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# Massive impact-induced release of carbon and sulfur gases in the early Earth's atmosphere

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ABSTRACT

Recent revisions to our understanding of the collisional history of the Hadean and early-Archean Earth indicate that large collisions may have been an important geophysical process. In this work we show that the early bombardment flux of large impactors (>100 km) facilitated the atmospheric release of greenhouse gases (particularly $CO_2$) from Earth's mantle. Depending on the timescale for the drawdown of atmospheric $CO_2$, the Earth's surface could have been subject to prolonged clement surface conditions or multiple freeze-thaw cycles. The bombardment also delivered and redistributed to the surface large quantities of sulfur, one of the most important elements for life. The stochastic occurrence of large collisions could provide insights on why the Earth and Venus, considered Earth's twin planet, exhibit radically different atmospheres.



## 1. Introduction

Atmospheric and surface conditions during the first billion years of Earth's history are poorly understood due to the paucity of geological and geochemical constraints. Early atmospheric models (Sagan and Muller, 1972; Owen et al., 1979; Kasting et al., 1984) indicated that the Earth could have been in a frozen state for hundreds of millions of years due to the reduced luminosity of the young Sun, which was approximately 20–30% less intense than today at visible wavelengths. However, the oldest terrestrial zircons dating back to $\sim$4.3–4.4 Gyr ago hint at protoliths that interacted with liquid water at or near the surface of the Earth (Wilde et al., 2001; Mojzsis et al., 2001; Cavosie et al., 2005) based on deviation of stable oxygen isotope ratios ($\delta^{18}O$) from mantle values. Additional support for the presence of surface or sub-surface liquid water is provided by the presence of muscovite and quartz inclusions in Hadean zircons, consistent with "S-type" granites formed from melting sedimentary protoliths including clays (Hopkins et al., 2010). In addition, chert $\delta^{18}O$ signatures (e.g., Blake et al., 2010) and the lack of glacial deposits prior to $\sim$3 Gyr ago (Young et al., 1998) have also been interpreted as evidence against snowball conditions in the early to mid-Archean. The apparent inconsistency between theoretical climate predictions and the rock record is referred to as the faint young Sun paradox (Sagan and Mullen, 1972).

The available Hadean zircon record, however, is sparse. For instance, the age of Hadean zircons is known with a typical error (1-$\sigma$) of 5–10 Myr, while their $\delta^{18}O$ vs. age distribution is characterized by gaps of several 10s Myr. The latter may be due to bias sampling and low number statistics, nevertheless current data are consistent with episodic or prolonged periods with liquid surface water and alteration of crustal material (Cavosie et al., 2005), or, perhaps, aqueous alteration beneath a global ice shell that might experience intermittent melting (Zahnle, 2006). Alternatively, Hf, Pb, O and Nd data have been interpreted as evidence that many of the observed Hadean zircons younger than $\sim$4.3–4.4 Gyr ago are due to the melting of older mafic crust (Kemp et al., 2010), and therefore do not require protracted clement surface conditions.

In this work, we assess the consequences of large impacts for Hadean and Eoarchean climate and surface conditions. The bombardment of the Earth by the debris of planet formation during the so-called late accretion from 4.5 Gyr ago to 3.5 Gyr ago, i.e. encompassing the Hadean and early Archean eons, was likely characterized by a plethora of large collisions (Marchi et al., 2014). Planetesimals exceeding 100 km in diameter pummeled the early Earth for hundreds of Myr, resulting in large volumes of melt produced both by immediate depressurization and by subsequent mantle convection driven by the impact (Elkins-Tanton and Hager, 2005; O'Neill et al., 2016). This buoyant melt would spread on the

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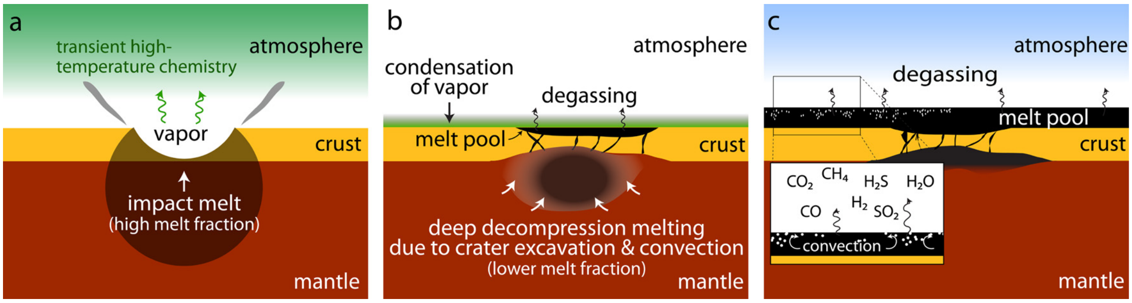


**Fig. 1.** Schematic cross section through an impact-generated melt pool and subsequent outgassing. a: A large impact results in the formation of a transient, silicate-rich high temperature atmosphere, prior to impact-generated melt spreading. b: Upon fast cooling ($\sim 10^3$ yr or less), the transient atmosphere condenses, while deep-seated, impact-generated melt spreads on the surface. c: As the impact-generated melt spreads, it releases gases. The outgassing indicated in panel c is expected to take place largely after the transient silicate vapors have condensed.

surface, a process further aided by the lack of significant surface topography due to a much warmer crust.

Impact-generated mantle melting and magmatism cannot be observed in the current terrestrial record due to the paucity of giant impacts. For example, the 1.85 Ga Sudbury structure is one of the largest extant impact structures on Earth (Grieve, 1987). However, the Sudbury impact (with a projectile size of ~12 km) was much smaller than the collisions we consider here. The granitic and noritic Sudbury impact melt sheet likely derived from melting of crustal and supracrustal protoliths (Zieg and Marsh, 2005). In contrast, we expect magma generation during the larger collisions that took place during late accretion to be dominated by mantle melting.

