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A consistent picture of early hydrodynamic escape of Venus atmosphere explaining present Ne and Ar isotopic ratios and low oxygen atmospheric content

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ABSTRACT

A time dependent model of hydrogen hydrodynamic escape powered by solar EUV flux and solar wind, and accounting for oxygen frictional escape, has been implemented in primitive Venus conditions. The model is constrained by the present $^{20}Ne/^{22}Ne$ and $^{36}Ar/^{38}Ar$ ratios in Venus atmosphere. It suggests that the net total amount of water delivered to the planet during accretion (≈10–100 Myr) is not in excess of the content of ≈5 Terrestrial Oceans (5 TO). In our preferred scenario, 60% of the oxygen (3 TO) is left behind the hydrogen during the first 100 Myr. From a comparison with Earth's case, we suggest that hydrodynamic escape has dried up Venus atmosphere early in its history (≈70 Myr), triggering the crystallization of the magma ocean, and leaving no available water in the atmosphere to condense out and form an Earth-size water ocean. On the contrary, Earth, possibly endowed with more water, and subject to a weaker hydrodynamic escape, would have remained wet after the crystallization of its magma ocean. We suggest that the oxygen left behind the escaping hydrogen during the main hydrodynamic phase on Venus has been dissolved in the magma ocean, and lost through oxidation. In the proposed scenario, the dense Venus CO_2 atmosphere doesn't result from an initial episode of runaway (or moist) greenhouse, but has been formed during the crystallization of the magma ocean, by progressive exsolution of carbon dioxide, at a time when the atmospheric partial pressure of water was of a few hundred bar. In the subsequent period, from ≈100 to ≈500 Myr, the hydrogen of the water delivered by comets may have been removed by continuing thermal escape, resulting at 500 Myr in a water global equivalent layer (GEL) of a few meters depth (or less), probably under the form of water vapor in the atmosphere, and a molecular oxygen atmosphere of ≈10 bar or so. At later times, pick-up ion escape may have removed most of the remaining water, and led to the present D/H atmospheric enhancement factor of 150. The ≈10 bar of oxygen may have been absorbed by crustal oxidation.

1. Introduction

It is thought that the massive greenhouse effect observed today in Venus atmosphere was initiated by the evaporation of an ocean of water at early times (Shimazu and Urabe, 1968; Rasool and de Bergh, 1970). Because water could not condense at temperatures prevailing in the inner solar nebula, planets have been supplied with water by planetary embryos, coming from more external zones of the solar nebula, where water could condense, with a water content of a few to a few tens Terrestrial Oceans (denoted by TO hereafter) (Morbidelli et al., 2000, Raymond et al., 2006).

It has been shown by Kasting and Pollack (1983) that, photolysis of water molecules followed by hydrodynamic escape of hydrogen is able to remove the total hydrogen content of 1 TO in less than 2 Gyr. What was the fate of the oxygen atoms produced by photolysis of water molecules? In the case of a large hydrogen escape flux, heavier species like oxygen can be dragged off along with hydrogen, according to the theory developed by Hunten (1973). Nevertheless, even by taking into account the higher values of the solar EUV flux at early epochs (Zahnle and Walker, 1982), the amount of oxygen lost is not expected to exceed ≈25% of the oxygen content of 1 TO (Chassefière, 1996a).

Another potential sink of oxygen is oxidation of FeO contained in surface basalts. The existing models of Venus interior composition greatly differ in terms of iron composition (Lodders and Fegley, 1998). Most of the planetary material is acquired through collisions with a small number of embryos originating in a wide region of the inner solar system: 0.7–3 AU (Morbidelli et al., 2000, Raymond et al., 2006), and similar compositions are therefore expected. The Earth value of the average FeO mass mixing ratio is 7.5%, and it is reasonable to assume a similar value for Venus. The present volcanism rate on Venus is estimated to be 0.1–0.2 km^3/yr, but it could have reached 3–10 km^3/yr during the emplacement of regional volcanic plains (Basilevsky et al., 1997). The crust production rate averaged over the whole lifetime of the planet is

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quite uncertain. This rate could have been of the order of ≈4–5 km^3/yr (Volkov and Frenkel, 1993, Matsui and Tajika, 1995), five times less than the present rate of crustal accretion at Earth's divergent margins (21–24 km^3/yr, Grimm and Hess, 1997), as a consequence of the fact that the atmospheric ^{40}Ar abundance normalized by planetary mass is 3 to 6 times less on Venus than Earth. Due to large uncertainties on Venus potassium budgets, and the details of outgassing processes, Namiki and Solomon (1998) do not exclude larger values of the crust production rate. Values as large as 50 km^3/yr, as derived from the convection model by Parmentier and Hess (1992), cannot be ruled out. A crustal growth rate of 50 km^3/yr translates in a volcanic rate of 10 km^3/yr. Assuming an average volcanism rate of 10 km^3/yr, it may be calculated that the oxygen content of 1 TO could have potentially been removed by oxidation of the crust over the last 4 Gyr (assuming that the totality of the FeO injected in the crust is converted into Fe_2O_3).

The ability of fresh lava to remove oxygen from the atmosphere seems limited. The characteristic diffusion depth of oxygen in basalt melts doesn't exceed ≈1 mm/day (Wendlandt, 1991). There is no reason why diffusion would be faster at the higher Venusian atmospheric temperature, since the diffusion velocity depends only on the temperature of the diffusive medium. Oxidation depths of tens of centimeters are observed for some lava samples from domes deposits (Saito et al., 2007). Detailed mechanisms of oxidation in this case are not known, but it could be due to the slow cooling time of endogenous lava (Saito et al., 2007). The typical thickness of lava flows on Venus is in the range from a few meters to a few tens of meters (Head and Wilson, 1986). Even by assuming that the diffusion of oxygen in the fresh, hot, lava occurs over a few tens of centimeters depth, only a few percents of the cooling lava can be oxidized during its emplacement. Even with a high average volcanism rate of 10 km^3/yr, assuming a value of 10% for the oxidation efficiency, the maximum amount of oxygen removed by crust oxidation may hardly exceed the oxygen content of 0.1 TO. Interestingly, Lécuyer et al. (2000), using a thermodynamic approach to show that hematite is stable at Venus pressure and temperature conditions, suggested that the surface of Venus could have been oxidized from ferrous iron to ferric iron by the oxygen left behind by hydrodynamic escape. They estimated that the oxygen contained in 1 TO would have to form a 50 km depth layer of oxidized, hematite-rich, crust. But the rate of such a reaction could be very slow. Moreover, the thick CO_2 atmosphere of Venus produces a surface pressure equivalent to depth of about 1000 m on the Earths' sea floor (Head and Wilson, 2003). At such pressures, exsolution of gases from the magma generally doesn't occur. If volatiles cannot be released from the magma, it is hardly believable that gas from the outside may diffuse inward efficiently. Another mechanism of oxidation could be the erosion of the upper basaltic layers, resulting in small grains, potentially able to be oxidized over reasonable time scales. Arvidson et al. (1992), estimated a degradation of Venus soils by this mechanism of 1 meter depth over 0.6 Gyr, which corresponds to ≈10^{-3} km^3/yr of eroded material, and this sink is therefore quite negligible. Due to large uncertainties on both the average crust production rate and the oxidation efficiency, it is difficult to put an upper limit on the quantity of oxygen removed by oxidation of the crust, but a maximum value of 0.1 TO seems to be a conservative assumption.

As shown by Chassefière (1996b), hydrodynamic escape powered by both EUV radiation and solar wind, according to a process involving charge exchange between escaping neutral atoms and solar wind protons, by multiplying the energy available for escape by a factor of 3 or more, is able to have removed significant oxygen amounts from Venus' atmosphere. In a different way, sputtering is also able to have significantly contributed to oxygen escape (Kulikov et al., 2006), provided Venus was not magnetized at early epochs. A strong primitive solar wind, is potentially able to stimulate an hydrodynamic flux high enough for oxygen atoms to be massively dragged off (Chassefière, 1997).

Much progress has been made in the last ten years in our understanding of Earth-like planet formation. Morbidelli et al. (2000) have shown that most of the initial water endowment of terrestrial planets was provided by a few planetary embryos in a relatively late stage of accretion. In typical scenarios, accretion starts at ≈10 Myr. Most of the water supplied by asteroids (1 TO) is delivered between 10 and 35 Myr. In the time between 35 and 70 Myr, accretion is completed and large amounts of water are delivered to the planet by a few large accreted embryos coming from large distances to the Sun (≈3 AU). At later times, comets from the Uranus–Neptune region and from the Kuiper–Belt may supply a late veneer of 10% of the present water content.

Looking at Fig. 5 of Raymond et al. (2006), it is seen that a Venus-type planet builds up in typically ≈20–30 Myr from embryos formed at less than 1 AU, most of the water being brought later (30–70 Myr). According to their calculations, a Venus-type planet may be less rich in water than a Mars-type, or Earth-type, planet. The feeding zone of the most inner planet doesn't significantly extend beyond ≈2.5 AU and, in an average, it is expected that it is endowed with less water than other planets. Indeed, the parent bodies of carbonaceous chondrites have been formed in the region beyond 2.5 AU, and most of the water of the terrestrial planets is expected to have been provided by embryos formed beyond 2.5 AU (O'Brien et al., 2006). Table 2 of Raymond et al. (2006) shows the results of five high-resolution simulations. In three cases, Venus is endowed with 4–6 times less water than Earth, in one case it is endowed with twice less water, and in one case with twice more water. The four simulations made by O'Brien et al. (2006) similarly show a depletion in material formed beyond 2.5 AU of the most inner planet(s): a factor of 5–10 in two cases, 2 in one case, and similar endowments in one case.

