

## ESA Technical Note

### THE (ANTICIPATED) DIVERSITY OF TERRESTRIAL PLANET ATMOSPHERES

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Recent exoplanet discoveries have profoundly changed our vision of the formation, structure, and composition of low mass planets. While it has been long thought, mostly based on the observation of our own Solar System, that there should be a gap between telluric planets with a thin, if any, secondary atmosphere and the so called icy giants that retained a substantial amount of hydrogen and helium accreted from the protoplanetary disk, this gap does not seem to exist in exoplanetary systems.

Indeed, as can be seen in Fig. 1, the distribution of the radius of *Kepler* planet candidates (Batalha et al., 2013) is quite continuous from 0.7 up to 10 Earth radii, and particularly between 2-4 Earth radii where the transition from Earth- to Neptune-like planets was thought to occur. Although these observations are still incomplete - especially when planets get smaller, or have a lower equilibrium temperature, or orbit bigger stars - they suggest that there is no clear cut distinction between low mass terrestrial planets and more massive planets for which the gaseous envelope represents a significant fraction of the bulk mass. If such a continuum exists in the bulk composition of low mass planets, one can also anticipate that the various atmospheric compositions seen in the Solar System are only particular outcomes of the continuum of possible atmospheres.

This raises several pending questions. What kind of atmospheres can we expect? Can we relate the global, measurable parameters of a planet (mass, radius, intensity and spectral distribution of the incoming stellar energy, ...) to the mass and composition of its atmosphere? How sensitive is the final atmosphere to the (yet) unconstrained initial conditions (mass and dispersal time of the gaseous disk, composition of the planetesimals, ...)? To start answering these questions, many theoretical studies have tried to understand and model the various processes controlling the formation and evolution of planetary atmospheres, with some success in the Solar System. As will be made clear in § 1, however, such atmosphere evolution models need heavy calibrations.

Therefore, to understand the zoology of exoplanet atmospheres, more observational constraints are needed. To that purpose, combined measurements of both the mass and radius of low mass exoplanets already provide some clues because they can constrain gas envelope/core mass fraction of the object (see Fig. 2). However, the atmospheric composition itself can only be probed through spectroscopic observations, and only dedicated missions like EChO (Tinetti et al., 2012) will be

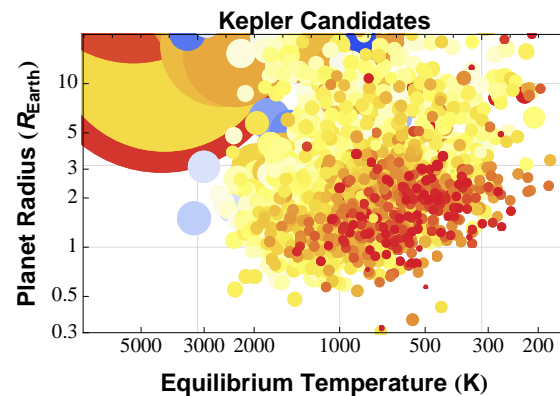


Figure 1: *Kepler* planet candidates in a radius-equilibrium temperature diagram. The size and the color of each dot are respectively representative of the size and color of the parent star. This diagram suggests the absence of any gap in the planet radius distribution between Earth- and Neptune-size planets.

able to produce such spectroscopic observations for a large enough number of target so that we can start to map out the diversity of low-mass exoplanet atmospheres.

Anticipating this wealth of data, in this note, we shortly review the various physical processes that contribute to the formation and evolution of planetary atmospheres (accretion, outgassing, escape; § 1 and 2) and we try to give an idea of the various type of atmospheres that these processes can create (§ 3). Then, in § 4, we will discuss how observations with a mission like EChO would help us unravel the link between a planet environment and its atmosphere.

## 1 THE VARIOUS ORIGINS OF THE ATMOSPHERE

To understand the various possible types of atmospheres, one first needs to consider the various sources of volatiles available during the formation of the planet. These sources have mainly two origins: the nebular gas present in the protoplanetary disk during the first 1 to 10 Myr of the planet formation, and the volatiles condensed and trapped into the planetesimals accreting on the nascent planet (mainly H<sub>2</sub>O and CO<sub>2</sub>). These volatiles initially incorporated in the bulk of the mantle can be released through two major channels, catastrophic outgassing and release by volcanism, with very different timescales.

As discussed in Section 2, because atmospheric escape is closely related to the stellar activity, it is strongly time dependent at early ages. The timescale on which the various species can be added to the atmosphere is thus critical in determining what is left in the matured atmosphere. Hence, we will discuss these three formation channels and their associated timescales separately.

