Cosmochim. Acta* 59 (1995) 1217–1232.
- [19] D.K. Rea, L.J. Ruff, Composition and mass flux of sediment entering the world's subduction zones: Implications for global sediment budgets, great earthquakes, and volcanism, *Earth Planet. Sci. Lett.* 140 (1996) 1–12.
- [20] R. Chester, *Marine Geochemistry*, Unwin Hyman, (1990) 698.
- [21] T.M. Donahue, New analysis of hydrogen and deuterium escape from Venus, *Icarus* 141 (1999) 226–235.
- [22] T.M. Donahue, D.H. Grinspoon, R.E. Hartle, R.R. Hodges Jr., Ion/neutral escape of hydrogen and deuterium: Evolution of water, in: S.W. Bougher, D.M. Hunten, R.J. Philipps (Ed.), *Venus II, Geology Geophysics Atmosphere and Solar Wind Environment*, University of Arizona Press, Tucson, AZ (1997) 385–414.
- [23] F.W. Taylor, D. Crisp, B. Bezar, Near-infrared sounding of the lower atmosphere of Venus, in: S.W. Bougher, D.M. Hunten, R.J. Philipps (Ed.), *Venus II, Geology Geophysics Atmosphere and Solar Wind Environment*, University of Arizona Press, Tucson, AZ (1997) 325–351.
- [24] T.M. Donahue, R.R. Hodges Jr., Past and present water budget of Venus, *J. Geophys. Res.* 97 (1992) 6083–6091.
- [25] R.R. Hodges, B.A. Tinsley, Charge exchange in the Venus ionosphere as the source of the hot exospheric hydrogen, *J. Geophys. Res.* 86 (1981) 7649–7656.
- [26] S. Kumar, D.M. Hunten, J.B. Pollack, Non-thermal es-

- cape of hydrogen and deuterium from Venus and implications for loss of water, *Icarus* 55 (1983) 369–375.
- [27] J.F. Kasting, J.B. Pollack, Loss of water from Venus. I, hydrodynamic escape of hydrogen, *Icarus* 53 (1983) 479–508.
- [28] J.M. Rodriguez, M.J. Prather, M.B. McElroy, Hydrogen on Venus: Exospheric distribution and escape, *Planet. Space Sci.* 32 (1984) 1235–1251.
- [29] J. Matas, Y. Ricard, L. Lemelle, F. Guyot, Thermodynamic equilibrium of metallic and silicate phases: Implications for chondrites and Earth core formation, *Phys. Earth Planet. Int.* (2000) in press.
- [30] Y.A. Surkov, V.L. Barukov, L.P. Moskalyeva, V.P. Kharyukova, A.L. Kemurdzhian, New data on the composition, structure, and properties of Venus rock obtained by Venera 13 and Venera 14, *Proc. Lunar Planet. Sci. Conf. 14th, J. Geophys. Res.* 89 (1984) 393–402.
- [31] J.S. Lewis and R.G. Prinn, *Planets and their atmospheres: origin and evolution*, Academic Press, Orlando, FL, 1984, 470 pp.
- [32] C.M. Pieters, J.W. Head, W. Patterson, S. Pratt, J. Garvin, V.L. Barsukov, A.T. Basilevsky, I.L. Khodakovsky, A.S. Selivanov, A.S. Panfilov, Y.M. Getkin, Y.M. Narayeva, The color of the surface of Venus, *Science* 234 (1986) 1379–1383.
- [33] A. Seiff, J.T. Schofield, A.J. Kliore, F.W. Taylor, S.S. Limaye, H.E. Revercomb, L.A. Stromovsky, V.V. Kerzhanovich, V.I. Moroz, M.Y. Marov, in: A.J. Kliore, V.I. Moroz, G.M. Keating (Eds.), *The Venus International Reference Atmosphere*, Pergamon Press, New York (1986) 3–32.
- [34] M.T. Zuber, Constraints on the lithospheric structure of Venus from mechanical models and tectonic surface features, *Proc. Lunar Planet. Sci. Conf. 17th, J. Geophys. Res.* 92 (1987) 541–551.
- [35] R.J. Phillips, Estimating lithospheric properties at Alta Regio, Venus, *Icarus* 112 (1994) 147–170.
- [36] A.H. MacDonald, W.S. Fyfe, Rate of serpentinization in seafloor environments, *Tectonophysics* 116 (1985) 123–135.
- [37] D.B. Campbell, D.A. Senske, J.W. Head, A.A. Hine, P.C. Fisher, Venus southern hemisphere Geologic character and age of terrains in the Themis–Alpha–Lada region, *Science* 251 (1991) 180–183.
- [38] R.J. Phillips, R.E. Arvidson, J.M. Boyce, D.B. Campbell, J.E. Guest, G.G. Schaber, L.A. Soderblom, Impact craters on Venus initial analysis from Magellan, *Science* 252 (1991) 288–297.
- [39] F. Nimmo, D. McKenzie, Volcanism and tectonics on Venus, *Annu. Rev. Earth Planet. Sci.* 26 (1998) 23–51.
- [40] T. Suzuoki, S. Epstein, Hydrogen isotope fractionation between OH-bearing minerals and water, *Geochim. Cosmochim. Acta* 40 (1976) 1229–1240.
- [41] M.A. Gurwell, Venus deuterium evolution and implications for primordial water, *Nature* 363 (1995) 1702–1704.
- [42] S.R. Taylor, S.M. McLennan, *The continental crust: its composition and evolution. An examination of the geochemical record preserved in sedimentary rocks*, Blackwell Scientific Publications, Oxford (1985) 312.
- [43] R.O. Pepin, Volatile inventories of the terrestrial planets, *Rev. Geophys.* 25 (1987) 293–296.
- [44] E.M. Galimov, A.A. Migdison, A.B. Ronov, Carbonate and organic carbon in sedimentary rocks during Earth's history, *Geochem. Int.* 12 (1975) 1–19.
- [45] J. Hoefs, Some peculiarities in the carbon isotope composition of 'juvenile' carbon, *Dep. Sci. Ind. Res. Bull.* 220 (1978) 181–184.
- [46] T.M. Donahue, J.H. Hoffman, R.R. Hodges Jr., A.J. Watson, Venus was wet: A measurement of the ratio of deuterium to hydrogen, *Science* 216 (1982) 630–633.
- [47] C. Lécuyer, P. Gillet, F. Robert, The hydrogen isotope composition of seawater and the global water cycle, *Chem. Geol.* 145 (1998) 249–261.
- [48] R.A. Robie, B.S. Hemingway, J.R. Fisher, *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10<sup>5</sup> Pa) pressure and at higher temperatures*, US Gov. Print. Office, 1452, Washington, DC, 1979, 456 pp.
- [49] T.J.B. Holland, R. Powell, A Compensated-Redlich-Kwong (CORK) equation for volumes and fugacities of CO<sub>2</sub> and H<sub>2</sub>O in the range 1 bar to 50 kbar and 100–1600°C, *Contrib. Mineral. Petrol.* 109 (1991) 265–273.
- [50] T.J.B. Holland, R. Powell, An internally consistent thermodynamic data set for phases of petrological interest, *J. Metamorph. Geol.* 16 (1998) 309–343.