Large igneous provinces may thus provide a more valid geological analogy, albeit without the near-instantaneous melting expected for impact-derived melt bodies. One key difference, however, is the volume of molten rocks. The largest known igneous provinces, such as the Ontong-Java Plateau, have an estimated volume approaching $10^7$ km$^3$ (Ross et al., 2005). For comparison, the volume of mantle-derived melt generated by a collision with a 100 km asteroid exceeds $10^7$ km$^3$, while for a 1000 km impactor it approaches $10^9$ km$^3$ (Marchi et al., 2014).

Outgassing of volatiles (such as $CO_2$, $SO_2$, CO, and $H_2S$) during the emplacement of large igneous provinces is thought to have significant—although transient—repercussions for atmospheric composition, surface temperatures, ocean chemistry, and planetary habitability (e.g., Self et al., 2014; Black et al., 2014). Likewise, the emplacement of large bodies of melt on the early Earth's surface could have resulted in voluminous outgassing. However, previous work on the effects of asteroidal bombardment on the early Earth's atmosphere (e.g., Sleep and Zahnle, 2001; Zahnle et al., 2007, 2010) or more recent terrestrial impacts (e.g., Kring et al., 1996) have chiefly considered impact-vaporized materials, instead of degassing from pools of impact-generated magma. Large-scale collisions also have the potential to drastically alter the composition and temperature of a pre-existing atmosphere by releasing significant amounts of silicate vapor. Such hot, transient atmospheres are estimated to cool off and precipitate quickly: on a time scale of a few months for the silicate to condense, and ~$10^3$ yr for the water to rain out (e.g., Sleep and Zahnle, 1998; Zahnle et al., 2007, 2010). On longer timescales, however, melt outgassing likely dominated the budget of released gases by virtue of the much larger melt volume compared to vapor volume (see Supplementary Information).

## 2. Impact-generated outgassing on the Hadean Earth

To investigate the environmental effects of large collisions on the early Earth we developed a model that combines the asteroidal bombardment flux with the quantities of gas released by the resulting impact-generated melt pools (Fig. 1). In our simulations we consider impactors larger than 10 km in diameter randomly generated using the main belt asteroid size-frequency distribution extrapolated to larger sizes to account for the budget of terrestrial highly siderophile elements (Marchi et al., 2014; see their Fig. 1). The time frame of interest is 3.5–4.5 Gyr, the latter being the assumed formation time of the Moon, although our results do not depend on the absolute time of the Moon's formation. The nominal impact flux is derived using an example of a successful simulation, as shown in Marchi et al. (2014). We also tracked the stochastic variability of large collisions by using $\sim 10^3$ simulations: the number of impactors ranges from 100–150 and 10–30, respectively for impactor size larger than 100 and 200 km (Fig. S1). As described in Marchi et al. (2014) (Fig. 1a), for each collision we estimated the volume of impact-generated melt by comparing the mantle solidus with pressure and temperature fields predicted from hydro-code simulations. We adjusted our estimates to account for thermally triggered mantle convection and subsequent decompression melting based on results from Elkins-Tanton and Hager (2005). The estimated melt volumes, which depend on the assumed background potential temperature of the mantle (Marchi et al., 2014), are used as inputs for our outgassing computations (Fig. 1b). The degassing efficiency will depend on volatile concentrations in the melt, degree of melting, solubility, and speciation (Fig. 1c). The latter is controlled by the oxygen fugacity of the lower crust and mantle, which is the source material for the impact-generated melt. Despite a developing consensus that the Hadean mantle and surface environments were relatively oxidizing (e.g., Kasting, 2014), some geological evidence points to more reducing conditions (e.g., Yang et al., 2014). Therefore we tracked the production of gases in two end-member scenarios for oxidizing and reducing conditions, with and without additional volatiles from the projectiles, and with a range of Hadean mantle concentrations (see Supplementary Information). Given the uncertainties in the above factors, our strategy is to develop a baseline model for each end-member scenario. Our baseline models are tailored to describe lower limit cases, and they are characterized by conservative assumptions for outgassing throughout. The major species in the gas phase under oxidizing magmatic conditions will be $CO_2$ and $SO_2$, as in modern basalts (e.g., Trail et al., 2011). The major species in the gas phase under reducing conditions will be CO, and to a lesser extent $CH_4$ and $H_2S$ (Iacono-Marziano et al., 2012; Yang et al., 2014; Kasting, 2014). In addition to the species above, it is expected that significant volumes of water vapor and $H_2$ were also released, although we do not specifically address them in this work.

### 2.1. Hadean Earth's volatile budget

We assume that little silica-rich continental crust existed in the Hadean, and furthermore our simulations suggest that for large Hadean impacts most melt derived from the mantle rather than from the crust (Marchi et al., 2014). Consequently, unlike Phanerozoic impact melt bodies, Hadean impact-generated melt pools were predominantly mantle-derived, initially silica undersaturated melts with correspondingly low viscosity (Giordano et al., 2008). Under these conditions, once melts ascend and spread, bubbles should quickly rise and escape. Because the solubility of $CO_2$ and CO is very low at upper crustal pressures (Papale, 1997; Iacono-Marziano et al., 2012), degassing of these species from melt pools was likely rapid and efficient.

We adopt a Hadean bulk silicate Earth volatile budget based on the current bulk silicate Earth budget less the contribution from late accretion. The latter is computed assuming a nominal late accreted mass of 0.35% of an Earth mass (Walker, 2009), although the results are not sensitive to the precise mass accreted within the uncertainty range (+0.15%–0.25%; 1-$\sigma$). In addition, some impactor material will vaporize, some will melt, and some refractory material will accrete to the Earth in solid form. As a lower limit on the fraction of impactor volatiles that will reach the atmosphere, we assume that upon collision the volatile content of the projectile will only outgas with the efficiencies we assume for mantle-derived volatiles escaping from impact melt pools (see Supplementary Information). The asteroidal budget of carbon and sulfur is derived from both carbonaceous and enstatite chondritic meteorites (Kring et al., 1996).

