The young Sun’s XUV-activity as a constraint for lower CO$_2$-limits in the Earth’s Archean atmosphere

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Abstract

Despite their importance for determining the evolution of the Earth’s atmosphere and surface conditions, the evolutionary histories of the Earth’s atmospheric CO$_2$ abundance during the Archean eon and the Sun’s activity are poorly constrained. In this study, we apply a state-of-the-art physical model for the upper atmosphere of the Archean Earth to study the effects of different atmospheric CO$_2$/N$_2$ mixing ratios and solar activity levels on the escape of the atmosphere to space. We find that unless CO$_2$ was a major constituent of the atmosphere during the Archean eon, enhanced heating of the thermosphere by the Sun’s strong X-ray and ultraviolet radiation would have caused rapid escape to space. We derive lower limits on the atmospheric CO$_2$ abundance of approximately 40% at 3.8 billion years ago, which is likely enough to counteract the faint young Sun and keep the Earth from being completely frozen. Furthermore, our results indicate that the Sun was most likely born as a slow to moderate rotating young G-star to prevent rapid escape, putting essential constraints on the Sun’s activity evolution.
throughout the solar system’s history. In case that there were yet unknown cooling mechanisms present in the Archean atmosphere, this could reduce our CO$_2$ stability limits, and it would allow a more active Sun.

Keywords:

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1. Introduction

During the Archean, extending from approximately 3.8 to 2.5 billion years ago (Ga), the Sun’s total luminosity was 75-82% of its current value (Gough 1981), meaning that the Earth with its current atmosphere would have been too cold to possess liquid oceans (Sagan and Mullen 1972). This is in contradiction to several lines of evidence that liquid water was already present at the surface during the Hadean (4.56 Ga to $\approx$ 4.0 Ga) and Archean eons ($\approx$ 4.0 Ga to 2.4 Ga) (e.g., Feulner 2012, Catling and Zahnle 2020) such as elevated $^{18}$O/$^{16}$O ratios in zircons from 4.3 Ga (Mojzsis et al., 2001; Wilde et al., 2001) and hydrothermal quartz with fluid inclusions of Archean seawater at 3.5 Ga (Foriel et al., 2004), and the problem is known as the Faint Young Sun Paradox. The most popular solutions involve a stronger greenhouse effect and many candidates have been proposed as the dominant greenhouse gas. Methane produced by microbes could have been present at levels of $> 10^{-4}$ bar (see, e.g., Robinson and Reinhard, 2018). Other suggestions involve higher N$_2$ surface pressures enhancing the greenhouse effect by

Please note that the Hadean eon is not strictly defined but 4.0 Ga is often used as the boundary to the Archean eon. See, e.g., Zahnle et al. (2007), and Goldblatt et al. (2010).
broadening the absorption lines of greenhouse gases such as CO$_2$ (Goldblatt et al. 2009) and the production of the strong greenhouse gas nitrous oxide by enhanced solar activity (Airapetian et al. 2016). However, N$_2$-dominated atmospheres with high surface pressures and negligible amounts of CO$_2$ as suggested by Johnson and Goldblatt 2018 are unlikely to build up due to high thermal escape and moreover one would expect a further increase of $\delta^{15}$N, which is not observed in the present atmosphere (Lammer et al. 2018, Lammer et al. 2019, Gebauer et al. 2020, Sproß et al. 2021).

The most obvious greenhouse candidate is CO$_2$ and several studies have attempted to quantify how much CO$_2$ must have been present to solve the problem (Kasting 1987; von Paris et al. 2008; Kienert et al. 2012; Wolf and Toon 2013; Charnay et al. 2013; Charnay et al. 2017; Charnay et al. 2020). Geochemical measurements extend back to the late Archean and suggest that the CO$_2$ partial pressure (pCO$_2$) was likely significantly higher than in the modern atmosphere (Rye et al. 1995; Hessler et al. 2004; Sheldon 2006; Driese et al. 2011; Kanzaki and Murakami 2015) though significant uncertainty exists and no measurements for the early Archean or the Hadean are available (see below for a summary of these constraints). It has been suggested that due to the removal of mass by the solar wind, the early Sun was slightly more massive and therefore more luminous than it in now which could solve the faint young Sun problem (Spalding et al. 2018). However, upper limits on the mass loss rates of young Sun-like stars from radio observations and considerations of how rapidly the rotation rates of Sun-like stars decrease with age rule out this solution (Gaidos et al. 2000; Johnstone et al. 2015; Fichtinger et al. 2017).
During the Archean, the Sun emitted higher levels of X-ray (< 10 nm), extreme ultraviolet (EUV; 10–91.2 nm), and far ultraviolet (FUV; 91.2–200 nm) radiation (where we use ‘XUV’ here to refer to the wavelength range 1-400 nm, which includes the ultraviolet between 200–400 nm). This radiation is important since it is absorbed high in the atmosphere where it drives heating and photochemistry such as the absorption line of CO$_2$ at 89.9 nm, and for N$_2$ at 79.6 nm (e.g., Roble et al. 1987; Rees 2004; Bauer and Lammer 2004). The early Sun’s XUV evolution is not known, with the major uncertainty being its early rotation rate (Johnstone et al. 2015; Tu et al. 2015). Rotation is important since it determines a star’s XUV luminosity, with rapid rotators being more luminous than slow rotators (Wright et al. 2011). Observations of young stellar clusters show that the Sun could have been born with a rotation rate between a few times to a few tens of times its current value (Bouvier et al. 2014), meaning that very different scenarios for the Sun’s activity evolution in the first billion years are possible (Tu et al. 2015). If the Sun was born as a rapid rotator, it would have remained at its maximum activity level for several hundred million years; if the Sun was born as a slow rotator, its activity level would have decreased to moderate levels within the first ∼20 million years.