This dispersion of the results unambiguously reflects the stochastic character of water accretion (A. Morbidelli, personal communication, 2009), showing that, in a statistically average way, a Venus-type is expected to receive less water than an Earth-type planet (typically 3 times less) but that in a few cases (10% here), the opposite may be true.

Using these fundamental new results about terrestrial planetary accretion time scales and source regions for the delivery of water, it is now possible to describe in a more accurate way primitive hydrodynamic escape. As shown hereafter, hydrodynamic escape is potentially able to remove large amounts of water, and if less water was available on Venus with respect to Earth for hydrodynamic escape, Venus atmosphere could have been dried up before Earth atmosphere. The main goal of the present paper is to assess the effect of a primitive phase of EUV-solar wind-powered hydrodynamic escape on the isotopic fractionation pattern of noble gases in Venus atmosphere (Ne, Ar, Kr, Xe). The case of Ne is of particular interest since its atomic mass is quite close to the mass of atomic oxygen. The escape of oxygen has therefore been accompanied by escape of neon. Another constraint for the model is the absence of oxygen in significant amounts in the present Venus atmosphere.

2. Present knowledge of noble gases in Venus atmosphere

Noble gases in the Venus atmosphere have been analyzed by mass spectrometry and gas chromatography on board Pioneer Venus and several Venera probes. Although a similar pattern is observed for the three terrestrial planets, there are several significant differences. Ne and Ar are more abundant than in Earth's atmosphere, by at least factors of 10 and 50, respectively. The ^{20}Ne/^{36}Ar ratio is depleted by a factor of ≈3 in Venus atmosphere relative to Earth (Table 1). The Venus noble gas elemental spectrum is more solar-like than those of Earth and Mars, Ar being slightly (factor of 10) depleted with respect to the Sun, whereas Ne is strongly depleted (factor of 1000).

The Venus pattern is quite different from the chondritic one, which resembles the patterns of Earth and Mars. It may be seen that the amount of carbon and nitrogen are similar on Earth and Venus, but that they are depleted by two orders of magnitude on Mars. The relative

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Table 1
Noble gas isotopic ratios in the atmosphere of Venus (from Wieler, 2002).

Element	Venus value	Earth value
$^3He/^4He$	$<3 \cdot 10^{-4}$	$1.4\ 10^{-4}$
$^{20}Ne/^{22}Ne$	11.2–12.6	9.8
$^{21}Ne/^{22}Ne$	<0.067	0.029
$^{36}Ar/^{38}Ar$	5.45 ± 0.1	5.32
$^{40}Ar/^{36}Ar$	1.11 ± 0.02	295.5

similarities of CO_2, N_2, Kr and Xe on Venus and Earth, compared to Mars (depleted by a factor of ≈100) suggest that Mars experienced a much stronger atmospheric escape. Neon is less fractionated in Venus atmosphere ($^{20}Ne/^{22}N = 11.9 \pm 0.7$) than in Earth atmosphere ($^{20}Ne/^{22}Ne = 9.8$) with respect to solar composition ($^{20}Ne/^{22}Ne = 13.5$). The Ne isotopic fractionation might be attributed to a phase of EUV-solar wind-driven hydrodynamic escape of only Ne during the first ten or hundred Myr. Because Ne is only slightly heavier than O, hydrodynamic escape of Ne implies hydrodynamic escape of oxygen, and Ne may be used as a tracer of oxygen escape at primitive stages. The fact that Ne is isotopically heavier on Venus than on Earth implies that oxygen effectively escaped. Because Ne on Earth is similarly fractionated with respect to the solar composition, significant amounts of oxygen probably also escaped from Earth atmosphere.

For the following calculations, the initial inventory of Venus atmosphere in noble gases and their isotopes have been calculated assuming that the primitive amount of Xe in Venus atmosphere was similar to the present amount, therefore assuming that Xe didn't escape, and using for calculating all noble gas isotopes using standard elemental and isotopic ratios of the solar atmosphere.

3. Hydrodynamic escape model

Our model calculates in a simplified way (energy-limited approach) the escape flux of hydrogen from a H_2O-rich thermosphere, where H_2O is permanently photodissociated by the solar UV flux, as a function of time. It takes into account the escape of oxygen atoms, dragged off along with hydrogen, and calculates the evolution and final value of the isotopes of noble gases (Ne, Ar, K, Xe). This is a step-by-step time dependent model, where escape fluxes are calculated as a function of the time evolving energy-limited rate. Our approach uses methods and inputs provided in the papers by Zanhle and Kasting (1986), Kasting and Pollack (1983), Hunten et al., (1987) and Chassefière (1996a,b) (Fig. 1).

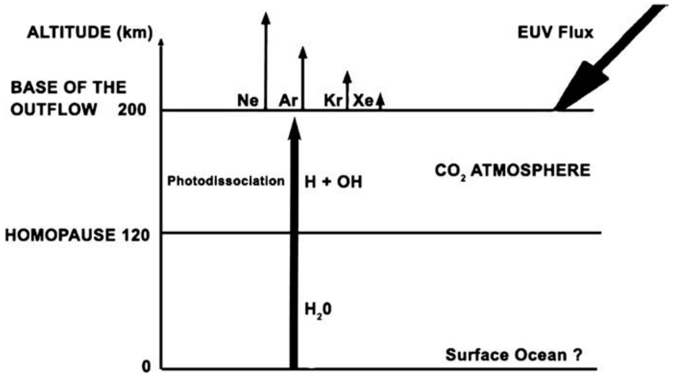

Fig. 1. Hydrodynamic escape on Venus. EUV flux and solar wind energy deposition rates in the outer layers of the atmosphere are at the origin of its hydrodynamic expansion. When H escapes, it drags noble gases along with it. The heavier the noble gas is, the smaller the effect. H_2O molecules are photodissociated into H and OH in the thermosphere at an altitude above 100 km.

3.1. Main principles and parameters of the model

The H escape flux is calculated at 200 km altitude, which is considered, from Kasting and Pollack (1983), as the base of the expansion. The choice of this altitude is of significant importance, since the amount of a minor species escaping together with hydrogen (and oxygen) depends on the mixing ratio of this minor species at the base of the expansion, due to diffusive separation between the homopause and the expansion level. From Figs. 9 and 10 of Kasting and Pollack (1983), atomic hydrogen becomes dominant above ≈180 km altitude, and its mass mixing ratio becomes close to unity above 200 km altitude. We will assume in the present study that the atmosphere below 200 km altitude is static, with vertical profiles of noble gas abundances controlled by hydrostatic equilibrium, in a background CO_2/H_2O dominated atmosphere. Above 200 km, the hydrogen-dominated atmosphere expands into the interplanetary medium: the input energy is directly converted into upward translational energy of the upward expanding flow. Tian et al. (2008) have shown that the thermosphere of the primitive Earth could have been in an hydrodynamic regime due to strong solar EUV illumination conditions. A significant consequence of this regime could have been an adiabatic cooling of the ascending flow, resulting in a substantial decrease of the exospheric temperature. This cooling occurs in the range from ≈200 km up to several thousand kilometers (see Fig. 7 of Tian et al., 2008) and strongly affects the altitude of the exobase. In the present work, the thermospheric temperature is assumed, for reasons of simplicity, to be constant in the range 120–200 km when calculating diffusive separation between the homopause and the expansion level, and is a free parameter.

The total available energy flux depends on:

(i) The efficiency ε of the solar EUV flux Φ_{EUV}, generally assumed to be 15%. Most of the rest of the energy is used for ionizing hydrogen atoms. Because electrons are not expected to recombine in the planetary corona, the part of the energy used for ionization is lost to space (Chassefière, 1996b). The heating efficiency cannot be greater than 30% (Chassefière, 1996b), and is generally assumed to be of the order of 15%.
(ii) The geometrical amplification factor *f* due to the fact that an extended corona is able to absorb more UV flux,
(iii) The relative contribution Φ_{sw} of solar wind energy deposition to the total energy deposition (EUV + solar wind) near the exobase (≈65% for present solar conditions, from Chassefière (1996b)).

The total energy flux engaged in escape:

$$\Phi = \varepsilon f \Phi_{EUV} + \Phi_{sw} \tag{1}$$

can be large at primitive epochs, and will be considered as a free parameter of the model. The range of:

$$\Phi = \eta \Phi_{EUV} \tag{2}$$

explored in this paper is from $\eta = 0.3$ to $\eta = 20$. Hydrogen is supposed to be supplied to the high atmosphere at the rate required for energy-limited escape, with no limitation due to diffusion. As shown below, the escape fluxes calculated hereafter correspond to a few TO lost over typically 100 Myr. According to the Eq. (50) in Kasting and Pollack (1983), and reducing the given number by a factor of 6, following the advice of these authors, to take into account the fact that H_2O is the major H-bearing species at homopause (case of large water vapor amounts in the thermosphere), the diffusion-limited flux is of the order of $6 \cdot 10^{13}\ cm^{-2}\ s^{-1}$, that is ≈10 TO per 100 Myr. Neglecting limitation by diffusion seems therefore appropriate.

The effect of H and O escape on the escape of noble gases and their isotopes is calculated by using the concentrations of noble gases

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calculated at 200 km altitude, assuming that the homopause is at 120 km, and using the barometric law between 120 km and 200 km, with an exponential decrease of the densities of the species according to their own scale height. The homopause altitude of 120 km is a little lower than the present Venus homopause (130 km), but representative of Earth and Mars cases. The determining parameter is the altitude difference between the homopause and the base of expansion, which value is 80 km in this study (which corresponds to the present situation). In primitive conditions, in the presence of very large amounts of water vapor (up to several hundred bars), this altitude gap of 80 km between the homopause and the expansion level may have been different. The goal of our simple parametric study is to find a consistent global picture of early escape, fitting neon and argon isotopic fractionation patterns, including not only atmospheric processes, but also solar activity, accretion history, and coupling between the solid planet (or magma ocean), the atmosphere and the various escape processes.