We assume melt concentrations of S species equivalent to the present-day S budget for the silicate Earth from McDonough and Sun (1995), minus ~150 ppm S delivered during late accretion. Estimates for the present-day carbon contents of the silicate Earth span a range of values (e.g., Hirschmann and Dasgupta, 2009; Dasgupta and Hirschmann, 2010). The depleted mantle sampled by Mid-Ocean Ridge Basalt (MORB) has been estimated to contain 10–330 ppm C (Saal et al., 2002; Hirschmann and Dasgupta, 2009; Helo et al., 2011), whereas more enriched mantle (such as the source for OIB) may contain up to 300–1300 ppm C (Dasgupta and Hirschmann, 2010). The proportions of these enriched and depleted materials within the mantle are uncertain, as is the fraction of Earth's primordial carbon that resides in the core (Dasgupta and Hirschmann, 2010; Dasgupta and Walker, 2008). Based on the assumption that depleted material comprises 40% of the mass of Earth's mantle, Dasgupta and Hirschmann (2010) estimated that the present bulk silicate Earth contains 68–312 ppm C. From C/N and C/$^4$He ratios (the latter in conjunction with a $^4$He/$^{40}$Ar production accumulation ratio and an estimate of bulk Earth $^{40}$Ar) Marty (2012) estimate a present-day bulk mantle inventory of $765 \pm 300$ ppm C. Drawing on similar lines of evidence, Halliday (2013) estimated a bulk mantle inventory of $647 \pm 410$ ppm C, with a lower estimate of $45 \pm 21$ ppm C inferred from the H/C ratio in the mantle and water concentrations in basaltic glasses from mid-ocean ridges and Hawaii. McDonough and Sun (1995) picked a present-day bulk mantle C of 120 ppm. Wood et al. (1996) estimate that if carbon in the core is negligible, the silicate earth may contain up to 900–3700 ppm C.

These estimates for mantle carbon address present-day carbon abundances. However, at least three processes have modified mantle carbon reservoirs since the start of the late accretion: the growth of the continental crust (e.g. Hofmann, 1988) the recycling and extraction of oceanic crust (e.g. Hofmann, 1988) and the late accretion itself (e.g., Walker, 2009). The segregation of a hypothesized early enriched reservoir—proposed to explain terrestrial $^{142}$Nd/$^{144}$Nd isotope ratios—could also have redistributed mantle carbon, but such a reservoir would have formed prior to the late accretion (Boyet and Carlson, 2005) and so does not directly affect our calculations. The extraction of the continental crust depleted the mantle of incompatible elements; extraction and recycling of the oceanic crust leads to further development of relatively enriched and depleted reservoirs (Hofmann, 1988). As summarized above, the present-day bulk mantle likely contains 10–765 ppm C. If significant quantities of C outgassed from the mantle during continental crust extraction, perhaps aided by hotter mantle potential temperatures (Herzberg et al., 2010; Dasgupta, 2013) the present-day carbon inventory of the mantle should provide a conservative starting point for back-calculation of mantle carbon in the Hadean. For the late accretion mass and projectile carbon contents we assume here, late accretion itself would have supplied ~50 ppm C to the bulk silicate Earth (Supplementary Table S1). Here we consider nominal Hadean mantle carbon concentrations of 60 ppm C, but note that significant uncertainties exist in both melt fraction (discussed below) and Hadean mantle carbon concentrations.

In the absence of graphite or diamond in the residue (e.g., Stagno et al., 2013), carbon is extremely incompatible during melting (Hauri et al., 2006). The effective melt fraction extracted during impact-induced melting integrates regions with high degrees of melting (for example, close to the impact site) and regions with lower degrees of melting (for example, regions where decompression and post-impact convection raise the mantle only slightly above its solidus; Elkins-Tanton and Hager, 2005; Marchi et al., 2014). The maximum degree of melting observed during simulations of post-excavation decompression and convection is ~15% (Elkins-Tanton and Hager, 2005). If the effective melt fraction is ~15%, bulk mantle carbon contents of 60 ppm C prior to late accretion would produce a melt with ~400 ppm C. For comparison, pre-degassing carbon concentrations in typical primary MORB melts are estimated to be ~500 ppm C (Michael and Graham, 2015). Ultimately, the outcomes we discuss in this work are not strongly sensitive to the carbon concentration we assume for impact-induced melt production. Carbon concentrations in mantle-derived melts as low as ~120 ppm C will still be sufficient to underwrite major carbon outgassing from impact melt pools.

### 2.2. Impact-generated melt outgassing and feedbacks

In this section we discuss the stability of atmospheric $CO_2$ which, as shown in Section 4, is expected to be the longest-lived and most abundant greenhouse gas released through outgassing of impact-generated melt pools. On the modern Earth over longer timescales, silicate weathering modulates the quantity of $CO_2$ in the atmosphere (e.g., Berner and Caldeira, 1997). Over much shorter timescales the composition of the atmosphere depends on equilibration with terrestrial and marine reservoirs. Aqueous equilibrium in the carbonate system:

$$CO_2\,(aq) + CO_3^{2-} + H_2O \Leftrightarrow 2HCO_3^-$$

depends in part on the abundance of each species and consequently on both dissolution of atmospheric $CO_2$ and on removal of $CO_3^{2-}$ as $CaCO_3$ (Ridgwell and Zeebe, 2005).

In the so-called Strangelove oceans of the Precambrian, calcium carbonate precipitation was abiotic (Ridgwell and Zeebe, 2005). Consequently the ocean–atmosphere system was likely to be poorly buffered, and subject to large swings in atmospheric $pCO_2$ (Ridgwell et al., 2003). In the Hadean, the specific buffering capacity in the oceans is unknown; as we discuss here (see also Zahnle, 2006), the oceans may even have been episodically frozen (effectively corresponding to zero buffering capacity). The extent of subaerial landmasses and the distribution of seafloor area with depth (important for abiogenic carbonate precipitation; Ridgwell et al., 2003) are similarly unknown.

