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Výzkum transformace atmosfér terestrických planet vlivem impaktů mimozemských těles a UV záření

Exploration of extraterrestrial body impact and UV-driven transformation of atmospheres of terrestrial planets

Disertační práce

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Dissertation thesis

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The presented thesis summarizes results of research performed as part of my Ph.D. studies at the Department of Spectroscopy, J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences and at the Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University.

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Prohlašuji, že jsem tuto práci vypracoval samostatně a že jsem řádně citoval všechny použité zdroje. Detailní popisy jednotlivých publikací, které jsou součástí této práce dále v textu vždy obsahují popis podílu mé práce na dané publikaci. Dále potvrzuji, že jsem tuto práci ani její část nepoužil k získání stejného nebo jiného akademického titulu. Jsem si vědom, že použití výsledků obsažených v této práci mimo Univerzitu Karlovu je možné pouze s písemným svolením této univerzity.

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Mgr. Antonín Knížek

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Abstract

Keywords: Exoplanets, Earth, Impact, Photochemistry, Infrared Spectroscopy, Atmospheric chemistry

Impacts and photochemistry are two very important driving forces for chemical transformation of planetary atmospheres. While strong UV radiation produced by young stars continuously provides a significant amount of energy, impacts are one-time events with far-reaching consequences. Especially important are then impacts on young rocky planets, including the early Earth, because these planets are likely exposed to much higher impact fluxes, commonly called 'heavy bombardment'. This bombardment is the final echo of the turbulent planetary accretion and has prominent significance for planetary environments, e.g., the chemical composition and shape of the planetary surface, the chemistry of atmospheres, aerosol production, and likely the origin of life. Future observations of exoplanets by space telescopes, such as the James Webb Space Telescope or Ariel, as well as ground-based telescopes, such as the Extremely Large Telescope currently under construction in Chile, could determine whether this heavy bombardment represents a common scenario for the evolution of terrestrial planets.

Both impacts and photochemistry can be efficiently simulated and studied in laboratory conditions by state-of-the-art methods. This thesis summarizes our results focused on identifying marker molecules of impacts and related thermodynamic disequilibria in planetary atmospheres. Key parts of this thesis involve the photocatalytic reduction of CO_2 to CH_4 in the context of Earth and Mars, the production of C_2H_2, OCS and CS_2 during impacts and their use as an impact marker, as well as the stability and chemistry of benzene and HCN during impacts. Each of the attached papers includes experimental results and shows what they imply for exoplanets. In some cases, the papers also contain predictions of specific consequences, such as the presence of spectral bands in observations provided by telescopes or concentrations of specific molecules in the soil detectable by landers. These parameters can be tested and our results directly proved or disproved.

Abstrakt

Klíčová slova: exoplanety, Země, impakty, fotochemie, infračervená spektroskopie, atmosférická chemie

Impakty a fotochemie jsou dvěma významnými hnacími silami pro chemické přeměny v planetárních atmosférách. Zatímco UV záření produkované mladými hvězdami kontinuálně poskytuje energii, impakty jsou jednorázové události s dalekosáhlými důsledky. Zvlášť významné jsou pak impakty na mladých kamenných planetách, protože tyto planety jsou vystavovány mnohem vyšším tokům dopadající hmoty, obvykle nazývané „těžké bombardování“. Toto bombardování je posledním dozvukem turbulentní planetární akrece a hraje důležitou roli při formování podmínek na planetách, včetně chemického složení, povrchu, chemie atmosfér, produkce aerosolů a pravděpodobně i vzniku života. Budoucí pozorování vesmírnými teleskopy, jako např. Vesmírný dalekohled Jamese Webba nebo Ariel, či pozemskými dalekohledy, jako např. Extrémně velký dalekohled, který je v současnosti konstruován v Chile, mohou určit, zda je toto těžké bombardování běžnou součástí evoluce terestrických planet.

Jak impakty, tak fotochemie mohou být efektivně simulovány a studovány v laboratorních podmínkách pomocí moderních metod. Tato práce shrnuje naše výsledky zaměřené na rozpoznávání markerových molekul impaktů a s tím souvisejících termodynamických nerovnováh v planetárních atmosférách. Klíčovými součástmi této práce jsou fotokatalytická redukce oxidu uhličitého na methan v kontextu Země a Marsu, produkce C_2H_2, OCS a CS_2 během impaktů a jejich použití jako markerů impaktů a v neposlední řadě stabilita a chemie benzenu a HCN během impaktů. Každý z přiložených článků obsahuje experimentální výsledky a ukazuje jejich důsledky pro exoplanety. Články obsahují také předpovědi, jako např. přítomnost spektrálních pásů v pozorováních z teleskopů nebo koncentrace specifických molekul v půdě detekovatelné vozítky na planetách. Tyto parametry mohou být testovány a naše výsledky tak přímo potvrzeny či vyvráceny.

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1 Aim of the work

This thesis presents work related to the exploration of planetary chemistry from the perspective of photochemistry and simulations of impacts in the laboratory. Most of the work presented here is experimental with the use of lasers and infrared spectroscopy as the connecting techniques. This thesis comprises seven publications, five of which are already published. Publications V and VII are currently under review in peer-reviewed journals and are included in this thesis, because they complete the story of this thesis, which describes both photochemistry and impacts as vital to our understanding of planetary chemistry. The seven publications present:

1) Oxygen isotope exchange, photocatalytic reduction of CO_2 to CH_4 in the context of the chemistry of Mars and the origin of biologically relevant molecules in connection with the origin of life (Publication I)
2) Exploration of the photocatalytic reduction of CO_2 to CH_4 – testing on a range of natural and synthetic catalysts (Publication II)
3) Application of the catalytic reduction of CO_2 to the chemistry of planetary atmospheres (Publication III)
4) The origin of acetylene in planetary atmospheres as a result of asteroid bombardment – experiments, planetary atmospheric model, and calculations of observability; acetylene as a marker of impacts (Publication IV)
5) The origin of CS_2 and OCS in planetary atmospheres as a result of asteroid bombardment – experiments, planetary atmospheric model, and calculations of observability by the James Webb Space telescope; CS_2 as a marker of impacts (Publication V)
6) The introduction of the ELISE experiment for extensive and detailed testing of asteroid and comet impacts into planetary atmospheres shown on the chemistry of benzene (Publication VI)
7) The stability of HCN in planetary atmospheres during impacts – description of impacts, extraction of rate constants for planetary atmospheric models, establishing of a general data reduction pipeline for future experiments (Publication VII)

2 Experimental planetary chemistry

In the landscape of contemporary science, the existence of worlds beyond our Solar System is no longer only a philosophical question. In 1917, Adriaan van Maanen discovered a first solitary white dwarf – the van Maanen's star. Walter Sydney Adams soon followed and captured its spectrum containing lines of calcium and other heavy elements. Through this discovery, he unknowingly provided the first evidence of an extrasolar planet, recognised only in 2015 (Zuckerman, 2014).

In 1938 (Belorizky, 1938) and lately in 1952 (Struve, 1952) postulated the radial velocity measurement as a method suitable for an exoplanet detection. However, the precision of measurement provided by spectrographs of that times was not sufficient. The first clue of exoplanet occurrence around the alien star has been provided by radial velocity measurements performed by (Campbell et al., 1988), and the first exoplanet orbiting a main sequence star was detected in 1995 (Mayor and Queloz, 1995). Today, over 5500 exo-worlds have been identified (Roques et al., 2023), but little is known about their physical and chemical environments. Upcoming deep spectral surveys with space telescopes will fill this gap (Tinetti et al., 2018). Exoplanets serve as a natural laboratory and new observational data will provide deep insights into their chemistry or will serve for an extrapolation of chemical and physical parameters to the early history of Earth and our Solar System (Ferus et al., 2022a).

Since the discovery of the first exoplanet orbiting a solar-type star (Mayor and Queloz, 1995), astronomers devoted much of their time to the development of techniques for the discovery, observation, and description of new exoplanets. Simultaneously, planetary scientists began developing models of their atmospheres, interiors, evolution, and other properties. Consequently, there arose the need for experimental data which would supply the models with parameters such as molecular absorption coefficients, collisional cross sections, new reactions, thermodynamic properties, and better radiative transfer models. These parameters can be determined by laboratory experiments and supplied to the existing models. Laboratory astrochemistry is therefore a necessary part of the exploration of exoplanets.

2.1 Observation of exoplanets

The cornerstone of experimental planetary chemistry is understanding astronomy and observations. Since the main goal of experiments is to complement observation and theory, the observation and theory provide guidelines on what is needed, required, or desired.

Five years before the first exoplanet was discovered, the Hubble Space telescope was launched to space. The instrument was constructed as a multipurpose optical telescope and yet, it was able to observe exoplanets with such precision that it discovered water vapour on super Earth K2-18b (Benneke et al., 2019). Another important satellite, the Spitzer Space Telescope, was launched in 2003 as an infrared telescope. It successfully mapped the atmospheric circulation of the gas giant HD 189733b (Grillmair et al., 2007). In 2006, the CoRoT (Convection, Rotation et Transits planétaires) telescope was launched with a primary focus on detecting transiting super Earth exoplanets and performing asteroseismology (CNES and ESA, 2006). The Kepler space telescope, initially launched in 2009 and later extended as the K2 mission, played a crucial role in exoplanet discovery. By monitoring the brightness of main sequence stars, Kepler identified over 2000 exoplanets, some of which are potentially habitable (NASA, 2018). The telescope concluded its observations in autumn 2018. Launched in 2013, the Gaia satellite was another telescope designed to map our galaxy. Its all-sky survey of stellar positions, brightness, and motion has provided a vast dataset for exoplanet searches (ESA, 2013).

Of the ongoing missions, TESS (Transiting Exoplanet Survey Satellite), launched in 2018, aims to discover Earth-sized planets. It recently found its first Earth-size planet, TOI 700 d, orbiting a red dwarf star within the habitable zone (NASA, 2020). The CHEOPS satellite (CHaracterising ExOPlanet Satellite) launched in 2019, is a precise photometric observatory that aims to characterize the mass and size distributions of exoplanets (ESA, 2019). The James Webb Telescope (JWST) launched in 2021, aims to observe at least 28 unique exoplanet targets, with 9 of them smaller than 2 Earth radii (Sharma, 2022). Additionally, the PLATO satellite, scheduled for 2026, will observe transits and characterize rocky extrasolar planets around yellow dwarf stars (ESA, n.d.). The upcoming Ariel telescope is scheduled to launch in 2028 aboard the Ariane 6-2 rocket to the L2 libration centre. Ariel's off-axis 1.1x0.7m Cassegrain telescope will observe approximately 1000 exoplanets using two infrared spectrometers: NIRSpec (NIR spectrometer) and AIRS (Ariel infrared spectrometer).

Furthermore, several other missions are already planned. For instance, HabEx (Habitable Exoplanet Observatory) (NASA, n.d.) is designed to detect atmospheric constituents that could potentially indicate biological activity, such as oxygen and ozone. HabEx is expected to launch in 2035. Another mission concept is the LUVOIR telescope (NASA, n.d.) (Large Ultraviolet Optical Infrared Surveyor), scheduled for a late 2030s launch, which aims to further enhance our exploration capabilities in the ultraviolet, optical, and infrared ranges.

2.2 Exoplanetary chemistry through experiments

In summary, observations set the requirements for experiments. Experimental exoplanetary chemistry then includes measurements of rate constants, thermodynamic properties of species, but also simulations of atmospheric chemistries unobserved on the Earth (such as hot Jupiters, ice giants, rocky planets around different stars…), or impacts, which constitute an important subject in this thesis.