A major parameter of the model is the thermospheric temperature T, assumed to be constant with altitude.

T is a free parameter of the model. We explore the range from 200 K to 4000 K. 200 K is the atmospheric temperature at the base of the expansion, as calculated by Kasting and Pollack (1983). In the case of primitive Earth, Tian et al. (2008) recently found a thermospheric temperature varying from 1000 K at 100 km altitude to 3000 K at 200 km altitude. The reason of the cold temperature in the case of Venus is the presence of CO_2 in the thermosphere, resulting in a strong cooling rate. We explain in Section 5.2, why a value of T of a few thousand K cannot be excluded.

3.2. Description of the model

3.2.1. Simple case of hydrogen escape alone (without oxygen escape)

Let's denote by $\Phi(t)$ the total energy flux (EUV, solar wind) engaged in H hydrodynamic escape (cf Eq. (1)). In the simplified energy-limited approach, the escape flux of hydrogen $F_1(t)$ obeys the simple relationship:

$$m_1 F_1(t) = \Phi(t)\, r\,/\,(MG), \tag{3}$$

where m_1 is the mass of one hydrogen atom, r the average distance from the planetary center at which the flux is deposited, M the mass of the planet and G the gravitational constant (see e.g. Chassefière, 1996a). The ratio between $\Phi(t)$ and $\Phi_{EUV}(t)$ is assumed for simplicity to remain constant with time during escape. Values of η up to 20 will be considered in the present study, although final results show that a moderate value of η (of the order of 1.2, or possibly twice more) is the preferred one.

We choose to use a law for the solar EUV flux time dependence that is proportional to $(t/t_0)^{-a}$. Thus we have:

$$F_1(t) = F_1(t_0) \times (t\,/\,t_0)^{-a} \tag{4}$$

where t_0 is the starting time of hydrodynamic escape, and a is a constant. At high atomic hydrogen column densities, ionization occurs mainly in the 80–90 nm range (see Fig. 1a of Chassefière, 1996b). From the most recent Sun in Time program (Ribas et al., 2005), it may be seen that the best value of a in this wavelength range is 0.85, that is the value of 5/6 used by Hunten et al. (2008). Photons in the 55–65 nm range also contribute to ionization, to a lesser extent, with an index a of ≈1. It has been checked that results are not changed depending on the selected value of a in this small range. We will use $a = 5/6$ in the following. Several values for t_0 ranging from 1 Myr to 100 Myr are considered. The intermediate value (10 Myr) is likely to be the most realistic, since water is mainly accreted in the time range from 10 Myr to ≈50 Myr (Morbidelli et al., 2000, Raymond et al., 2006).

This enables us to obtain the hydrogen density at the base of the expansion z_{exp} since the hydrogen flux is defined by:

$$F_1\left(z_{exp}\right) = n_H\left(z_{exp}\right) \times v_{exp}\left(z_{exp}\right), \tag{5}$$

where n_H is the hydrogen density and v_{exp} is the expansion velocity of the flow at the base of expansion. This velocity is of the order of 5 cm s^{-1} but typically varies from 3 to 10 cm s^{-1} (Kasting and Pollack, 1983, Chassefière, 1996b). The source of hydrogen is supposed to be unlimited.

The densities of noble gases and of their isotopes at the base of the expansion are calculated from their values in the global atmosphere, by applying gravitational separation between the homopause and z_{exp} with a constant temperature.

A species is dragged if its molar mass is lower than the crossover mass m_c (Hunten et al., 1987):

$$m_c = m_1 + (kTF_1)\,/\,(bgX_1) \tag{6}$$

where m_1 is the molar mass of the light component (hydrogen), k the Boltzmann constant, T the temperature at escape level, b the (temperature and element-dependent) diffusion parameter, g the acceleration due to gravity on Venus and X_1 is the light component mole fraction.

Parameter b_i (for species i) is given by the following approximation law:

$$b_i = C_b \times T^q, \tag{7}$$

where C_b and q are parameters that depend on both the background and diffusing gases. Both are determined by experiments (see Chamberlain and Hunten, 1987).

In this case, the flux F_2 of the heavy species (a noble gas isotope of molar mass m_2 and mole fraction χ^2) can be found by using the following law:

$$F_2 = (m_c - m_2)\,/\,(m_c - m_1) \times (X_2\,/\,X_1) \times F_1 \tag{8}$$

Since the solar flux is time-dependent, so is the crossover mass. It follows that light species will escape faster than heavier ones, producing fractionation. When the only main species in the atmosphere is hydrogen (species 1), species 2 is a noble gas isotope (Ne, Ar, Kr and Xe). Despite the high mass of the noble gases, they are only present as minor constituents and don't require any significant amount of energy to be dragged along with the hydrogen, so almost all the available incoming solar energy is converted into hydrogen escape energy.

3.2.2. Case of simultaneous escape of hydrogen and oxygen — dragged off by hydrogen

The second major species in the early high atmosphere of Venus is oxygen. With H_2O being the major constituent of the high atmosphere, we follow Kasting and Pollack (1983) and use the simple relationship $n(H) = 2 \times n(O)$. We study the joint escape of two main species where the contribution of species 2 to the total energy is no longer negligible. The energy available is thus split between the two fluxes, as proposed by Chassefière (1996a):

$$m_h F_h + m_o F_o = \Phi(t)\, r\,/\,(MG) \tag{9}$$

In the following simplified approach, we assume that oxygen escape is entirely driven by hydrogen escape due to the friction between H and

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O atoms as direct hydrodynamic escape of O is expected to be a minor effect.

We use a direct calculation method to determine both oxygen and hydrogen flux for each time step by determining first the reference hydrogen flux:

$$M_{\mathrm{h}} F_h^{ref} = \Phi r / (MG) \tag{10}$$

with the reference hydrogen flux $F_{\mathrm{h}}^{\mathrm{ref}}$ being the hydrogen flux powered by the total amount of available energy. Then, we calculate the reference cross-over mass corresponding to the reference hydrogen flux. We deduce that:

$$(m_{\mathrm{c}} - m_1) / \left(m_{\mathrm{c}}^{\mathrm{ref}} - m_1\right) = F_1 / F_1^{\mathrm{ref}} \tag{11}$$

Following Chassefière (1996a,b) we then obtain the cross-over mass corresponding to the oxygen escape:

$$m_{\mathrm{c}} = m_2 + \gamma\left(m_{\mathrm{c}}^{\mathrm{ref}} - m_2\right) \tag{12}$$

and:

$$m_{\mathrm{c}} / m_{\mathrm{c}}^{\mathrm{ref}} = F_1 / F_1^{\mathrm{ref}} \tag{13}$$

where γ is a constant equal to 1/9. The oxygen escape rate is then calculated from the new value of the hydrogen escape flux using Eqs. (9) and (10).

Eq. (8) applies again for each noble gas isotope, but both hydrogen and oxygen escape fluxes contribute to the total loss of secondary species and Eq. (8) becomes:

$$\begin{aligned} F_{\mathrm{ng}} = {} & \left(m_{\mathrm{ch}} - m_{\mathrm{ng}}\right) / (m_{\mathrm{ch}} - m_{\mathrm{h}}) \times \left(X_{\mathrm{ng}} / X_{\mathrm{h}}\right) \\ & \times F_{\mathrm{h}} + \left(m_{\mathrm{co}} - m_{\mathrm{ng}}\right) / (m_{\mathrm{co}} - m_{\mathrm{o}}) \times \left(X_{\mathrm{ng}} / X_{\mathrm{o}}\right) \times F_{\mathrm{o}} \end{aligned} \tag{14}$$

with two different crossover masses depending on what the species that causes the noble gas to be dragged off along is. These are calculated using Eq. (6). It is important to note that the diffusion parameter b is not the same for H and O.

4. Results

4.1. Case of hydrogen escape alone (without oxygen escape)

We first focus on the simplest case when hydrogen escapes and drags along only noble gases. The hydrogen flux is directly linked to the evolution of the solar flux and diminishes with time. The bulk of the escape is taking place during the first few tens of millions years. The later we set the escape to start, the less important the total escape will be.

Several parameters are investigated such as the time t_0 when the escape starts, the temperature T of the thermosphere and the η factor, which results from a combination of the heating efficiency ε, the geometrical amplification factor f and the relative contribution $r = \Phi_{\mathrm{SW}} / \Phi_{\mathrm{EUV}}$ of solar wind deposited energy ($\eta = \varepsilon f(1+r)$, see Eqs. (1) and (2). Concerning η, we have mainly explored the range from 0.6 to 2.4, corresponding to the typical situations given in the following list, always with a fixed ε factor of 0.15.

i) $\eta = 0.6$ which corresponds to a geometrical factor f of 4 (exobase at 1 planetary radius) and no contribution of the solar wind.
ii) $\eta = 1.2$, corresponding to $f = 4$ and a relative solar wind contribution $r = 1$ (meaning half of the energy comes from the solar wind).
iii) $\eta = 1.8$ with $f = 4$ and $r = 2$ (2/3 of the energy from solar wind).
iv) $\eta = 2.4$ with $f = 8$ (exobase at ≈2 planetary radii) and $r = 1$.

The Ne and Ar isotopic ratios generated by escape are calculated by the model and are used as a diagnostic by comparing them to values measured in the Venus atmosphere.

