Chapter 7
Implication of Impacts in the Young Earth Sun Paradox and the Evolution of Earth's Atmosphere

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Abstract The role of impacts in the evolution of the Earth's atmosphere is discussed. Impacts could have been significant heating sources during the Hadean eon, and likely promoted thermal escape of atmospheric species to differing degrees. Large impacts, that are regularly delivering enough energy to Earth's atmosphere to cause significant erosion, can also bring metal particles with catalytic properties in the right conditions. That impact-induced chemistry is poorly known, but recent laboratory studies emphasize its key role in the production of greenhouse gases and organic compounds. A better understanding of the phases associated with re-entry and cooling phases of a bolide plume evolving in the aftermath of a huge impact is needed. In the right range of temperature and pressure conditions, impacts can produce ammonia, methane and other organic compounds through the Haber and Fischer-Tropsch catalytic processes, but mixing and decay of those compounds in different models of the atmosphere needs to be explored. Hadean-atmosphere models proposed so far are reviewed also discussing the scarcely available geological evidence. Simple thermodynamic equilibrium calculations for probable Hadean atmosphere conditions are presented. Several scenarios of reducing (H_2-rich) and oxidizing (CO_2-rich) atmospheres are considered to study the stability of CH_4 and NH_3 and the formation of organic compounds. Searching for chemical signatures in similar evolutionary stages of recently formed Earth-like exoplanets could be an interesting future field of research. New evidence in this regard can contribute to a better understanding of the transition point to a habitable world.

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Introduction

Oparin (1924) was one of the first authors to speculate about the composition of the primeval atmosphere and its implications on the origin of life. He proposed a strongly reducing atmosphere rich in hydrogen (H_2), ammonia (NH_3), methane (CH_4) and other hydrocarbons, and suggested that the reactions between those compounds led to the production of organic compounds with increasing complexity, which then rained into the primordial ocean. A few years later Haldane (1928) proposed that carbon dioxide (CO_2) was the dominant carbon source in the early atmosphere, on the basis that volcanic degassing formed the primeval atmosphere. Despite being speculative, Oparin's scenario was innovative for his time because, not only did it propose an early atmosphere based on quite reasonable assumptions, but also provided a direct link between its evolution and the origin of life. Nowadays, many authors share this view and make the study of the origin of the atmosphere an interdisciplinary and exciting subject.

The first author to give a theoretical foundation to Oparin's ideas was Urey (1952) who developed the first relatively quantitative model of the primeval atmosphere. The successful synthesis of amino acids in laboratory by Miller (1953) and later by Miller and Urey (1959) gave additional value to Oparin and Urey's hypothesis of the reducing conditions of the early atmosphere. Practically at the same time Rubey (1951, 1955) challenged this hypothesis proposing instead an oxidizing atmospheric composition. According to this author the first atmosphere came from degassing of the Earth's interior and the volcanic gases would have released oxidized species, but quite different to those observed nowadays. Rubey proposed that the major hydrogen species was H_2O rather than H_2, CO_2 rather than CO and N_2 rather than NH_3. In this scenario the bulk of the early atmosphere would have been in a neutral oxidation state due to the presence of small amounts of reduced compounds (Table 7.1).

Although both hypotheses are difficult to reconcile, Holland (1962) tried it by proposing that the primitive atmosphere passed through both stages: in a first period the Earth would have a reducing atmosphere because the volcanic gases released prior to core formation would have been rich in metallic iron; then progressively it evolved to a more neutral atmosphere but still anoxic. The absence of oxygen in the early atmosphere is usually granted (cf. Holland 1984).

Now we know that all these first models about the origin and evolution of the early atmosphere are unrealistic, because we have additional information about some processes that happened in on the surface of the primeval Earth and,

Table 7.1 Main chemical species depending on the oxidation state of an early-Earth atmosphere

Atmosphere	H species	C species	N species	O species
Reducing	H_2	CH_4	NH_3	CO
Oxidized	H_2O	CO_2/CO	N_2	CO_2

moreover, we know that the Earth formed in a shorter accretion process than proposed in the past (Safronov 1969). Taking into account a period for Earth's accretion close to the actual calculations (10–100 Ma, with a preferred value of 50 Ma), the planet's interior probably was heated to several thousand Kelvin by gravitational energy released during impacts with planetesimals (Kaula 1979). In consequence core formation occurred probably at a faster rate than assumed in preliminary models, and differentiation was essentially complete in a short time scale (Stevenson 1983; Lammer et al. 2011). It is usually considered that the earliest atmosphere of the Earth was produced by primitive mantle outgassing, but it seems obvious that stochastic massive impacts could have also been an important factor in its composition. Impacts probably delivered organic compounds promoting catalytic reactions as consequence of the disruption in the atmosphere of metal-rich chondritic bodies. Endogenous and exogenous sources need to be evaluated and balanced in accordance with the geological and lunar evidence, but also laboratory experiments could be crucial for explaining the evolution of the terrestrial atmosphere in that period. This is a complex puzzle because such an atmosphere would have contained H_2, H_2O, CO, CO_2, CH_4, and NH_3, but also because of the scarce geological evidence available for that period.