### 1.1 Nebular gas and protoatmospheres

When a dense, cold molecular cloud gravitationally collapses to form a protostar, conservation of angular momentum forces a fraction of the gas to remain in an extended disk where planets can form. This gas is mainly composed of hydrogen and helium. The abundances of heavier elements are expected to be close to the stellar ones, except for some elements that can be trapped in condensing molecules. While these disks are quickly dispersed by stellar radiation and winds (on timescales on the order of 3 Myr), planetary embryos more massive than  $\sim 0.1 M_{\text{Earth}}$  can retain a significant mass of nebular gas, depending of course on the local conditions in the nebula, on the core mass and on the accretion luminosity.

An extreme case occurs when the embryo becomes massive enough and the mass of the atmosphere becomes similar to the core mass. Then, the so called core instability can be triggered, resulting in an unstable gas accretion that can proceed almost until all the available gas in this region of the disk is fed to the planet (Mizuno, 1980; Stevenson, 1982; Pollack et al., 1996). This is the mechanism that is thought to have formed the four giant planets in our Solar System. The critical core mass above which the core instability is triggered could be as low as a few Earth masses, and a substantial primitive atmosphere could be accreted by much smaller planets (Ikoma & Hori, 2012).

This is well illustrated on Fig. 2 where the masses and radii of all the observed low mass transiting planets are reported. If one object exhibits a radius that is bigger than the radius that would have a pure water world (water being the less dense, most abundant material except for H/He) of the same mass (dashed curve), this tells us that at least a few percents of the total mass of the planet are made of low density species, most likely H<sub>2</sub> and He gas. The fact that many objects less massive than Neptune are in this regime indeed confirms the possibility to accrete a large fraction of gas down to  $2\text{-}3 M_{\text{Earth}}$ , the mass of Kepler-11 f.

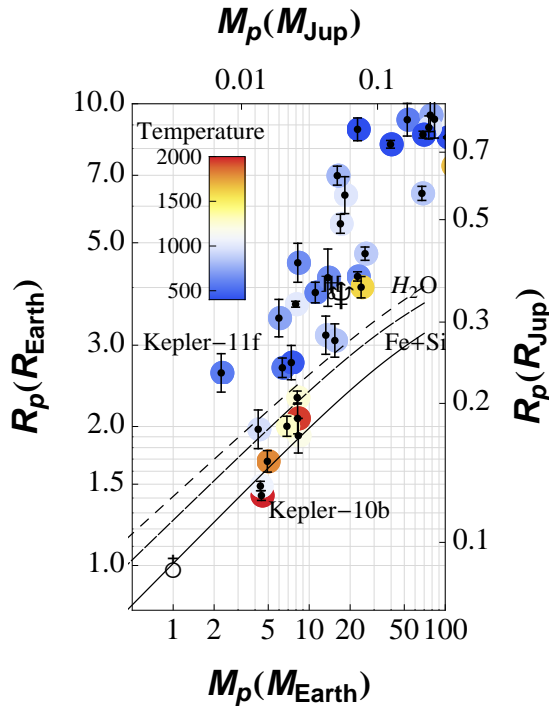


Figure 2: Mass-radius diagram of planets in the Earth to Saturn mass regime. The color of each dot is related to the equilibrium temperature of the planet (see color bar in K). Curves represent the mass radius relationship for an Earth like planet with a water mass fraction of 0, 0.5 and 1 from bottom to top. Planets above the top curve must have a massive gaseous envelope to explain their large radii. One can see that in the low mass regime, hotter planets preferentially have a higher density that is either due to the more efficient escape or to lower gas accretion efficiency in hot regions of the disk.

The fact that, in a given mass range, radii can easily vary by a factor of two reminds us, if need be, that the early gas accretion depends on many parameters that are not well understood (mass and dispersal time of the disk that can change from one system to another, location of the protoplanet, ...). The determination of the gas mass fraction of a given object, even knowing its current properties, is far from being a trivial task.

## 1.2 Catastrophically outgassed $\text{H}_2\text{O}/\text{CO}_2$ atmospheres

The other source of volatiles are the planetesimals that accrete to form the bulk of the planet itself. These will be the major sources of carbon compounds (mainly  $\text{CO}_2$  and possibly  $\text{CH}_4$ ), water (especially if they formed beyond the ice line), and, to a lesser extent,  $\text{N}_2/\text{NH}_3$  and other trace gases.

