

Univerzita Karlova
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Phosphine and nitrous oxide as false-positive biosignature gases in planetary spectra

Fosfan a oxid dusný jako falešně pozitivní biosignatury ve spektrech planet

Diplomová práce

Vedoucí práce: RNDr. Martin Ferus, Ph.D.

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Prohlášení

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Abstract

This study is dedicated to evaluating the potential for a novel pathway of abiotic synthesis of phosphine (PH_3) from phosphorus trioxide (P_4O_6) by a photocatalytic mechanism on aerosols. The mechanism might explain the recent possible detection of phosphine on Venus. This scenario has recently been suggested theoretically by our team based on an analogy with methane production from carbon dioxide on acidic photochemically-active surfaces of materials, which may account for a possible source of methane on Mars. Methane, just like phosphine, was suggested as an indicator of life on terrestrial planets, including Mars. The theoretical testing of photochemical phosphine generation suggests that even if this gas is present in the atmosphere of Venus it cannot be considered as an indicator of life until the suggested mechanism is excluded theoretically, or by experimental results, or direct evidence of life on Venus. This thesis will be followed by preparation of sophisticated experiments and intensive laboratory research addressing this. Furthermore, the role of nitrous oxide as another false positive biosignature was evaluated in this study. The presence of nitrous oxide can also be explained by processes other than biological, particularly on early planets. This study specifically demonstrates the synthesis of nitrous oxide by unexpected plasmochemistry taking place during a simulated hypervelocity atmospheric entry asteroid impact event. In order to evaluate the production, sinks and stability of both biosignature gasses, a 1D Lagrangian planetary atmosphere model (ARGO) was used. For assessing the potential of the newly introduced reaction mechanisms, models of the Venus and early Earth atmospheres in ARGO code and modified STAND chemical network were created and verified. Results of both models have been discussed in terms of detection limits of both gasses. The modifications needed in ARGO in order to achieve better precision were identified and discussed. As the result of this theoretical study, proposition for a new experiment was formulated.

Abstrakt

Tato práce je zaměřena na zhodnocení potenciální role zcela nové abiotické cesty syntézy fosfanu (PH_3) z oxidu fosforitého (P_4O_6) mechanismem kyselé fotokatalýzy na aerosolech. Tento mechanismus by mohl objasnit nedávnou detekci fosfanu na Venuši. Tento teoretický scénář byl navržen naším týmem v analogii s produkcí metanu z oxidu uhličitého na kyselých fotochemicky aktivních površích, která může být vysvětlením přítomnosti metanu na Marsu. Metan je spolu s fosfanem jedním z možných indikátorů života na terestrických planetách. Teoretická verifikace fotochemické produkce fosfanu potenciálně může znamenat, že ani přítomnost tohoto plynu v atmosféře Venuše nemůže být považována za indikátor života na Venuši, dokud námi navržený mechanismus nebude teoreticky vyvrácen na základě experimentu či přímé detekce života na Venuši. Z tohoto důvodu bude na tuto studii navázáno sofistikovaným experimentem a intenzivním laboratorním výzkumem. Práce dále hodnotí roli oxidu dusného jakožto další falešně pozitivní biosignatury, jejíž přítomnost lze vysvětlit jinými procesy než přítomností života – konkrétně ve spojení s jeho syntézou plazmatem vzniklým při vstupu asteroidů do atmosféry planety. K evaluaci vzniku, zániku a stability obou plynů nově objevenými a neočekávanými fotochemickými a plazmochemickými procesy byl použit 1D Lagrangovský model planetární atmosféry. Za účelem zhodnocení potenciálu nových reakčních mechanismů byly vyvinuty modely pro atmosféry Venuše a rané Země v kódu ARGO a upravena reakční síť STAND. Výsledky obou modelů byly diskutovány vzhledem k limitům detekce obou plynů. Byly rovněž identifikovány a diskutovány postupy, kterými lze použité 1D atmosférické modely nadále zpřesnit. Jako výsledek teoretické studie je navržen experiment.

Content

Acknowledgements	4
Abstract	5
Abstrakt	6
Content	7
The list of abbreviations	9
1. Introduction	12
2. Theoretical part	15
2.1. Biosignatures	15
2.1.1 False positives and controversial data suggesting life beyond Earth.	15
2.1.2 Drake Equation and habitability of a planet	17
2.1.3 Habitability of the planet	18
2.2 Atmospheric biosignatures	25
2.2.1 Earth-like atmospheres	25
2.2.2 Other atmospheres	27
2.3 PH ₃ and N ₂ O as false positive biosignatures	29
2.3.1 N ₂ O as a biosignature on Early planets	29
2.3.2 PH ₃ as a biosignature on Venus and other terrestrial worlds	31
2.3.2.1 Surface of Venus	32
2.3.2.2.1 Surface/atmosphere interaction	35
2.3.2.3 Atmosphere	37
2.3.2.1 <i>The composition:</i>	Chyba! Záložka není definována.
2.3.2.1.1 Clouds	40
2.3.2.1.1 S- compounds	40
2.3.2.1.2 UV absorbent	41
2.3.2.1.3 Phosphorus compound:	41
2.3.2.2 Phosphine	43
2.3.2.2.1 Detection of PH ₃	43
3 Modelling part	48
3.1 ARGO 1D Lagrangian High Energy Chemistry/Diffusion Code for Planetary Atmospheres	48