A very dense primitive atmosphere, containing CO_2 and H_2O may have efficiently trapped the heat from the Sun (weaker at visible and longer wavelengths) and also participated in retaining the primordial accretionary energy. Consequently, it has been envisioned that the surface temperature of the proto-Earth rose to above 1,500 K creating a "magma ocean" on the surface (Matsui and Abe 1986; Zahnle et al. 1988). These authors suggested that such conditions prevailed because a massive atmosphere prevented the rapid freezing of the magma ocean during the first tens of Ma in the Earth surface, coinciding with the period of high accretion. A stable magma ocean requires that the volatile outgassing together with the exogenous delivery be of at least of the same order as the atmospheric mass loss by Jeans escape. Kaula (1979) obtained the Earth's thermal evolution taking into account the impactor's frequency. He found that the surface's temperature probably stayed between 2,000 and 3,500 K during the Earth's accretion period (about 50 Ma). The upper mantle was probably more reduced than today, although progressively became more oxidized as a result of the release of reduced volcanic gases and the subduction of hydrated, oxidized seafloor (Kasting et al. 1993).

It has been shown that the cataclysmic impact forming the Moon probably did not completely erode the atmosphere of the Earth (Genda and Abe 2003, 2005; Newman et al. 1999). This inflexion point was followed by other less massive impacts bringing volatile-rich materials that could have released reduced gases when subjected to subduction. Bukvic (1979) and more recently Schaefer and Fegley (2007) have modeled the equilibrium gas chemistry of an outgassed chondritic-vaporized reducing atmosphere, but several processes that can take place in the aftermath of the impacts are scarcely known. Other authors have an opposite view where the outgassed vapors (Delano 2001), or the degassed vapors during impacts (Ahrens et al. 1989) produced oxidizing products ($H_2O + CO_2$). Both scenarios are explored here, and also the influence of an enhanced shortwave solar activity during the early Hadean.

Composition of Impactors and Their Impact in the Chemistry

In this section we analyze the role of impacts inducing significant compositional changes in the terrestrial atmosphere. We will particularly focus on the key role of carbon- and water-rich bodies that, due to their relative low bulk density, tensile strength, and volatile abundance experience catastrophic disruption in the upper atmosphere. Typically, about 60% of the large fireballs recorded and measured by the Prairie Network experience one or several fragmentations along their path, and in about 20% of the cases the bolide practically ends up in a sudden overwhelming fragmentation (Ceplecha et al. 2003). In simple terms, it happens because when the meteoroid penetrates the atmosphere it feels an increasing dynamic pressure ($p = \rho \cdot v^2$). When the loading pressure surpasses the material strength required for fragmentation the body breaks apart and, as consequence of the flight and the shock wave shaking, disruption is imminent. The properties of the above-mentioned large meteoroids are probably not identical to volatile-rich asteroids or comets because, among other things, meter-sized meteoroids arriving at our planet are biased towards high-strength materials that have survived an excavating impact in their parent bodies and long-exposures to interplanetary space. It is well known, for example that Near Earth Objects (NEO) are delivered to near-Earth space from the Main Belt in typical periods of millions of years. Blum et al. 2006) reasoned from accretionary and evolutionary arguments that hundred- to km-sized primitive asteroids and comets should exhibit a fragile nature: extremely low bulk density, and high porosity.

Water-rich asteroids and comets impacting the atmosphere of Earth are directly delivering volatile species as consequence of the disruption behavior, but the amounts of surviving materials are scarce if the impact geometry and velocity are not favorable for a moderate deceleration and settling of the materials in the atmosphere (Blanck et al. 2001). On the basis of fireball spectroscopy it is suspected that catastrophic disruptions can disperse dust far from the shock wave frontal region where bolide experiences higher temperatures (Borovicka 1993, 1994; Trigo-Rodríguez et al. 2003). Consequently, the peak temperature and the exposure to heat are both minimized and there is room for a percentage of the body to survive, at least, as small fragments that are slowly settling down towards the surface.