The four main experimental approaches to studying impacts in the laboratory involve: (a) hypervelocity gun experiments, (b) shock tube experiments, (c) air plasma flows and (d) high power lasers. All these approaches have advantages and limitations, which are discussed below.

2.2.1 Hypervelocity gun experiments

Hypervelocity gun target experiments are widely used in impact physics (Libourel et al., 2019), but have certain limitations. The typical velocities achieved by these projectiles range from 3-7 km s^{-1} (Hibbert et al., 2017), which falls short of simulating meteor plasma during atmospheric entry, where meteoroids reach much higher velocities. The minimum velocity of a meteoroid, determined by Earth's gravity, is approximately 11.2 km s^{-1} (Ceplecha et al., 1998).

Moreover, meteor ablation initiates during atmospheric entry at altitudes around 120 ± 10 km, depending on the meteoroid's mechanical strength and composition (Adolfsson and Gustafson, 1994; Ceplecha et al., 1998), velocity, shape and other parameters. In hypervelocity gun experiments, the formation of plasma occurs only upon collision with the target. Projectiles used in these experiments are typically made of synthetic materials like steel or hard natural materials such as basalt or dunite. The composition of these materials does not accurately represent chondritic materials found in meteoroids, or the atmosphere. Chondritic materials cannot be used as projectiles due to their inability to withstand the compression forces generated by the gun (Libourel et al., 2019).

Overall, gun experiments remain valuable tools for studying various phenomena, including target experiments with impact-induced formation of biologically relevant materials (Blank et al., 2001; Furukawa et al., 2009; Martins et al., 2013). Nonetheless, experimental simulation of gas phase, aerosol or liquid impact chemistry or airglow plasma is not possible through this approach.

2.2.2 Shock tube experiments

Shock tube experiments play a crucial role in understanding fundamental impact plasma chemistry (Dremin, 1989; Roy et al., 2022). These experiments provide valuable insights into the survival potential, decomposition lifetime, and de novo synthesis of molecules in the context of cometary impact (Rubin et al., 2019) or asteroid impact events (Singh et al., 2022).

For instance, a recent study has employed piston-driven shock tube experiments to investigate the heating of an Ar and N_2 gas mixture (Jayaram et al., 2013). These experiments generated temperatures ranging from 9,100 to 12,300 K, along with reflected shock pressures of approximately 59 to 70 bar, over a duration of 2 to 4 milliseconds. As a result, shock tube experiments offer essential data for simulating impact plasmas generated in the gas phase, particularly in terms of their chemical implications.

2.2.3 Air plasma flows

An alternative approach to simulating impact plasmas involves subjecting meteorite samples to intense heat sources, such as high-enthalpy subsonic air plasma flows in a wind tunnel (Agrawal et al., 2018; Drouard et al., 2018; Helber et al., 2019; Loehle et al., 2022, 2017). These experiments serve the purpose of replicating the atmospheric entry of various objects, including spacecraft components, meteoroids, or space debris.

These simulations have been utilized for basic spectral line identification by analysing emission spectra from chondrites, achondrites, and iron meteorites (Drouard et al., 2018). However, there are limitations to these experiments. The simulated meteor plasmas generated in wind tunnels typically reach temperatures of up to 2,400 K (Loehle et al., 2017). In reality, meteor plasmas possess a more complex structure, featuring high-temperature regions that can exceed 4,400 – 20,000 K (Silber et al., 2018). Additionally, the high-enthalpy experiments involve treating the specimen material with plasma in large chambers that may not be fully vacuum sealed, chemically clean, or filled with various gas mixtures, thereby introducing further limitations and excluding the possibility to reliably study isolated chemical processes.

2.2.4 Laser experiments

An additional approach to simulating meteor plasmas involves the use of lasers. This technique offers versatility and allows for the experimental simulation of various phenomena, including supernova explosion shocks, gas giant interiors, explosions, plasma jets (Villagrán-Muniz et al., 2003), accretion processes, nuclear fusion, hypervelocity atmospheric entries, impacts and meteors (Ferus et al., 2017b; Ferusa et al., 2015; Rimmer et al., 2019), and lightning discharges (Borucki, 1985; Borucki et al., 1988; Borucki and McKay, 1987; Navarro-González et al., 2001a; Sobral et al., 2002, 2000; Villagrán-Muniz et al., 2003; Wooding, 1972).

Using lasers in these simulations presents several advantages, such as exclusion of chemical contamination from electrode materials (Borucki et al., 1988), potentially small gas volumes, a generally chemically clean and isolated system (Sobral et al., 2000), and the ability to apply lasers on mineral surfaces at the meso- to microscale, allowing experimentation on single phases (Sobral et al., 2000). The properties of laser-induced dielectric breakdown are characterized by parameters such as pulse duration, energy density, laser wavelength, photon fluency, the chemical nature of the irradiated material or gas density, and the chemical composition of the surrounding atmosphere (Babánková et al., 2006; McKay and Borucki, 1997; Saeidfirozeh et al., 2022; Villagrán-Muniz et al., 2003; Zakuskin et al., 2023). These adjustable parameters make lasers suitable for simulating various phenomena based on the desired properties.

The use of lasers for simulating impact events was initially proposed by (Rae and Hertzberg, 1964) and later experimentally explored by others (Hapke et al., 1975). The authors simulated impact evaporation processes, and subsequent studies used lasers to explore meteorites and meteors (Pirri, 1977). Laser-based experiments have also been suggested for simulating ball lightning and lightning discharges (Borucki, 1985; Borucki and McKay, 1987; Jebens et al., 1992; Wooding, 1972). Lasers have recently been used to study nitrogen oxide synthesis by impact plasma (Heays et al., 2022; Navarro-González et al., 2019), or lightning plasma (Navarro-González et al., 2001b).

The connection between laser and lightning physics was established by identifying similarities in electron density, temperature, energy dissipation, and chemical freeze-out temperature (Borucki, 1985; Borucki and McKay, 1987; Jebens et al., 1992). However, the hydrodynamic evolution of laser-induced dielectric breakdown leads to faster cooling compared to lightning (Navarro-González et al., 2001a; Sobral et al., 2002; Stark et al., 1996). High-power laser facilities like the Prague Asterix Laser System (PALS) can generate plasma fireballs with electron densities ranging from 1.5×10^{17} to 10^{20} cm^{-3} and temperatures decreasing from 10^5 K to 9,300 K after the pulse (Babánková et al., 2006; Šmíd et al., 2019). These conditions align with the findings related to lightning (Sobral et al., 2000).

Studies using lasers for the simulation of meteor and impact plasma include for instance the synthesis of silicon oligomers and simple hydrocarbons (Managadze et al., 2003), hydrogen cyanide and acetylene formation (McKay and Borucki, 1997; Scattergood et al., 1989), or origin of nitrates on early Mars (Navarro-

González et al., 2019). Subsequent studies successfully demonstrated the crucial role of impact plasma in the origin of canonical nucleobases (Ferus et al., 2017b, 2015, 2014, 2012; Ferusa et al., 2015), sugars (Civiš et al., 2016b) and amino acids (Civiš et al., 2004). Studies with this and other lasers also showed the transformation of simple molecules in early terrestrial planet environments (Civiš et al., 2008), such as hydrogen cyanide (Ferus et al., 2017a), acetylene (Civiš et al., 2016a), methane (Civiš et al., 2017), carbon monoxide (Civiš et al., 2008) and aromatic compounds (Petera et al., 2023).

Furthermore, laser-based experiments can be efficiently used to evaluate environmental changes triggered by large impacts. Impact events can chemically transform atmospheres or surfaces, produce new chemicals and aerosols, or enrich the surface of a meteoroid with heavy elements, supporting chemical catalysis (Ferus et al., 2021). This is especially relevant for early planets experiencing heavy bombardment (Ferus et al., 2021; Koeberl, 2006; Reimold and Gibson, 2006). An example of an apparatus with lasers for the studying of planetary chemistry is shown in Figure 1.

Figure 1: A laser-based experiment ELISE for studying planetary chemistry induced or affected by impacts built in our laboratory.

In summary, lasers provide a powerful tool for simulating meteor and impact plasmas, and plasma interaction with solids, liquids and gases, offering versatility, controllable parameters, and the ability to study a wide range of phenomena. While there are some differences between laser-induced plasmas and real meteor plasmas, lasers have proven valuable in understanding impact processes, synthesizing compounds, simulating space weathering, and studying asteroid deflection.

2.3 Impacts on exoplanets

Laser experiments play a crucial role in identifying markers of impacts and studying impact processes. For example, the impact of the comet Shoemaker-Levy 9 on Jupiter in 1994 resulted in the observation of various species such as S_2, CS_2, OCS, NH_3, HCN, H_2O, and CO (Zahnle et al., 1995). Recent studies have also tentatively detected PH_3 in the atmosphere of Venus, which could be attributed to atmospheric corrosion caused by a single giant impactor or a random increase in the impact flux (Bains et al., 2022, 2021; Omran et al., 2021; Schulze-Makuch, 2021; Truong and Lunine, 2021).

In the future, spectroscopic studies of exoplanets are expected to enable the detection of very large meteors and impacts in their atmospheres (Schneider, 2018). However, it has been speculated that even an impact event as significant as the Chicxulub event, which occurred 65 million years ago and likely wiped the dinosaurs off the planet, would be barely detectable from 10 light-years away (Paine, 2006). Regular meteors may be too faint to be observed with telescopes like ARIEL or JWST. Nevertheless, in nearby exoplanetary systems, occasional observations of large impact events, explosions, or collisions may be possible. For instance, a recent large impact event led to the creation of different twins in the Kepler-107 exoplanet system (Bonomo et al., 2019).

Models suggest that in young planetary systems, giant impacts dominate the oligarchic growth, late accretion, and early stages of planetary evolution within the first few hundred million years (Koeberl et al., 2005; De Niem et al., 2012; Quintana et al., 2016; Reimold and Gibson, 2006). This is supported by evidence from the Moon's cratering history and the presence of late veneer on Earth

(Brasser et al., 2016; Geiss and Rossi, 2013; Morbidelli et al., 2018). The history of impact mass delivery and size distribution remains unresolved, and it is unknown whether other planetary systems have experienced similar impact histories due to different predictions from planet formation models (Ferus et al., 2022b, 2021, 2020, 2017b; Ferusa et al., 2015; Morbidelli et al., 2018; Quintana et al., 2016).

Understanding impact history is important for questions of habitability, as the delivery of chemical compounds from outside a planet is crucial for the evolution of environments capable of supporting life. Impact plasmas play a role in the origin of life's building blocks, post-impact processes, and the generation of feedstock molecules for prebiotic synthesis through impact-induced atmospheric and surface chemistry (Todd and Öberg, 2020).

Experiments involving lasers simulating impact plasmas on the atmosphere, surface, or impactors have shown the synthesis of various species, such as C_2H_2, HCN, N_2O, HNCO, and $HCONH_2$ (Civiš et al., 2016a; Ferus et al., 2019, 2017a; Heays et al., 2022; Rimmer et al., 2019). These findings are significant for recognizing impact processes on young planets (Ferus et al., 2022a, 2021). However, it should be noted that recognizing impacts directly on early Earth-like planets can be challenging due to the complex interplay among geochemical, physical, and geological processes, requiring the elimination of other possible sources. An elevation in impact frequency may be inferred from the detection of unexplained imbalances in the mixing ratios of molecular species associated with impact chemistry or their temporal variations linked to formation and decomposition processes.