3.2 Photocatalytic reduction of phosphorus oxides to phosphine	59
3.2.1 Model conditions	60
3.3 N ₂ O steady state model	64
3.3.1 Modelling of Early Earth atmosphere	66
4. Results	70
4.1 Photocatalytic reduction of phosphorus oxide to phosphine.	70
4.1.1 Abiotic production (excluding our mechanism):	75
4.1.2 Comparison to our production rate	77
4.2 N ₂ O stable state model:	82
5. Discussion	85
5.1 Detectability	85
5.2 Could discovery of PH ₃ mean life on Venus?	86
5.3 Comparison to biomass	87
5.4 Other possible sources of phosphine in Venus atmosphere	88
5.5 N ₂ O other abiotic productions	90
1D vs 3D models.	91
5.7 PH ₃ and CH ₄ parallel	93
6. Conclusion	95
References	96
Appendix	102

The list of abbreviations

Abs – Absolute units

Ariel - the Atmospheric Remote-sensing Infrared Exoplanet Large-survey

AU – Astronomical Unit

DMDS – Dimethyl disulphide

DMS – Dimethyl sulphide

ESI – Earth Similarity Index

EUV – Extreme Ultra-Violet radiation

FP – False Positive

Hab – Ex – Habitable Exoplanet Imaging Mission

IR – Infra-red

JWST - James Webb Space Telescope

LHB – Late Heavy Bombardment

MIR – Middle Infra-Red radiation

M.p. – Melting point

NASA – National Aeronautics and Space Administration

NIR – Near Infra-Red radiation

PAH – Polycyclic Aromatic Hydrocarbon

PAL – Present Atmospheric Level

Pc – Parsec

PDE – Partial Differential Equation

UV – Ultra-Violet radiation

Vis – Visible light

V.p. – Vapour pressure

XRF – X-Ray Fluorescence



**Are we or are we not the only life form in the Universe?
That is the question...**

**Jsme či nejsme jediní živoucí ve vesmíru?
Tot' otázka...**

1. Introduction

One burning question in humanity's collective mind, tracing back to the ages of philosophers and still one of the questions fuelling space exploration, is whether we are alone in the universe and if with the decay of life on our planet life in the universe will cease to exist. While in the past this question was a rather philosophical one, in today's age we are approaching truly sophisticated answers supported by theoretical and experimental findings in chemistry, physics and biology. This question has become a central motivation in interdisciplinary fields such as cosmochemistry and astrobiology. Its answer will be supported by direct observation of celestial bodies with space telescopes such as JWST, Ariel or HabEx. Based on spectral data and a great supporting laboratory experiments and theoretical modelling we will be able to elucidate the detailed chemical and physical conditions on other planets, with an important role also played by the exploration of solar system bodies, such as Venus, Mars, Europa, Titan, asteroids, and comets. Modern science will be able to determine whether an observed planet is likely to bear life. However, our understanding of "what is life" is truly limited only to its manifestation and properties of living entities on Earth. Therefore, even the definition of life is nonuniform.¹

One could say that the desire to understand life from its creation to the limiting forms it could possibly take, is a driver of the evolution of our society, entire religions, philosophies and all natural sciences. For a scientist, we postulate 3 conventional approaches to getting a better understanding of life as a concept.

- A concept of laboratory and theoretical research; established in the Theory of Scientific Abiogenesis formulated by Alexander Oparin in his work "Origin of life" ². Experimental approaches were then pioneered by Stanley Lloyd Miller in 1952³ the concept of such laboratory studies is well reflected by a proclamation formulated by Albert Eschenmoser: "The origin of Life cannot be discovered; it has to be reinvented."⁴

- A second approach is offered by exploration of solar system bodies. The importance of this research is reflected, for example, in the way that the entire scientific community and common people tensely watched the Perseverance rover land on Mars because a successful landing we are one step closer to better understanding the possible origin of life on Mars. Outer regions of the solar system have been recently visited by the JUNO spacecraft (Jupiter, 2016), and deeper space was visited by the New Horizons spacecraft (Pluto and Charon, 2015) which is now on its way to the Kuiper belt. Such research explores the pristine matter from which our world was created.
- The observation of exoplanets in other solar systems and, in future, also exploration of their chemical and physical conditions, climate and atmospheres, and estimation of their habitability. All this is possible only by spectroscopic methods. This research can be conducted mainly by space telescopes such as JWST or Ariel.