Other important aspect to consider is the thermal processing that affects the materials subjected to ablation in the fireball column. As a consequence of the heat associated with the collision with atmospheric gases, meteoric minerals are ablated, vaporized and dissociated. Elemental lines and molecular bands are remarkable features in bolide spectra (Fig. 7.1). It has been demonstrated that most of the fireball chemistry behind radiating light can be perfectly fit with a thermodynamic equilibrium model (Borovicka 2001; Trigo-Rodríguez et al. 2003). This behavior is probably a consequence of the quick mixing of air and meteoric plasma promoted by the supersonic movement, meteoroid spinning, and subsequent induced turbulence around the bolide. In this work we are assuming thermodynamic equilibrium to study some of the processes that could take place in bolide plumes.

It is important to remark, however, that the production of different gases can be avoided in environments with different chemistry and radiative flux. Results are then preliminary, with the main aim of exploring unknown aspects of the delivery of pristine materials to Earth's atmosphere.

The reentry and ablation of cometary dust was studied thanks to the accurate spectroscopic study of the impact plumes produced in Jupiter's atmosphere as a consequence of the impact of comet Shoemaker-Levy 9 in July 1994 (Fitzsimmons et al. 1996). Interestingly these authors found that most of the light emission came from silicate grains ablated in the different phases. In the case of a chondritic (asteroidal) body with larger metal abundance at least two key processes are envisioned to participate in greenhouse gas production in the aftermath of the bolide interaction:

1. A rapid conversion of N_2 to NH_3 is feasible in the aftermatch of impacts, particularly during the final stage in which the bolide plume stops its adiabatic expansion, and falls back to the surface. The catalysis producing abundant ammonia, known as the Haber process, requires the surface of metal grains acting as catalyzers.
2. At the same time, metal grains can catalyze a plethora of different organic compounds when abundant CO and H_2 are available via Fischer-Tropsch catalysis (Sekine et al. 2003, 2006). This has been found to be a key process occurring in impact plumes produced by comets and carbonaceous asteroids atmospheric disruptions.

Survival of Greenhouse Gases: CH_4 *and* NH_3

The tendency of NH_3 and CH_4 to decompose has been the main criticism against the long-term stability of these compounds and the possibility of having a strongly reduced Hadean environment. Sagan and Chyba (1997) attempted to solve the faint young Sun dilemma by proposing the formation of particles of organic polymers (tholins) by the action of UV light in an atmosphere with $CO_2/CH_4 < 1$. Suspended in the stratosphere, those polymers would protect the lower atmosphere from UV photolysis, acting as a screen capable of avoiding the photodecomposition of these greenhouse gases. Protected by tholins from ultraviolet radiation, they would have enhanced the early greenhouse in an amount enough to keep warm temperatures despite the weakness of the young Sun.

The proportions of C and O in the atmosphere are also important. This is because a $C/O > 1$ ratio promotes polymerization of CH_4 whereas $C/O < 1$ led primarily to oxidation (Sagan and Chyba 1997). In an anoxic atmosphere the primary reservoirs of oxygen are CO_2 and H_2O. Probably CO_2 outgassing was important in the Hadean. However, Kasting (1997) and Sleep and Zahnle (2001) proposed that the rapid weathering of the ejecta from frequent large impacts could have provided a sink for atmospheric CO_2. According to their model, methane and ammonia participated in a kind of feedback cycle, working together in two main ways: (i) methane's presence produced an organic haze due its capacity to polymerize and (ii) this haze protected ammonia from UV photodissociation. This cycle could yield longer lifetimes for these gases, in turn allowing the greenhouse effect in the primeval atmosphere