Thus, while the detailed features of the Hadean carbon cycle present a compelling area for future research, a full treatment of the interactions between surface carbon reservoirs is beyond the scope of this work. Instead, we consider the Hadean carbon cycle through the lens of a simple exponential decay, which is intended to represent all processes that modulate atmospheric $CO_2$. On the modern Earth, the timescale for the silicate weathering feedback is approximately $10^5$–$10^6$ yr (e.g. Berner et al., 1983). In the Hadean, the efficiency of silicate weathering (and the availability of exposed silicate material for weathering) is poorly constrained, although efficiency is generally assumed to be lower than on the present-day Earth due to cooler temperatures and less continental area exposed to weathering (Zahnle et al., 2007). Conversely, more efficient seafloor alteration in the Hadean would accelerate $CO_2$ drawdown timescales (Sleep and Zahnle, 2001). We therefore consider an e-folding decay timescale ($\tau$) for the drawdown of $CO_2$ ranging from $10^6$–$30 \times 10^6$ yr (Zahnle et al., 2007). Longer or shorter decay constants for $CO_2$ drawdown would imply more stable or more intermittent climatic conditions respectively.

We utilize a similar approach for other gases. The e-folding decay times in Table S1 express the assumed removal timescale for exponential drawdown. While this assumption may not rigorously apply to all gases investigated (depending on the chemistry and environmental parameters such as temperature), it provides a convenient way to look at first order evolutions of major gases. For the most reactive species we set the drawdown time scale to the temporal resolution of the simulations ($10^3$ yr).

### 2.3. Transient effects of large collisions

Large collisions are expected to generate significant volumes of silicate vapors (Zahnle et al., 2010). For instance, assuming that the amount of vaporized target material is of the same order of the projectile's volume (see Supplementary Information), we estimate that impactors exceeding 200 km diameter would produce a mass of silicate vapor comparable to that of Earth's present atmosphere. At temperatures between 2000 K–3000 K, the vapor will be dominated by Na, SiO, Zn, Mg, Fe, FeO, $O_2$ and O (Visscher and Fegley, 2013). Outgassing of volatiles directly from projectiles may also influence atmospheric chemistry (Schaefer and Fegley, 2007, 2010). Schaefer and Fegley (2010) find that under equilibrium conditions, carbonaceous chondrite outgassing will produce a gas rich in $H_2O$ and $CO_2$, whereas ordinary and enstatite chondrites yield a reduced gas rich in a combination of CO, $CH_4$ and $H_2$. Schaefer and Fegley (2007, 2010) consider a vapor derived entirely from the projectile, whereas for the Hadean Earth we expect vapors from large impacts to be dominated by target material. Fe and Mg are expected to condense out of the atmosphere on timescales of a few months or less as the atmosphere cools (Sleep and Zahnle, 1998; Zahnle et al., 2010). Similar conclusions have also been found for impacts on Mars (e.g., Segura et al., 2008). During this relatively brief condensation interval, drawdown of carbon through reaction with Fe and Mg may be governed by the solubility of $CO_2$ in silicate magma (Zahnle et al., 2010)—the same constraint we consider when calculating outgassing from the mantle-derived melt sheets. Zahnle et al. (2010) suggest that after Fe, Mg and other more refractory elements condense (Lodders, 2003), the atmosphere will remain rich in $H_2O$ and $CO_2$ (though the water vapor may also ultimately condense as the atmosphere cools further). The timescale for spreading of buoyant melt can vary from $10^3$ yr to $10^6$ yr, depending on the size of the impactor (O'Neill et al., 2016). For comparison, the timescale for melt extraction at mid-ocean ridges has been estimated at $\sim 10^3$ yr (e.g., Connolly et al., 2009). Silicate atmospheres are typically short-lived (Zahnle et al., 2010), and only after decompression melts have percolated out of the mantle can they reach the surface and outgas. We therefore expect outgassing from impact melt sheets to largely postdate and be relatively unaffected by high temperature chemistry in impact vapors, except insofar as these processes alter the pre-impact atmosphere.

It is also expected that 500-km or larger impactors would result in global vaporization of the ocean leaving behind a steam atmosphere after the condensation of the silicate vapors (Sleep et al., 1989; Zahnle et al., 2010). Similar timescales as described above apply also to these extremely large collisions (Zahnle et al., 2010). In summary, in this work we do not consider the transient atmospheric chemistry that is likely to accompany vaporization of silicate materials during the most energetic collisions. Future work to investigate the residual state of the atmosphere after condensation of silicate materials would shed light on the extent to which impact vaporization is capable of resetting background atmospheric composition.

## 3. Impact vs. volcanic outgassing

Volcanism at plate boundaries, hotspots, and other intraplate settings also produces greenhouse gases including $CO_2$. To sustain sufficient atmospheric $CO_2$ abundances to support liquid water in the Hadean ($\sim 7 \times 10^{17}$ kg; von Paris et al., 2008), continuous outgassing from volcanoes or other non-impact related sources must exceed $\sim 700 \times 10^9$–$7000 \times 10^9$ kg $CO_2$/yr (for $\tau = 1$ Myr or $\tau = 0.1$ Myr respectively). For comparison, for the modern Earth, Williams et al. (1992) estimate a global subaerial volcanic flux of $\sim 65 \times 10^9$ kg $CO_2$/yr. Based on $CO_2/^3He$ ratios and estimates for mid-ocean ridge, arc, and mantle plume melt production rates, global magmatic transfer of $CO_2$ to the atmosphere and hydrosphere has been estimated to total $4$–$10 \times 10^{12}$ mol/yr (Marty and Tolstikhin, 1998), which corresponds to a range of $176$–$440 \times 10^9$ kg $CO_2$/yr. Recently, Burton et al. (2013) have estimated even higher subaerial volcanic fluxes of $540 \times 10^9$ kg $CO_2$/yr, balanced by alteration of oceanic crust (Alt and Teagle, 1999) and large ingassing fluxes of carbon in subduction zones (Dasgupta and Hirschmann, 2010). Just a few volcanic systems contribute disproportionately to modern volcanic $CO_2$ outgassing. In particular, Mt. Etna and Mt. Vesuvius contribute >20% of the global arc volcanic flux (Williams et al., 1992; Dasgupta, 2013). This $CO_2$ has been hypothesized to derive from metamorphism of crustal carbonate platforms (e.g., Iacono-Marziano et al., 2009), which may not have been widespread in the Hadean. The net contribution of mid-ocean ridges to surface carbon may be negligible, because of the sequestration of $CO_2$ during alteration of mid-ocean ridges (Alt and Teagle, 1999). If fluxes of subducted carbon were lower in the Hadean, presumably the outgassing fluxes at arc volcanoes (if plate tectonics was already operating) were also lower. Likewise if the late accretion delivered a significant fraction of present-day mantle carbon, volcanism at the start of the Hadean may have liberated less $CO_2$. The recent flux of $CO_2$ from plumes alone is at most $\sim 3 \times 10^{12}$ mol/yr (Marty and Tolstikhin, 1998), or $132 \times 10^9$ kg $CO_2$/yr, which is approximately 5 to 50 times smaller than the steady $CO_2$ flux required to sustain clement conditions in the Hadean.