With state-of-the-art technology, remote spectral surveys is our best option for investigating biosignatures on celestial bodies outside of our solar system. Solar system planets can however be explored in situ. Similarly to the situation regarding exoplanetary research now, the only available method at the beginning of the 20th century for exploring chemistry on planets such as Mars and Venus was remote spectroscopic observation. In 1894, Percival Lowell was convinced shadows observed on Mars are actually artificial canals built by Martians. Detailed surveys clearly show that no artificial structures can be observed on Mars so far.⁵ It can be expected that such a misunderstanding will happen also in the future regarding over-confidence in our spectral methods and list of molecules attributable to life and other fascinating features on exoplanets.

On the other hand, we have better tools for interpreting raw observational data (which can actually be of worse quality than spectra of Mars or Venus recorded during the early 20th century).

How can we avoid jumping to a quick conclusion of life, where there in fact might be none? What does the discovery of a biosignature gas on a terrestrial planet mean? Remote observations, even provided by state-of-the-art techniques, are limited even for the solar system. The discovery of phosphine on Venus⁶ has definitely resulted in a reassessment of our knowledge, and raises question about how indubitable biosignatures can be observed^{7, 8}, the conditions under which life could thrive, planetary chemistry and atmospheric chemistry, ethics, where does the popularization of science end and the twisting of scientific results to more sensational scenarios start. The presence of a biosignature gas in the atmosphere of a planet does not automatically mean it was produced by life. Biosignatures are truly a sign of life only once all other possibilities have been proven implausible!¹

To evaluate the plausibility of an abiotic production pathway to a biosignature, we have handy tools, which scientists from 100 years ago did not have, and sophisticated models allowing us to study processes in the atmosphere computationally.

The aim of this study is to investigate a new kind of abiotic production of phosphine and nitrous oxide. This work will hopefully enrich our understanding of biosignatures. Furthermore, our laboratory is participating in the preparation of the Ariel mission; this study could bear results which should be taken into account whilst evaluating Ariel data.

2. Theoretical part

2.1. Biosignatures

Biosignature is generally defined as an object, substance or pattern, whose origin specifically requires biological agent. In terms of exoplanets, we usually speak about spectral feature of a molecule typically produced by (or related to existence of) a biosphere.^{9,10} In this context, a biosignature should not be understood as unambiguous evidence of life – biosignature only indicates possible biological agent. We can postulate that:

Only after all other scenarios leading to the presence of biosignature have been deemed implausible, only after that, can we call biosignature a biosignature.

2.1.1 False positives and controversial data suggesting life beyond Earth.

In search of life outside of our planet, several controversial discoveries have already occurred. Some of them are summarized in the book “Astrobiology: A Brief Introduction” by Kevin W. Plaxco and Michael Gross.¹¹ Many of them suggest the possibility of life on Mars, since 1976 theories of life on Mars resurface every few years. In 1976, NASAs landers from mission Viking mixed soil with radioactively labelled carbon nutrients to see if any metabolism occurs. One of those experiments recorded a production of radioactively labelled methane, however, they were not able to reproduce this experiment with the same results. For this reason, NASA deemed this finding a false positive. Later in the year of 1996, during the study of Martian meteorite ALH84001 found in Antarctica, a formation inside the meteorite that highly resembled fossilised microbes was discovered. After further analysis, NASA discovered organic molecules and tiny crystals of mineral magnetite; this discovery was subjected to the analogy with Earth magnetotactic bacteria (Figure 1).¹² However, the result was dismissed and challenged multiple times. PAH discovered in ALH84001 were not

as diverse as they should have been if their origin was biological, furthermore nanofossils seemed to be too small to have real functioning metabolism. This argument is however highly controversial, because cyanobacteria range in size from 500 nm to 60 micrometres. The size of 500 nm is comparable to structures observed in ALH84001 (see Figure 1). Also, the size of cyanobacteria represents the largest prokaryotic organism, because the average diameter of most bacteria ranges between 200 nm to 2.0 microns. However, it is generally agreed that at the first glance promising evidence of life in ALH84001 can be tentatively considered to be false positive.