3 The environment of the early Earth

To the best of our knowledge, Earth is the only planet known to host life. Yet very little is known about its earliest history and its appearance at the time of the origin of life. Most of the geological record has been erased by tectonics, the only exception being ancient zircons, which in themselves are very rare. With the ever increasing amount of known rocky exoplanets, we have more and more opportunities to glimpse rocky planets of similar size and age around stars similar to our Sun. Observing and describing their properties could show us all the possible evolution paths the Earth could have taken and if it is really unique or rather average (Ferus et al., 2022a).

3.1 Emergence of life on Earth

The dating of the origin of life on Earth is uncertain. Most common lines of evidence for early life include microfossils, carbon isotopic ratios, and stromatolites. In 2017, (Dodd et al., 2017) presented putative evidence for the discovery of fossilized microorganisms from the Nuvvuagittuq belt in Quebec, Canada, which are at least 3.770 Gyr old and possibly even 4.280 Gyr old, which would be the oldest known evidence of life on Earth to-date. These microfossils were found in ferruginous rocks, interpreted as seafloor-hydrothermal vent-related precipitates. The claim is based on the observations of micrometer-scale hematite tubes, which are similar in appearance to modern microorganisms and ancient microfossils, while at the same time the reported carbon isotopic ratios from this finding are consistent with biological activity at that age.

Next, carbon isotopic ratios have been used as evidence of life. Organisms typically fractionate carbon isotopes, because ^{12}C fixation is typically kinetically favored relative to ^{13}C (Catling and Kasting, 2017). The oldest such evidence to date is the discovery of a graphite inclusion in a single grain of zirconium silicate from Jack Hills, Australia, dated at 4.10 ± 0.1 Gyr, with a biogenic $\delta^{13}C$ value -24 ± 5 ‰ (Bell et al., 2015).

A different, younger, of evidence of early life are stromatolites, which are laminated sedimentary structures formed as a result of the existence of microbes. The oldest stromatolites were found in the Dresser Formation of the Warrawoona Group in northwestern Australia (Buick et al., 1995), possibly as old as 3.500 Gyr. Many other stromatolites of younger age were described as well (Allwood et al., 2009, 2006; Hofmann, 2000; Lepot et al., 2008). As the earliest findings are often disputed (Buick et al., 1995; Grotzinger and Rothman, 1996; Grotzinger and Knoll, 1999; Lowe, 1994; McLoughlin et al., 2008), their discovery should not be considered as an absolute proof but rather as consistent with the existence of life at that time (Wacey, 2009).

It is at the critical age around 4 Gya, where we know very little about the early Earth. In the following sections, we focus on what is and is not known about this era of Earth's development and what are the preceding and consequent processes that shaped our planetary environment.

3.2 The formation of rocky planets

At the age of the origin of life, the Earth was at most 500 Myr old, or rather, young. Young planets can be expected around young stars, but determining stellar ages is inherently difficult. There exists a variety of established methods, such as measuring the lithium depletion boundary, kinematics of young groups of stars, placing stars in Hertzsprung-Russell diagrams, pulsations and seismology, surface gravity measurement, rotation and activity or lithium abundance. Each of these methods has its uses as well as drawbacks, but generally, determining stellar ages below ~20 Myr has much more uncertainties due to the possibility of age spreads and lack of reliable absolute ages. Each method is also suited for a different star mass- and age ranges in the HR diagram, as summarized in Table 2 in (Soderblom et al., 2014). Some methods for the estimation of the age of young stars therefore exist and it is around these stars that young planets can be expected.

A star is formed from the collapse of an interstellar cloud. The remaining material after the formation of the star is spun out and flattened into a protoplanetary disk. Matter in the plane of rotation is affected by a centrifugal force and gas pressure, which act in opposite to gravitational pull of the central star. Such disks are called protoplanetary disks and are the cornerstone of the formation of planets. A famous disk has been observed around the star HL Tauri by ALMA ((NRAO/ESO/NAOJ et al., 2016). The published image (see Figure 2) shows a series of lighter and darker concentric rings. The star is a T-Tauri star (pre-main sequence variable star with age <10 Myr) and planetary formation should be taking place. The dark rings are therefore often explained as orbital trajectories cleared out by the forming planets.

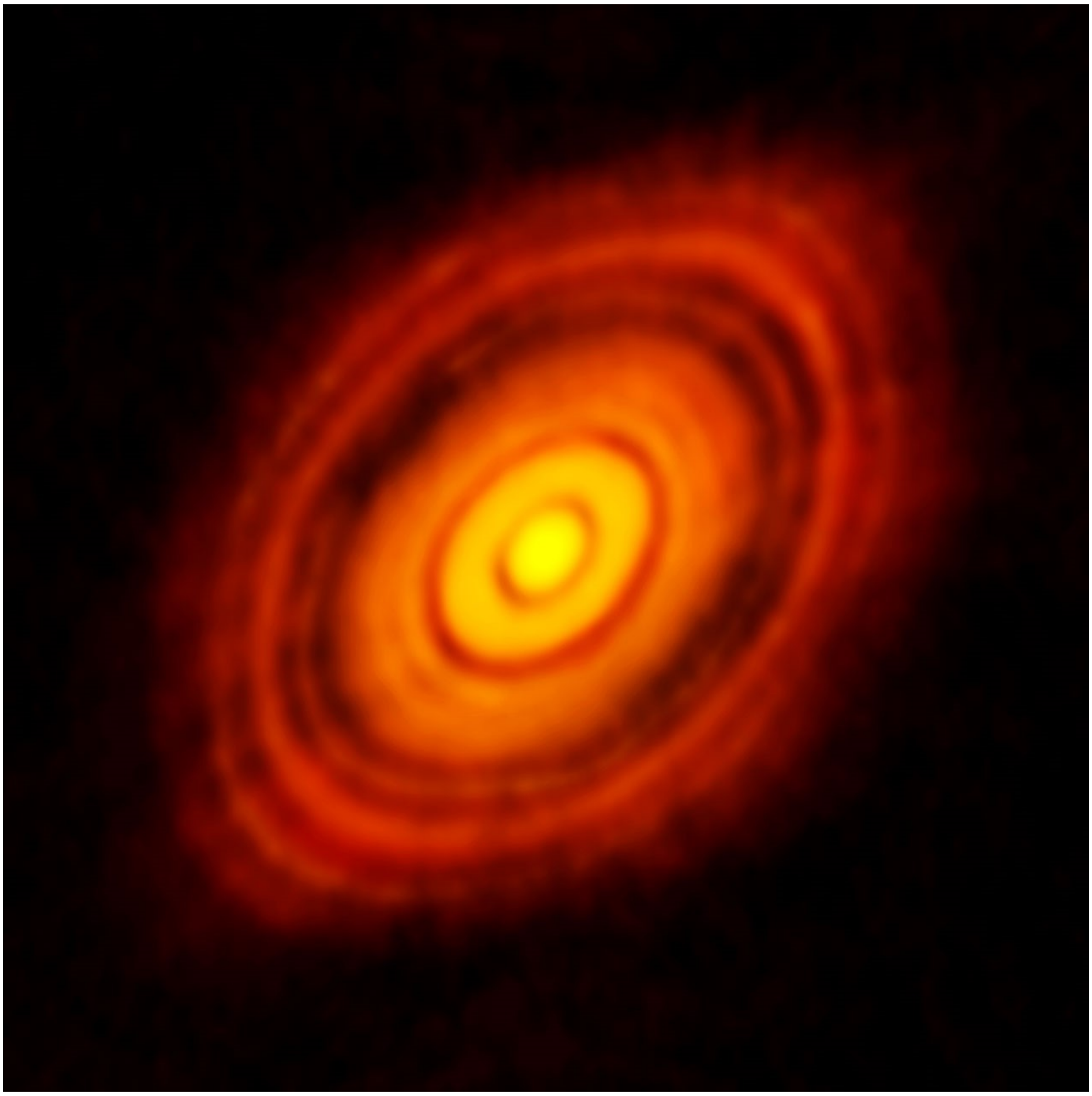

Figure 2: The protoplanetary disk observed around the HL Tauri star. The black rings are thought to be trajectories cleared out by forming planets. Image credit: ALMA (ESO/NAOJ/NRAO). For full reference see ((NRAO/ESO/NAOJ et al., 2016).

Planets form in the protoplanetary disk by collapse and subsequent accretion of solid material from the disk. One of the theories for the formation of planets was proposed by (Safronov, 1972). In his core accretion model, the orbiting particles first form planetesimals (0.1 – 10 km diameter objects). In some regions, the growth may trigger runway accretion leading to planetary embryos or protoplanets (10^3 - 10^4 km diameter) and eventually to planets. If Jupiter and Saturn, for example, formed through this process, then after they grew 10 - 15 Earth masses solid cores, their gravity was sufficient to capture hydrogen. In the original core accretion model, dust, gas and solid particles would be attracted to the disk midplane, where they would collide and form larger and larger particles, followed by four stages of growth: formation of planetesimals, runaway growth, oligarchic growth and late state accretion (Izidoro and Raymond, 2018).

A competing theory is that of pebble accretion, where centimeter-sized pebbles rapidly collapse to make planetary embryos while gas is still in the disk (Wahlberg Jansson and Johansen, 2014). A recent paper by (Lyra et al., 2023) outlines an analytical theory for the growth of planetesimals by polydisperse accretion. That theory predicts that pebble accretion is a viable theory over a wide parameter space and alleviates the need for mutual planetesimal collisions as a major contributor to planetary growth, which has been a common point of criticism in the core accretion model.

Some models favor a third mechanism, the streaming instability, as the main mechanism of the formation of 100 km-sized planetesimals. In that scenario, the planetesimals then continue their growth to Mars-sized planetary embryos by a combination of planetesimal and pebble accretion (Chambers, 2023). From that size onwards, models tend to be specific and include the architecture of the planetary systems (Izidoro and Raymond, 2018). Notably, in all these models, terrestrial planets form as gas-free.

It is worth noting that there exist other approaches, such as the Hayashi approach to accretion, where terrestrial planets grow in presence of dust and gas (Hayashi et al., 1979), or disk instability, where Jupiter forms directly from the gravitational collapse of the disk (Helled et al., 2014).

The evolution of the architecture of planetary systems can trigger further effects, such as migration of planets. For example, according to the Grand Tack model (O'Brien et al., 2014), Jupiter may have migrated inwards and stunted the growth of Mars, etc. This would have influenced for example water delivery to Earth (Ogihara et al., 2023). Therefore, there is enough space for uncertainty such that it is impossible to definitively describe the formation of the Solar system and the formation of the Earth, let alone exoplanetary systems. For example, it has been previously assumed that the formation of rocky planets ends with a series of late-stage giant impacts, which would produce warm dusty debris. This debris was not observed on exoplanets so far, implying that the debris is removed (e.g., by a tenuous gas disk, or by solar wind) or that rocky planets form very early and emerge fully formed from the nebular phase, which would challenge the view of the current accretion models (Najita and Kenyon, 2023). On the other hand, (Kessler and Alibert, 2023) argue that late-stage giant impacts and critical for the formation of giant planets, at least in models which combine core and pebble accretion approaches.

3.3 The origin of Earth's atmosphere

Even though we do not precisely know how, the Earth has formed and must have obtained an atmosphere. More generally, the Earth must have obtained volatiles - compounds which are liquid or gaseous on the surface or in the atmosphere.