At higher levels of solar XUV radiation, the Earth’s atmosphere is hotter and more expanded (Tian et al. 2008; Tian et al. 2009; Kuramoto et al. 2013), leading to more rapid losses to space (Lammer et al. 2008; Lichtenegger et al. 2010; Lammer et al. 2018). Under the very high XUV flux that we would expect for the young Sun during the early Hadean, the Earth’s modern atmosphere would be heated so much that it would escape to space at
rates high enough to rapidly remove the entire atmosphere (Johnstone et al. 2019). Also important is the atmosphere’s composition, which has changed significantly during the Earth’s lifetime (Lammer et al. 2018). For example, high amounts of CO$_2$ in the atmosphere would lead to cooling of the upper atmosphere and reduced loss rates (Kulikov et al. 2007; Lichtenegger et al. 2010). Although the fractionation of the heavy Xe isotopes suggests some evidence for hydrogen escape from the Archean atmosphere (Zahnle et al. 2019), the very small atmospheric $^{14}$N/$^{15}$N fractionation compared to the deep mantle (Cartigny and Marty 2013; Füri and Marty 2015) on the other hand suggests only minor escape of nitrogen (Lammer et al. 2018).

N$_2$ likely has been outgassed and built up during the Archean eon (Mikhail and Sverjensky 2014; Som et al. 2016; Lammer et al. 2018; Lammer et al. 2019; Stüeken et al. 2020; Sproß et al. 2021), and became the main atmospheric species besides CO$_2$. The amount of N$_2$ present in the atmosphere when life evolved is important for understanding the production of prebiotic molecules (Airapetian et al. 2016; Zerkle et al. 2017; Zerkle and Mikhail 2017; Lammer et al. 2018; Lammer et al. 2019; Gebauer et al. 2020; Sproß et al. 2021). However, estimates of atmospheric molecular CO$_2$ and N$_2$ partial surface pressures during the Archean eon widely vary in the literature. So far previous studies focused on hydrodynamic hydrogen escape from early Earth’s atmosphere during the Archean (Tian et al. 2005; Kuramoto et al. 2013) with the main aim to reproduce the observed fractionation of heavy Xe isotopes (Zahnle et al. 2019; Avice and Marty 2020). While Tian et al. 2005 and Kuramoto et al. 2013 neglected the atmospheric bulk gases, CO$_2$ and N$_2$, Zahnle et al. (2019) developed a hydrodynamic diffusion-limited hy-
drogen escape model where he included CO$_2$ as the main atmospheric gas and considered CO$_2$-H$_2$-H atmospheres. These authors have chosen CO$_2$ rather than N$_2$ because CO$_2$ is important for the energy budget in the thermosphere where its mixing has a great effect on the radiative cooling and heating (Gordiets and Markov 1978; Gordiets et al. 1982; Gordiets and Kulikov 1985; Kulikov et al. 2006; Kulikov et al. 2007; Johnstone et al. 2018; Zahnle et al. 2019). Although Zahnle et al. (2019) included radiative cooling of CO$_2$ in their study of hydrogen escape from a CO$_2$-dominated atmosphere, they neglected dissociation of CO$_2$ molecules and escape of its dissociation products.

The aim of this particular study is to investigate various CO$_2$/N$_2$ mixing ratios and the escape of early Earth’s bulk atmosphere during the Archean eon exposed to a possible range of higher XUV fluxes from the young Sun as inferred from stellar rotation rates of solar-like stars (Tu et al. 2015). In Section 2, we summarize the applied state-of-the-art physical-chemical thermosphere and escape model, and in Section 3 we present model results. In Section 4, we discuss the limitations of the Archean CO$_2$-levels, and in Section 5 we address possible influences of minor atmospheric species that are not included in the present study. Finally in Section 6, we address the implications of our findings for the faint young Sun problem and the young Sun’s activity evolution before we conclude our investigations in Section 7.