As seen in Fig. 2, where resulting Ne and Ar fractionation patterns are plotted, there exist scenarios consistent with present values of isotopic ratios. For high thermospheric temperatures (>1000 K), isotopic fractionation is too large, because the densities of Ne and Ar, and therefore their escape fluxes are large. On the contrary, at low thermospheric temperature (<400 K), Ne is not fractionated enough to fit present value due to its low abundance at escape level.

We also investigated the amount of hydrogen lost in each case, first as the amount lost during the escape of neon (10–300 Myr), and then as the total amount lost over the first three billion years. Hydrogen lost during the escape of neon can range from the quantity of hydrogen contained in about 3 to 7 TO for $\eta = 0.3$ depending on the temperature at the base of the expansion. It can however reach up to 12 for $\eta = 0.6$ and to 30 to 40 for $\eta = 1.2$. Finally, for $\eta = 2.4$, the amount of lost water can reach 150 TO, which is an unrealistically large value according to recent accretion scenarios recently published. From Table 2, it can be seen that at least 10 TO of hydrogen must be lost in order to fit the present neon isotopic ratio.

Table 2 gives a summary of results fitting the observed Ar and Ne isotope ratios. In order to fit the low temperatures given by existing models of hydrodynamic escape (Kasting and Pollack, 1983), of the order of 200–300 K, the preferred η value is 2.4. But, in this case, the number of terrestrial oceans lost during neon escape is clearly too large and unrealistic. By limiting to ten the number of terrestrial oceans available, the preferred sets of parameters (η, t_0, T) are (0.6, 1–10 Myr, 750 K) and (1.2, 100 Myr, 400 K). In the (quite implausible) case of a start at 100 Myr, a higher energy input is required, and the thermospheric temperature is allowed to be smaller. The energy input

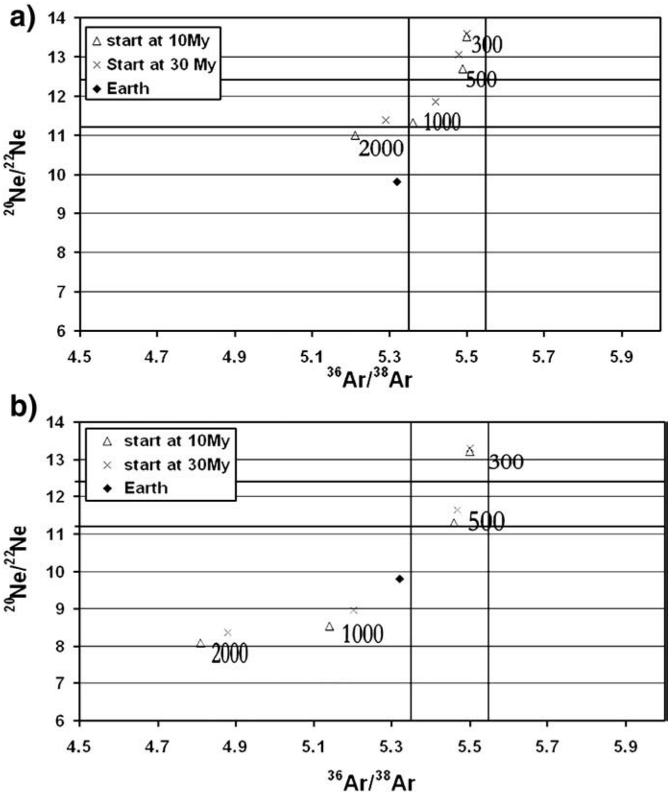

Fig. 2. Isotopic ratios according to different scenarios of the escape of the atmosphere of Venus when O doesn't escape. a) $\eta = 0.6$. b) $\eta = 1.2$. The ranges of the measured values of the isotopic ratios of Ne and Ar are limited by dashed straight lines. They delineate a box inside which measured isotopic ratios are satisfied. The point representing Earth atmosphere isotopic ratio is represented.

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Table 2
Summary of results fitting the observed Ar and Ne isotope ratios for different values of η.

Parameters	^{20}Ne/^{22}Ne [11.2–12.6]	^{36}Ar/^{38}Ar [5.35–5.55]	Number of TO lost during Ne escape (10–300 Myr)
$\eta = 0.6$ $t_0 = 1$ Myr $T = 750$ K	11.5	5.4	10
$\eta = 0.6$ $t_0 = 10$ Myr $T = 750$ K	11.8	5.4	11
$\eta = 1.2$ $t_0 = 10$ Myr $T = 400$ K	11.3	5.5	32
$\eta = 1.2$ $t_0 = 100$ Myr $T = 400$ K	11.4	5.4	11
$\eta = 2.4$ $t_0 = 10$ Myr $T = 300$ K	12.5	5.50	84

corresponds to typically one full EUV flux, requiring that part of the escape energy is provided by solar wind, which agrees reasonably well with previous studies (Chassefière, 1996b).

We made similar calculations with other expansion velocities at 200 km altitude that were deemed realistic (Kasting and Pollack, 1983, Chassefière, 1996b). With respect to our standard value of 5 cm/s, we have tested lower (3 cm/s) and higher (10 cm/s) values. It results in a shift of the preferred parameter sets toward higher (for a lower velocity) or lower (for higher velocities) temperatures. In the model, high escape velocities translate into low hydrogen density at the base of the expansion and an increased isotopic fractionation. In most conditions, the results don't change significantly.

4.2. Case of simultaneous escape of hydrogen and oxygen

We take now into account the fact that O atoms are dragged off along with H atoms. When taking into account the escape of a second major component, we have to distribute the total solar EUV incoming flux between the two species. It means, according to Eq. (8), that at high energy input the escape flux of hydrogen will be lower by roughly one order of magnitude. Fig. 3 shows an example of the evolution of the hydrogen and oxygen fluxes with time.

The fluxes are lower than when neglecting oxygen escape and decrease steeply with time during the first hundred million years. The large amount of oxygen lost to space consumes most of the energy input. As the crossover mass is decreasing, oxygen escape flux is decreasing too until it only consumes a small fraction of the solar energy input. Just before 600 Myr, the crossover mass becomes lower than the mass of the oxygen and its escape completely ceases.

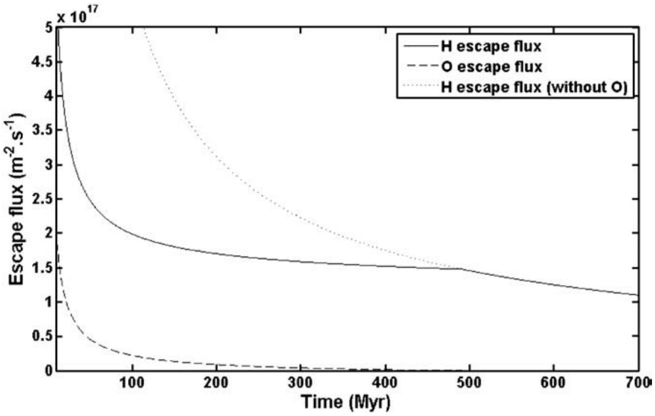

Fig. 3. Estimation of the escape flux of H and O in our “preferred case” ($\eta = 1.2$, $T = 750$ K, start at 10 Myr). Comparison is made with the “Hydrogen only” escape flux.

As the noble gases we study are all heavier than oxygen, they stop escaping before oxygen. Additionally, due to the slowing effect of oxygen, the effective crossover mass is reduced and noble gases escape less easily. Ne escape vanishes at ≈200 Myr (Fig. 4), instead of 300 Myr before. Most of the Ne isotopic fractionation occurs at early times, before 100 Myr (see Table 3). Kr and Xe don't escape significantly, and even Ar stops escaping very soon. Neon 20 is depleted by about 50% with respect to its initial value, and neon 22 by 30%. The cumulative amounts of escaped hydrogen and oxygen, and of the oxygen left behind hydrogen, are given as a function of time in Fig. 5.

A few possible sets of parameters fitting Ne and Ar isotopic ratios are given in Table 3. Several solutions exist for reasonable values of the parameters, but the preferred temperature is 500–750 K. A low temperature of 200–300 K is incompatible with significant fractionation of Ne. The preferred sets of parameters (η, t_0, T) are (1.2, 1–10 Myr, 750–1250 K), (1.8, 1–10 Myr, 750 K) and (2.4, 10 Myr, 500 K). Escape must start earlier (1–10 Myr vs 10–100 Myr), requires twice more energy ($\eta = 1.2$–2.4 vs $\eta = 0.6$–1.2), and a hotter thermosphere (500–1250 K vs 400–750 K).

5. Discussion

5.1. Escape at early times (10–500 Myr)

Despite the simplicity of the used model, and the uncertainties existing on Venus noble gas isotopic ratios, the present work underlines a few new results.

First, the gravitational separation between the homopause and the base of the outflow results in a relatively weak fractionation of noble gases. Xenon and krypton are not fractionated at all, whereas argon is marginally fractionated and neon moderately fractionated. Interestingly, Ne can be used as a tracer of oxygen escape and the present model shows that there is good qualitative agreement between the idea that a significant amount of oxygen was lost together with hydrogen and the measured moderate fractionation of neon in Venus' atmosphere with respect to solar values. It is relatively straightforward to attribute the moderate fractionation of Ne in Venus atmosphere to the escape of the primitive ocean.