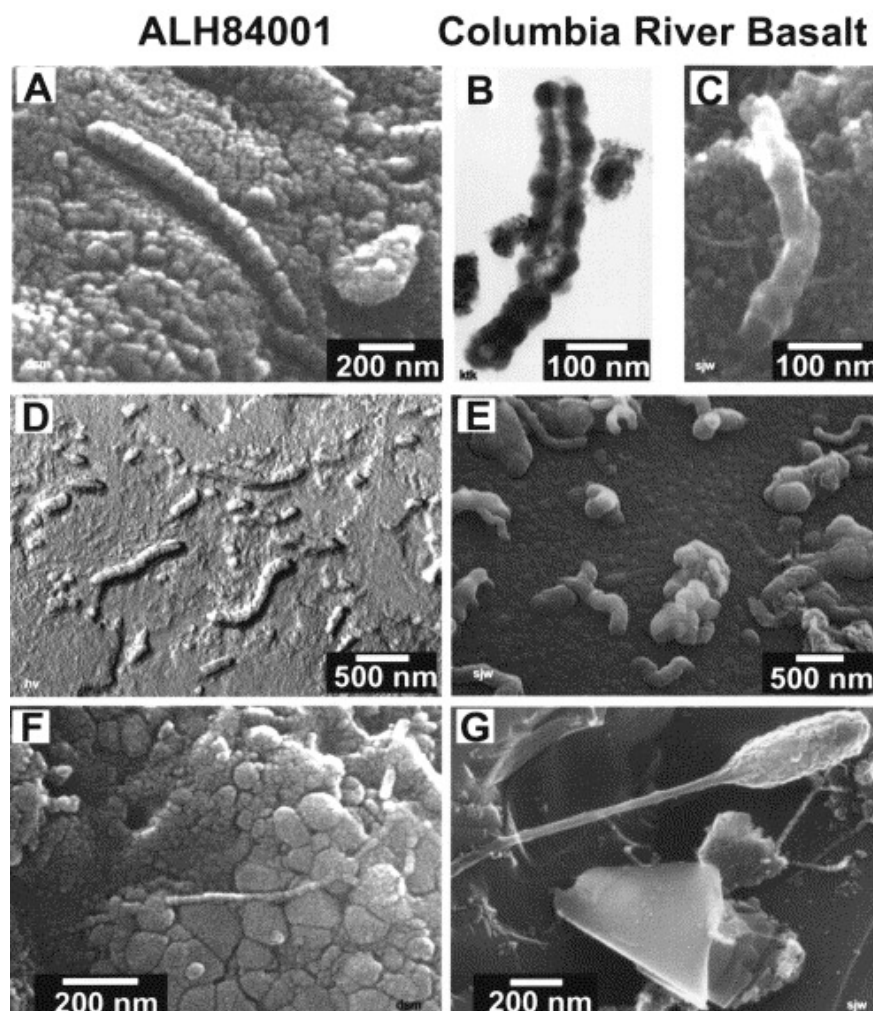


Figure 1: Comparison of ALH84001 to basalts found on Earth, Figures A, D and F are electron microscope images of ALH84001, the rest are Figures by Thomas Keppta et al. 1998. Figure taken from E.K. Gibson, Jr et al. 1999.¹²

After many measurements with negative results starting in late 80s, methane was finally discovered in Mars' atmosphere by three individual groups of scientists in 2004. Methane is considered to be a very persuasive biosignature, therefore the discovery provoked strong discussion in scientific community and public. Could there be life on Mars? Philosophy of biosignatures dictates us to first disprove any other possible reasons for methane presence on Mars before we conclude the existence of life on Mars. Several scenarios describing abiotic production of methane on Mars have been proposed since, one of which suggests photocatalytic synthesis of methane from CO₂.^{13,14}

Several features have been debated as signs of life on other celestial bodies. The Venus atmosphere shows significant inconsistencies with our understanding of atmospheric chemistry. Data from Pioneer, Magellan and Vega missions discovered significant lack of CO, which should be generated by lightning and solar radiation. Furthermore, a fine balance of H₂S and SO₂ have been observed, even though these two have not been considered coexisting species ever before. Mysterious absorber of UV in the atmosphere of Venus was not explained by any of these missions. Finally, CS₂, a molecule produced only by catalysis and microbes on Earth, have been detected. Since the beginning of this century, the possibility of life on Venus has been presented as the answer to these inconsistencies.^{15,16} After detection of phosphine on Venus this topic is even more frequently debated.^{7,17}

Once discoveries like these occur, one needs to ask what the probability is, that life really exists under such conditions.

2.1.2 Drake Equation and habitability of a planet

Search for biosignatures is also closely connected to quantitative expression of probability of a habitable planet discovery?

In order to provide a scientific answer, the American astrophysicist Frank Donald Drake formulated Equation (3):¹⁸

$$N_c = R_s f_p n f_L f_I f_c L \quad (3)$$

Drake equation enables to estimate the distribution of civilisations in our galaxy that are intelligent and capable to communicate. Their total number is expressed by a factor N_c , which can be calculated by multiplication of other factors important to calculation: the rate of star formation in our galaxy R_s ; the percentage of them that are orbited by planetary system f_p ; average number of habitable planets in one solar system n ; then we need to estimate how many of those planets bear life f_L and finally frictions of habituated planets with intelligent forms of life f_I and friction of those who bear potential and desire to communicate f_c ; all multiplied by the average lifetime of the civilisation L .