In current terrestrial planet formation models, planets are usually formed in less than 100 Myr. During this phase, the energy produced by the impacts of the planetesimals and planetary embryos is generally large enough to melt the upper mantle, creating a planet-wide magma ocean. When the accretion luminosity decreases, however, this magma ocean starts to solidify. Because solidification is more easily initiated at high pressures and molten magma is less dense than the solid phase, this solidification proceeds from the bottom upward (Elkins-Tanton, 2008). During this phase which can last from  $10^5$  yr to 3 Myr depending on the volatile fraction,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , which cannot be trapped in the solid phase in large quantities, are rapidly outgassed.

The mass of the resulting atmosphere then depends on the composition of the planetesimals, and thus on their initial location as well as on the metallicity of the star. For a planet like the Earth formed at warm temperatures (where water ice is not stable), the available amount of volatiles should be limited because the water mass fraction in the planetesimal should be low. It is estimated that no more than a few Earth oceans equivalent mass ( $\text{EO} \approx 1.4 \times 10^{21}$  kg  $\approx$  270 bar on Earth) of water and 50-70 bar of  $\text{CO}_2$  were released that way (Lammer 2013, and reference Therein).

If the planet is formed much closer to, or even beyond, the snow line, the water content of the planetesimals could be much larger (a few 10wt%), and tens to thousands of Earth oceans of water could be accreted (Elkins-Tanton, 2011). This suggests the existence of a vast population of planets with deep oceans (aqua-planets) or even whose bulk composition is dominated by water (ocean planets; Léger et al. 2004). In that case, the physical state of the outer water layer (supercritical, steam, liquid water, ice), depends on the temperature that is first controlled by the cooling mantle during the first tens of Myr and then by the insolation received.

### 1.3 Volcanically degassed secondary atmospheres

On a much longer, geological timescale, the volatiles that remained trapped in the mantle during the solidification can be released through volcanic outgassing. Along H<sub>2</sub>O and CO<sub>2</sub>, this process can bring trace gases at the surface, such as H<sub>2</sub>S, SO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, HF, H<sub>2</sub>, CO, and noble gases such as Ar, Xe, etc.

On Earth and Mars, there are strong evidences that this secondary outgassing has played a major role in shaping the present atmosphere. However, the importance of this process on other planets will depend on the strength of the tectonic activity, if tectonic activity there is.

On Earth and Mars, there are strong evidences that this secondary outgassing has played a major role in shaping the present atmosphere. In particular, Tian et al. (2009) showed that the thermal escape (see below) induced by the extreme ultraviolet flux from the young sun was so strong that a CO<sub>2</sub> atmosphere could not have been maintained on Mars until about 4.1 billion years ago. Nevertheless, a late secondary atmosphere is thought to have been degassed, in particular via the magmas that formed the large volcanic Tharsis province. Phillips et al. (2001) estimated that the integrated equivalent of a 1.5-bar CO<sub>2</sub> atmosphere could have accumulated, but more realistic models have significantly lower this value (Hirschmann & Withers, 2008; Grott et al., 2011). Similarly, the 5% of photochemically unstable methane present in the present-day Titan atmosphere are thought to originate from episodic outgassing of methane stored as clathrate hydrates within an icy shell in the interior of Titan (Tobie et al., 2006).

## 2 ATMOSPHERIC SINKS

While tens to thousands of bars of H/He and CO<sub>2</sub> may have been present in the early Earth atmosphere, they are obviously not there anymore (the water now being into liquid form in the oceans). This tells us that some processes, e.g. atmospheric escape and weathering/ingassing, can play the role of atmospheric sinks, and that these processes are powerful enough to remove completely massive protoatmospheres if the right conditions are met.

Considering the fact that there are three main successive delivery of different volatiles during the early stages of the planet's evolution, the main questions are to know when these atmospheric sinks are most efficient and if they can selectively deplete some species with respect to the others. This is what we will now discuss.

### 2.1 Atmospheric escape

Atmospheric molecules can leave the planet's attraction if they go upward with a speed exceeding the escape velocity (Jeans, 1925). However, in the lower part of the atmosphere, the gas density is large enough to ensure a high collision rate, preventing hot particles with a sufficient velocity to leave the planet. As the density decreases with height, this assumptions breaks down when the

mean free path of the particles becomes bigger than the scale height of the atmosphere. Around this level, called the exobase, stellar excitation by radiation and plasma flows is important, and fast enough atmospheric particles can actually escape.