2. Upper atmosphere model

We model the Earth’s mesosphere and thermosphere using The Kompot Code, which is a sophisticated state-of-the-art physical and chemical
model for planetary thermospheres developed by Johnstone et al. (2018) and Johnstone et al. (2019) that considers heating from the absorption of solar X-ray, UV, and IR radiation, electron heating from collisions with non-thermal photoelectrons, heating from exothermic reactions, Joule heating, radiative cooling from IR emission by several species, thermal conduction, and energy exchange between the electron gas, ions and neutrals. For the chemical structure, relevant chemical reactions, eddy and molecular diffusion, and advection are included. A major strength of this model is its comprehensive and first-principles treatment of the main physical processes including a first principles treatment of the atmospheric heating that does not require the use of any free parameters such as the commonly used heating efficiency. The model can successfully reproduce the upper atmospheric structures of modern Venus, and Earth (Johnstone et al. 2018). The model also handles a possible transition from hydrostatic to hydrodynamic atmospheric conditions by solving the hydrodynamic equations.

In all simulations presented in this study, we calculate the 1D physical structure of the atmosphere between the lower boundary at 50 km altitude and the upper boundary at the exobase level where the atmospheric gas becomes non-collisional. The simulations start with a set of arbitrary initial conditions and evolve through a large number of time steps until the atmospheres come to steady states. The exobase altitude is allowed to vary freely during the simulation. Within the simulation domain, the gas is composed of 30 molecular and atomic species, including 11 ions. The reactions of the chemical network of the model can be seen in Table H.1. of Johnstone et al. (2018). The neutral, ion, and electron components of the gas are assumed to
have separate temperatures. The composition of the gas in the bulk atmosphere at the lower boundary is assumed to be N$_2$ and CO$_2$, with the relative mixing ratios of the two being the most important parameters that we study here. We will discuss the effects of possible existing minor species that are not included in this particular study to our results in Section 5.

The lower boundary temperatures and particle densities are assumed to be 267 K and $5 \times 10^{16}$ cm$^{-3}$ in all simulations. These are approximately the values that we use in our modern Earth simulation (Johnstone et al. 2018) and are to a large extent arbitrary. Our results do not vary significantly with reasonable changes in the lower boundary temperature since what matters the most is the absorbed solar XUV energy, and our assumed temperature is approximately the planet’s effective temperature which is a reasonable assumption. The exact value of the base density is not important as long as it is sufficiently high that all of the input X-ray, EUV, and FUV radiation is absorbed in the simulation domain. Making this value larger or smaller only has the effect of making small changes in the altitudes at which the various processes take place, which is unimportant since the base altitude in our simulation is anyway negligible compared to the radius of the Earth.

The thermal structure of the atmosphere is evolved in time by heating from several processes, cooling by infrared radiation to space by CO$_2$, NO, and O, thermal conduction applied to the neutral, ion, and electron components separately, and energy exchanges between these components by several elastic and inelastic collisional processes. Our physical model for the heating of the gas is a particular strength since we do not assume any free parameters and calculate the heating rate from first principles. Heating takes place due
to the absorption of XUV radiation, which directly heats the gas, leads to the release of heat from exothermic chemical reactions (see also Fig. 5 and Table H1 in [Johnstone et al., 2018]), and creates a spectrum of high energy electrons which heat the thermal electron gas through elastic collisions. Additionally, the absorption of solar photospheric infrared radiation by CO$_2$ is included and can be important in simulations with large CO$_2$ mixing ratios.

Our model for CO$_2$ cooling makes no assumption about local thermodynamic equilibrium and is able to realistically calculate the cooling rates for very different CO$_2$ abundances, as can be seen from our calculations of modern Earth and Venus ([Johnstone et al., 2018]). Finally, in some cases in our model simulations, hydrodynamic advection driven by strong escape at the exobase is strong enough to cool the atmosphere significantly by adiabatic cooling.

Since our model is a 1D model, we have to simplify radiation transfer. In [Johnstone et al., 2018], we assumed that the computational domain is pointing in an arbitrary direction relative to the position of the star, with the angle between this direction and the direction that points directly to the star being defined as zenith angle $\theta$. We then calculated the XUV spectrum at each point in the atmosphere along this direction by doing the radiation transfer from the exobase to each point separately (see Fig. 1 in [Johnstone et al., 2018] for a demonstration of this geometry) and found that for the Earth an angle of $\theta = 66^\circ$ gives the best representation of the atmosphere averaged over all zenith angles. We, therefore, also used $\theta = 66^\circ$ within our current study.