This equation was then broadened for distribution of all biospheres in our galaxy (Equation 4):

$$N_B = R_s f_p n f_L L_B \quad (4)$$

Where N_B is the distribution of biospheres in our galaxy, and L_B is the lifetime of the biosphere.

All of these terms explained above are important to understanding and correct assessment of life distribution throughout our galaxy, however, for this thesis the most important term here is the number of habitable planets in a solar system.

2.1.3 Habitability of the planet

It is expected that existence of liquid water is a key parameter for habitability of a planet and life evolution.¹⁹ Water ocean on surface also distinguishes Earth from other planets. Even though any direct evidence is missing, it is expected that several planetary candidates provide plausible conditions for existence of liquid water on surface. The list of them is provided in

Table 3, page 23. It has also been hypothesised that liquid water existed on Mars and Venus in their history.

If water is central for life, habitability can be estimated in terms of the ability of the planet to bear liquid water. Such an evaluation can be very complicated. Occurrence of surface liquid water depends e.g. on distance of a particular planet from its parent star, on the star type, planetary rotation, chemical and physical evolution, composition and dynamics of the atmosphere, planetary albedo, glacier albedo, the greenhouse effect, tectonics etc.

Simplified definition concept has been introduced by Su-Shu Huang.²⁰ Habitable Zone is defined as the range of distances from the star where planets with a certain atmosphere can support existence of liquid water. Habitable Zone is again dependent on multiple factors such as the atmosphere of the planet (there are Habitable Zones defined for no greenhouse planets to Habitable Zones defined for atmospheres with maximal greenhouse effect), albedo of the planet but most importantly the star type. O and B star type orbiting planets are not considered to be habitable by any significant possibility due to higher levels of stellar radiation. For other star types the decreasing trend in temperatures can be observed as such: $A \rightarrow F \rightarrow G \rightarrow K \rightarrow M$.²¹ This is illustrated in Figure 2 on the next page.

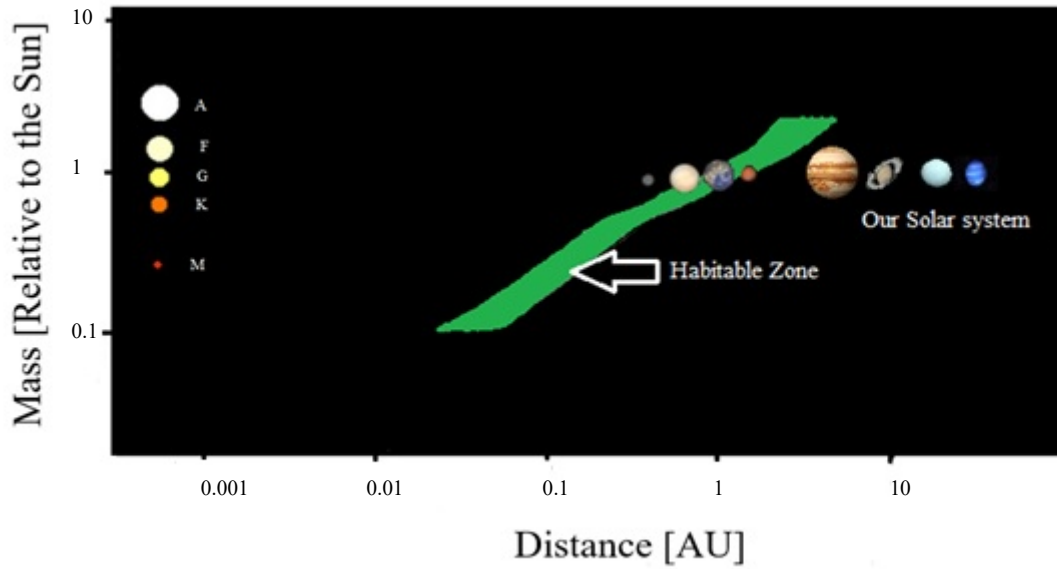


Figure 2: Diagram showing dependence of habitable zone as a function of distance from the star and its spectroscopic type. Recreated from Kasting, Whitmire and Reynolds (1993).²¹

However, higher albedo of the planet can shift Habitable Zone towards the star. This is particularly important for icy planets including Early Earth. Our planet may have gone through the period of ice age during Hadean era due to lower brightness of the Sun.²² Possible solution to this problem is greenhouse effect, induced by gasses absorbing in NIR – H₂O,^{22,23} CH₄,²⁴ NH₃,²⁴ CO₂,^{22,25,26} N₂O.²⁷

In case of our solar system, optimistic Habitable Zone includes Mars and even Venus. However, the most common approach has been in 1993 proposed by James F. Kasting et al.²¹ by setting limits for Habitable Zone to 0.95 to 1.37 AU (Venus orbits at 0.72 AU and Mars at 1.52 AU). This model works for planets with N₂-CO₂-H₂O atmosphere and includes greenhouse effect with carbonate silicate feedback.