There are several ways for the particles to reach escape velocities, defining the various escape mechanisms that can be separated into two families: thermal and non-thermal escape (see Lammer (2013) for a review). Thermal escape characterizes atmospheric escape primarily caused by the stellar radiative excitation of the upper atmosphere. To first order, it depends on the gravity, and on the temperature of the exobase. This temperature is not controlled by the total bolometric insolation which heats the surface and the lower atmosphere, but by the flux of energetic radiations and the plasma flow from the star (especially the extreme ultraviolet which is absorbed by the upper atmosphere). It also depends on the ability of the atmospheric molecules to radiatively cool to space by emitting infrared radiation; to simplify, greenhouse gases like  $\text{CO}_2$  can efficiently cool, whereas other gases like  $\text{N}_2$  cannot. Thermal escape exhibits two regimes:

- *Jeans escape* when the exosphere is in hydrostatic equilibrium, and only the particles in the high energy tail of the Maxwell distribution can leave the planet. Lighter atoms and molecules like hydrogen and helium are more affected because they reach a much higher velocity at a given thermospheric temperature.
- *hydrodynamic escape*, the so-called *blow-off* regime, when radiative heating can only be compensated by an adiabatic expansion and escape of the whole exosphere. On the terrestrial planets in our solar system such conditions may have been reached in H- or He-rich thermospheres heated by the strong EUV flux of the young Sun.

Non-thermal escape result from energetic chemical reactions or interactions with the stellar wind (*ion pick-up, plasma instabilities, cool ion outflow, polar wind*, etc. See Lammer (2013) for a more complete description of these processes).

While it is clearly out of the scope of this note to go into the details of each of these mechanisms, it is interesting to derive an order of magnitude estimate for the maximum escape that can be expected for a given planet. This can be done by considering the hypothetical case of *energy limited escape*. This limit is obtained by assuming that a given fraction  $\eta$  (the heating efficiency) of the radiative flux available to be absorbed in the upper atmosphere is actually used to extract gas from the gravitational potential well of the planet. Because the exospheric levels are only sensitive to the very energetic photons in the X-EUV range (wavelength below 100 nm), the energy limited escape rate  $F_{\text{esc}}$  can be written

$$F_{\text{esc}} = \eta \frac{R_p F_{\text{XUV}}}{GM_p} \quad (\text{kg m}^{-2} \text{s}^{-1}), \quad (1)$$

where  $F_{\text{XUV}}$  is the averaged XUV flux received by the planet (i.e. divided by 4 compared to the

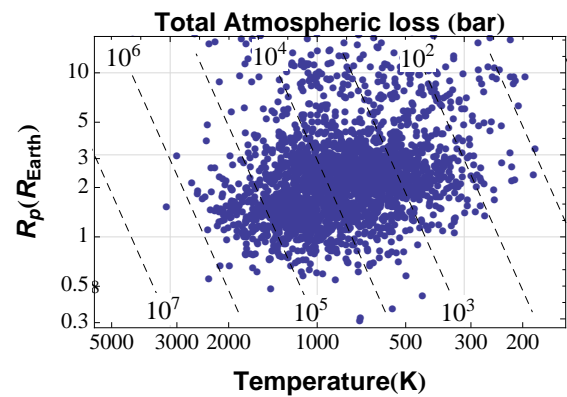


Figure 3: *Kepler* planet candidates in a radius-equilibrium temperature diagram. Dashed lines represent contours of the average total amount of atmosphere that should be lost by a planet at the given position in the diagram in bars (atmospheric loss is integrated over 5 Gyr and accounts for the early active phase of the star).

flux at the substellar point),  $G$  is the universal gravitational constant, and  $R_p$  and  $M_p$  are the planetary radius and mass.

Unlike the total bolometric luminosity, the stellar luminosity in the X-EUV range  $F_{XUV}$  is correlated with the stellar activity, which is very high at young ages and declines over time. Therefore, the escape rate strongly varies with time. For example, the solar EUV flux is believed to have been 100 times stronger than today during the first hundred million years of our Sun's life, to later decrease following a power law (Ribas et al., 2005; Lammer et al., 2011). Thermal escape is thus most relevant during the first tens to hundreds of Myr after the star formation, i.e. on a timescale which is similar to the atmosphere formation process! The implications of the coincidence will be discussed in Section 3.

To give an idea of how strong this escape can be, we computed the total atmospheric pressure that can be lost during the planet lifetime

$$p_{\text{esc}} = \int \frac{GM_p}{R_p^2} F_{\text{esc}}(t) dt = \frac{\eta}{R_p} \int F_{XUV}(t) dt, \quad (2)$$

as a function of the planetary radius and for an efficiency  $\eta = 0.15$  (Murray-Clay et al., 2009; Lammer, 2013; Lammer et al., 2013). The variation over time of the XUV to bolometric flux ratio (so that the results can be expressed in terms of the equilibrium temperature of the planet) is modeled for a solar type star using the parametrization of Sanz-Forcada et al. (2011). The results are shown in Fig. 3 (dashed labeled contours). As expected, atmospheres are more sensitive to escape when the planet receives more flux (higher equilibrium temperature) and is smaller (weaker gravity). Interesting enough, current planet candidates (purple dots in Fig. 3) are expected to exhibit very different levels of atmospheric losses, with cold giant planets for which the effect of escape on the atmospheric content can almost be neglected, and highly irradiated Earth-like objects for which the whole atmosphere has probably been blown away (see § 3; Léger et al. 2011).