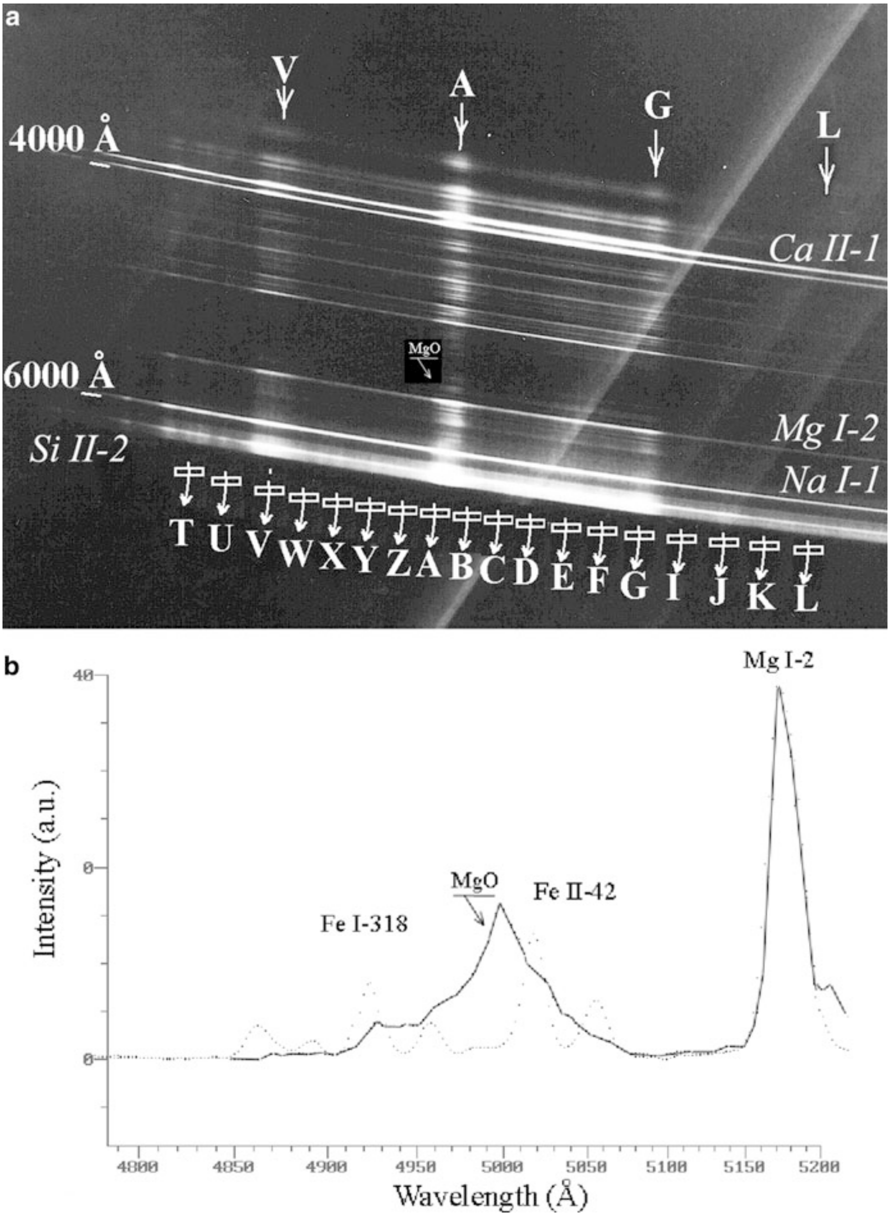

Fig. 7.1 A photographic spectrum of a Perseid fireball associated with comet 109P/Swift-Tuttle recorded in photographic plate from Ondrejov Observatory. The meteoroid producing this bolide was about 30 g in mass, and appeared on Aug. 11, 1969 at 21h06m UTC. (**a**) Detailed image of the ending part of the fireball luminous path showing the scanned slots with a microdensitometer as discussed in Trigo-Rodríguez (2002) and Trigo-Rodríguez et al. (2003). The main emission lines are shown: the Ca II-1 doublet, the Mg I-2, the Na I-1, and finally the Si II-2 line associated with the high temperature component. (**b**) A small part of the *center* image shows a MgO band that cannot be fitted to elemental emission lines. The scanned signal in this graph appears discontinuous, while a *darker, continuous line* shows the modeled spectrum (Original image courtesy of Jiri Borovicka (Ondrejov Observatory, Czech Republic))

during longer time scales than when each is considered separately. Such a high amounts of these greenhouse gases are supported by evidence for a CH_4 mixing ratio of 10^{-4} (100 ppmv) in paleosol data 2.8 Ga old (see e.g. Pavlov et al. 2000). In fact, Catling, Zahnle and McKay (2001) suggested that the concentration of methane in the Archean atmosphere was even larger than this given by Pavlov et al. (2000). The main pros and cons of these arguments are given on Table 7.2.