Looking in more details, results show that hydrodynamic escape and related isotopic fractionation occur early because massive oxygen escape drastically reduces the effective crossover mass. According to our model, neon can escape until 200 Myr, but most of Ne isotopic fractionation occurs during the first 100 Myr. This chronology is consistent with the results of terrestrial planet accretion modeling (Morbidelli et al., 2000, Raymond et al., 2006). Whereas the equivalent of up to 1 TO, may be delivered to the planet from 10 to 35 Myr, much more (up to a few 10 TO) are brought by a few large

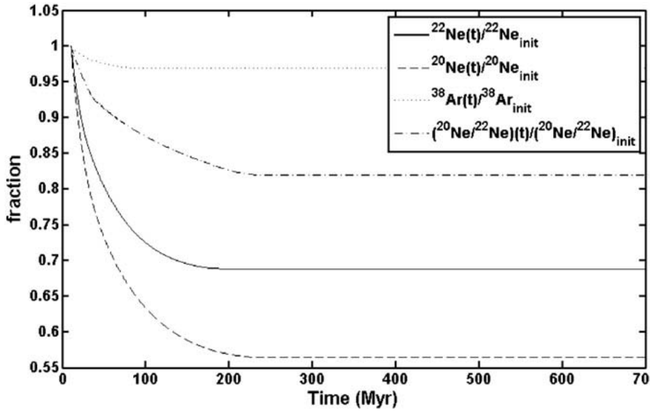

Fig. 4. Evolution of the relative amounts of Ne and Ar with time during the linked escapes of H and O, and of the ^{20}Ne/^{22}Ne ratio. This scenario uses the following parameters: $\eta = 1.2$, $T = 750$ K, start at 10 Myr.

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Table 3
Summary of results fitting the observed Ar and Ne isotope ratios for different values of η.

Parameters	$^{20}Ne/^{22}Ne$ [11.2–12.6]	$^{36}Ar/^{38}Ar$ [5.35–5.55]	$^{20}Ne/^{22}Ne$ at 100 Myr.	Number of TO of O finally released to the atmosphere at 100 Myr.
$\eta = 1.2$ $t_0 = 1$ Myr $T = 750$ K	12.1	5.4	12.4	3.5
$\eta = 1.2$ $t_0 = 10$ Myr $T = 750$ K	11.2	5.4	12	3
$\eta = 1.8$ $t_0 = 1$ Myr $T = 500$ K	11.2	5.5	12	3.7
$\eta = 1.8$ $t_0 = 10$ Myr $T = 500$ K	11.4	5.4	12.3	3.1
$\eta = 2.4$ $t_0 = 10$ Myr $T = 500$ K	10.6	5.5	11.9	3.7

embryos in the 35–100 Myr period. Only 0.1 TO is expected to be provided at later times by comets. Fig. 5 shows that the typical time of escape to space of 13 TO is ≈300 Myr. Nevertheless, in this case, large amounts of oxygen (the content of ≈10 TO) are left behind in the atmosphere. Such a huge quantity cannot be physically removed at later stages by crust oxidation. Even at 100 Myr, when ≈5 TO have been lost to space, the content of 3 TO of oxygen is left in the atmosphere, much larger than our reasonable upper limit of 0.1 TO. If a magma ocean survived 100 Myr at the surface of Venus, this magma ocean could have dissolved oxygen. We therefore suggest that hydrodynamic escape stopped at the time when the magma ocean crystallized (likely ≈100 Myr, but possibly earlier), in such a way that most of the oxygen left in the atmosphere was lost to the magma.

From an isotopic analysis of SNC meteorites, Debaille et al. (2007) have shown that a magma ocean lasting at least 100 Myr has been present on Mars, which can be explained only if Mars has been covered by a thick atmosphere. A 300 bar atmosphere of water vapor, roughly corresponding to the water content of 1 TO vaporized to the atmosphere, results in a temperature at the surface of 1500 K (Abe and Matsui, 1988), therefore sufficient to keep rocks molten at the surface. It is now generally thought that Earth similarly developed a magma ocean during 100 Myr or so (Elkins-Tanton, 2008), resulting today in a surviving layer of dense melt at the base of the mantle (Labrosse et al., 2007). Although no observational data exist, it is tempting to assume that Venus developed a magma ocean at the beginning of its history.

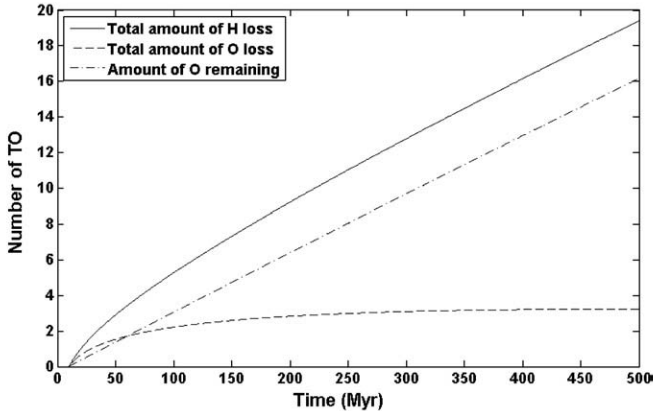

Fig. 5. Summary of the number of Terrestrial Oceans lost through the escape of H and O during the escape of Ne and O. We also added the amount of oxygen left behind hydrogen in the atmosphere of Venus. Preferred case ($\eta = 1.2$, $T = 750$ K, Start at 10 Myr).

Due to the accretion of water from the top, water is expected to be delivered to the atmosphere and upper layers of the magma ocean. Let us assume that 1 TO is delivered to the atmosphere, generating a pressure of 300 bar of water vapor in the atmosphere. At 300 bars, the solubility of water in the magma is 1.5 wt.% (Moore et al., 1995). If the mantle is totally molten, it may be calculated that the atmosphere is in this case at equilibrium with a molten mantle containing 36 TO. Such a high content is implausible when most of the accreted water has been lost. If the total content of the ocean is smaller, it results that the water vapor in the atmosphere cannot be at dissolution equilibrium, and therefore further dissolves in the magma. But, in this case, due to decreasing greenhouse effect, magma begins to cool by radiating to space and solidify at the base of the magma ocean (Elkins-Tanton, 2008). Solidification results in the exsolution of water and resupplying of the atmosphere in water vapor. The equilibrium is reached when the thickness of the upper molten layer of the mantle is such as there is a dissolution equilibrium between 300 bar of atmospheric water vapor and the subjacent magma layer containing 1.5 wt.% water. Assuming that the total amount of water contained in the atmosphere-magma ocean system is N TO, it may be calculated that the thickness Δz of the magma layer overlying solid mantle is $\Delta z = 60 \times (N - 1)$ km for a planet of 6000 km radius. Assuming that, at some time, there are 6 TO in the atmosphere-magma ocean system, the depth of the magma ocean is 300 km, overlying an already thick layer (2700 km) of crystallized magma. This equilibrium state is stable. This reasoning applies only if the dissolution rate doesn't depend on the temperature in the considered (p, T) range (0.3 kbar, 1500 K), which is nearly the case (Yamashita, 1999).

This negative feedback has already been pointed out by Matsui and Abe (1986). As shown by existing models (Zahnle et al., 1988, Elkins-Tanton, 2008), this process, although simplistic and probably not occurring during the main accretion period, must be true on average during quiet periods when no large impact occurs. Collisions are expected to remove a fraction, of the existing atmosphere at impact (Genda and Abe, 2005), but also provide it with fresh water. The system is expected to relax to the equilibrium over a few million years (Zahnle et al., 1988, Elkins-Tanton, 2008). At ≈100 Myr, after the bulk of accretion, stability of a ≈300 bar steam atmosphere could provide a rather exact view of the end of the magma ocean phase.

Indeed, hydrodynamic escape continuously occurs at the top of the atmosphere. In order to maintain the equilibrium, water is released from the magma to the atmosphere at a rate equal to the escape rate of hydrogen at the top. In this way, water is pumped from the magma by hydrodynamic escape, thus indirectly controlling the solidification rate of the magma. After most of the water of the magma has been removed, the water vapor amount in the atmosphere decreases over a characteristic time of ≈10 Myr (time for 1 TO of hydrogen to escape to space at 100 Myr, see Fig. 6). When the water mixing ratio in the global atmosphere becomes smaller than ≈10 wt.% (Kasting and Pollack, 1983), that is about 20 bar of water vapor partial pressure, hydrodynamic escape converts into Jeans thermal escape and massive escape virtually stops. At that time, the ocean has fully crystallized.

On Mars, the estimated duration of the magma ocean is ≈100 Myr (Debaille et al., 2007). On Earth, studies of single zircons suggest that some continental crust formed as early as 4.4 Gyr, 160 Myr after accretion of the Earth, and that surface temperatures were low enough for liquid water (Valley et al., 2002). Consistently, we assume that Venus' magma ocean crystallized before ≈100 Myr. It results from the present work that, at this time, ≈5 TO had escaped, and that the oxygen content of 3 TO had been left behind. These 3 TO of oxygen may have been dissolved in the magma ocean. It is difficult to put precise error estimates for these numbers, but a factor of 2 seems reasonable in view of the different sources of uncertainty, and of what we know about accretion and primitive solar conditions.

We therefore suggest that the main phase of hydrodynamic escape of hydrogen and oxygen at Venus ended before ≈100 Myr, at about the same time as the magma ocean, because most of the delivered water had

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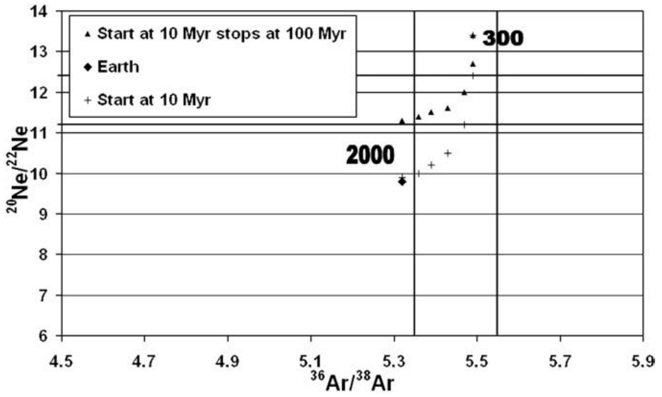

Fig. 6. Isotopic ratios according to different scenarios of the escape of the atmosphere of Venus when O escapes with $\eta = 1.2$. The ranges of the measured values of the isotopic ratios of Ne and Ar are limited by dashed straight lines. They delineate a box inside which measured isotopic ratios are satisfied. The point representing Earth atmosphere isotopic ratio is represented. Two scenarios are represented, one when the escape stops around 100 Myr (see discussion section), the other when there is enough water to continue until the H and O escape flux are too low to sustain the escape of neon. The successive points correspond to different temperatures: 300 K, 500 K, 750 K, 1000 K, 1250 K, 1500 K and 2000 K.

escaped at this time and, sufficient amounts of hydrogen were not available to power the escape. Argon and neon had been fractionated at a level comparable with their presently observed fractionation degree.