The volcanic activity of the Hadean Earth is highly dependent on the tectonic history of the planet. In particular, hotter mantle potential temperatures (Herzberg et al., 2010) may have increased volcanic activity relative to today's Earth. On the other hand, modeling suggests that volcanic activity was at most several times more intense than at present (e.g., O'Neill et al., 2013). If volcanism was particularly vigorous, it is possible that the combined effects of impact-induced magmatism and other volcanism may have been sufficient to offset the faint young Sun and maintain clement surface conditions. However, our model (and the atmospheric evolution depicted in Fig. 3) addresses only impact-related outgassing, and we do not explicitly consider the effects of variations in background volcanism.

In this work we argue that, irrespective of the intensity of background volcanic activity, the same process responsible for the delivery of highly siderophile elements to the Earth's mantle was

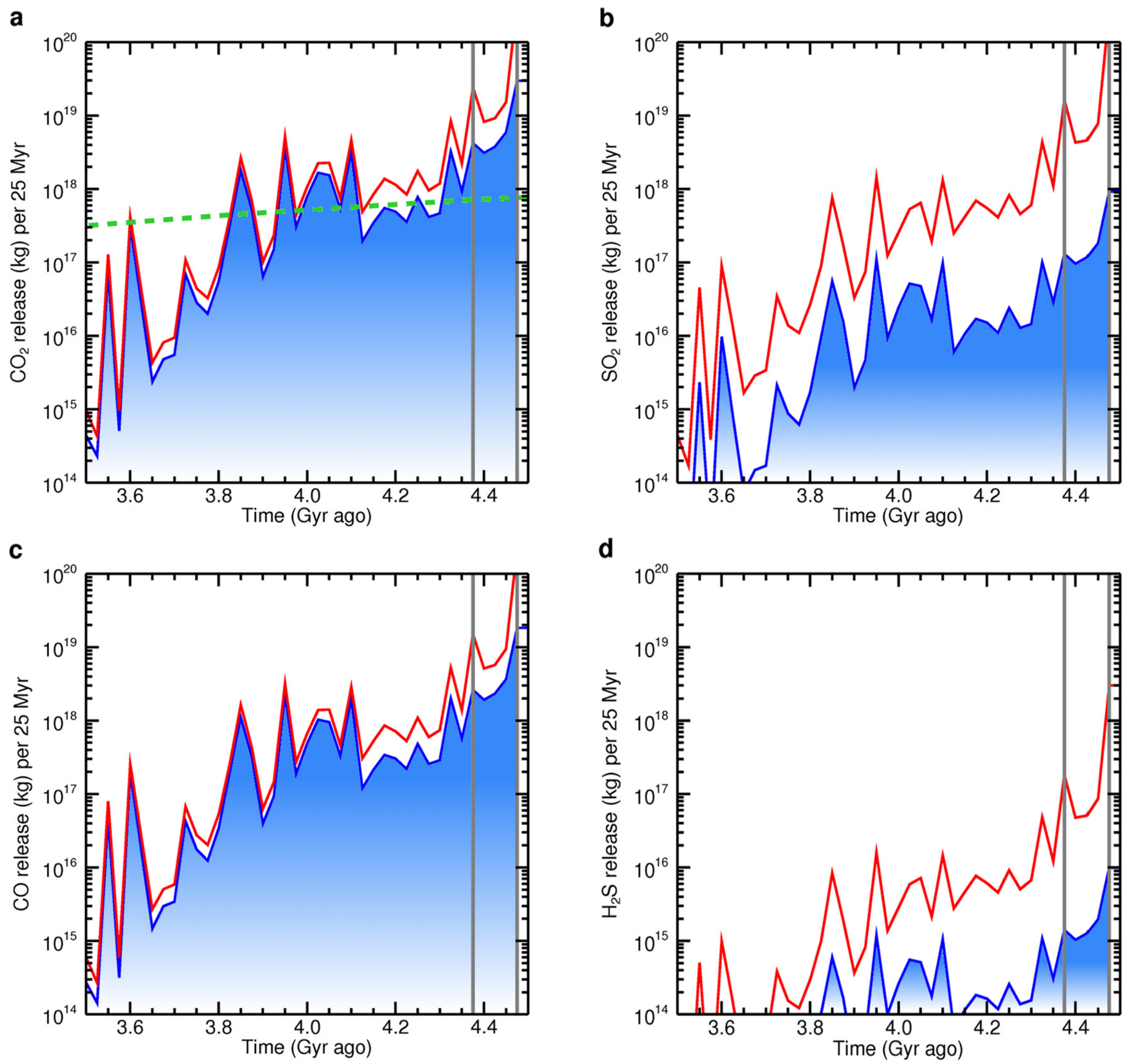


**Fig. 2.** Impact-generated outgassing on the early Earth. Outgassing for oxidizing (a: $CO_2$; b: $SO_2$) and reducing conditions (c: CO; d: $H_2S$). Each panel indicates the amount of gas released into the atmosphere in time bins of 25 Myr, with and without the contribution of impactors' volatiles (red and blue curve, respectively) for one specific simulation. For the case of carbon dioxide (a), the horizontal dashed green line indicates an estimate of the amount of atmospheric $CO_2$ needed to give an average surface temperature of 273 K based on a 1D model (von Paris et al., 2008). The vertical grey lines indicate the timing of major collisions (diameter ≥500 km), which could have potentially added large volume of water vapor into the atmosphere (see Supplementary Information).

also capable of triggering massive venting of greenhouse gases to the Hadean Earth's atmosphere, while sporadic sizeable impactors (10–100 km in diameter) could also have contributed from time to time during the middle to late Archean.