3.3.1 Accretion and the primary atmosphere

First and foremost, volatiles can be co-accreted with the solids during the formation of the planet. One of the possible mechanisms is the equilibrium condensation model (Read, 1985). In this model, the protoplanetary disk has the same composition and mass as the Sun and undergoes a temperature evolution. The disk is first heated because it is very dense and radiation from the protostar can't escape to outer space, friction generates heat and gravitational energy converted to kinetic energy during transport of material adds to the mix. After reaching a peak temperature, the disk begins to cool. Material condenses at distances from the protostar where it meets its boiling point temperature. The materials condense approximately in order: (i) highly refractory metals and oxides, (ii) Ni-Fe metal, (iii) silicates, (iv) sulfides, (v) hydrated minerals and (vi) ices (Catling and Kasting, 2017; Johansen et al., 2023a, 2023b). Notably, H_2 and He are considered as always gaseous due to their low vaporization temperatures. Details of the model are disputed nowadays, but the main explanation of why rocky planets are closer to the Sun and gas giants are farther away holds. Modern models of the origin of the Solar system's architecture give varied and more detailed predictions on the composition of bodies. For example, Jupiter's and Saturn's rapid gas accretion scatters nearby planetesimals, some of which are thrown into the inner Solar system. This mechanism would explain the presence of carbonaceous asteroids (which are rich in volatiles, e.g., have 5 - 20 % of water

(Kerridge, 1985)) in the outer main asteroid belt. Similarly, many of these scattered bodies would collide with rocky planets and bring in volatiles. The origin of water on Earth would therefore be explained as a simple byproduct of giant planet growth (Raymond and Izidoro, 2017). A similar mechanism could be expected in exoplanetary systems and rocky exoplanets would have to have water as well.

The nature of the scattered accreting bodies is unknown, but some information about the early Solar system can be obtained from meteorites. Generally, chondritic meteorites are meteorites with nearly solar-like composition, excluding gas-forming elements (Catling and Kasting, 2017). In contrast, achondrites are meteorites originating from already differentiated bodies. Primitive chondrites are a third division of meteorites, which formed from bodies heated to the point of melting but did not experience large-scale differentiation (Weisberg et al., 2021).

In any case, meteorites must have delivered both refractory and volatile elements to the Earth and directly contributed to the formation of the primary atmosphere. Thermal outgassing of CI and CM carbonaceous chondrites produces mostly H_2O-rich atmospheres. Ordinary H, L and LL chondrites and enstatite chondrites produce H_2-rich atmospheres with CO and H_2O as second and third most abundant gases. Low iron enstatite chondrites give rise to CO-rich atmospheres with significant amounts of H_2, CO_2 and H_2O. Atmospheres outgassed from CV chondrites give mostly CO_2-rich atmospheres with H_2O as the second most abundant compound. In contrast, (Newcombe et al., 2023) show that H_2O content in achondrites is very low (≤ 2 μg g^{-1}) from both the inner and outer parts of the early Solar System. Such low values imply that differentiated planetesimals must have efficiently degassed before or during melting. This suggests that most of the delivered water must have been delivered to Earth in unmelted material, such as chondrites. Simulations by (Schaefer and Fegley, 2010) then predict that atmospheres of Earth and Mars formed during accretion were H_2-rich.

3.3.2 Loss of primary atmospheres

Primary atmospheres of planets formed during accretion were lost to space, likely even before the accretion was completed. It is therefore suitable to think about primary atmospheres of planetary embryos rather than planets. For instance, planetary embryos larger than Mars would be able to capture some nebula gas rich in H_2 and He (Inaba and Ikoma, 2003). Importantly, the model by Inaba and Ikoma gives a formula for the calculation of the accretion of smaller particles. Due to gas drag from the atmosphere, an Earth-size object, and a 100 m planetesimal would have 10 times enhanced collisional rate relative to the collisional rate calculated from crossing of direct trajectories, making accretion much more efficient. In the case of terrestrial planets, we do not nowadays observe H_2 and He dominated atmospheres. Even if the planets started with a solar-composition atmospheres and if the helium and hydrogen escaped to space, the result would be ~60% CO_2, ~20% Ne and ~10% N_2, which, obviously, is not the case (Catling and Kasting, 2017).

For temperate planets, such as the early Earth, impact erosion during late-stage accretion is considered as the main mass loss mechanism. If the contribution of pebble accretion to the formation of planets is higher than currently thought, other processes may have significant (but likely not dominant) influence, such as photoevaporation via X-ray and UV ionization or photoionization and photodissociation of H_2 (Howe et al., 2020).

3.3.3 Evidence from noble gases

(Catling and Kasting, 2017) in their book show that Earth, Venus and Mars are depleted in noble gases relative to solar composition. Information embedded in the noble gas ratios points to the existence of atmospheric escape, but also gives insight into the evolution of planets. The noble gas depletion relative to solar values is different for each planet, but the patterns across gases are the same. Since noble gases are the most atmophilic volatile elements due to their little reactivity, they must have been part of the primary atmosphere on the planetary embryo. Their lack implies that the Earth either did not obtain those gases from the solar nebula or must have lost the primary atmosphere.

The source of the noble gases on Earth has not been definitively resolved. There are three possible sources of noble gases: implantation by solar wind, accretion from the solar nebula gas (already disputed above) and delivery by chondrites and comets (Péron et al., 2018). On Earth, $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios are higher in the mantle than in the atmosphere, i.e., the mantle is richer in the lighter neon isotopes. It has been shown that lunar soils reflect the composition of the solar wind and also exhibit $^{20}Ne/^{22}Ne$ ratios very close to that of ocean island basalts, which are inferred to be close to primitive mantle. This, together with mantle transport effects, points to early solar wind as the source of light volatiles in the mantle. The gases would have been implanted into the precursor grains from which the Earth accreted during the first few Myr after the formation of the Solar system. The atmospheric $^{20}Ne/^{22}Ne$ ratio, which is lower than in the mantle, can then be explained as a mix of mantle-degassed neon and delivery from chondritic gases, again disfavoring the accretion of an atmosphere from the solar nebula and supporting the idea of the accretion of volatiles from solids. In line with this, (Zhang et al., 2023) predict a low $^{20}Ne/^{22}Ne$ ratio ~ 9.7 in Archean atmospheric samples.

Next, Ar isotopic evolution is primarily sensitive to mantle processing rate history, hence being unsuitable for tracking continental crust growth. On the other hand, Ar isotopic composition can be used to track mantle processing rates. The model presented by (Zhang et al., 2023) suggests that ^{36}Ar was directly delivered by chondritic material and not outgassed from the mantle.

When the noble gas isotopic ratios are examined for Earth, Mars and Venus, even more information can be deduced. For example, argon and neon are more abundant on Venus than Earth, respectively (Owen and Bar-Nun, 1995). This could be explained by Venus colliding with a large body rich in Ar and Ne early on. Another explanation can be that Venus did not have an ocean (or that it was removed by a runaway greenhouse effect), the presence of which enhances the loss of an atmosphere during giant impacts (as explained below). On Earth, which does have an ocean, the primary atmosphere would be removed, whereas on Venus, remnants of the primary atmosphere would have survived (Genda and Abe, 2005).

On the other hand, atmospheric argon on Venus is depleted in radiogenic ^{40}Ar relative to Earth. This argon isotope is produced from the decay of ^{40}K with a half-life 1.25 Gyr. If volcanic outgassing from the interior of a planet is efficient, the argon should enter the atmosphere eventually. The difference between Earth and Venus suggests that volcanism on Venus is less significant, a likely result of the non-existence of plate tectonics (Catling and Kasting, 2017).

Further, noble gases are generally less depleted with increasing atomic mass, which is explained by the idea that lighter noble gases escaped more easily than heavier gases. Even heavy/light stable isotopes ratios of these elements are higher than their solar values. An exception to this is terrestrial xenon. Xenon has 9 stable isotopes, some of which are products of extinct radionuclides. Xenon is heavier than krypton, and if it was captured as part of the primary atmosphere from the nebula and then subjected to escape, krypton should be more depleted in the Earth's atmosphere than xenon. The contrary is true, however, which is known as the missing xenon paradox (Ozima and Podosek, 2001; Pepin, 1991; Tolstikhin and O'Nions, 1994). One proposed mechanism for the loss of xenon the drag of xenon ions (xenon is relatively easily ionized) by hydrogen escaping to space, implying at the same time that hydrogen rapidly escaped and the Earth was progressively oxidized (Ostrander et al., 2021). An alternative explanation is that the xenon actually fractionated to the core in the form of xenon iron oxides (Peng et al., 2020). Xenon would not be so inert after all.

3.3.4 Early carbon and nitrogen

As we have shown, the Earth must have accreted its present atmosphere from solids. For example, carbon (Catling and Kasting, 2017) and nitrogen (Catling and Kasting, 2017; Zhang et al., 2023) were largely delivered in organic ices and macromolecular organic material (refractory or carbonaceous dust). The C/N ratio across the interstellar medium, comets, chondritic meteorites and terrestrial planet shows an increase between volatile-rich pristine bodies and larger volatile-depleted objects subjected to thermal or accretional metamorphism. As a result, the C/N ratios in material accreted to terrestrial planets should be higher than in carbonaceous chondrites or comets. Indeed, the bulk silicate Earth has a C/N ratio of 49.0 ± 9.3, whereas the nebular ratios in the disk are ~1 - 12. A likely explanation for that is that the Earth accreted thermally processed objects and then experienced a large-scale atmospheric loss (Li et al., 2023). A model by (Johansen et al., 2023c) shows that in the case of pebble accretion, nitrogen partitions relatively evenly between the core and the atmosphere due to its low solubility in the magma. The model thus favors nitrogen delivery to Earth by pebble snow. As a consequence for terrestrial planets in general, they should be readily supplied by both C and N, but the ratios will strongly depend on the accretion history and evolution.

3.3.5 Giant impacts, Moon formation and the post-impact atmosphere

The elemental compositions of the Moon and Earth's mantle are quite similar, both in terms of macroscopic elements, such as Si and Mg (Wänke, 1999) and isotopic composition, such as ^{16}O, ^{17}O and ^{18}O (Herwartz et al., 2014). This suggests that both the Earth and Moon share a common origin. The most widely accepted explanation for this is that the formation of the Moon happened by a giant impact of a small planetesimal called Theia (Hartmann and Davis, 1975; Jöns, 1985). This impact likely happened around 4.47 Gyr ago (Bottke et al., 2015), when the Earth was already mostly differentiated (Kleine and Rudge, 2011). The impact may have melted the surface of the whole Earth and launched significant amounts of impact ejecta into orbit. Some calculations even argue that the temperature and pressure were so high that they exceeded the mantle critical point and the surface magma ocean-atmosphere boundary was not defined for a time (Caracas and Stewart, 2023). Calculations have shown that 2,000 – 2,700 km diameter impactor would be required to completely melt the Earth's surface, while >700 km impactor would be required to evaporate surface oceans (Citron and Stewart, 2022). Theia is thought to have been big enough to have melted the surface. The Moon then accreted from the melted and ejected material. Immediately after the moon-forming impact, the atmosphere would consist of melted and vaporized rock at ~2,500 K. This initial stage would last $\sim 10^3$ years. Outgassing and escape during this period are poorly constrained, but some proposals exist. The mantle redox state has a significant effect on both these processes. Reduced/thin atmospheres and reduced mantles rich in H_2 would emit more radiation to space as compared to oxidized, H_2O and CO_2-rich atmospheres. H_2 outgassing rates after the impact would be ten times larger than diffusion limited escape and the total mass loss of H_2 outgassed from the atmosphere is a few tens of Myr (Katyal et al., 2020). For another ~2 Myr after the impact, species would condense out of the atmosphere, and partly dissolve in the melted surface. Since all water is evaporated, the atmosphere would be opaque and slowly radiatively cools to space. Eventually, the surface starts to solidify. Then, for up to $\sim 10^8$ yr after impact, a solid surface is formed, the ocean condenses, and CO_2 is gradually incorporated into the crust.