Assuming a static magma, and an oxygen diffusion coefficient of the order of 10^{-6} cm^2 s^{-1} (Wendlandt, 1991), the oxidation depth over 100 Myr is of the order of only 1 km. But the magma is likely highly convective, with a vertical mixing scale, over 100 Myr, of the order of the total mantle thickness (3000 km). From Lécuyer et al. (2000), it may be calculated that the oxygen content of 3 TO oxidizing ferrous iron results in a global equivalent hematite-rich crust layer of ≈ 150 km thickness.

Our scenario for the first 100 Myr is therefore self-consistent. During accretion, between 10 and 100 Myr, a net amount of water equivalent to the content of 5 TO is provided to the planet. Most of the hydrogen is progressively lost to space by hydrodynamic escape, whereas ≈ 3 TO of oxygen left behind is lost to the magma ocean before crystallization, assumed to occur at 100 Myr. Neon is fractionated to the present observed ^{20}Ne/^{22}Ne value during the first ≈ 100 Myr. The main phase of hydrodynamic escape ends up at 100 Myr because all the accreted water has been consumed in escape at this time, and consequently the magma ocean crystallizes at about the same time.

In the subsequent period (100–500 Myr), a maximum of ≈ 0.1 TO of water in order of magnitude is expected to have been delivered to the planet by comets and to have escaped by thermal escape. This order of magnitude is obtained by assuming that the probability of collision of a comet with the Earth is 10^{-6}, that the total mass of cometary matter is 100 Earth mass, and that 50% of cometary material is water (Morbidelli, personal communication, 2009), yielding a number of 0.2 TO, that is a 0.1 TO order of magnitude for the upper limit. Less than 10% of the oxygen contained in this water can escape together with hydrogen, and the O_2 content of the atmosphere at 500 Myr is expected to be of the order of ≈ 10 bars of O_2. In this way, a dense atmosphere of O_2 may have formed on Venus between 100 Myr and 500 Myr. This oxygen could have been removed at later stage by crust oxidation, and to a lesser extent non-thermal escape.

5.2. Comparison between Venus' and Earth' cases

Interestingly, Ar and Ne in Earth atmosphere are fractionated in a way which is consistent with the scenario proposed for Venus. The terrestrial value can be obtained for a value of η of 2.4 (twice our best case for Venus) and a thermospheric temperature larger than 1000 K. From Fig. 6, it may be seen that a reason why Ne is more fractionated on Earth could be that escape stopped earlier on Venus. Let's assume $\eta_{\mathrm{Venus}} = 2.4$, therefore $\eta_{\mathrm{Earth}} = 1.2$. Since the EUV flux at Earth level is twice smaller, and although the solar wind contribution can vary in a different way from Venus to Earth, assuming a twice lower energy input at Earth level is reasonable. In this case, provided the thermospheric temperature on Earth is larger than 1000 K, the present Earth's Ne fractionation pattern is reached on Earth after typically 100 Myr. In this case, in order to fit the Venus Ne fractionation pattern, we need to assume that water escape stopped on Venus at ≈ 50–70 Myr.

First, is such a Venus–Earth relative timing explainable? As previously mentioned, the most recent accretion simulations published in the literature point toward a lower water content of the accreting Venus by a factor of 3 in an average although it is not excluded that Venus has been endowed with as much water as Earth. A lower initial endowment in water of Venus, combined with a larger hydrodynamic escape rate, seems to favour the hypothesis that Venus has been dried up early. In this case, if 5 TO have been accreted by the proto-Venus, and mostly lost shortly after the end of water accretion, that is before ≈ 70 Myr, Ne has been fractionated during the first 70 Myr. It would imply that the initial Venus magma ocean crystallized early, at ≈ 50–70 Myr, triggered by fast dessication of mantle and atmosphere.

Second, is a thermospheric temperature of 500–1000 K, more than twice the present value, realistic? During most of the hydrodynamic escape phase, a substantial amount of CO_2 was dissolved in the magma ocean. Using CO_2 solubility data in molten basalt (Stolpen and Holloway, 1988), it may be calculated that a magma ocean of 100 km depth would reduce the present amount of atmospheric CO_2 by a factor of ≈ 2 (50 bar). For a depth of the magma ocean of 1000 km, the reduction factor is of ≈ 20 (5 bar). According to calculations of Kulikov et al. (2006), such a reduction of CO_2 may result in a thermospheric temperature larger than 500 K. It is difficult to precisely determine the primitive temperature of Venus thermosphere, in particular if much water was present in the atmosphere, but a higher temperature during the magma ocean, atmospheric CO_2-depleted, phase doesn't seem unrealistic.

Third, is a η factor of 2.4 for Venus realistic? Such a factor could be accounted for if $f = 8$ (exobase at ≈ 2 planetary radii) and $r = 1$ (one half of energy from solar wind), or $f = 16$ (exobase at ≈ 3 planetary radii) and $r = 0$ (no solar wind contribution). As suggested by Chassefière (1997), and proved by Tian et al. (2008) for Earth, the altitude of the exobase can reach very large values of several planetary radii (up to ≈ 15). Our assumption is therefore not unrealistic.

Assuming that Venus was endowed with 3 times less water than Earth, Earth would have accreted the water content of 15 TO. Assuming that the present water content of Earth is ≈ 2 TO, Earth must have lost ≈ 13 TO. From Fig. 6, which can be applied to the case of Earth if $\eta_{\mathrm{Venus}} = 2.4$ (in this case: $\eta_{\mathrm{Earth}} = 1.2$), it is seen that the time for 13 TO to be lost is of the order of 300 Myr. We know that the continental crust of Earth formed not later than 160 Myr (Valley et al., 2002). It results that Earth would have remained wet after the crystallization of its magma ocean, allowing the subsequent formation of a liquid water ocean.

5.3. Escape postdating heavy bombardment (500 Mr–present epoch)

The escape postdating 500 Myr could have been dominated by non-thermal escape of hydrogen and oxygen (Kulikov et al., 2006). At the present time, it is known that, at minimum solar activity, the H^+ escape flux from the upper Venus atmosphere by non-thermal escape is at least $\approx 10^{25}$ s^{-1} and that H and O escape in stoichiometric proportion (2 H for 1 O) (Barabash et al., 2007). This lower limit, recently obtained from the measurements of the ASPERA instrument on Venus Express, corresponds

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to an average flux of $\approx 3\cdot 10^6$ cm^{-2} s^{-1}. It is consistent with the values obtained from the plasma analyzer and ion-neutral spectrometer of the Pioneer Venus mission (Donahue, 1999). A H^+ escape flux of 107 cm^{-2} s^{-1} translates into a GEL of water of 10 cm depth per billion years. The deuterium fractionation factor is estimated to be 0.14 (Donahue and Hodges, 1992). Assuming a global average mixing ratio of 30 ppmv of water in the atmosphere (Marcq et al., 2008), the amount of water in the atmosphere is equivalent to a GEL of 1.3 cm (in STP conditions). Since deuterium in Venus atmosphere is enriched by a factor of ≈ 150 with respect to terrestrial ocean water (Donahue et al., 1982, De Bergh et al., 1991), the deuterium presently in the atmosphere corresponds to a GEL of 2 m depth, or $\approx 10^{-3}$ TO. Interestingly, this quantity fits rather well the amount which could have been lost by ion escape since 4 Gyr (Kulikov et al., 2006). A residual amount of water of 10^{-3} TO at 500 Myr may have escaped by non-thermal escape and the generated hydrogen fractionation is of the order of the value observed today.

This amount of 10^{-3} TO of water present at 500 Myr at the surface of Venus (or more likely in the atmosphere under the form of water vapor) is estimated assuming that no water has been released to the atmosphere by volcanism, or by impactors, during the last 4 Gyr. The cometary source is relatively modest (Donahue, 1999). Much less is known about outgassing. Possibly, the present atmospheric water vapor could be the remnant of the water vapor outgassed during the last resurfacing event, or the previous ones. According to Basilevsky et al. (1997), the average thickness of the basalt layer emplaced during the last resurfacing event, is 1–3 km. Assuming a water content of 2% (mass wt), typical of Earth conditions, the content of a water GEL of 10 m depth should have been released to the atmosphere. Since the deuterium present today in Venus' atmosphere corresponds to a GEL of 2 m depth, and because deuterium doesn't escape significantly, it means that the strict upper limit on the water vapor content of the extruded magma is 0.2%, assuming that the D/H ratio in the mantle is terrestrial. This limit should have to be reduced if other resurfacing events have occurred since 4 Gyr. From Head and Wilson (1986), the minimum content of water in Venus magma sources required to ensure explosive activity is 1%, and it results that Venusian volcanism is very likely not explosive, with the consequence that very little water can be released to the atmosphere by volcanism. If hydrogen presently escapes at the rate of a GEL of 10 cm depth per Gyr, no more than a few centimeters should have escaped since the last resurfacing event, corresponding to a magma water content of 100 ppm if all water is outgassed from the magma.