The chemical structure of the atmosphere is evolved in time by chemical reactions, molecular and eddy diffusion, and hydrodynamic advection. The
chemical network used here is the network presented in Johnstone et al. (2018), with the only difference here being that we exclude all reactions that involve elements other than N, C, and O. The chemical network consists of 241 reactions in total, of which 42 are XUV driven photoionization or photodissociation reactions. Each of these photoreactions have their own wavelength dependent cross-sections. In Fig. [1] we show the evolution of the Sun’s X-ray (<10 nm) flux at the orbit of the Earth during the Archean eon assuming modern values for the orbital parameters, where the different evolutionary tracks are for different cases for the Sun’s rotational evolution (Tu et al. 2015). Our atmosphere model considers the full solar spectrum in the wavelength range 1-400 nm, and for this spectrum, we use empirical models developed for use in atmospheric studies (Claire et al. 2012), with two examples shown in Fig. [1]. At each point on the X-ray evolution tracks, we assume the XUV spectrum from Claire et al. (2012) with the same total X-ray flux.

Here, we do not consider atmospheres that are heated to such high temperatures that they reach fully hydrodynamic states with the outflow velocities exceeding the escape velocity below the exobase. Although our model can be used for such cases (Johnstone et al. 2019; Johnstone 2020), we find very high atmospheric loss rates of the assumed bulk atmospheric species can take place already before reaching the transonic hydrodynamic regime. As in Tian et al. (2008) and Johnstone et al. (2018), we solve the hydrodynamic structure of the atmosphere assuming steady states for the total mass density and velocity structure (i.e. assuming $\partial \rho / \partial t = 0$ and $\partial v / \partial t = 0$). As described in Johnstone et al. (2018), we solve the full time-dependent hydro-
dynamic energy equations separately for the neutral, ion, and electron gases, with no steady state assumption and the effects of adiabatic cooling of the gas due to the outward expansion are taken into account.

As seen below, we are interested here in which sets of atmospheric and solar parameters would lead to rapid expansion of the Earth’s atmosphere driven by XUV heating, and for this purpose it is not necessary to consider each of the individual atmospheric loss mechanisms and we consider Jeans escape at the exobase only. Considering hydrodynamic escape would not affect our results, since in such a case the atmosphere would anyway be lost completely.

3. CO\textsubscript{2}/N\textsubscript{2} mixing ratios and the expansion of the thermosphere

Using our atmosphere model, we simulate the Earth’s upper atmosphere throughout the Archean, from 3.8 to 2.5 Ga ago, assuming an atmosphere composed of CO\textsubscript{2} and N\textsubscript{2} as the main species. We first calculate a grid of upper atmosphere models with a range of solar activity levels and atmospheric CO\textsubscript{2} mixing ratios. At each activity level, we calculate models with CO\textsubscript{2} mixing ratios at the base of the simulation domain of 0.99, 0.75, 0.50, 0.25, 0.1, 0.01, and 0.001, and with N\textsubscript{2} making up the rest of the atmosphere. We consider solar XUV spectra having X-ray fluxes between approximately 2 to 15 erg s\textsuperscript{-1} cm\textsuperscript{-2}. It is important to note that for our simulations, the chemical composition of the atmosphere is more important than the total amount of atmosphere since the processes that we model take place at the densities where the XUV radiation is absorbed. Changes to the atmosphere’s mass would lead to small changes in the altitudes of the lower boundaries of our
Figure 1: The evolution of the Sun’s X-ray flux at the orbit of the Earth during the Archean for three cases of the Sun rotational evolution. These cases are for the Sun being a slow (10th percentile), medium (50th percentile), and fast (90th percentile) rotator. The initial rotation periods (at 1 Myr after solar system formation) for the Sun in these three scenarios are 9, 4, and 0.7 days respectively. Two of the X-ray and ultraviolet spectra from Claire et al. (2012) that we use at two different values for the X-ray flux are shown in the insert.
Figure 2: The vertical structures of temperature (upper-panel), heating (middle-panel), and cooling (lower-panel) for our example simulation.
As an example we show model results in Figs. 2 and 3 of an atmosphere that is composed of 50% CO$_2$ and 50% N$_2$ for a solar XUV spectrum with an X-ray flux of 7.3 erg s$^{-1}$ cm$^{-2}$ which is about 11 times the average present-day solar X-ray flux, i.e., 0.66 erg s$^{-1}$ cm$^{-2}$ (with a minimum of 0.22 erg s$^{-1}$ cm$^{-2}$, and a maximum of 2.82 erg s$^{-1}$ cm$^{-2}$, see Judge et al. (2003)). The vertical structure of the atmospheric temperature of this example is shown in the upper panel of Fig. 2. Heating and cooling rates are shown in the middle and lower panels, respectively. The corresponding density profiles for neutral (left) and ion species (right) are shown in Fig. 3. An interesting result that can be seen in Fig. 2 is that the heating by the Sun’s infrared spectrum is negligible compared to the XUV heating despite the very high CO$_2$ abundance. This is different to the cases of modern Venus and Mars in which infrared heating is very important (Fox and Bougher 1991), and this difference is due simply...
Figure 4:  
**Upper panel:** the dependence of the exobase altitude on the X-ray flux at 1 au for different CO\textsubscript{2} mixing ratios.  
**Middle panel:** the evolution of the Earth’s exobase altitude for cases of the Sun being a slow rotator for different CO\textsubscript{2} mixing ratios.  
**Lower panel:** the evolution of the Earth’s exobase altitude for cases of the Sun being a fast rotator for different CO\textsubscript{2} mixing ratios. In each case, circles show results of individual atmosphere models and the solid lines are derived from functional fits to the relationship between F\textsubscript{X} and exobase altitude (shown in the upper panel) combined with the F\textsubscript{X} evolution tracks. The black circle depicts our example simulation.
to the fact that the XUV heating scales with the Sun’s activity whereas the infrared heating (which depends on the Sun’s photospheric emission) remains approximately constant in time.