## 4. Results

We present first the results concerning the total budget of released gases corresponding to our nominal model described above (Fig. 2). A first important conclusion is that the total amount of carbon species released throughout the Hadean exceeds by a factor of 10–100 the current mass of the atmosphere ($\sim 5.15 \times 10^{18}$ kg). The amount of sulfur species released into the atmosphere is also significant, although we note that under our assumptions the outgassing of impactor material has a much more important role than for carbon species. Furthermore, the intense outgassing of impact melt sheets during the Hadean is followed by a rapid drop of several orders of magnitude by 3.5 Gyr ago compatible with the level of atmospheric $CO_2$ inferred from the Archean geological record (<3.5–2.5 Gyr ago; e.g., Rye et al., 1995).

To assess the effects of outgassing from melt pools on Hadean climate and surface habitability, we developed a model that tracks the quantity of gas released in each impact and follows its overall evolution in the atmosphere, as discussed in Section 2.2. The latter is done through a simple parameterization of the major loss mechanisms, including the carbonate–silicate Urey cycle, photodissociation and precipitation. The model does not track the complex chemistry of the atmosphere nor the details of atmospheric interactions with the surface (i.e., between rock and water). We also neglect the complex chemistry of temporary, hot silicate-rich atmospheres as previously discussed.

We first focus on carbon. In the oxidizing case, $CO_2$ is directly released by the melt. We initially assumed an exponential decay of atmospheric $CO_2$ with a conservative e-folding decay timescale of $\tau = 1$ Myr. Fig. 3a reports the results for the case without impactor volatiles. These simulations show that impact outgassing could have intermittently sustained a level of atmospheric $CO_2$ above the inferred minimum condition for liquid water in the early Archean and Hadean ($\sim$4–7 $\times 10^{17}$ kg; von Paris et al., 2008) for a cumulative time span of several 10s Myr up to 100 Myr.

We further explore the effect of $\tau$ on the budget of atmospheric $CO_2$, as Hadean $CO_2$ weathering may have differed significantly from the Phanerozoic (Zahnle et al., 2007) due to reduced con-

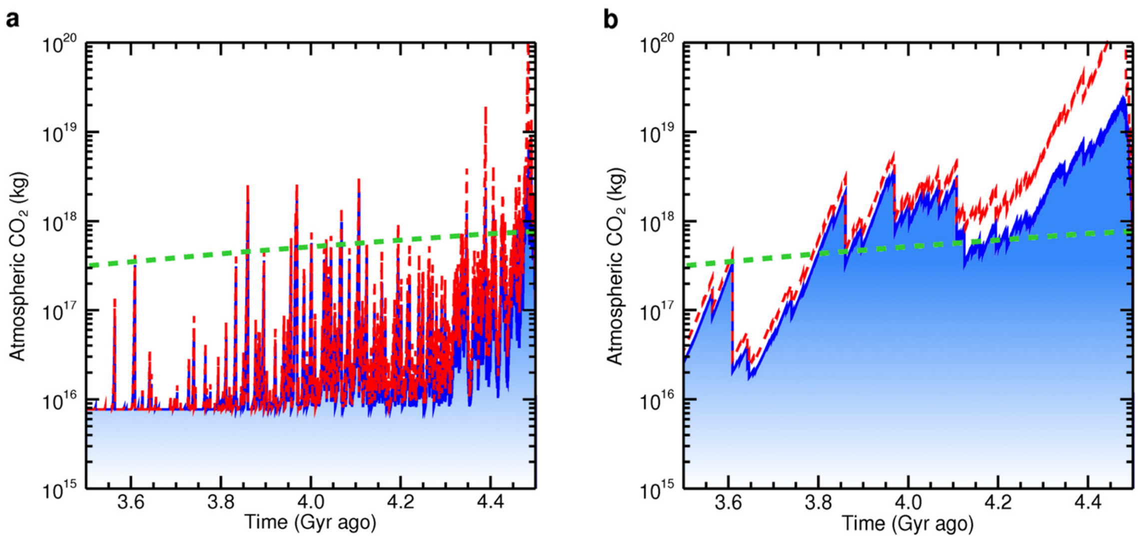


**Fig. 3.** Effects of weathering timescale on atmospheric $CO_2$. Evolution of carbon dioxide for oxidizing conditions and an e-folding removal time scale of 1 Myr (a), and 30 Myr (b). Symbols and colors as in Fig. 2. Similar results apply for reducing conditions. Note that the exact timing and number of major impacts (represented by spikes in a) is highly stochastic and their time locations depend on the actual simulation (Marchi et al., 2014).

tinental land area and perhaps reduced surface temperature. We estimate that for $\tau = 10$ Myr, a clement surface condition is obtained for a cumulative time span of 100–200 Myr. Furthermore, impacts would have resulted in surface temperatures above freezing until ~3.8 Gyr ago and ~3.5 Gyr ago (Fig. 3b), respectively for $\tau \sim 30$ Myr and ~90 Myr.