The question to know if the present water vapor on Venus is the remnant of a primordial reservoir or is at steady state has been extensively discussed by Grinspoon (1993) and Donahue (1999). Giving the uncertainty still existing on the hydrogen escape rate, it is not possible to give a definitive answer at this stage. Assuming a steady state, Grinspoon (1993) proposed that the average water content of Venusian magmas could be as low as ≈ 50 ppm by weight. In such a case, the mantle could be extremely desiccated, one thousand times dryer than the Earth mantle. He also proposed that the D/H ratio in the mantle could be non-terrestrial (typically ≈ 10 SMOW), with a fractionation resulting from a "massive hydrogen escape which occurred very early in the planet's history and was frozen into the mantle when an early magma ocean solidified". If so, the present atmosphere would be outgassed by the mantle and the high atmospheric D/H would reflect a signature preserved in the mantle. This idea of a quite desiccated mantle fits rather well the general conclusion of the present paper. Nevertheless, it cannot be excluded that the present mantle is not extremely dry (although drier than Earth mantle). If the water content of the magma is a fraction of percent, water is not (or only marginally) outgassed and remains within the magma during solidification. Interestingly, some water could be extracted later from volatile-rich basalts by erosion. Assuming an erosion rate of 1 nm/yr (Arvidson et al., 1992), and a water mixing ratio of surface basalts of 1%, and assuming that water in the eroded grains is released to the atmosphere, a GEL of ≈ 10 cm depth of water is released by this mechanism to the atmosphere in 1 Gyr, consistently with the present escape rate. Future measurements of the water content of surface rocks is of crucial importance to go further.

5.4. Global view of escape history

In this way, the initial hydrodynamic escape of hydrogen and oxygen (the equivalent of ≈ 5 TO), between 10 and 100 Myr, would have fractionated Ne, and Ar. At this time, the fraction of oxygen left behind hydrogen (≈ 3 TO) had been dissolved in the magma ocean and ultimately consumed in iron oxidation. The main phase of hydrodynamic escape would have ceased at 100 Myr, or earlier (≈ 50–70 Myr), when all the accreted water has been consumed in escape, resulting in the early crystallization of the magma ocean. In the subsequent period, from 100 Myr to 500 Myr, comets would have brought 0.1 TO of water, lost again by thermal escape, with a residual at 500 Myr of ≈ 10 bars of molecular oxygen, potentially removed later by oxidation of the crust during episodic volcanic events. At 500 Myr, based on the present D/H ratio and assuming no significant volcanic source of water at later stage, the amount of water remaining on Venus (at the surface or more likely in the atmosphere) should have been of the order of 10^{-3} TO (or less), subsequently lost to space by non-thermal escape, resulting in the today observed D/H ratio. Such a scenario, which explains H, Ne and Ar isotopic ratios observed today in the atmosphere, and the absence of significant amounts of oxygen in the present atmosphere, is self-consistent. It requires the existence of a magma ocean, maintained by the dense steam atmosphere, during the first ≈ 100 Myr (or less: 50–70 Myr), able to efficiently remove oxygen left behind hydrogen during the first phase of hydrodynamic escape. This scenario is summarized in Fig. 7.

6. Conclusion

The scenario presented in this paper must be considered as a possible, globally self-consistent, scenario. A major question remains to know what precisely happened after the closure of the magma ocean at ≈ 100 Myr, or even before (≈ 50–70 Myr). In this paper, we have proposed that the water atmospheric content, no more buffered at 300 bars after the solidification of the ocean, was removed quickly, over a time scale of ≈ 10 Myr, by hydrodynamic escape without condensation of water vapor into an ocean.

We don't know at the present time if such a condensation was possible or not from a thermodynamical point of view, due to large uncertainties on the results of existing radiative transfer codes of H_2O–CO_2 massive atmospheres. The critical point of H_2O is located at 647 K. As shown by Matsui and Abe (1986), the surface temperature of Earth at the end of accretion could have been ≈ 600 K, therefore lower than the critical temperature, and water would have been able to condense. From the same authors, the temperature of Venus surface at the end of the accretion was ≈ 700 K, larger than the critical temperature, potentially preventing atmospheric water from condensing out. But, as shown by Liu (2004), a dense supercritical H_2O–CO_2 mixture can condense at temperature lower than ≈ 720 K, and the condensation of atmospheric water on Venus seems thermodynamically possible in primitive Venus conditions. As suggested by Kasting (1988), who took also into account the effects of clouds, a water ocean could have formed on Venus if "its initial water endowment was close to that of Earth". The main result of the present study it that it could not have been the case. The initial endowment of Venus could have been smaller, by typically a factor of 3, than the endowment of Earth (typically 5 TO for Venus, 15 TO for the Earth). Because Venus is closer to the Sun, hydrodynamic escape would have been (twice) more efficient on Venus. Due to the combination of these two factors, most of the ≈ 5 TO accreted by Venus could have been removed before 70–100 Myr, triggering the early crystallization of the magma ocean and

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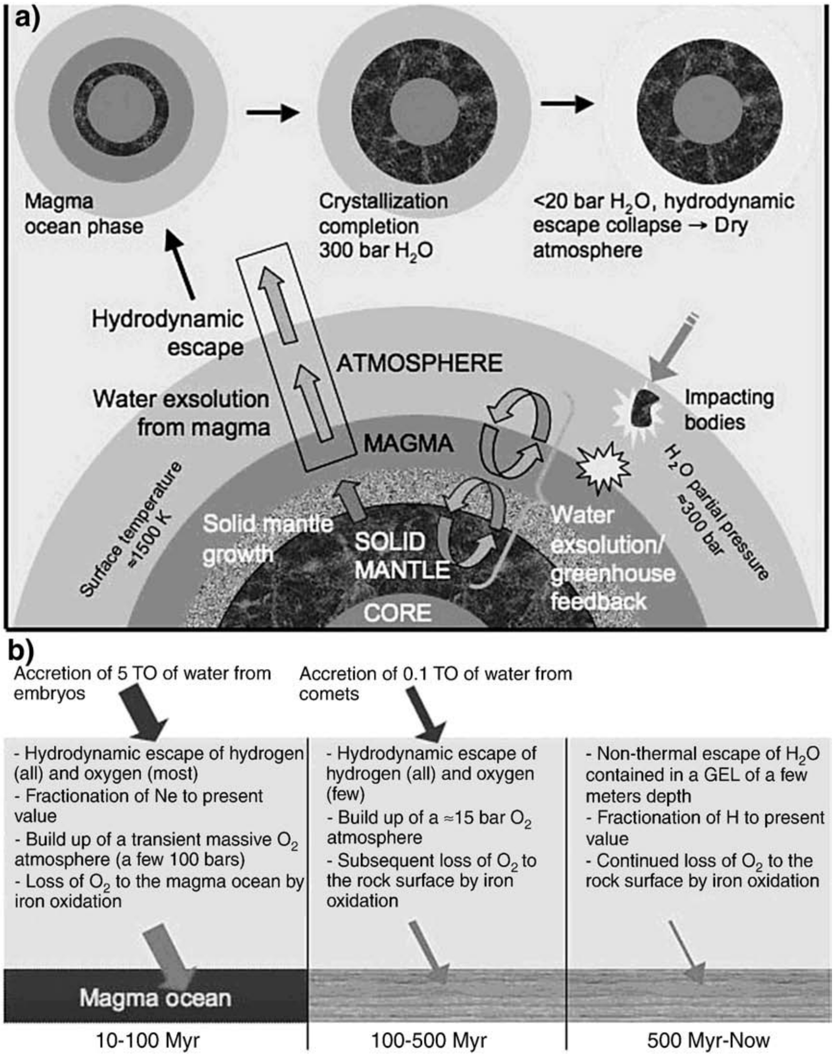

Fig. 7. a) Schematic diagram of (i) the coupling between magma ocean, atmosphere and hydrodynamic escape at the primitive Venus and (ii) the evolution of Venus until hydrodynamic escape collapse at ≈100 Myr. b) Possible scenario of Venus water history and later evolution.

leaving no significant amounts of available water for the formation of an Earth-size water ocean. On the contrary, Earth would have retained a significant fraction of its large initial water endowment after the solidification of its magma ocean, which occurred no later than 160 Myr (Valley et al., 2002), with possibly several TO still present in the mantle and/or the atmosphere at this date. If such a scenario is confirmed, it has strong potential implications on the history of the interior of the planet.

In the proposed scenario, the dense Venus CO_2 atmosphere doesn't result from an initial episode of runaway (or moist) greenhouse, but has been formed during the crystallization of the magma ocean, by progressive exsolution of carbon dioxide, at a time when the atmospheric partial pressure of water was of a few hundred bar. Due to strong hydrodynamic escape, pumping out water from the magma through the atmosphere, Venus' atmosphere has been dried up early, yielding crystallization of the magma, with no subsequent formation of an Earth-size ocean.

According to our model, Venus has developed in the 100–500 Myr time period a dense molecular oxygen atmosphere (typically ≈10 bar), with substantial amounts of water vapor (a few precipitable meters). Such a kind of planet, if observed in extrasolar planetary systems, should by a false–positive of a planet hosting life. The study of Venus is therefore of paramount interest to prepare the spectroscopic observation and interpretation of Earth-like extrasolar planets. An in-situ mission to Venus to measure more precisely the light noble gas isotopic ratios, and the heavy noble gas elemental and isotopic ratios, is a key element of further progress in comparative planetology. Measuring the water content and oxidation state of surface rocks would similarly be of paramount interest.