The dependence of exobase altitude on X-ray flux at 1 AU and the evolution of the exobase altitude for the slow and fast solar rotator tracks for different CO$_2$ mixing ratios are shown in Fig. 4. Higher X-ray fluxes lead to more heating and lower CO$_2$ mixing ratios lead to less cooling, meaning that the atmospheres in the high-activity and low-CO$_2$ cases are hotter and more expanded. This also means that the transition between the collision-dominated to collisionless regime, i.e., the exobase level, occurs at higher altitudes, becomes less gravitationally bound and the upper atmosphere will be consequently lost to space more rapidly. For high XUV fluxes the thermosphere can be heated to high temperatures and the upper atmosphere starts to expand very efficiently so that losses at the exobase cause a large scale outward flow of material, and the resulting adiabatic cooling to some extent counters the strong heating (Tian et al. 2005; Tian et al. 2008; Murray-Clay et al. 2009).

Going backwards in time, for many of the CO$_2$ mixing ratio cases the expansion of the atmosphere becomes very rapid due to the stronger solar XUV emission. In such cases, escape of the main atmospheric constituents at the exobase (atomic N, O, and C) by thermal escape becomes high enough to remove the entire atmosphere in a very short time period. When specifically this takes place differs for each CO$_2$ mixing ratio and for different solar activity tracks. Such rapid loss could not have taken place during the Archean since it would have meant no significant atmosphere could have been present.
meaning that only cases in which such rapid escape does not take place are likely to be realistic. The most striking feature shown in Fig. 4 is that at ages before approximately 3.5 billion years ago, massive atmospheric expansion cannot be avoided in the early Archean and the exobase level starts to expand upwards to above 10 000 km if the Sun was a fast rotator even with very high concentrations of CO$_2$. For the Hadean eon, however, not even a slow rotating Sun might have prevented the complete erosion of the atmosphere, if no yet unknown cooling agents had been present.

4. Limits on Archean CO$_2$-levels

The fact that large amounts of atmospheric CO$_2$ are needed to prevent rapid escape allows us to derive restrictive lower limits on the Archean CO$_2$ content. This is based on the assumption that the Earth had a substantial atmosphere throughout the Archean, and there is significant geological evidence to support this assumption (Catling and Zahnle 2020), including evidence for liquid water and life being present during the early Archean and possibly before (Mojzsis et al. 1996, Javaux 2019). To derive these lower limits, we first derive them as a function of activity level (see Fig. 5), and then convert these limits into functions of age for the different solar activity tracks. To do this, we define a threshold mass loss rate of 0.1 bar Myr$^{-1}$ (the value at which a 1 bar atmosphere would be removed in 10 million years). When the mass loss rate of the atmosphere is above this threshold, we consider this to be unrealistically large for the Archean. Since our mass loss rates are very sensitive to the CO$_2$ mixing ratio, the threshold CO$_2$ mixing ratios are not sensitive to this exact definition for the threshold mass
loss rate. Assuming threshold mass loss rates of ten times larger or smaller would lead to almost identical results. For each solar activity level, we use the model grid presented in the previous section and by extrapolation or interpolation we calculate the CO\(_2\) mixing ratio at which the mass loss rate crosses the threshold value. For many of the solar activity levels considered, we then tested the accuracy of our extrapolations/interpolations by running new models around the derived threshold CO\(_2\) mixing ratio and found in each case that our original estimates were accurate.