From then onwards, the nature of the Hadean climate is unknown, but would have been mostly influenced by the content of greenhouse gases (Heays et al., 2022; Sleep and Zahnle, 2001; Walker, 1985). Notably, during such impact, the ocean would be vaporized rather explosively. Little water would actually escape, but the shock evaporation would push away any primary atmosphere (Abe, 2011). The atmosphere which then formed on Earth originated mainly from degassing of the mantle.

It is worth noting, though, that (Tucker and Mukhopadhyay, 2014) suggest that the Earth experienced at least two magma ocean outgassing episodes, but both happened before the Moon-forming impact and that the Moon-forming impact did not induce a complete surface melting.

One notable period in the Earth's impact record is the Late Heavy Bombardment. Cratering on the Moon and models of the evolution of the Solar system led to the proposal of a period of intense bombardment of the Earth by asteroids from the Main belt ejected by gravitational resonance between Jupiter and Saturn (Gomes et al., 2005; Nesvorný and Morbidelli, 2012; Tsiganis et al., 2005). Nowadays, the existence of this period is still debated (Bottke and Norman, 2017). In any case, the craters on the Moon prove that the Earth was subjected to heavy bombardment during its history, be it gradual or concentrated. Although incomparable to the Moon-forming impact, the impacts would also have had a strong effect on the atmospheric evolution and could have vaporized the ocean and sterilized any possible life (Sleep and Zahnle, 1998), partially melt the crust (Reimink et al., 2023), or at least vaporize the several hundred meters of the ocean and induce significant warming (Lowe and Byerly, 2015; Segura et al., 2013).

One important aspect is discussed in (Catling and Kasting, 2017), and that is that the composition of the surface also influences the post-impact evolution. In the case of smaller impacts, if the impactor hits a reduced crust, the impact ejecta would also be reduced. For example, impacts on yet undifferentiated planets would produce mostly reduced gases, such as CH_4, NH_3 and H_2. A similar situation would happen after the Moon-forming impact, when the iron from Theia would be melted, but not yet differentiated to the Earth's core. Late veneer could also bring enough reducing power in the form of iron to produce reduced atmospheres, which would progressively oxidize as hydrogen would escape to space and iron would sink into the core (Zahnle et al., 2020). On the other hand, impacts onto already differentiated bodies would produce mostly neutral and oxidized gases, such as CO_2, H_2O, N_2, and CO. The redox state of the mantle would therefore determine the nature of the forming atmosphere.

3.3.6 The evolution of the mantle and mantle outgassing

According to (Stevenson, 1983), the Earth formed during 10^7 - 10^8 years through collisions with increasingly larger bodies. During this relatively short period, the mantle was melted by the impacts and the Earth differentiated even during its accretion. Since the iron sank to the core, the mantle became more oxidized. Even today, some Fe^{3+} iron can be found in the mantle, as opposed to the core, where iron is mostly neutral. (Trail et al., 2011) show that ancient magmas from ~4.4 Gya exhibit oxygen fugacities, f_{O_2}, consistent with oxidation state defined by the fayallite-magnetite-quartz (FMQ) buffer and hence similar to present-day oxidized conditions. From this, they imply that the mantle was oxidized very quickly, and any forming atmosphere would be either weakly reduced or oxidized (containing CO_2, H_2O, N_2, and SO_2 w/ H_2), but likely not reduced (CH_4, NH_3, H_2S). Notably, though, (Yang et al., 2014) propose that the atmosphere may have been oxidized more slowly. According to that paper, the Hadean crust was probably very weak, the continental crust was much more reduced than in the post-Hadean times and progressively oxidized until ~3.6 Gya. In such a case, the atmosphere would have been reduced as well.

Nowadays, the mantle is relatively oxidized, mostly with f_{O_2} corresponding to the FMQ buffer. Calculations by (Maurice et al., 2023) show that a possible magma ocean after a giant impact would last ≤1.5 Myr and the magma ocean during this time evolves from reduced to highly oxidized, releasing more and more oxidized gases, such as CO_2 and H_2O. The origin of this and the evolution of the oxidation state is still debated.

Thermal evolution models of the Earth's past are often constructed using modern outgassing rates, which are modified or constrained accordingly. For this reason, modern outgassing rates need to be understood first. Major outgassed species, such as CO_2, SO_2, H_2S, and N_2 are outgassed nowadays from both subaerial and submarine outgassing. Outgassing rates of reduced species, such as CH_4, can be then estimated from thermodynamic equilibrium of magmas in the upper mantle. Supposing the estimates of outgassing rates of all those species from all the various sources are known (which they are, but are not relevant to this text), differences between past rates and modern rates can be discussed. Overall, geothermal heat flow, volcanism and plate tectonics have changed from the past, but a general agreement on how has not been reached in the scientific community. One point which is agreed upon in that the Earth's interior was hotter in the past, e.g., because of higher radiogenic heat production (Pastorek et al., 2020) or leftover heat from accretion. (Davies, 1980) estimated past heat flow 2 - 5 times higher 3.0 Gya and 4 - 8 times higher at 3.5 Gya. (Sleep and Zahnle, 2001) estimated 2 - 3 times higher surface heat flux for the early Earth compared to modern surface with significant uncertainty. It is fair to say that there exists some evidence for low surface heat flow in the past (Hopkins et al., 2008). This evidence comes from Jack Hills zircons, which probably sat above a subduction zone, where the crust would be thicker and the surface heat flux correspondingly lower. Nevertheless, this evidence could also mean that models of plate tectonics in the past are incorrect (Korenaga, 2008b, 2008a, 2007, 2006). Furthermore, the prevalence of komatiites in Archean greenstone belts (Herzberg et al., 2010) suggests that different types of rocks existed in the past. This fact has also been used to define the Archean-Proterozoic boundary (Windley, 1984). Since komatiites are ultramafic rocks, this also suggests that the outgassing fluxes of H_2 and CH_4 may have been higher. In summary, the debate on the redox state of the Hadean and Archean atmosphere has not been settled and there are indications that both, it was similar to the modern state, and more reduced than today.

3.3.7 The prebiotic atmosphere

The only possible approach to discussing the composition of the prebiotic atmosphere is to construct an atmospheric chemistry model. A logical approach to this is to assume an atmospheric composition based on available estimates and then test the sensitivity of the model to changes in those parameters.

For example, the most abundant molecule in today's atmosphere is N_2 with a mixing ratio ~0.78, and this amount constitutes about one fourth of Earth's total hydrogen. About 0.4 present atmospheric level of nitrogen (PAN) is the crust and >1.4 PAN is in the mantle (Catling and Kasting, 2017), probably emplaced as early as in the Hadean (Wordsworth, 2016). Evidence from $N_2/^{36}Ar$ ratios in ancient fluid inclusions (Marty et al., 2013), raindrop imprints (Som et al., 2012), and bubbles in lava flows (Som et al., 2016) suggests that the N_2 partial pressure may have been lower in the past. Since N_2 is relatively unreactive in Earth's atmospheric conditions, however, effects on the atmospheric chemistry should be small. Some noteworthy effects could include altered shortwave radiation surface fluxes due to Rayleigh scattering of the incoming radiation by nitrogen or altered three-body reaction fluxes where nitrogen serves as a third body which can remove excess energy.

Another important gas in the atmosphere is CO_2. It is a greenhouse gas and it is likely that higher concentrations were needed to compensate for the lower luminosity of the young Sun, although many other theories which attempted to explain the faint young Sun paradox exist (Goldblatt and Zahnle, 2011; Heays et al., 2022; Rosing et al., 2010). The general approach in modelling and discussing the composition of the atmosphere is therefore to assume a given level, e.g., 300 ppm as the preindustrial atmospheric level (PAL), and then explore the sensitivity to changes in this value in a planetary atmospheric model.

Further, balancing outgassing of H_2 with hydrogen escape rate (diffusion limited escape) for a weakly reduced atmosphere gives about 1×10^{-4} steady state mixing ratio of H_2 for the early Earth (Catling and Kasting, 2017). This number can be used to estimate the amount of some other species in the Earth's atmosphere before the emergence of life.

Aside from the major atmospheric constituents, there existed trace components, of which O_2 is possibly very important for both the redox and the emergence of life. Oxygen is produced in the atmosphere by several processes, one of which is the photolysis of H_2O (BRINKMANN RT, 1969). Oxygen can also be produced from photodissociation of CO_2. This would imply that photochemistry would produce more O_2 the more CO_2 and H_2O would be present. This O_2 would react with outgassed H_2 at lower altitudes to produce water again. The steady state of oxygen would therefore be most influenced by the amount of CO_2 and H_2.

With regards to CO_2, (Catling and Kasting, 2017) constructed an atmospheric model where they predict that the O_2 volume mixing ratio would be about 10^{-5} – 10^{-3} at 100 km altitude if the 1× - 1000× the preindustrial atmospheric level of CO_2 is used. On the other hand, even in the highest CO_2 content case 1000 PAL, surface mixing ratios would be $<10^{-9}$.

Comparatively, also explore the effect of various H_2 outgassing fluxes at a constant CO_2 surface mixing ratio 0.2. Their model shows that although surface O_2 concentrations are affected by this, at 60 km the mixing ratio levels of at around 10^{-4} for all explored cases.

The presence of molecular oxygen together with a reduced partner in an atmosphere is considered a potential biosignature. In some cases, O_2 may not be detectable in (exo)planetary atmospheres (e.g., at mid-IR wavelengths) and O_3 has been suggested as a possible proxy (Kozakis et al., 2022). As it turns out, the UV radiation from the host star has a significant effect on the amounts of O_3 on a given planet, so using ozone as a proxy for O_2 is only possible with good constraint on the incident UV flux.

Similar models that deal with the nature of the early prebiotic atmosphere are many and the one presented here is just a drop in the ocean. Other models include the works of (Airapetian et al., 2016; Canuto et al., 1982; Hu et al., 2013, 2012; Hu and Seager, 2014; Kasting, 2014; Segura et al., 2007; Trainer, 2013; Yung and McElroy, 1979), to name just a few.

(Eistrup, 2023) provides a review on the state of modelling of planetary evolution from protoplanetary disks to exoplanetary atmospheres. The review discusses differences between simpler "iceline" chemistry models and rigorous approaches.

Another important feature of early rocky planetary atmospheres are hazes. Hazes are common in known planetary atmospheres with significant consequences for atmospheric opacity (Arney et al., 2016, 2017). They likely form from photochemical reaction of methane with the surrounding atmosphere and take on the form of a fractal organic haze. High UV fluxes and presence of oxygen radicals destroy the haze precursors and, on such planets, hazes do not form. The hazes influence surface chemistry by shielding the surface from UV radiation and surface cooling. Natural waters on the prebiotic Earth are likely niches for the origin of life, on which UV transmission and atmospheric opacity would have a strong effect. For example, natural freshwaters would be largely transparent to UV radiation, while high-salinity waters would be opaque to ≤220 nm radiation. On the contrary, ferrous waters would be shielded. Since prebiotic chemistry can be both hindered and enhanced by UV radiation, discussion on this topic is potentially important and atmospheric opacity is a necessary part (Ranjan et al., 2022) of any relevant discussion.

Aside from hazes, another phenomenon which would alter the surface flux of radiation and shield the surface would be clouds (Herbort et al., 2022). On rocky planets with higher temperatures (~400 - ~1,000 K), the most important stable condensates are KCl[s], NaCl[s], FeS[s], FeO[s], Fe_2O_3[s], FeS_2[s], and Fe_3O_4[s]. On colder planets with $T \lesssim 400$ K, thermally stable condensates are H_2O[l,s], C[s], NH_3[s], NH_4Cl[s], and NH_4SH[s]. For even colder atmospheres with temperatures $\lesssim 150$ K, even CO_2[s], CH_4[s], NH_3[s], and H_2S[s] become stable.