Discussion and Conclusions

Today most researchers seem to prefer a mildly reducing atmosphere based on mantle degassing and bolide impact but there is still controversy. The different components considered in the literature are compiled in Table 7.2. Stellar evolution models show that the solar luminosity has increased through time, with the solar constant (S) around 30% smaller 4 Ga ago than nowadays. At the same time, the integrated high-energy emission was about one order of magnitude higher than in the present about 3.9 Gyrs ago (Ribas et al. 2005). All these changes probably had important consequences for the Earth's atmosphere, like the non-thermal escape processes produced by magnetic-induced solar forcing (Lundin et al. 2007).

Was the Hadean atmosphere anoxic? Several authors have widely presented the rise of oxygen in the Earth's atmosphere as an evolutionary process. Walker et al. (1983) and Kasting (1987) developed simple models involving the atmosphere-ocean system. They proposed the evolution of oxygen in three main stages. During the first stage (stage I), the entire atmosphere/ocean system was essentially devoid of free oxygen under reducing conditions. The main basis of this argument is that the supply rate of reduced substances as H_2, CO and H_2S from volcanoes and Fe^{2+} from seawater/basalt interaction exceeded the production of O_2 from photolysis followed by the escape of hydrogen to space. A few authors do not share that view (e.g Towe 1981) and support the presence of O_2 in the primeval environment. According to Kasting et al. (1992) at some point during the Archean or the Early Proterozoic, the supply of reduced substances decreased or the oxygen rate increased. As volcanic activity and impact plumes were the principal sources of reducing gases, the transition to an O_2-rich atmosphere probably happened when the LHB ceased at the end of the Hadean. The process was probably slow, induced by stromatolitic bacteria near the surface where local oxic conditions can be reached. The deep ocean remained anoxic, carrying ppm abundances of ferrous iron in solution. Such conditions are necessary to create banded iron sediments formed until the mid-Proterozoic. The presence of an oxidized surface and a reduced deep ocean identifies the Stage II of Walter-Kasting model for the early Proterozoic (Kasting and Chang 1992) under increasing O_2 abundance originated from photosynthetic organisms. Finally in Stage III is characterized by extended oxic conditions.

The geological evidence for an anoxic Archean (and presumably late Hadean) environment has been recently obtained. Farquhar et al. (2001) presented recently the evidence of Mass Independent Fractionation (MIF) of sulfur isotopes in sediment deposited prior to 2.3 Ga. By MIF we understand that sulfur isotopes do

Table 7.2 Main pros and cons for the presence of two greenhouse gases, NH_3 and CH_4 in the primeval atmosphere

	Pros	Cons
NH_3	1. A small quantity $[NH_3] \sim 10^{-5}$ in a 1 bar atmosphere can increase the global temperature enough to avoid a glacial era	1. Soluble in water and subject to rapid rainout
	2. Can come from different endogenous and exogenous sources	2. The proposed amount of NH_3 can be photodissociated by UV light to produce N_2 in a few decades
	3. Produced by cometary impacts (Lellouch 1996)	3. NH_3 can be destroyed by reaction with OH to produce N_2
	4. If CH_4 was present forming an organic haze, the NH_3 could substantially shield from photolysis	4. NH_3 constitutes less than 1% of the volatile mass of comets
CH_4	1. Photodissociation is only produced by $\lambda < 1{,}450$ Å photons	
	2. It's possible to polymerize the methane with UV photons (oxidation is replaced by polymerization happens when C/O ratio passes unity)	1. The CH_4 lifetime (under present conditions) is of the order of centuries
	3. Endogenous source: some CH_4 is produced by serpentinization in mid ocean ridge basalts	2. No probable exogenous source is known; CH_4 constitutes less than 1% of the mass of comets
	4. Possible production of CH_4 during cometary impacts (Zahnle 1996; Lellouch 1996)	
	5. In the low O_2 Archean atmosphere CH_4 is not oxidized	

not obey the standard mass-dependent relationship of S isotopes in aqueous solution. The penetration of UV radiation in the 190–220 nm spectral region can produce MIF as was demonstrated by Farquhar et al. (2001). In order for this radiation to penetrate deep into the atmosphere the columns of O_2 and O_3 must have been much lower than at present. In this way, under reduced atmospheric conditions S can be removed from the terrestrial atmosphere in a variety of different oxidation states. Additional evidence for an anoxic Archean atmosphere is the presence of sedimentary deposits (red beds) more than 2.45 Ga ago containing uraninite, siderite and pyrite, the reduced shallow-water facies of Fe formations, the presence of highly carbonaceous shales not enriched in redox-sensitive elements and, in general, the general observation than the older palaeosols are not oxidized (Pavlov and Kasting 2002).