Our lower limit on the CO\(_2\) abundance naturally depends on the Sun’s activity level, and therefore its initial rotation rate and age. In Fig. 5 we show the minimum CO\(_2\) level needed to prevent rapid atmospheric escape as a function of the solar X-ray flux at 1 AU. At a flux of 2 erg s\(^{-1}\) cm\(^{-2}\), which is similar to that experienced by the Earth soon after the end of the Archean for all solar rotation scenarios, our lower limit is at a CO\(_2\) mixing ratio of approximately 10\(^{-3}\). At fluxes above approximately 13 erg s\(^{-1}\) cm\(^{-2}\), rapid escape would take place even in a completely CO\(_2\) atmosphere. This is above the X-ray flux at the start of the Archean for the slow rotator case, and therefore CO\(_2\) cooling is able to prevent rapid escape in this case, but below the fluxes from the medium and fast rotator cases.

In Fig. 6 we show how our lower limits on the atmospheric CO\(_2\) mixing ratio evolves throughout the Archean for the three solar evolution cases, and compare these limits to geochemical measurements from the literature (Rye et al. 1995, Hessler et al. 2004, Sheldon 2006, Driese et al. 2011, Kanzaki and Murakami 2015). Our results are consistent with all of the measurements if we assume a total surface pressure of \(\sim\)1 bar. It has been argued that
the mineralogy of Archaean sediments is inconsistent with a pCO\textsubscript{2} during the late Archean that is significantly higher than today (Rosing et al. 2010), though this interpretation is a matter of debate (Goldblatt and Zahnle 2011; Dauphas and Kasting 2011; Reinhard and Planavsky 2011). Our results are inconsistent with such a low pCO\textsubscript{2} since rapid atmospheric escape would be unavoidable in this scenario.

5. Possible influences of minor atmospheric species

Besides the main atmospheric species CO\textsubscript{2} and N\textsubscript{2} there is much evidence that H\textsubscript{2}O and biogenic CH\textsubscript{4} were most likely also present around 2.6 – 2.8 Ga (Hinrichs 2002; Zahnle et al. 2010; Zerkle et al. 2012; Lammer et al. 2018). Below the cold trap for water vapor, H\textsubscript{2} will be produced from H\textsubscript{2}O molecules by photolysis, and photosynthesis followed by fermentation or diagenesis of organic matter. Highly reduced gases such as CH\textsubscript{4} or NH\textsubscript{3} are also dissociated by photolysis due to the high XUV flux of the young Sun and by reactions with OH and O radicals produced from the photolysis of H\textsubscript{2}O and CO\textsubscript{2} molecules (Kuhn and Atreya 1979; Kasting 1982; Kasting 1993; Zahnle et al. 2010; Wordsworth 2016). Above the cold trap, mainly the light dissociation products H\textsubscript{2}, and H will be abundant, as discussed in detail by Zahnle et al. 2019.

In agreement with our study, Zahnle et al. 2019 assumed that the bulk atmosphere during the Archean eon consisted mainly of CO\textsubscript{2} and N\textsubscript{2}. However, these authors simplified their model by neglecting N\textsubscript{2} and considering only CO\textsubscript{2}-H\textsubscript{2} atmospheres for the investigation of Xe escape. Zahnle et al. 2019 developed a 1D hydrodynamic diffusion-limited hydrogen escape model that
was applied to highly irradiated CO$_2$-H$_2$-H atmospheres. Although their study includes CO$_2$-related radiative cooling, the CO$_2$-related photo- and ion-chemistry was also simplified, so that dissociation of CO$_2$ molecules was not included in their model. It was assumed that CO$_2$ does not escape but hydrogen diffuses through the CO$_2$ into the thermosphere and drags the embedded Xe$^+$ ions, which are considered as trace gas, upwards to the exobase from where it then escapes. It was shown in their study that the forces that act on the heavy Xe$^+$ ions are the collisions between the escaping neutral and ionized hydrogen that push Xe$^+$ ions outwards while collisions with CO$_2$ molecules block it. [Zahnle et al. 2019] could reproduce Earth’s present Xe isotope paradox if the assumed CO$_2$-dominated atmospheres had mixing ratios of at least 1% hydrogen or 0.5% CH$_4$ above the H$_2$O cold trap if they are exposed to a solar EUV irradiation that was $\geq 10$ times higher than today’s solar value.

Results very similar to those of [Zahnle et al. 2019] were also derived from hydro-code models that studied the losses caused by transonic escape of pure H$_2$ atmospheres; in those simulations, the lower boundary temperatures were fixed; they can also be seen as an infinite heat sink caused for instance by radiative cooling of CO$_2$. The differences that are attributable to the CO$_2$-related photochemistry that was included in the model of [Zahnle et al. 2019] but neglected by [Tian et al. 2005] and [Kuramoto et al. 2013] were more or less negligible. [Zahnle et al. 2019] also found that under their assumptions in the homosphere (lower thermosphere) where CO$_2$ is abundant, radiative heating and radiative cooling are in balance, the temperature of the gas is determined by the bulk gas and very little energy is channeled into hydrogen
escape. This is also in agreement with a study of Yoshida and Kuramoto (2020) who investigated the hydrodynamic hydrogen escape from an assumed reduced early Mars’ atmosphere where they considered carbon compounds as radiative coolants.