Lowest limit is estimated for a planet with runaway greenhouse scenario that we could observe in case of Venus.^{28,29} In this scenario, greenhouse effect becomes so strong to suppress thermal radiation of the planet, it then leads to evaporation of water, which is then hydrodynamically lost into universe and eventual outgassing and take-over of CO₂ as a major atmospheric gas.^{28,29}

Upper Limit of Habitable Zone is then given by temperature of CO₂ condensation. When CO₂ freezes, not only is it impossible for it to take participate in greenhouse effect build-up, but it also enhances the albedo of the planet.

Concept of Habitable Zone however does not include other important features exhibited by a planet supporting life. In our limited perception of life, the only habitable planets are of the terrestrial type. Category of terrestrial planets that have habitable potential is further restricted by the mass of the planet. If the mass of the planet is too low, the planet could become geologically inactive after a short period of time after its formation, because its core cools off quicker than in case of planets with bigger mass and slowly becomes solid.^{30,31}

Magnetic field of Mars and Mercury is negligible compared to Earth. Magnetosphere of a planet is created by magnetic field induced by movements of the liquid iron core. Magnetic field protects the atmosphere from solar wind and cosmic radiation. Unprotected atmosphere is lost by solar wind erosion and escape of molecules. Therefore, atmosphere of Mars is thinner than atmosphere of Earth. Mercury has no atmosphere at all – this fact is also in correlation to lower gravitation – lower mass of the planet. Comparison in the Table 1:

Table 1: Comparison of Mercury, Earth, and Mars; their mass and the magnitude of their atmosphere.

Planet	Mass [Relative to Earth]	Atmosphere [kPa]
Mercury	0.055	~0
Earth	1	101
Mars	0.107	0.7-0.9

Furthermore, lowering in geological activity correlates with tectonics and volcanism. In such a case, robust surface-atmosphere chemical exchange cannot be expected. This means consequences to carbonate – silicate cycle. On Super-Earths, tectonic activity is also inhibited. This suppression results in the lack of continents and in insufficient surface – atmosphere chemical exchange. However, studies supporting possibility of life on bigger terrestrial planets have been published.^{32,33}

While evaluating the Kepler data, Dressing and Charbonneau calculated occurrences of Earth-sized and Super-Earth-sized planets in habitable zone of M dwarfs to find an occurrence rate of 0.16 for Earth-sized planets and 0.12 for Super-Earths.³⁴ Their results are summarized in

Table 2:

Table 2: Comparison of Earth-sized and Super-Earth-sized planetary radius relative to Earth, occurrence rates of both classes for Habitable Zone defined as 0.95 – 1.37 AU and Habitable Zone defined in borders of Venus to Early Mars and the closest probable distance between next habitable planet and our solar system in parsec.

	R [relative to Earth]	Occurrence in Habitable Zone		Nearest potentially habitable planet
		0.95-1.37 AU	Venus-Early Mars	
Earth size	1-1.5	0.16	0.24	2.6±0.4 pc
Super-Earth size	1.5-2	0.12	0.21	10.6±0.7 pc

To conclude this summary of habitability, the list of 24 terrestrial planets that are most likely to maintain surface water is provided by Table 3, however it is important to note that our understanding of life nature is very limited and constrained to Earth, our understanding of planetary systems and conditions on other planets and other solar systems is also very incomplete and needs further exploration.

Table 3: List of 24 terrestrial planets most probable to bear life, their mass or a radius, solar flux, equatorial temperature, orbital period, and Earth Similarity Index (ESI).³⁵

Name	Mass [M _e]	Radius [R _e]	Flux [S _e]	T _{eq} [K]	Orbital Period	ESI
Teegarden's Star b	≥1.05	—	1.15	264	12	0.95
TOI-700 d (N)	—	1.14	0.87	246	101	0.93
K2-72 e	—	1.29	1.11	261	217	0.90
TRAPPIST-1 d	0.41	0.77	1.14	263	41	0.90
Kepler-1649 c (N)	—	1.06	0.75	237	301	0.90
Proxima Cen b	≥1.27	—	0.70	228	4.2	0.87
GJ 1061 d (N)	≥1.64	—	0.69	218	12	0.86
GJ 1061 c (N)	≥1.74	—	1.45	275	12	0.86
Ross 128 b	≥1.40	—	1.48	280	11	0.86
GJ 273 b	≥2.89	—	1.06	258	12	0.85
TRAPPIST-1 e	0.62	0.92	0.66	230	41	0.85
Kepler-442 b	—	1.35	0.70	233	1193	0.84
Wolf 1061 c	≥3.41	—	1.30	271	14	0.80
GJ 667 C c	≥3.81	—	0.88	247	24	0.80
GJ 667 C f	≥2.54	—	0.56	221	24	0.77

Table 3 continuation:

Kepler-1229 b	—	1.40	0.49	213	865	0.73
TRAPPIST-1 f	0.68	1.04	0.38	200	41	0.68
Kepler-62 f	—	1.41	0.41	204	981	0.68
Teegarden's Star c	≥ 1.11	—	0.37	199	12	0.68
Kepler-186 f	—	1.17	0.29	188	579	0.61
GJ 667 C e	≥ 2.54	—	0.30	189	24	0.60
tau Cet f	≥ 3.93	—	0.32	190	12	0.58
TRAPPIST-1 g	1.34	1.13	0.26	181	41	0.58
GJ 682 b	≥ 4.40	—	0.31	190	16	0.57

2.2 Atmospheric biosignatures

2.2.1 Earth-like atmospheres

Numerous gasses are considered biosignatures for Earth type of atmosphere dominated by N_2 , CO_2 , and H_2O vapour. The most important biosignature is probably represented by molecular oxygen produced by photosynthesis. Infrared bands of oxygen in the ground electronic state cannot be observed, because it is a homonuclear diatomic molecule. Transitions of other types such as magnetic dipole transitions and electric quadrupole infrared transitions are well known and should be observable on exoplanets in IR and Vis spectral ranges.³⁶

Abiotic processes (e.g. by water vapour photolysis) are unable to produce high concentrations of molecular oxygen in the atmosphere of Earth, but some scenarios suggest abiotic formation of O_2 on exoplanets.^{37–41} Ozone, the reaction product of oxygen, is also considered to be a biosignature. However, also for its formation, several abiotic pathways have been suggested.^{39,41,42}

Another promising and observable biosignature in atmosphere of a terrestrial planet is methane. This product of an anaerobic microbial metabolism exhibits strong absorption bands ranging from Vis to MIR. However, it should be noted again that abiotic sources of methane have been proposed on rocky planets,^{14,40,41,43} including the scenario central for this study: synthesis of methane from carbon dioxide over acidic surfaces upon UV light on surface of Mars and an analogical process, origin of phosphine from gaseous phosphorous trioxide in Venus clouds. Biosignatures also account compounds of sulphur: DMS, DMDS and CH_3SH considered to be direct or indirect metabolites.^{41,44–46} Table 4 summarizes the most important biosignatures discussed so far in the scientific community. Above mentioned and some other gaseous biosignatures spectra important for Earth-like atmospheres are depicted in Figure 3 (Page 27):⁴¹

Table 4: Summary of some of the most important or obvious biosignatures, their biological source is listed, their method of remote detection; index m – multiple bands, index w- weak band, index s- strong band, the most dominant method of detection is written down in bold letters. Negatives of each species are written down, including some of the possible false positives (FP).^{41,47}

Species	Source	Observation	Negatives
Oxygen (O ₂)	Oxygenic photosynthesis	Vis/NIR^m ; MIR ^w ; UV ^s ;	Destroyed by aerobic respiration, some FP are possible.
Ozone (O ₃)	Photochemical reactions of biotic O ₂	NIR^m ; Vis ^m ; UV ^h	Favourable abiotic production near M dwarfs and F dwarfs.
Methane (CH ₄)	Anaerobic methanogenesis metabolism	NIR^m ; UV/Vis ^m ; MIR ^m	Big number of FP (H ₂ atmospheres). Probably abiotic production on Mars. Biosignature only in tandem with oxidizing gasses. Hard to detect in LR.
Nitrous oxide (N ₂ O)	Denitrification of nitrile	Vis/NIR ^m ; NIR ^m / MIR ^m	Higher build-up in younger systems (results in modelling errors), chemodenitrification FP, FP around young and magnetically active star systems, etc. Challenging detection.
Organosulfur gases (DMS, DMDS, CH ₃ SH)	Biodegradation of DMSP, Decomposition of methionine	Can be detectable via C ₂ H ₆ imbalance.	Rapid photolysis - hard to build up to the detectable level. Since the detection is indirect, extensive modelling is needed in every case.
Chloromethane (CH ₃ Cl)	Natural and anthropogenic sources	NIR ^m	Volcanism abiotic production, unclear abiotic and biotic production mechanisms even on Earth.
Organic haze		Inconsistencies in albedo	Need extensive modelling to compute probable albedo of the planet without the haze.
Hydrogen sulphide (H ₂ S)	Many biotic sources	NIR ^m , MIR ^m	Many abiotic sources.
Carbonyl sulphide (OCS)	Lichens in soil	NIR ^m , MIR ^m	Abiotic sources such as volcanism.
Methyl iodide (CH ₃ I)	Marine bacteria	NIR ^m , MIR ^m	Fast abiotic degradation and abiotic sources.
Dimethyl sulphide	Plankton	NIR ^m , MIR ^m	Volcanism FP.
Phosphine (PH ₃)	Anthropogenic activity, anaerobic biotic sources	NIR ^m , MIR^m	