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References

Abe, Y., Matsui, T., 1988. Evolution of an impact-generated H_2O–CO_2 atmosphere and formation of a hot proto-ocean on Earth. J. Atmos. Sci. 45 (21), 3081–3101.

Arvidson, R.E., Greeley, R., Malin, M.C., Saunders, R.S., Izemberg, N., Plaut, J.J., Stofan, E.R., Shepard, M.K., 1992. Surface modification of Venus as inferred from Magella, observations of plains. J. Geophys. Res. 97 (E8), 13,303–13,317.

Barabash, S., 2007. The loss of ions from Venus through the plasma wake. Nature 450, 650–652.

Basilevsky, A.T., Head, J.W., Schaber, G.G., Strom, R.G., 1997. The resurfacing history of Venus. In: Bougher, S.W., Hunten, D.M., Phillips, R.J. (Eds.), Venus II. University of Arizona Press, pp. 1047–1086.

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Chamberlain, J.W., Hunten, D.M., 1987. Theory of planetary atmospheres: an introduction to their physics and chemistry. Academic Press, Inc., Orlando, FL. (book).

Chassefière, E., 1996a. Hydrodynamic escape of oxygen from primitive atmospheres: applications to the cases of Venus and Mars. Icarus 124, 537–552.

Chassefière, E., 1996b. Hydrodynamic escape of hydrogen from a hot water-rich atmosphere: the case of Venus. J. Geophys. Res. 101, 26039–26056.

Chassefière, E., 1997. Loss of water on the young Venus: the effect of a strong primitive solar wind. Icarus 126, 229–232.

Debaille, V., Brandon, A.D., Yin, Q.Y., Jacobsen, B., 2007. Coupled ^{142}Nd–^{143}Nd evidence for a protracted magma ocean in Mars. Nature 450, 525–528.

De Bergh, B., Bézardn, T., Owen, D., Crisp, Mailllard, J.-P., Lutz, B.L., 1991. Deuterium on Venus: observations from Earth. Science 251, 547–549.

Donahue, T.M., 1999. New analysis of hydrogen and deuterium escape from Venus. Icarus 141, 226–235.

Donahue, T.M., Hodges, R.R., 1992. Methane measurement by the Pioneer Venus large probe neutral mass spectrometer. Lunar and Planetary Inst., Papers Presented to the International Colloquium on Venus, p. 29.

Donahue, T.M., Hoffmann, J.H., Hodges Jr., R.R., Watson, A.J., 1982. Venus was wet: a measurement of the ratio of deuterium to hydrogen. Science 216, 630–633.

Elkins-Tanton, L.T., 2008. Linked magma ocean solidification and atmospheric growth for Earth and Mars. Earth Planet. Sci. Lett. 271, 181–191.

Genda, H., Abe, Y., 2005. Enhanced atmospheric loss on protoplanets at the giant impact phase in the presence of oceans. Nature 433, 842–844.

Grimm, R.E., Hess, P.C., 1997. The crust of Venus. In: Bougher, S.W., Hunten, D.M., Phillips, R.J. (Eds.), Venus II. University of Arizona Press, pp. 1205–1244.

Grinspoon, D.H., 1993. Implications of the high D/H ratio for the sources of water in Venus' atmosphere. Nature 363, 428–430.

Head, J.W., Wilson, L., 1986. Volcanic processes and landforms on Venus : theory, predictions, and observations. J. Geophys. Res. 91, 9407–9446.

Head, J.W., Wilson, L., 2003. Deep submarine pyroclastic eruptions : theory and predicted landforms and deposits. J. Volcanol. Geotherm. Res. 121, 155–193.

Hunten, D.M., 1973. The escape of light gases from planetary atmospheres. J. Atmos. Sci. 30, 1481–1494.

Hunten, D., Pepin, R., Walker, J., 1987. Mass fractionation in hydrodynamic escape (of gases from planetary atmospheres). Icarus 69, 532–549.

Kasting, J.F., 1988. Runaway and moist greenhouse atmospheres and the evolution of Earth and Venus. Icarus 74, 472–494.

Kasting, J.F., Pollack, J.B., 1983. Loss of water from Venus. I. Hydrodynamic escape of hydrogen. Icarus 53, 479–508.

Kulikov, Yu. N., Lammer, H., Lichtenegger, H.I.M., Terada, N., Ribas, I., Kolb, C., Langmayr, D., Lundin, R., Guinan, E.F., Barabash, S., Biernat, H.K., 2006. Planet. Space Sci. 54 (13–14), 1425–1444.

Labrosse, S., Hernlund, J.W., Coltice, N., 2007. A crystallizing dense magma ocean at the base of the Earth's mantle. Nature 450 doi:10.1038.

Lécuyer, C., Simon, L., Guyot, F., 2000. Comparison of carbon, nitrogen and water budgets on Venus and the Earth. Earth Planet. Sci. Lett. 181, 33–40.

Liu, L., 2004. The inception of the oceans and CO$_2$-atmosphere in the early history of Earth. Earth Planet. Sci. Let. 227, 179–184.

Lodders, K., Fegley Jr., B., 1998. The Planetary Scientist Companion. Oxford University Press, p. 124.

Marcq, E., Bézard, B., Drossart, P., Piccioni, G., Reess, J.M., Henry, F., 2008. A latitudinal survey of CO, OCS, H$_2$O, and SO$_2$ in the lower atmosphere of Venus: spectroscopic studies using VIRTIS-H. J. Geophys. Res. 113.

Matsui, T., Abe, Y., 1986. Evolution of an impact-induced atmosphere and magma ocean on the accreting Earth. Nature 319, 303–305.

Matsui, T., Tajika, E., 1995. Comparative Study of Crustal Production Rates of Mars, Venus and the Earth. Abstracts of the Lunar and Planetary Science Conference, vol 26 p. 909.

Moore, G., Vennemann, T., Carmichael, I.S.E., 1995. Solubility of water in magmas to 2 kbar. Geology 23, 12,1099–12,1102.

Morbidelli, A., personal communication, 2009.

Morbidelli, A., Chambers, J., Lunine, J.I., Petit, J.-M., Robert, F., Valsecchi, G.B., Cyr, K.E., 2000. Source regions and timescales for the delivery of water to the Earth. Meteor. Planet. Sci. 35, 1309–1320.

Namiki, N., Solomon, S.C., 1998. Volcanic degassing of argon and helium and the history of crustal production on Venus. J. Geophys. Res. 103, 2, 3655–3677.

O'Brien, D.P., Morbidelli, A., Levison, H.F., 2006. Terrestrial planet formation with strong dynamical friction. Icarus 184, 39–58.

Parmentier, E.M., Hess, P.C., 1992. Chemical differentiation of a convecting planetary interior : consequences for a one plate planet such as Venus. Geophys. Res. Let. 19 (20), 2015–2018.

Raymond, S.N., Quinn, Lunine, J.I., 2006. High-resolution simulations of the final assembly of Earth-like planets. I. Terrestrial accretion and dynamics. Icarus 183, 265–282.

Rasool, S.I., de Bergh, C., 1970. The runaway greenhouse and accumulation of CO$_2$ in the Venus atmosphere. Nature 226, 1037–1039.

Ribas, I., Guinan, E.F., Güdel, M., Audard, M., 2005. Evolution of the solar activity over time and effects on planetary atmospheres. I. High-energy irradiances (1–1700 Å). Astrphys. J. 622, 680–694.

Saito, T., Ishikawa, N., Kamata, H., 2007. Magnetic petrology of the 1991–1995 dacite lava of Unzen volcano, Japan: degree of oxidation and implications for the growth of lava domes. J. Volcanol. Geotherm. Res. 164, 268–283.

Shimazu, Y., Urabe, T., 1968. An energetic study of the evolution of the terrestrial and cytherean atmospheres. Icarus 9, 498–506.

Stolpen, E., Holloway, J.R., 1988. Experimental determination of the solubility of carbon dioxide in molten basalt at low pressure. Earth Planet. Sci. Lett. 87, 397–408.

Tian, F., Kasting, J.F., Liu, H., Roble, R.G., 2008. Hydrodynamic planetary thermosphere model: 1. Response of the Earth's thermosphere to extreme solar EUV conditions and the significance of adiabatic cooling. J. Geophys. Res. 113.

Valley, J.W., Peck, W.H., King, E.M., Wilde, S.A., 2002. A cool early Earth. Geology 30 (4), 351–354.

Volkov, V.P., Frenkel, M.Y., 1993. The modeling of Venus' degassing in terms of K–Ar system. Earth Moon Planets 62, 117–129.

Wendlandt, R.F., 1991. Oxygen diffusion in basalt and andesite melts: experimental results and discussion of chemical versus tracer diffusion. Contrib. Mineral. Petrol. 198, 463–471.

Wieler, R., 2002. Noble gases in the solar system. In: Porcelli, D., Ballentine, C.J., Wieler, R. (Eds.), Noble Gases in Geochemistry and Cosmochemistry, pp. 21–70 (Geochemical Society, Mineralogical Society of America).

Yamashita, S., 1999. Experimental study of the effect of temperature on water solubility in natural rhyolite melt to 100 MPa. J. Petrology 40 (10), 1497–1507.

Zahnle, K.J., Walker, J.C.G., 1982. The evolution of solar ultraviolet luminosity. Rev. Geophys. Space Phys. 20, 280–292.

Zahnle, K.J., Kasting, J.F., 1986. Mass fractionation during transonic escape and implications for loss of water from Mars and Venus. Icarus 68, 462–480.

Zahnle, K.J., Kasting, J.F., Pollack, J.B., 1988. Evolution of a steam atmosphere during Earth's accretion. Icarus 74, 62–97.

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