These results hold also under reducing conditions assuming that CO is converted gradually into $CO_2$ (e.g., Kasting, 2014; Table S1). Methane, which is a strong greenhouse gas, has also been invoked as a partial solution to the faint young sun paradox (Kiehl and Dickinson, 1987; Wolf and Toon, 2014). Accounting for volatiles from the projectile, if ~1% of the available C outgassed as methane (Iacono-Marziano et al., 2012) under reducing conditions, even moderately sized impacts could have released sufficient $CH_4$ to push atmospheric $CH_4$ above $10^{-4}$ bars. This quantity of $CH_4$ would increase global mean surface temperatures by ~6 K (Wolf and Toon, 2014). These computations have been performed with a nominal melt concentration of 400 ppm C, and our conclusions remain valid down to ~120–150 ppm C, irrespective of the extent of carbon outgassing from the impactors themselves. At melt carbon concentrations less than ~120 ppm, however (corresponding to Hadean mantle with less than ~20 ppm C), the contribution of the projectiles themselves to atmospheric $CO_2$ release outweighs that of the mantle-derived melt.

In summary, our findings suggest that following the transient aftermath of large impacts, impact-derived outgassing could have resulted in episodes of clement surface conditions prior to ~3.5–3.8 Gyr ago.

## 5. A closer look at Hadean zircons

Ancient zircons provide the only direct record of environmental conditions during the Hadean. As discussed in Section 1, the prevailing view holds that elevated Hadean zircon $^{18}O/^{16}O$ ratios (expressed in the conventional $\delta^{18}O$ notation) likely reflect crystallization in magmas contaminated with material previously weathered or altered at low-temperatures in the presence of liquid water (e.g., Mojzsis et al., 2001; Bell et al., 2014). The age distribution of zircons older than about 3.5 Gyr ago (Fig. 4a), however, does not allow us to precisely constrain the temporal stability of liquid water, and either a sustained clement climate or freeze-thaw episodes (with initial acquisition of the elevated $\delta^{18}O$ signature during thaw intervals) are compatible with the zircon data. We used an ensemble of 20 Monte Carlo simulations (Fig. S1; Marchi et al., 2014) to compute the likelihood that impacts alone could result in clement conditions (Fig. 4b). After accounting for the age distribution of extant and analyzed Jack Hills zircons (which are biased towards older ages due to targeting of the most ancient crystals), our modeled Hadean climatic evolution predicts a distribution that is consistent with the observed pattern of $\delta^{18}O$-enrichment in ancient zircons (Fig. 4c). In particular, the influence of impact melt pool degassing on Hadean climate may explain the prevalence of 4.0–4.2 Gyr-old zircons with oxygen isotopic signatures that reflect interaction with surface liquid water. As discussed in Section 3, background levels of volcanism in the Hadean may have further contributed to Earth's climate state.

Our model shows that, depending on the characteristic timescale for drawdown of gases from the atmosphere, late accretion impactors could have resulted in either sustained clement climate or alternating episodes of warmer and icehouse conditions throughout the Hadean and early Archean. While we acknowledge that high $\delta^{18}O$ values do not prove the presence of surface water, the capacity of our model to provide a quantitative explanation of the observed zircon $\delta^{18}O$ distribution is noteworthy.

In the context of the middle to late Archean, our model shows that impact-driven outgassing alone is unlikely to have sustained liquid water and possibly warm ocean temperatures (e.g., Blake et al., 2010) after ~3.5–3.8 Gyr ago (Fig. 4b), with the exception of sporadic intervals after sizeable impacts.

## 6. Implications for the emergence of life

Our results emphasize that impacts were a major geophysical and geologic process on the Hadean and Eoarchean Earth. Large impacts may have yielded direct consequences for environmental conditions prior to and during the emergence of life. In particular, carbon and sulfur are key elements for life and their circulation at the surface is therefore important to constrain the conditions under which the first organisms may have emerged. The earliest geochemical signature of life dates to ~3.5 Gyr ago (Schopf, 2006). Some of the earliest known organisms (e.g., Shen et al., 2001) relied on sulfur for key metabolic functions. However, because the vast majority of Earth's primordial sulfur likely partitioned into the core during core formation (e.g., Labidi et al., 2013; Wang and Becker, 2013) its availability could have been