In Fig. 3, we assume a solar type star, but in reality, at a given bolometric insolation, escape is also expected to be more intense around low mass stars as they emit a larger fraction of their flux in the XUV range. This can be seen in Fig. 4. It is due to the increased duration of the active phase of lower mass stars.

Finally, let us mention the fact that, because escape originates from the upper atmosphere, only the particles present there are substantially affected. This explains why low mass atoms and molecules, which are more abundant in the high levels of the atmosphere, escape more easily. Hydrogen, whether it comes from the photodissociation of  $H_2$  or  $H_2O$ , is a perfect example and is generally the first gas to escape, although it can drag heavier atoms along if escape occurs in the hydrodynamic regime (Hunten et al., 1987).

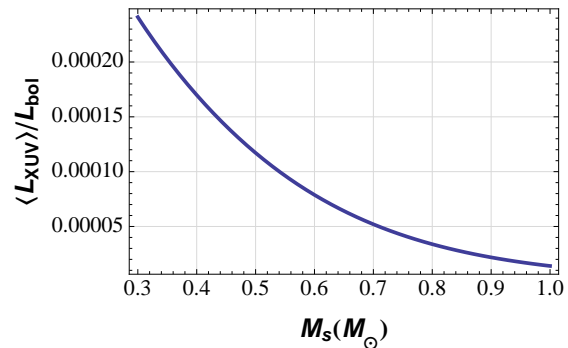
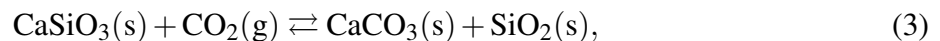


Figure 4: Ratio between the mean XUV luminosity (integrated over time) and the bolometric luminosity of a star as a function of its mass. Computed using Sanz-Forcada et al. (2011) parametrization for  $L_{XUV}$ . The greater ratio for lower mass stars stems from the longer early activity phase and results in a more efficient escape around smaller stars (at a given bolometric flux).

## 2.2 Weathering and ingassing

The atmospheric composition can also be altered by interactions with the surface. Indeed, if the right conditions are met, some constituent of the atmosphere can chemically react with the surface and get trapped there. In addition to this process, called weathering, the aforementioned surface can be buried by lava flows or subducted by plate tectonics, re-enriching the mantle in the volatiles that have been trapped; volatiles that will eventually be released by volcanic activity later.

An example of such process is the chemical weathering of silicate minerals in presence of liquid water and CO<sub>2</sub>. Atmospheric CO<sub>2</sub> goes into solution in liquid water relatively easily and the resulting fluid, carbonic acid (H<sub>2</sub>CO<sub>3</sub>), reacts with the silicate minerals of the crust to weather the rock and release calcium, magnesium, and iron ions into the water. These ions can promote the precipitation of solid carbonates, (Ca,Mg,Fe)CO<sub>3</sub>. To simplify, the following net reaction



can occur. This reaction traps carbon dioxide into carbonates that can accumulate before being buried by subduction.

A very interesting property of this *carbonate-silicate cycle*, is that it provides a powerful stabilizing feedback on planetary climates on geological timescales (Walker et al., 1981). Indeed, because the reaction occurs in an aqueous phase and is made easier by the erosion of the ground by rainfalls, weathering rates increase when precipitations, and thus temperatures, increase. On the other extreme, weathering is fairly limited when the surface is frozen. As a result, high (low) temperatures will increase (decrease) the weathering, leading to a lower (higher) greenhouse effect by carbon dioxide. This feedback, which is believed to have stabilized Earth climate over time, is at the very heart of the modern vision of the concept of "habitable zone", the zone around a star where liquid water can be stable at the surface of the planet (Kasting et al., 1993).

On the other hand, this means that the climate itself can have a strong feedback on the atmospheric composition. For example, in the absence of liquid water, the capture of CO<sub>2</sub> is very inefficient. Thus, while Venus and the Earth may have accreted a comparable amount of CO<sub>2</sub> during their formation, it might be because Venus climate has entered a runaway greenhouse state for which no liquid water could be stable at the surface that the planet ended up with a thick, 93 bar CO<sub>2</sub> atmosphere (Rasool & de Bergh, 1970). On Earth, most of the initial CO<sub>2</sub> inventory is thought to be trapped in form of carbonates in the crust after chemical precipitation.