Selected molecular species then each have amounts of work done on their possible origin, stability, and destruction on the early Earth and in exoplanetary atmospheres. For example, the detection of SO_2 in the atmosphere of WASP-39b has been considered a first confirmation of photochemistry on an exoplanet (Tsai et al., 2023). Short wave photochemistry may have also contributed to the production of HCN on the early Earth (Pearce et al., 2022), but would not be the only source (Chyba and Sagan, 1992; Todd and Öberg, 2020). Volcanic activity was likely higher on the early Earth. In mixtures with low CO_2 content, i.e., in mixtures at $T > 1400$ °C due to thermal decomposition of H_2O and CO_2, magmatic outgassing produces reactive trace species such as NO, OH, Cl, Br and I. Photochemistry also likely produced polycyclic aromatic hydrocarbons on both Earth and Mars (Kopacz et al., 2023).

3.3.8 The Archean atmosphere

The end of Hadean the beginning of Archean eons is defined at 4.0 Gya. The Earth during the Archean probably witnessed the origin of life, which influenced the composition of the Earth’s atmosphere once it became a worldwide phenomenon. The Archean eon (4.0 Gya to 2.5 Gya) represents a third of Earth’s history and yet very little is known about the atmosphere. Some information can be deduced from the combination of geological proxies in combination with models (Catling and Zahnle, 2020). This approach implies surface O_2 levels $<10^{-6}$ times the present atmospheric level, N_2 levels similar to today or lower, CO_2 amounts ~10 – 2,500 times the modern amounts and CH_4 levels 10^2 - 10^4 times the present atmospheric level. These concentrations would have been enough to counter the fainter Sun and long-term climate moderation, but the carbon cycle would produce surface temperatures 0 – 40°C. In this model, the isotopic mass fractionation of xenon is best explained by drag of xenon ions by hydrogen escaping to space, implying at the same time that hydrogen rapidly escaped and the Earth was progressively oxidized (Ostrander et al., 2021). As with all the text above, we have indications and indirect evidence about the conditions on the early Earth during and after its formation, but definitive information is, unfortunately, impossible to obtain.

4 List of attached publications

1. Civiš, Svatopluk; Ferus, Martin; Knížek, Antonín; Carbon Dioxide and the Effects on Climate, 2019, Springer Nature, Cham, Switzerland, ISBN: 978-3-030-24031-8
2. Knížek, Antonín; Kubelík, Petr; Bouša, Milan et al.; ACS Earth and Space Chemistry, 4, 1001-1009, 2020
3. Civiš, Svalopluk; Knížek, Antonín; ACS Earth Space Chem., 5, 1172-1179, 2021
4. Rimmer, Paul B.; Ferus, Martin; Waldmann, Ingo P.; The Astrophysical journal, 888, (21), 12pp, 2020
5. Ferus, Martin; Rimmer, Paul B.; Cassone, Giuseppe; Science Advances, under review
6. Petera, Lukáš; Knížek, Antonín; Laitl, Vojtěch et al.; The Astrophysical Journal, 945, (149), 10pp, 2023
7. Knížek, Antonín; Petera, Lukáš; Laitl, Vojtěch; Monthly Notices of the Royal Astronomical Society, under review

5 The Chemistry of CO_2 and TiO_2: From breathing Minerals to life on Mars (Publication I)

The first publication of this thesis is a book which summarizes research on the chemistry of CO_2 and its photocatalytic reduction of CO_2 on mineral surfaces performed in our laboratory and with special emphasis on planetary atmospheres.

The first chapter introduces the properties and uses of CO_2 as well as its effect on climate. It also discusses its potential uses and its connections to energy storage.

The second chapter summarizes research on the surface interactions of CO_2 and TiO_2. At room temperature, CO_2 spontaneously adsorbs on various lattice defects on the surface of TiO_2 and other minerals and clays (montmorillonite, basalt, siderite, calcite, etc.). The CO_2 forms CO_3^{2-} anions adsorbed on the surface. Then, due to its symmetry, the CO_3^{2-} anion can rotate. After desorption, the originally lattice oxygen may in this way become part of the desorbed CO_2. If any of the oxygen atoms are isotopically different, then isotopic exchange between the surface and the gas occurs. This process has a very low barrier and spontaneously occurs at room temperature. Tested minerals which exhibit this behaviour include both synthetic materials and natural samples, proving that this process occurs on a regular basis.

The third chapter then goes on the investigate the effect of UV radiation on this experimental system. As it turns out, CO_2 adsorbed on the surface of selected minerals (e.g., TiO_2) is photocatalytically reduced to CO, CH_4 and CH_3OH. This process of photocatalytic reduction of CO_2 is widely studied in connection to the global climate change and the rising global temperature. Efficient means of reducing atmospheric CO_2 levels using solar light to produce fuels or chemical reagents is highly desirable. Our papers and this book introduced a different perspective, which is the photocatalytic reduction of CO_2 as a natural process, possibly important in space. We conducted a case study on Mars, where the conditions are potentially favourable for this process. Mars has a thin atmosphere and UV radiation penetrates as low as to the surface of the planet. Its atmosphere is also mainly composed of CO_2 (~95%) and its surface is covered with regolith, a fine material which contains Fe_2O_3 and TiO_2, both minerals active in the photocatalytic reduction process.

A supporting claim was made using the Nakhla meteorite (a Martian meteorite) as catalyst for this process. It has been shown that this meteorite work as a catalyst of the photocatalytic reduction of CO_2 as well.

Moreover, since CH_4 is the reduced carbon counterpart to CO_2, as attempt was made to discover the oxidation products. X-Ray photoelectron spectroscopy analysis showed that the oxidation products are chlorates and perchlorates. Both compounds were found on Mars. Using the rates observed in our experiments, we therefore estimated the depth of the perchlorate-containing layer on Mars, should this process have occurred with the same efficiency since the formation of Mars. That was a testable prediction, which still awaits experimental verification on site.

The fourth chapter describes the bearing of these results on prebiotic chemistry and the origin of life in the universe. It is generally known that reduced atmospheres (containing CH_4, NH_3, H_2S) are more favourable towards prebiotic synthesis than oxidized atmospheres (rich in CO_2, N_xO_y, SO_2,…), at least from the experimental point of view. The photocatalytic reduction of CO_2 to CH_4 could therefore render planetary atmospheres susceptible to prebiotic synthesis. No comprehensive planetary chemistry model was made, and we do not expect this process to wholly change the redox state of the atmosphere, but rather, we expect local changes based on the exposed minerals, which would also be limited in duration due to atmospheric mixing and lifetimes of the reduced compounds. Overall, however, in specific environments, the photocatalytic reduction could be the missing impulse to initiate the synthesis of prebiotically more relevant compounds.

Last, the fifth chapter provides a short discussion on the environmental and industrial applications of the photocatalytic reduction of CO_2 to CH_4. Overview of basic principles and properties to be studied as well as overview of the current literature on the topic (at the time of writing) is also included.

6 Acidic Hydrogen Enhanced Photocatalytic Reduction of CO_2 on Planetary Surfaces (Publication II)

The second publication broadens the previous work by testing 18 mineral and rock samples for their activity in the photocatalytic reduction of CO_2. The tested samples were Al_2O_3, kaolinite, MgO, $CaCO_3$, TiO_2 (for reference). Natural sodium montmorillonite, acidic montmorillonite, ferruginous smectite, a field clay sample from the Sokolov coal basin, natural rutile from Golčův Jeníkov, siderite, basalt, ilmenite, natural clay with a montmorillonite admixture, clay with kaolinite admixture and samples of diatomaceous earth from the Soos Nature Reserve, Czechia.

Each experiment consisted of CO_2 and HCl in contact with a catalytic material irradiated for 3500 h. The composition was monitored using FTIR and activity of some sample was detected. Overall, the materials were classified into three categories based on their efficiency – active efficient minerals, active inefficient minerals, and inactive minerals. The active efficient minerals produced enough methane to allow retrieval of a pseudo-first order rate constant of methane production. It should be noted that the pseudo-first order kinetics approach was employed, because the mechanism is unknown and in the studied minerals, this rate equation describes the system reasonably well, at least for comparison's sake. Active inefficient minerals produced methane enough to be detected by IR at the end of irradiation, but not enough to reliably fit the rate constant of its formation, and inactive minerals did not produce any methane at all. The three active and efficient minerals were Al_2O_3, ilmenite (sample from Jizerská louka) and sample 1 from Soos natural reserve, Czechia. In an attempt to find out what is the reason for the varied activity across the tested minerals, band gap for each mineral was estimated. This was done by measuring reflectance spectra in a 200-800 nm range. Using the Kubelka-Munk theory of diffuse reflectance, the band gap was determined from the absorption edge. In sample where no absorption edge appeared, the reflectivity/absorption at 350 nm was determined. The wavelength 350 nm was chosen because the irradiation lamp in the original experiment was a broadband Hg lamp with emission maximum at ~350 nm. Unfortunately, no clear correlation between activity and band gap was not observed.

On the other hand, the band gap is a closely followed and tweaked property of many industrial catalysts. Lower band gap in general means that the material is able to absorb radiation at longer wavelengths/lower energies and so become more efficient at solar energy capture. However, too small a band gap means that the excited electron does not have enough energy to activate the adsorbed CO_2 and start the photoreduction cascade. As seen in the literature, acids lower the band gap of the semiconductor minerals. The paper shows that presence of HCl in general reduced the reflectance at 350 nm. This means that the minerals are more apt to absorbing radiation in presence of HCl and HCl increases the efficiency of the photocatalytic reduction as a whole.

The discussion on the applicability of these results then proposes that it could be possible to observe both methane and oxygen in an atmosphere, where the methane would be photochemically generated. Even though not long-lasting, the presence of these two species at the same time would be a false positive biosignature. Care is therefore needed when considering the possible redox disequilibrium pairs as markers of life on planets.

7 Abiotic Formation of Methane and Prebiotic Molecules on Mars and Other Planets (Publication III)

The research on the photocatalytic reduction of CO_2 which began with my diploma thesis and continued during my PhD studies culminates in this publication with a proposal of a planetary carbon cycle. This cycle contains of four separate processes – the photocatalytic reduction of CO_2, spontaneous oxygen atom exchange between CO_2 and surfaces, plasma-induced synthesis of organic molecules and oxidation back to CO_2. Overall, the dominant carbon cycles are different on the different planet types. On Earth, the biogeochemical cycle encompasses carbon exchange between the atmosphere, ocean, sediments, the interior, and the biosphere. Notably, much of the contribution of the biosphere is realised through the cycling of organic carbon. On Earth-like planets, the cycle is expected to be similar with the exception of the biosphere. On the giant planets, the cycles are completely different and consist of atmospheric upwards diffusion, photolysis, sinking of heavier products and thermolysis again. On a side note, these cycles produce hydrogen in the upper atmospheric layers. This hydrogen then escapes, and the atmospheres are irreversibly oxidized. On exoplanets, both of these and any other cycles may be expected. The cycle proposed in this paper is expected to be usually a minor contributor to the overall carbon cycle, but in certain conditions, such as on Mars, its role may be more significant.

The spontaneous oxygen atom exchange between CO_2 and minerals has been described in Publication I of this thesis and was only summarized in this Publication III. Briefly, CO_2 adsorbs on the surface of minerals where it reacts to form a CO_3^{2-} ion. After overcoming a 16.5 kcal mol^{-1} barrier, the ion rotates and releases CO_2 with the lattice oxygen atom incorporated in its structure and leaves behind one of its former oxygens.