Where is the outgassed CO_2? The total amount of carbon dioxide tied up in carbonate rocks today is some 3×10^{20} kg, the equivalent of about 60 bar if introduced in the atmosphere. Ronov and Yaroshevskiy (1967) initially used this evidence for suggesting a massive CO_2 early atmosphere, and the idea was also adopted by other authors (Holland 1978; Kasting 1983). They proposed that this carbon, along with other volatile elements reached the Earth during planetesimals' accretion, with carbonaceous chondrites and comets being the main sources of this carbon (see also Chyba et al. 1990; Chyba and Sagan 1992). This simple view of an extraordinary amount of carbon in the primeval atmosphere is unrealistic based in two arguments. First, the carbon-rich bodies reached the Earth separated by large time intervals, therefore gradually incorporating this carbon directly into the Earth crust, where it was retained (Oró 1961; Sagan and Khare 1971). Second, the presence of a global water ocean, supported by the isotopic studies of a 4.4 Ga zircon (Valley et al. 2001), makes it possible that the injection of large quantities of CO_2 into the atmosphere during impacts or degassing was quickly removed by the ocean feedback. Probably the Earth developed a mechanism to remove efficiently the excess of carbon in its atmosphere as evidence that nowadays the oceans are able to absorb 6×10^{15},g C/year as estimated Keeling (1983, 1993). Nowadays it depends on biological sequestering of CO_2 as carbonates, but if one inorganic sink existed in the past producing a similar rate, the oceans would be capable to remove this carbon from the atmosphere in only 50 Ma. This is just an upper limit because seems reasonable that not all this carbon was brought to the atmosphere at the same time and, moreover, the presumed overabundance of water in the primeval environment could participate accelerating the absorption rate of CO_2 by the ocean.

The absence of glacial deposits prior to 3 Ga was the main reason argued by Owen et al. (1978) and Kasting (1993) to support a dense primeval CO_2 atmosphere. This greenhouse gas had increased the temperature of the Earth to keep water in liquid state. Sagan and Chyba (1997) cast doubt on these arguments by suggesting the presence of other greenhouse gases capable to solve the "early faint-Sun dilemma" without the necessity to invoke a massive CO_2 atmosphere. Probably the carbonate-silicate geochemical cycle (Schidlowski et al. 1983) had an inorganic counterpoint in the early Earth by over-saturation of the oceans because silicate minerals were also common from that epoch. Currently the task to precipitate $CaCO_3$ is being mainly performed by living organisms, producing the isotopic fractionation of carbon. Support for this process is found in the data on C-isotopic compositions; transformation of inorganic carbon into living matter entails a marked bias towards the light isotope (^{12}C) with the heavy one (^{13}C)

retained in the inorganic reservoir (Schidlowski 1987, 1988). The first evidence for organic production of carbonate rocks comes from mat-forming bacteria, producing sedimentary rocks and stromatolites around 3.8 Ga ago (Maher and Stevenson 1988; Kasting and Chang 1992). Moreover sedimentary rocks rich in oxidized iron containing smaller quantities of carbon also formed in abundance in the Archean when the atmosphere was anaerobic (Walker 1987). Nowadays principally living organisms, particularly by calcareous plankton, performs this task.

Biogenic sinks of CO_2 were probably not present during the Hadean, but water was abundant as inferred from zircon data (Peck et al. 2001). Sleep and Zahnle (2001) proposed as a solution that the dynamic mantle buffer dominated over the crustal one on the early Earth. As a consequence, the mantle cycle would maintain low atmospheric and oceanic CO_2 levels, capable to produce a cold climate unless another greenhouse gas was important. The Hadean was also marked by collisions that participate in the sink of CO_2. For example, Sleep and Zahnle (2001) proposed that the huge production of basaltic glass ejecta in these impacts was weathered in a similar way as modern mafic and ultramafic volcanic glasses producing *palagonite*. After it, the hydration of such minerals progresses very quickly, being a direct sink for CO_2. The efficiency of this reaction depends of the access of reactable seawater or rainwater to the ejecta grains. This process is even plausible at temperatures close to the freezing point of water although are expected to be higher at temperate conditions (Brady and Gislason 1997).

To summarize, we think that an open view to explore different plausible scenarios for the Hadean terrestrial environment is needed. Physico-chemical processes associated with impacts must be taken into account in future models. Consequently, we wish to encourage new theoretical and laboratory approaches to get a more complete picture of the first stages in atmospheric evolution, also considering the role of impacts in an environment marked by a very different solar irradiance flux than nowadays (Ribas et al. 2005).

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