The formation of carbonates has also been suggested on early Mars when abundant liquid water seems to have flowed on the surface, possibly explaining the fate of an early thick CO<sub>2</sub> atmosphere (Pollack et al., 1987). However, almost no carbonates were initially detected by the OMEGA imaging spectrometer in spite of its high sensitivity to the spectral signature of carbonates (Bibring et al., 2005). Recently, several observations from orbiters (Ehlmann et al., 2008) and landers (Boynton et al., 2009; Morris et al., 2010) have revived the carbonate hypothesis and reasserted the importance of carbon dioxide chemistry in martian climate history (Harvey, 2010).

## 3 MAJOR CLASSES OF ATMOSPHERES

Let's make an attempt to see how the processes described above fit together to produce the diversity of atmospheres that we know, or can expect. Indeed, we have seen that they have the ability to build or get rid of an entire atmosphere. The key is now to identify the mechanism(s) that are most relevant to a given planetary environment. The result of this process is summarized in the diagram shown in Fig. 5 and discussed below.

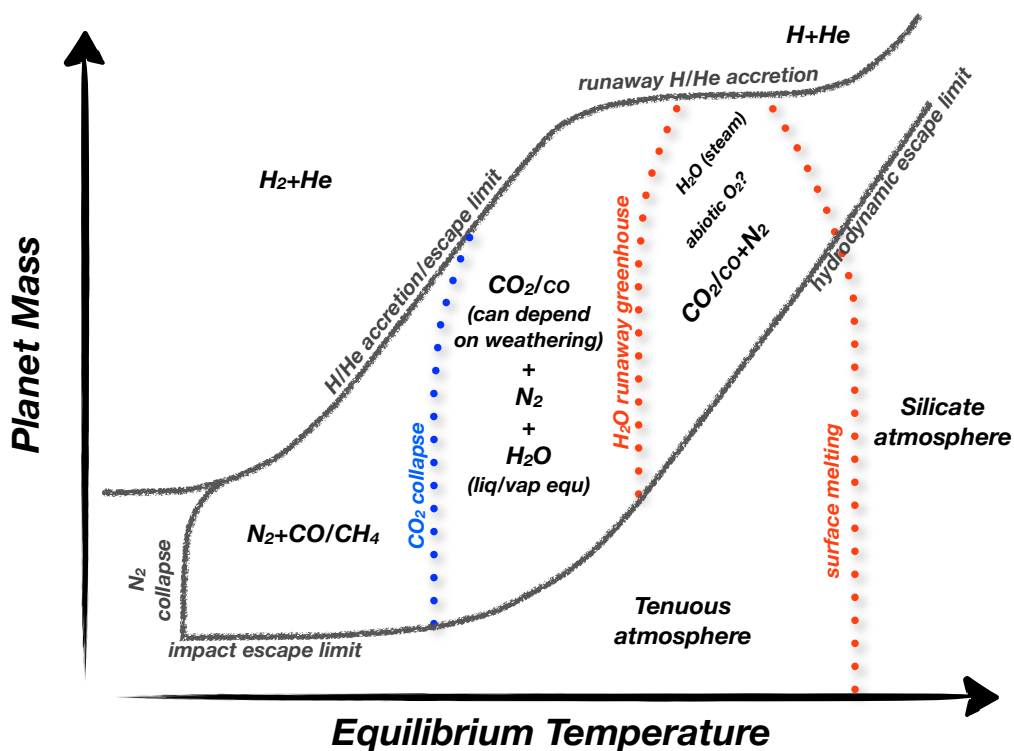


Figure 5: Schematic summary of the various class of atmospheres. Each line represent a transition from one regime to another, but note that these "transitions" are in no way hard limits. Only the expected dominant species are indicated, but other trace gas should of course be present.



### 3.1 H/He dominated

Hydrogen and helium being the lightest elements and the first to be accreted, they can most easily escape. The occurrence of H/He dominated atmosphere should thus be limited to objects more massive than the Earth. Indeed, in the Solar System, none of the terrestrial planetary body managed to accrete or keep a potential primordial H/He envelope, even the coldest ones which are less prone to escape.

Fig. 2 suggests that a mass as low as  $2M_{\text{Earth}}$  can be sufficient to build and keep such an atmosphere. But it also suggests that being more massive than that is by no means a sufficient condition. Indeed, some objects have a bulk density similar to the Earth up to  $8-10M_{\text{Earth}}$ . Although these high density planets receive a stronger stellar insolation on average, it is not clear yet whether this correlation stems from the fact that planets forming on closer orbits can accrete less nebular gas (Ikoma & Hori, 2012), or from the fact that hotter planets exhibit higher escape rates. Note that the first hypothesis assumes that such close-in planets are formed in-situ.