From these results one can expect that the amount of hydrogen that is produced from the expected H\textsubscript{2}O vapor and/or CH\textsubscript{4} molecules, which diffused through the water cold trap up to the exosphere was strong enough to drag heavy Xe\textsuperscript{+} ions. However, the hydrogen flow does not contribute much to the adiabatic cooling that we obtain from our model simulations for expanded CO\textsubscript{2}/N\textsubscript{2}-dominated bulk atmospheres. Therefore, one can expect that our heating and cooling rates shown in Fig. 2 as well as the resulting temperature and atmospheric profiles as shown in Figs. 2 and 3 will not change much.

The hypothesis proposed by Zahnle et al. (2019), namely that hydrodynamic-diffusion-limited hydrogen escape is most likely the explanation for the observed Xe paradox, seems to be a solid one. However, when they neglect N\textsubscript{2} as a second main atmospheric species and neglect dissociation of CO\textsubscript{2} molecules and escape of its dissociation products, then their simplified model will not yield accurate results. As one can see from our study, different CO\textsubscript{2}/N\textsubscript{2} mixing ratios exposed to various XUV fluxes from the young Sun will yield differently expanded bulk atmosphere structures, and, hence, potentially high escape rates of C, O and N atoms.

For higher solar XUV fluxes as expected during the Hadean > 4 Ga, other processes such as solar wind stripping and cold ion outflows of the bulk atmosphere could be important, which might be an additional challenge for sustaining a stable CO\textsubscript{2}-dominated atmosphere. That ion outflow might have
been significant during the Hadean eon is already indicated by recent findings of Kislyakova et al. (2020) who studied the evolution of early Earth’s polar outflow from the mid-Archean to present and already found loss rates due to polar outflow at $\approx 3$ Ga of $\approx 3.3 \times 10^{27} \text{ s}^{-1}$ and $\approx 2.5 \times 10^{27} \text{ s}^{-1}$ for $\text{O}^+$ and $\text{N}^+$ ions. According to their results, the main parameters that governed the atmospheric escape during the studied time period are the evolution of the young Sun’s XUV radiation and the atmosphere composition, while the evolution of the Earth’s magnetic field had a less important role.

The cold trap, however, might not have existed continuously during the Archean eon due to fluctuations to very low total atmospheric surface pressures (Som et al. 2016; Lammer et al. 2018; Stüeken et al. 2020). If it did not exist, $\text{H}_2\text{O}$ could have reached the thermosphere but would have subsequently been dissociated (Zahnle and Buick 2016). That such conditions at least periodically existed and $\text{H}_2\text{O}$ was then indeed dissociated can be derived from $\approx 2.4$ Ga old micrometeorites which were oxidized in the upper atmosphere (Tomkins et al. 2016; Zahnle and Buick 2016; Rimmer et al. 2020). If $\text{H}_2\text{O}$ was then indeed dissociated, it could not have contributed efficiently as cooling agent during this period.

Since our results have consequences for $\text{H}_2$ and the related Xe fractionation process, future studies should redo the study by Zahnle et al. (2019) by including $\text{N}_2$ as a second major atmospheric constituent, CO$_2$ dissociation and the escape of C, O, and N atoms. The observed Xe isotope ratio might then be reproduced more easily with lower XUV fluxes and even lower $\text{H}_2$ and/or $\text{CH}_4$ mixing ratios.
6. The Faint Young Sun Paradox and the solar activity evolution

Several studies have estimated the amount of CO\textsubscript{2} that would be needed during the Archean to solve the faint young Sun problem \cite{Kasting1987,vonParis2008,Kienert2012}. Estimates using 3D global climate models that include ice-albedo feedback suggest that a very high amount of CO\textsubscript{2} of up to 0.4 bar are needed in the early Archean \cite{Kienert2012}. Other 3D climate models suggest temperate climates can be achieved at 3.8 billion years ago with a pCO\textsubscript{2} of 0.1 to 0.36 bar \cite{Charnay2017,Charnay2020}. In Fig. 6, we compare our lower limit on the CO\textsubscript{2} mixing ratios for the slow solar rotator case to these results assuming again a total surface pressure of \(\sim\)1 bar. Our results show that the amount of CO\textsubscript{2} in the atmosphere during the early Archean was enough for the greenhouse effect from CO\textsubscript{2} alone to counter the faint young Sun.