Photocatalytic reduction of CO_2 to CH_4 has been described in Publication I and Publication II as well. Again, briefly, CO_2 may adsorb on the surface of photoactive minerals (often semiconductors). The mineral adsorbs UV radiation and excites the adsorbed CO_2. This then decomposes and is reduced by reacting with available protons (in our experiments from HCl, but other sources are also possible) to CO and CH_4. In environments with a source of CO_2, a photoactive mineral, a source of protons and UV radiation, methane can be produced in the atmosphere. The three most important photoactive minerals for this process on Earth and Mars are TiO_2, FeO_T and Al_2O_3. Using rate constants of the formation of CH_4 from our previous works in some simple calculations, we estimate a Martian methane surface flux 2.81×10^7 cm^{-2} s^{-1} and a Martian methane destruction rate 2.37×10^5 cm^{-2} s^{-1}. Therefore, we predict methane formation rate two orders of magnitude higher than the destruction rate and therefore sufficient to explain the methane level observed by Curiosity on Mars. It should be noted that the detection of methane on Mars is still tentative and other missions, such as the Trace Gas Orbiter did not detect any. Through a similar calculation, we calculate methane surface flux for Earth. To determine the effect of this process on the overall redox of the Earth's atmosphere, we also calculate the H_2 budget in a prebiotic atmosphere. Through this calculation, we determine that the contribution to the hydrogen steady state concentration is roughly 4 orders of magnitude less than from other processes. However, there are many unknowns in this calculation, because it applies to the early Earth about which a lot is not known, and the influence of this process may have been both higher and lower.

The methane produced in this abiotic way as a part of its surrounding atmosphere containing N_2 and H_2O, both of which are common in planetary atmospheres, can be exposed to high-energy density environments, such as asteroid or comet impacts. The ensuing chemistry produces organic molecules, including biomolecules. Specifically, mixtures of CH_4, CO, H_2O and N_2 in presence of montmorillonite exposed to laser sparks in the laboratory (experimental model of an impact) produces adenine, glycine, uracil, cytosine, and glycine. The former claim that more reduced atmospheres are more favourable to prebiotic synthesis are repeated.

In the last step, the produced molecules are oxidized back to CO_2. In the case of methane, its lifetime in the Earth's atmosphere is about 10-12 years. It is most efficiently oxidized by $\cdot OH$ to CO_2. Apart from that, in all atmospheres, common destruction pathways include lightning storms, fires, atmospheric discharges or selective chemical reactions on surfaces.

Overall, we conclude that the process, or in general, formation of reduced compounds on aerosols, is important enough to merit inclusion into atmospheric chemistry models, where it is currently missing. In some environments, such as Mars, this process may be of importance. Direct proofs of this process outside the laboratory are still non-existent. But since more and more exoplanets are discovered every day, proofs of this cycle may be observed in the future.

8 Identifiable Acetylene Features Predicted for Young Earth-like Exoplanets with Reducing Atmospheres Undergoing Heavy Bombardment (Publication IV)

UV radiation is a process that exerts its influence on the atmosphere continually over long timescales. A contrast to this is singular events with far-reaching consequences, e.g., asteroid or comet impacts. These events are immediate, on-time events, which, given their magnitude have the potential to alter atmospheric composition of the whole planet. Other such events include volcanic activity, stellar flares, or dust storms (e. g. on Mars).

In this Publication IV, we explored the effect of impacts on the transformation of an atmosphere containing and equimolar mixture of CH_4, CO and N_2 (~240 Torr each). The atmosphere was enclosed in a 1 L borosilicate glass cell, which also contained 1 mL of water (which in turn produced about 23.8 Torr of water vapour) and montmorillonite powder as a catalyst. The sample was irradiated with a high-power iodine photodissociation laser system (PALS, Institute of plasma physics, CAS, Czechia). A total of 25 pulses was delivered to the sample. Each pulse has energy 150 J, is 350 ps wide and has wavelength 1,315 nm. One pulse was delivered every 20 mins, because the laser system needs to cool down after each pulse. The laser beam was focused into the sample cell and LIDB was induced approximately in the middle of the sample cell (not on any surface). This experimental approach, as mentioned above, represents a viable laboratory model of a high-velocity impact.

The composition of the gas phase was monitored by FTIR before and well after the irradiation. The main observed products were CO_2, HCN, C_2H_2 and NH_3. The majority of N_2 and CO in the experiment was left intact, but a significant portion (~2/3) of the methane was consumed, indicating that the origin of the HCN and C_2H_2 includes carbon from the methane. The experimental results were then used by Dr. Rimmer at the Cambridge University. The initial and boundary conditions were applied to the ATMOS 1D Global Climate model to calculate the temperature profile of a hypothetical planet with this atmospheric composition. Then, yield of products in terms of molecules per Joule, the energy deposited via impact and the frequency of impacts were combined to calculate outgassing rates and surface mixing ratios of the products in question. The calculated parameters (temperature profile, surface mixing ratios, outgassing rates) were then incorporated into ARGO, a Lagrangian photochemistry and cosmic-ray atmospheric chemistry model. The model calculated a full atmospheric profile with pressures of all monitored species.

The atmospheric profiles calculated from ARGO along with other parameters were used to calculate atmospheric transmission spectra using TauREx. The calculation was performed by Dr. Waldmann and his team. The spectra were calculated for an Earth-sized planet orbiting a Sun-like star. The first result from the model with this atmospheric composition is that the methane absorption signal obscures many usually important molecular features. Despite that, the bulk composition of the atmosphere including C_2H_2 can be observed. Specifically, with a resolving power $R = 300$, CH_4 can be detected at 3.3 μm, the CO feature can be observed at 4.9 μm, and H_2O at 6.5 μm. The acetylene can be detected as a shoulder to the methane 3.3 μm feature and at 10.5 μm as a lone feature. HCN cannot be detected, with all its signals masked by the other absorbers. For this reason, it turns out that C_2H_2 is a viable tracer of impacts on methane-rich rocky exoplanets whereas HCN is not.

Even though acetylene is a good tracer of impacts, it is important to not consider it as a marker of impacts as its sole presence can be potentially explained by other means, such as UV photochemistry, thermochemistry in specific environments, etc. Temporal variations on acetylene signals, however, could be indicative of impact chemistry on the observed planet.

The experiment in this paper was carried out with a single atmospheric composition, rather arbitrarily chosen, and an arbitrary number of pulses was applied to the system. Both of these drawbacks were enforced by the technical limitations of the laser system and the available beam time. Care is therefore needed when extrapolating the results to different atmospheric compositions, which, however, is necessary. The experiment was also carried out at ~1 bar atmospheric pressure and at room temperature. As discussed in the paper, however, even though the composition of the mixture does not represent any chemical equilibrium, results in this paper and the referenced papers indicate trends in the experimental results, which follow trends in chemical equilibrium at temperatures ~2,000-5,000 K. The results of these calculations are shown to be rather insensitive to changes in $N_2/(CO + CH_4)$ and CO/CH_4. The changes in abundances are within one order of magnitude for both species over a wide range of values. The C/O ratio, however, make a big difference on the results. Specifically, observable quantities of acetylene would between C/O ~ 1.1 – 1.2. Below C/O ~1.1, its abundance would drop off significantly and would not be observable anymore.

Overall, the experiment in this paper combined with the effects of UV radiation, energetic particles on the loss of methane and the accompanying escape of H_2 imply significant methane outgassing rates to replenish the lost amount. This possibility can be realized, as it seems, on Titan, 55 Cnc e as well as on the early Earth. Importantly, though, since there exist scenarios which could produce significant amounts of acetylene through outgassing or photochemistry, acetylene is a reliable impact signature only when the planet-star system is taken in context.

9 Carbon disulfide as a tracer of asteroid impacts on young volcanically active exoplanets (Publication V)

Similar to publication IV, this paper follows a similar process of impacts as the source of energy for atmospheric processes. Future observation of exoplanets by space telescopes and ground-based telescopes will observe potentially more and more atmospheres of exoplanets. From those observations, models will be able to say much about the conditions on the given planet. Current understanding of planetary evolution models predicts that after the accretion of a planet, material lingering on unstable trajectories is destabilized and bombards that planetary surface in what is called 'heavy bombardment'. Impacts are therefore considered as very important in the shaping of planetary atmospheric properties during late-stage accretion and early after its formation. However, impacts themselves are very unlikely to be observed directly, because the plasma that forms during impact is 1) too faint to be observed, and 2) temporally limited, so that even if observable, astronomers would have to be very lucky to capture it. What could be observable, though, are changes in the atmospheric composition after impacts through specific markers.

This paper focuses on the chemistry of young rocky planets, such as the early Earth, or LHS 1140b, whose atmospheres as nitrogen-dominated and contain water, carbon species and sulfur-bearing species. Namely, SO_2 and H_2S are considered as common volcanic gases and likely constituents of an atmosphere on a volcanically active young planet. Here, SO_2 is more likely in oxidized atmospheres and H_2S in more reduced atmospheres. The experiment in this paper, similar to the previous paper, simulated asteroid impact with a high-power laser PALS. Artificial atmospheric mixtures were irradiated with 15 pulses of this laser, each with ~150 J energy, 1,315 nm wavelength and 350 ps duration. Changes composition of the mixture before and after irradiation were monitored with high-resolution FTIR spectroscopy. The results were expressed in yield of molecules J^{-1}. Significant products include OCS, CS_2, NO, C_2H_2 and HCN. Here OCS and CS_2 are the major sulfur-bearing products.

The resulting yields were included in a planetary post-impact chemistry model ARGO with the STAND2020 reaction network, which predicted the vertical mixing ratios of OCS and CS_2 for a supposed early Earth and LHS 1140b atmospheric compositions. Different surface mixing ratios of SO_2 were used (ranging from 1 ppm to 1%) to test the sensitivity of the result.

A radiative transfer model TauREx3 was imposed on a modelled atmosphere of LHS 1140b with manually varied concentrations of OCS and CS_2. The model was used to predict observability of OCS and CS_2 in its atmosphere by the James Webb Space Telescope. Combined results from the chemical and radiative transfer model show that CS_2 and OCS would be observable by JWST after 10 transits on rocky planets experiencing mass delivery rates $>10^3$ g year^{-1} within 20 pc of the telescope.

Discussion in the paper goes on to show that CS_2 is a suitable tracer of impacts. On the other hand, OCS is more ambiguous, because other sources of OCS may exist. OCS/SO_2 disequilibrium may be also indicative of impacts, although not a definitive signature.

Note: This publication is currently submitted for review.

10 Decomposition of Benzene during Impacts in N_2-dominated Atmospheres (Publication VI)

Research presented in publications IV and V introduces the topic of impacts into planetary atmospheres with special focus on the chemistry and kinetics of the impacts. Experiments for both of these papers were carried out using the PALS laser. The parameters spaces that could be explored in the experiment are strictly limited by the available beam time, the specifics of the experimental apparatus, and the fact that the analysis is a one-time analysis in a different building. For these reasons, we constructed a new apparatus called ELISE (Experimental Laboratory Impact Simulator for Exoplanets). The apparatus is desribed in this publication and shown in Figure 3 in this thesis. In short, it is a glass apparatus equipped with a laboratory Nd:YAG laser with tuneable energy (up to 450 mJ) and includes a FTIR measurement cell for online analysis without the need to compromise the sample. The system also boasts a fan which simulates mixing as well as negates the slow diffusion which otherwise hinders the FTIR analysis. The sample further contains a gas handling section and is vacuum tight. The experiment can be run both in flow and as a closed circuit. The materials used for construction were limited to borosilicate glass for the body, stainless steel and rubber O-rings for vacuum connections and Teflon for the fan. This minimizes possible surface interactions of the sample. The system is modular, and we have constructed two cells for sample irradiation. One is a spherical cell for the irradiation of gaseous mixtures and the other is a cell with a Teflon holder which is connected to a rotating stepper motor designed for the irradiation of mineral and rock samples, or tablets.