Then, the presence of a large fraction of primordial nebular gas in the atmosphere of warm to cold planets above a few Earth masses should be fairly common. The real question will be to know the atmosphere mass and by how much these atmospheres will be enriched in heavy elements compared to the parent star? Such information will be critical to better understand the early stage of planet and atmosphere formation during the nebular phase.

### 3.2 H<sub>2</sub>O/CO<sub>2</sub>/N<sub>2</sub> atmospheres

Then, if, for some reason, the planet ends up its accretion phase with a thin enough H/He atmosphere so that surface temperatures can be cold enough for the solidification, a significant amount of H<sub>2</sub>O and CO<sub>2</sub> should be released (envelope between gray curves in Fig. 5). To understand what will happen to these volatiles, however, one needs to understand in which climate regime the planet will settle.

#### 3.2.1 Which physical state for H<sub>2</sub>O?

Saving for later the very hot temperatures for which the surface itself is molten, let us go through the different available regime from the upper left to the lower right part of Fig. 5.

Above a certain critical flux, the so called runaway greenhouse limit, the positive radiative feedback of water is so strong that the atmosphere warms up until surface water is vaporized (Kasting, 1988)<sup>1</sup>. In this case, the absence of surface water hampers CO<sub>2</sub> weathering, leaving most of the CO<sub>2</sub> inventory in the atmosphere.

In this case, a key question concerns the conservation of the water itself. Indeed, if H<sub>2</sub>O is a major constituent of the atmosphere, it can easily be photo-dissociated high up. This produces H atoms that are ready to escape. Although this seemed to occur on Venus, more massive planets with a higher gravity to counteract escape, or object that accreted more water may still possess a significant fraction of atmospheric water (see for example the debate on the atmospheric composition of GJ 1214 b; Miller-Ricci & Fortney 2010; de Mooij et al. 2012)

Below the runaway greenhouse limit, water can condense at the surface. Except for a few planets very near the limit, water vapor should thus remain a trace gas in liquid/vapor equilibrium with the surface. Thus, the atmosphere could be dominated by species that are less abundant in the initial inventory but have been slowly outgassed such as N<sub>2</sub>, among others. In such a state,

<sup>1</sup>Although this limit is not that well defined when the water inventory is very limited (Abe et al., 2011; Leconte, J. et al., 2013).

CO<sub>2</sub> weathering can be efficient so that the amount of carbon dioxide might depend smoothly on the surface temperature (Abbot et al., 2012). However, if water is lost due to atmospheric escape, especially for lower mass planets such as Mars, or hotter ones, CO<sub>2</sub> could build up in the atmosphere and become the dominant gas.

For colder climates, even CO<sub>2</sub> greenhouse warming is insufficient to prevent its condensation indefinitely. When this CO<sub>2</sub> collapse occurs, water of course, but also CO<sub>2</sub> itself can only be found in trace amounts. As is seen in the solar system (e.g. Titan), N<sub>2</sub> thus becomes the only stable abundant species (apart from H<sub>2</sub>/He). Carbon compounds can be found in the form of CO or CH<sub>4</sub> depending on the oxidizing/reducing power of the atmosphere. This can continue until the triple point of nitrogen itself is reached. At that point N<sub>2</sub> ice albedo feedback favors a very cold climate where nitrogen is in condensation/sublimation equilibrium with the surface, leaving only tenuous atmospheres such as the ones found on Pluto and Triton.

### 3.2.2 the possibility of abiotic O<sub>2</sub>

Molecular oxygen O<sub>2</sub> cannot easily become a dominating species in a planetary atmosphere because it is chemically reactive and is not among the volatile species provided by planetesimals. Most of the O<sub>2</sub> in Earth present atmosphere is thought to have been produced by oxygenic photosynthesis. Nevertheless, several abiotic scenarios that could lead to oxygen-rich atmosphere have been suggested and studied in details, because the presence of O<sub>2</sub> and the related species O<sub>3</sub> (easier to detect) in the atmosphere of an exoplanet are considered to be possible biomarker compounds (Owen, 1980; Leger et al., 1993)