Later in the Archean, our results are less restrictive and we require, as a lower limit, less CO\textsubscript{2} to prevent rapid escape than is necessary to keep the surface warm. It has been suggested that 2.5 billion years ago, a higher surface pressure of N\textsubscript{2} would have enhanced the greenhouse effect through pressure broadening of the absorption lines of greenhouse gases, and that with a pCO\textsubscript{2} of \(10^{-2}\) bar at 2.5 billion years ago, a pN\textsubscript{2} of 2 bar would be needed to counter the fainter Sun \cite{Goldblatt2009}. In this scenario, the CO\textsubscript{2} mixing ratio is \(5 \times 10^{-3}\), which is slightly above our lower limit at 2.5 billion years ago. The situation is different at slightly earlier ages; this lower limit on the CO\textsubscript{2} mixing ratio is \(10^{-2}\) and \(2 \times 10^{-2}\) at 2.7 and 2.9 billion years ago respectively, suggesting that a higher pN\textsubscript{2} is unlikely to be realistic before the end of the Archean unless also accompanied by a correspondingly
larger pCO$_2$.

We show in both Fig. 4 and Fig. 6 that the Sun was most likely born as a slow to intermediately rotating young G-star. No amount of CO$_2$ in the atmosphere would have prevented rapid escape to space had the Sun been more rapidly rotating. This can be seen in Fig. 6 where the minimum CO$_2$ mixing ratios in both the medium and fast rotator cases exceed unity. By putting important constraints on the Sun’s activity evolution, our results are also important for our understanding of the Earth’s atmosphere evolution during the Hadean, and for the atmospheric evolutionary histories of Venus and Mars. Since the Sun could not have been a fast rotator, its high level of activity must have decayed to low or moderate levels already very early in its lifetime, likely within the first 20-50 million years after the start of the solar system formation (Tu et al. 2015) and was therefore not at its maximum activity level for the first 100 Myr as is commonly believed. Such lower activity levels for slowly rotating stars can already be seen in the 12 million year old stellar cluster h Per (Argiroffi et al. 2016).

The finding that the young Sun was most likely a slow to intermediately rotating young G-star also agrees with recent studies by Lammer et al. (2020a, 2020b, 2021) where Venus’ and Earth’s present atmospheric Ar, Ne isotope and bulk K/U ratios can be reproduced only if the young Sun was between a slow and a moderately rotating young G-type star.

It is interesting also to consider how important the slow rotation of the young Sun was for the formation of the habitable surface conditions of the Earth. Had the Sun been a rapid rotator, our results suggest that the Earth’s atmosphere would not have been able to survive during the Archean, and
Figure 5: The minimum amount of CO$_2$ needed in the atmosphere to prevent rapid atmospheric escape as a function of the X-ray flux at 1 au. Note that the entire solar X-ray and ultraviolet spectrum (1-400 nm) is considered in our models calculations.

warm habitable surface conditions could not have been maintained.

7. Conclusions

In this study, we use a state-of-the-art model for the Earth’s upper atmosphere to put sensitive constraints on several parameters that are important for the evolution of the Earth’s CO$_2$/N$_2$ atmosphere and surface conditions during the Archean. These constraints come from considerations of the conditions necessary to prevent the bulk atmosphere from rapidly escaping to space during the Archean eon due to the young Sun’s higher X-ray and EUV activity. We derive lower limits on the amount of CO$_2$ that must have been present in the atmosphere to prevent such escape, finding that at the start of the Archean 3.8 billion years ago, the atmospheric CO$_2$ level must have been
Figure 6: **Upper-panel:** Our results for the minimum CO\textsubscript{2} mixing ratio throughout the Archean for the slow, medium, and fast rotating solar evolution scenarios. The ranges and limits represent geochemical measurements from the literature. **Lower-panel:** A comparison of our lower limit on the CO\textsubscript{2} with estimates for the pCO\textsubscript{2} needed to keep the Archean Earth warm despite the fainter young Sun. The red shaded area is ruled out by our results. The green and black lines show respectively the estimates for pCO\textsubscript{2} required from 1D models (von Paris et al. 2008) and 3D models (Kienert et al. 2012), where the 3D models require a higher CO\textsubscript{2} concentration due to the ice-albedo feedback effect. The grey lines indicate the total pressure at 2.7 Ga of 0.23 ± 0.32 bar as inferred from gas bubbles in basaltic lava flows by Som et al. (2016).
at least 40% of the atmosphere. This is important because no geochemical measurements of CO$_2$ from this time period or earlier are currently available and CO$_2$ is an important greenhouse gas. Assuming an atmospheric surface pressure similar to that of the modern Earth, this is likely enough CO$_2$ to solve the faint young Sun problem during the early Archean. Importantly, our results give constraints on the activity evolution of the young Sun which would have depended on its initial rotation rate. Cooling by CO$_2$ is only able to prevent rapid atmospheric escape if the Sun was born as a slow rotator. This result is very important not just for the Archean Earth, but for our understanding of atmospheric losses for the entire evolutionary history of the Earth and for terrestrial exoplanets as well.

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