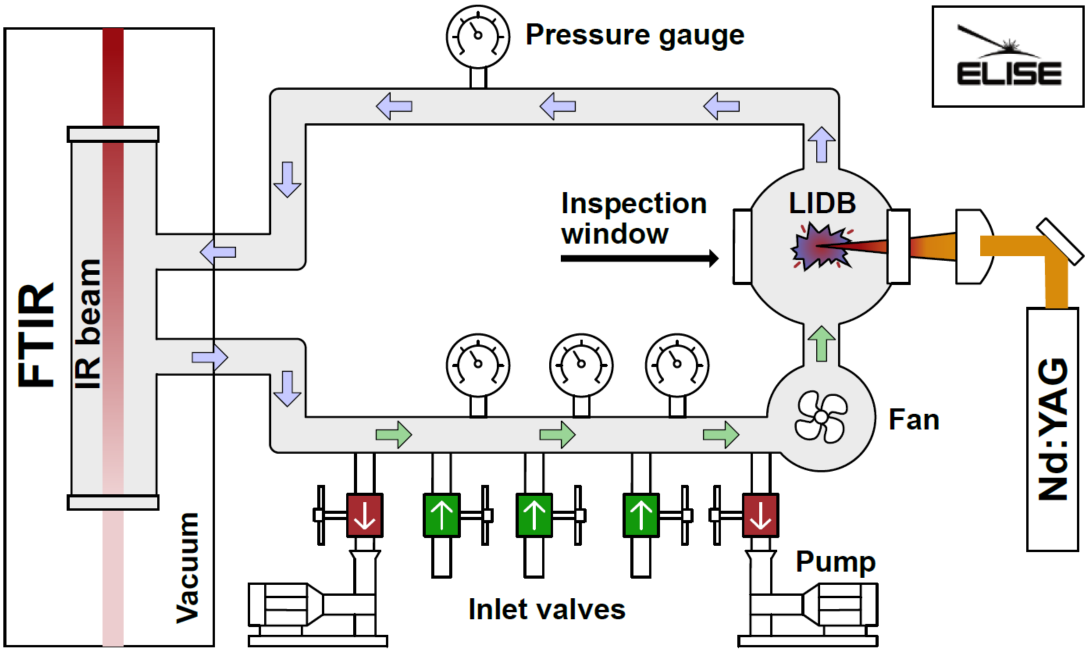

Figure 3: The ELISE (Experimental Laboratory Impacts Simulator for Exoplanets) apparatus. This figure was created by Antonín Knížek, Lukáš Petera and David Černý and is part of Publication VII in this thesis. The paper is unpublished at the time of writing of this thesis (14 August 2023) and may become subject to copyright in the future. The reader is therefore referred to this paper for reference.

The first experiment carried out on this system were focused on the decomposition of benzene during impacts in N_2-dominated planetary atmospheres. A significant amount of carbon in space is in the form of polyaromatic hydrocarbons. A project START 'Heterogeneous chemistry of polycyclic aromatic hydrocarbons in astrochemical context' was dedicated to the investigation of the behaviour of the PAHs during impacts in various conditions and in various atmospheres. Benzene was selected as a PAH prototype and the simplest carbon species containing a benzene ring. We therefore prepared atmospheres containing benzene and water vapour in nitrogen as the background gas and exposed them to the impact-simulating laser radiation. Thanks to the new apparatus, we were able to explore the concentration parameter space more thoroughly. The model ~1 bar atmospheres contained ~0.08%-0.7% of benzene and ~0.02%-2% of water vapour. In total, we performed 16 experiments with different concentrations of each specie. This experiment simulated an asteroid or comet impact into a nitrogen-rich planetary atmosphere. Benzene and water are unlikely to coexist for longer timescales in a planetary atmosphere since they represent the opposite ends of the redox equilibrium, but in this model, water can be brought in by the impactor and the benzene can be already present in the atmosphere. This would be the case of the Saturn's moon Titan, which has a reduced ~1.5 bar atmosphere containing benzene.

Benzene decomposes during the simulated impact. The main products are HCN (yield 3.1%-24.0%), acetylene (yield 0%-11.7%) and CH_4 (yield 0.5%-3.3%). In the presence of water, CO (yield 2.4%-35.1%) and CO_2 (yield 0.01%-4.8%) are formed as well.

To better describe the process, the kinetics of the decomposition of benzene was investigated first. The mechanism of the decomposition would require detailed knowledge of the behaviour of the plasma discharge including a radiative transfer model with coupled kinetics which was beyond the scope of the publication. We considered the kinetics of the overall reaction in which benzene decomposes to products. The rate equation used in the paper combined zeroth and first order rate equation such that at higher benzene partial pressures (beginning of the experiment), the decomposition is limited by the available amount of energy in the pulse and the decomposition follows a zeroth order kinetics, and at lower benzene pressures (as the experiment progresses), the kinetics gradually transforms into a first order kinetics because the decomposition is limited by the amount of available benzene. We note that we consider this reaction forward only, because reverse reaction of e.g., three acetylenes in unlikely and has not been observed. This rate equation was fitted to the data and after extraction of the effect of mixing, two rate constants were obtained. These constants should be valid in the tested experimental range and describe the decomposition of benzene regardless of the formed products.

As mentioned above, the main products are HCN, C_2H_2, CH_4, CO and CO_2. The obtained data were not sufficient to describe the kinetics of the formation of the products. However, some trends in the composition of the product mixture could be extracted. First and foremost, as could be expected, with the increasing amount of water at the beginning, the product mixture contained more of the oxidized products CO and CO_2. Furthermore, higher initial content of water enhances the formation of the terminally oxidized product CO_2. Examination of the time-resolved experimental mixture composition also shows that the formation of CO_2 is a successive reaction following the formation of CO.

Furthermore, the data show that a higher initial benzene partial pressure favours the production of acetylene over HCN. This is likely due to the different chemical properties of CN and C2 radicals, the precursors of HCN and C_2H_2, respectively.

On the other hand, the yield of methane clearly correlates with the amount of water in the experiment. This implies that the methane formation mechanism includes an OH radical.

The formation of a solid phase was also observed. The solid phase was collected and analysed with scanning electron microscopy (SEM). This preliminary SEM measurement was published as well, but the solid phase was not analysed in more detail as it would merit a study of its own. The amount of products in the solid phase and the gas phase attains a constant ratio 0.42:0.58.

These experiments provided much more information on the behaviour of the system than previous experiments with the PALS laser (publications IV, V), but still were limited to ~1 bar total pressure and 300 K temperature. The temperature requirement is to a certain degree arbitrary because the reactions take place in the plasma after the LIDB and so long as the temperature of the whole mixture is significantly less than that, the results should be valid. Only one energy was used for the experiments, and that was 450 mJ per pulse at the entrance to the cell. Our calculations show that 100 pulses of this laser emplace energy comparable to a 22-cm in diameter asteroid impacting at 45° with average density 1500 kg m^{-3} and impact velocity 17 km s^{-1} into current Earth's atmosphere. Experiments with different laser pulse energies would be necessary for safe extrapolation of the results to different asteroid sizes. To be able to construct a full model, a full-size distribution of the impacting bodies would have to be included, which would require orders of magnitude more experiments. There are many other possible follow up to this study besides experiments with different energies – atmospheric kinetics model, radiative transfer model of the plasma, examination of the solid phase, etc. Overall, however, the fact that benzene is decomposed and that the main products are HCN, C_2H_2, CH_4, CO and CO_2, holds.

Finally, given that these follow-up studies are successful, benzene may prove to be indicative of recent impact events. If the atmosphere exhibits less of benzene than expected from thermochemistry and photochemistry as well as elevated abundances of HCN, C_2H_2, CH_4, CO and CO_2, impact may be possible. The ratio of $(CO+CO_2)/(HCN+C_2H_2+CH_4)$ as well as CO/CO_2 could also be used to trace the amount of water in the impactor. These claim, however, would require a full planetary chemistry model as well as the planetary neighbourhood behaviour for context and is currently a very far-off target.

11 Survival of HCN during impacts in N_2-dominated planetary atmospheres (Publication VII)

HCN is an important molecule in planetary chemistry. It is a ubiquitous molecule in space and the precursor of tholins, various organic molecules and possibly also hazes. Toxic to organisms, it is a possible precursor of nucleic acid bases, amino acids and possibly lipids and carbohydrates in prebiotic chemistry. Its synthesis and decomposition in planetary atmospheres have been widely examined in the literature. We focused on the stability and chemistry of HCN in planetary atmospheres subjected to impacts.

The experiments were again carried out on the ELISE apparatus. HCN and H_2O containing atmosphere with N_2 as the background gas. The decomposition of HCN in the laser-simulated impact and the ensuing chemistry were described. We performed nine 'main' experiments. Each sample in this experiment was irradiated for 7,000 s. This time was chosen as the time it takes to fully decompose the HCN in all experiments. The composition of the gas phase was monitored by FTIR again. A simple kinetic model was constructed, which describes both the decomposition of HCN into solid phase products as well as reaction with H_2O to produce CO and then CO_2. To extract the rate constants and fit the model, however, we developed a data reduction and analysis pipeline which starts with defining adsorption multipliers for HCN and H_2O. It has been observed that HCN and H_2O adsorb on the walls of the apparatus (and much more than Co and CO_2 at that). This adsorption is impossible to quantify in the current setup. For this reason, adsorption multipliers to the data were added and the model was executed with 64 possible combinations of the adsorption multipliers. The goodness of fit in terms or R^2 was determined and for each experiment, the six rate constants of the model were determined in each experiment as a mean of the fitted constants for the fits with the adsorption multipliers with R^2 value in the 2σ of the mean R^2 value. Covariances were also calculated in order to determine if the fitted parameters depend on the defined multipliers. As was verified, they do not, and this approach is valid. Then, the mean of the fitted rate constants was calculated. Standard deviations were calculated in each step and propagated throughout the whole calculation, so the obtained results area applicable to the studied range. The data analysis pipeline is described in the paper in detail along with all the plots with all the intermediate results.

To then test the results on a wider range of initial parameters, several other experiments were performed. For those, only the initial composition and the composition after 420 s of uninterrupted irradiation were determined. The kinetics model with the obtained rate constants and the initial partial pressures was then applied to predict the partial pressures at 420 s and compared to the experimental results. The data show that the model is reasonably applicable in the tested range 0-13 Torr of initial HCN and 0-25 Torr of initial H_2O.

The obtained rate constants can be directly included in a planetary atmospheric chemistry model. Again, the experiments were performed at room temperature, but the temperature in the plasma is higher and may reach tens of thousands of K after the discharge. The products form in the afterglow of the discharge and the results should be insensitive to changes in surrounding temperature so long as it is sufficiently lower than the plasma temperature. As such, it is probably impossible to apply to hot Jupiters with temperatures often exceeding 2,000 K.

12 Conclusion

The presented thesis introduces impacts and photochemistry as significant driving forces for planetary chemistry. The attached papers summarize various experiments with the photocatalytic reduction of CO_2 to CH_4 in the context of planetary atmospheres and surfaces and the role of impacts on atmospheric transformation in selected cases. Special care is given to the history of Earth in both the introduction and the attached papers, because Earth is our home planet and also a planet which we know most about. Understanding the chemistry, history and evolution of the Earth's environment is ever more important in the era of a rapidly changing climate. At the same time, the experimental and theoretical results can be directly applied to the modelling of exoplanets, to support observations by telescopes and in this way, broaden our knowledge about the Universe about us.

13 Literature

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