The most likely situation in which O<sub>2</sub> might accumulate and become a dominant species is in a runaway greenhouse planet, like early Venus, on which large amounts of hydrogen escape from a hot, moist atmosphere (See Lammer et al. 2011, and reference therein). Because the hydrogen originates from H<sub>2</sub>O, oxygen is left behind. The escape of a terrestrial ocean equivalent of hydrogen, unaccompanied by oxygen sinks, could leave an atmosphere containing up to 240 bars of O<sub>2</sub> (Segura et al., 2007). Alternatively O<sub>2</sub> could be produced by photosynthesis of CO<sub>2</sub> in a very dry environment, but its concentration is then not likely to reach more than a few percents (Selsis et al., 2002; Segura et al., 2007)

### 3.2.3 Photochemistry and CO

CO<sub>2</sub> atmosphere may not be photochemically stable. In fact, the abundance of CO<sub>2</sub> on Mars and Venus seemed puzzling early in the space age, because CO<sub>2</sub> is readily photo-dissociated. The direct three-body recombination,  $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$ , is spin-forbidden and therefore extremely slow at atmospheric temperatures. The solution for Mars is that photolysis of water vapor produces OH radicals that react readily with CO to make CO<sub>2</sub>; in effect water vapor photolysis catalyses the recombination of CO<sub>2</sub>. Could the equilibrium be reversed in favor of CO in some conditions? Zahnle et al. (2008) showed that this may happen in thick cold (and thus relatively dry) atmosphere, although they noted that in reality CO could react with the surface (Fe) and be recycled as CO<sub>2</sub> by another path. Another interesting point is that the stability question is asymmetric. Under plausible conditions a significant CO atmosphere can be converted to a CO<sub>2</sub> atmosphere quickly in case of any event (impact, volcanism) that may provide water vapor, whereas it takes tens to hundreds of millions of years to convert CO<sub>2</sub> back to CO. In any cases, the behavior of CO atmosphere would be somewhat different than CO<sub>2</sub>. CO is a weaker greenhouse gas than CO<sub>2</sub>, but

it condenses at significantly lower temperature (or higher pressure) than CO<sub>2</sub>. In very cold cases, conversion to CO may thus prevent atmospheric collapse into CO<sub>2</sub> ice glaciers.

### 3.3 Thin silicate atmospheres

For very hot or low mass objects (lower part of Fig. 5), escape is supposed to be efficient. Bodies in this part of the diagram are thus expected to have a very tenuous atmosphere, if any. This class actually encompasses most Solar System bodies: Mercury, Pluto, all outer-planet satellites but Titan, etc... However, in the Solar System, the only examples we have imply condensation/sublimation equilibrium of the atmosphere with ices present at the surface.

In extrasolar systems, another exotic situation can arise. Indeed, some planets, such as CoRoT-7 b (Léger et al., 2009), are so close to their host star that the temperatures reached on the dayside are sufficient to melt the surface itself. As a result, some element usually referred to as "refractory" become more volatile and can form a thin "silicate" atmosphere (Schaefer & Fegley, 2009; Léger et al., 2011). Depending on the composition of the crust, the most abundant species should be, by decreasing abundance, Na, K, O<sub>2</sub>, O and SiO. Interestingly enough, the energy-redistribution effect of such an atmosphere could be limited to the day side of the planet as condensation occurs rapidly near the terminators (Castan & Menou, 2011). In addition, silicate clouds could form. Both of these effects should have a significant impact on the shape of both primary- and secondary-transit lightcurves, allowing us to constrain this scenario in a near future.

## 4 OUTSTANDING QUESTIONS AND OPPORTUNITIES FOR ECHO

Because in our Solar System we often have only one or two particular examples of planets, if any, in each of the aforementioned classes, it is difficult to quantify the location of the various transitions in Fig. 5. This is where extrasolar planets can prove an invaluable asset. Indeed, if we are able to identify the main constituents of tens to hundreds of exoplanets in various mass/temperature regimes, we will not be looking at individual cases anymore, but at populations.

Such a global view is critical if we truly want to understand the process of atmosphere formation as a whole, and how it behaves in various environments. Indeed, to that purpose, we need to know what is the fraction of super-Venuses compared to super-Mercuries or mini-Neptunes, for example. Only a dedicated transit spectroscopy mission can tackle such an issue. Interestingly, many atmospheric-regime transitions occur in the high-mass/high-temperature part of Fig. 5 which is exactly where observatories like EChO are most sensitive. This means that, even before being able to characterize an Earth-like planet in the habitable zone, we will be able to characterize exotic terrestrial-planet atmospheres in key regimes that are mostly unheard of in the Solar System. Thus, the first observations of terrestrial exoplanet atmospheres, whatever they show, will allow us to make a major progress in our understanding of planetary climates and therefore in our estimation of the likeliness of life elsewhere in the universe.

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