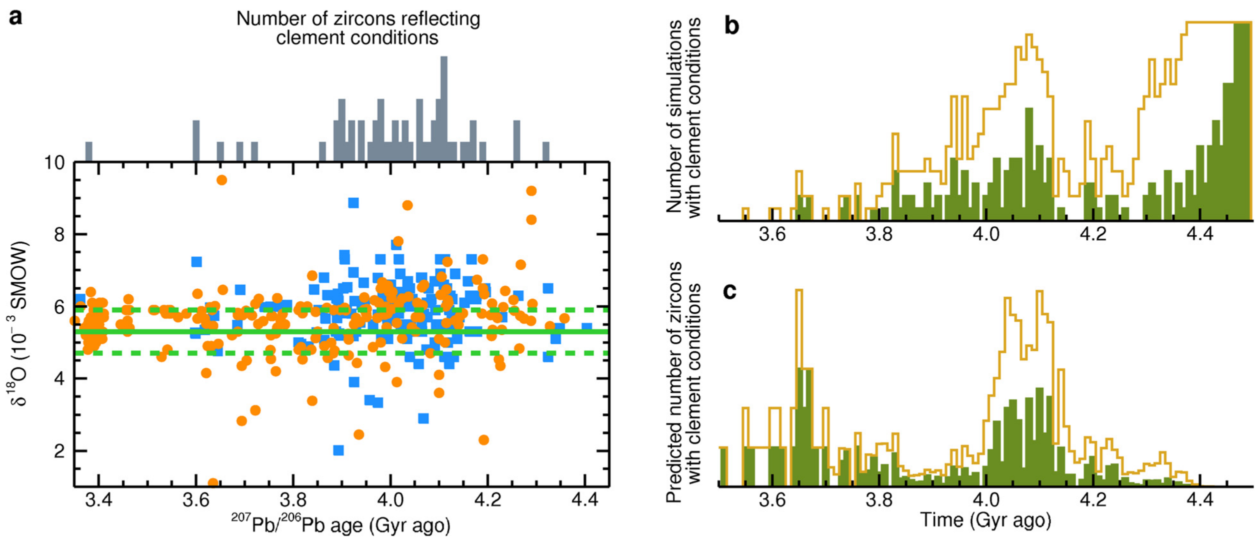


**Fig. 4.** Early Earth's surface conditions. a: Oxygen isotope ratio values ($\delta^{18}$O; relative to Standard Mean Ocean Water, SMOW) for zircons older than 3.4 Gyr ago (Bell et al., 2014): data in blue squares indicate zircons that were imaged with electron microprobe and show no contamination by cracks or inclusions; data in orange circles indicate no imaging available or unclear interpretation. Zircons with clear indications of contamination have been excluded (Bell et al., 2014). The solid green line indicates the mean mantle $\delta^{18}$O (dashed lines are $\pm 2-\sigma$). The grey histogram at the top indicates the number of concordant zircons of a given age with $\delta^{18}$O in excess of mantle values (Bell et al., 2014). Time bins of 10 Myr. Note that due to deliberate pursuit of the most ancient zircons, the number of data points are biased toward older ages, and the histogram may be incomplete for ages younger than ∼3.8 Gyr ago. b: Frequency of simulations resulting in $CO_2$ levels above freezing conditions (see Fig. 2) from an ensemble of 20 Monte Carlo simulations, for an e-folding removal time scale of 1 Myr (green) and 10 Myr (yellow). c: Same as above, but now the distributions have been convolved with an ancient zircon age distribution (Griffin et al., 2014; which contains over 700 individual zircon ages older than 3.5 Gyr ago) to give the distribution of $\delta^{18}$O in Hadean zircons expected from the climatic influence of impact melt pool degassing. Because this convolution accounts for the number of zircons of a given age that have been analyzed, assuming that the dataset of Bell et al. reflects a similar bias towards older zircons, the shape of the gray distribution in Fig. 4a and the green distribution in Fig. 4c should be directly comparable.

very limited at the Earth's surface in the aftermath of the giant impact that resulted in the formation of the Moon. Assuming typical chondritic sulfur abundances for late accreted material, we compute that more than ∼50% of the current bulk silicate Earth sulfur may have been delivered between ∼4.5 to ∼4.0 Gyr ago, compatible with geochemical data (Labidi et al., 2013; Wang and Becker, 2013). Here we demonstrate that impact melt pool degassing redistributes mantle carbon and (chiefly impactor-derived) sulfur towards surface environments, drastically increasing the amount of sulfur available for Archean biological processes. The surface redistribution of carbon and sulfur species could alter oceanic pH, with major repercussions for metabolic pathways.

Given the uncertainties in oceanic buffering capacity and silicate weathering described above, any calculation of pH in Hadean oceans is illustrative rather than quantitative. That said, to calculate ocean pH given variable atmospheric $CO_2$ partial pressure, we follow the approach described by Follows et al. (2006) and Tans (1998), a variant of which is implemented at http://biocycle.atmos.colostate.edu/shiny/carbonate/. We assume titration alkalinity of 2000 µeq/kg and seawater temperatures of 293 K, and we further assume an elevated Precambrian salinity of 0.054 ppm (Knauth, 2005) to obtain total dissolved inorganic Boron. We neglect dissolved phosphorus and silica. We then solve the carbonate equilibria for [H+], using a script adapted from Follows et al. (2006) and from http://biocycle.atmos.colostate.edu/shiny/carbonate/.

We estimate that $CO_2$ partial pressures of ∼0.1 bar (which we expect following the largest collisions) would acidify Hadean oceans to pH $< 6$. For comparison, seawater pH during the end-Permian mass extinction may have dropped below pH $= 7.5$ (Clarkson et al., 2015). Even such acidic pH levels would not inherently deter extremophile organisms (e.g., Johnson, 1998). However, repeated episodes of impact degassing could cause major swings in acidity in tandem with shifts in temperature (and occasional impact vaporization of the oceans), rendering the Hadean Earth particularly inhospitable for the earliest possible biota while setting the stage for life in the Archean.

## 7. Conclusions

In this work we have explored the environmental effects of large collisions during the Hadean and early Archean. The picture emerging is one in which after the transient havoc of hot, silicate-rich atmospheres has passed, impact-generated melt outgassing could have substantially altered surface conditions. Release of greenhouse gases such as $CO_2$ may have been sufficient to temporarily offset weaker insolation from the faint young Sun. Depending on the timescale for atmospheric $CO_2$ drawdown, impact-induced outgassing could have sustained clement surface conditions episodically (1–10 Myr) or for a protracted time (100s Myr). While detailed investigation of the consequences of background volcanism is beyond the scope of this work, elevated Hadean volcanism could have supported additional greenhouse warming.

The bombardment also redistributed or delivered to the surface and subsurface C and S, both important elements for life, with important implications for oceanic pH and early metabolic chemistry. Our work supports a view of the early Earth in which impacts were responsible for environmental catastrophes (local or global, depending on the impactor size), followed by more benevolent global effects.

Finally, because the late accretion is a highly stochastic process the end result of these collisions could have been radically different among terrestrial planets, and in particular on Venus. In contrast to Earth, at present the Venusian atmosphere is predominantly $CO_2$ and lacks a significant inventory of water. Under the young Sun's strong UV, X-ray and EUV fluxes (Kasting and Pollack, 1983), large amounts of atmospheric H and O (from photodissociation of water vapor) could have been removed from Venus on a relatively short time scale of 70–100 Myr (e.g., Gillmann et al., 2009). We hypothesize that early bombardment and impact melt degassing may have facilitated the Venusian greenhouse state, both by extracting water and $CO_2$ from the solid planet and by vaporizing surface reservoirs. Particularly interesting is the occurrence of very large collisions. Our terrestrial impact flux shows that impactors larger than 500 km can randomly occur over a protracted time and 10% of the simulations have a minimum impact time of 4 Gyr ago or less. A similar result is expected for Venus. Thus, because the late accretion process is stochastic, and because the efficiency of hydrogen escape declines with time, the precise atmospheric conditions on Venus today may result from the vagaries of planetary collisions more than four billion years ago.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.05.032.

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