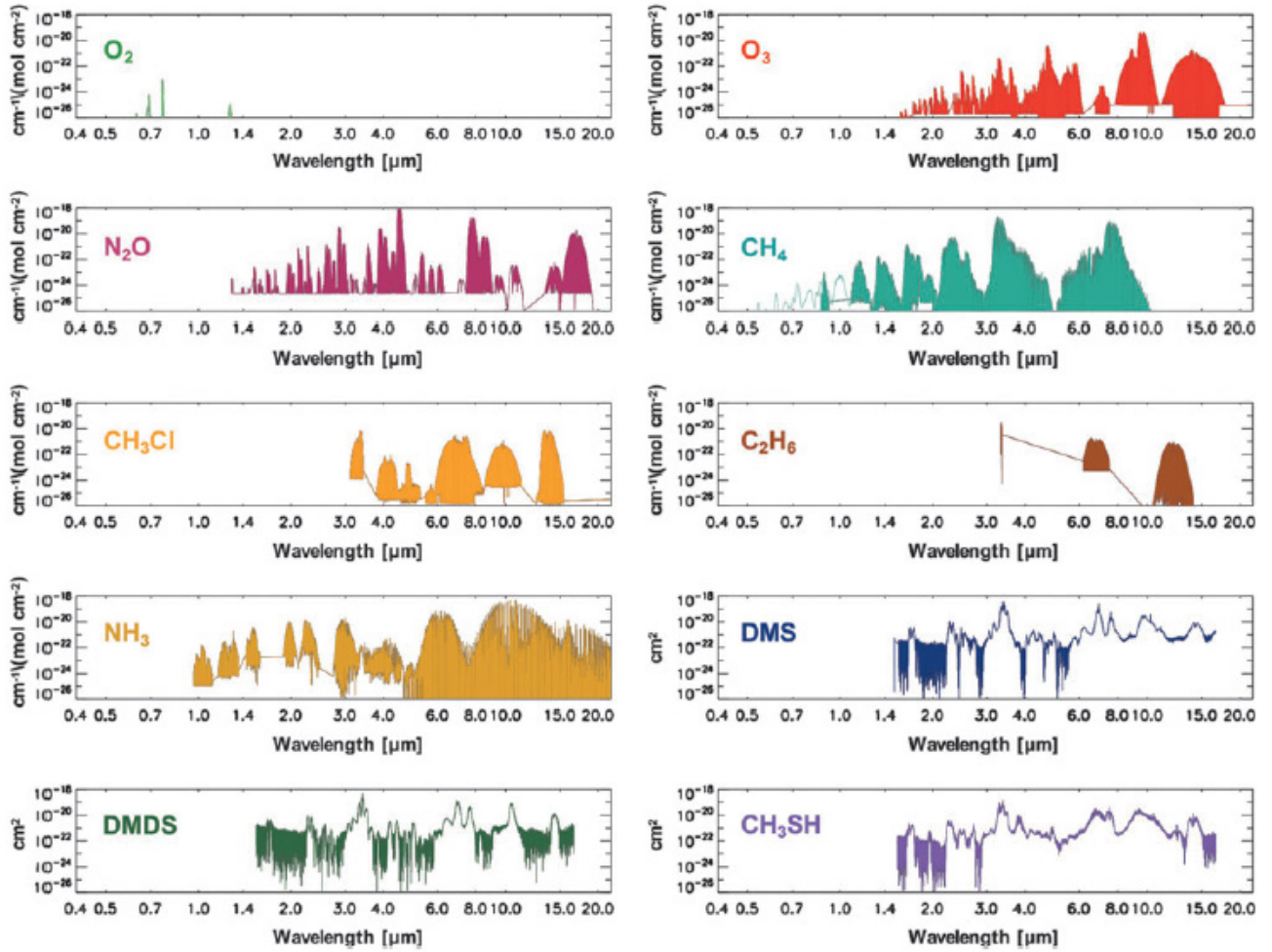


Figure 3: Absorption features of most common biosignatures. O_2 , O_3 , N_2O , CH_4 , CH_3Cl , C_2H_6 and NH_3 in terms of ($cm^{-1}/molecule \times cm^{-2}$) and rest in cross sections (cm^2).

2.2.2 Other atmospheres

Hydrogen is the most common species in the universe and therefore, the most common exoplanetary atmosphere prototype is assumed to be consisted of H_2 . It has been shown that these atmospheres could support life with only a small amount of CO_2 present. Most of the signatures mentioned above cannot be used in case of such atmospheres, since production of for example CH_4 , C_2H_6 or H_2S goes well with significant rates in abiotic pathways.^{41,48–50} Chemical composition of the atmosphere is assumed to be determined by planetary mass and

equilibrium temperature as suggested in Figure 4, this model however needs better calibration, which should be provided by mission Ariel.

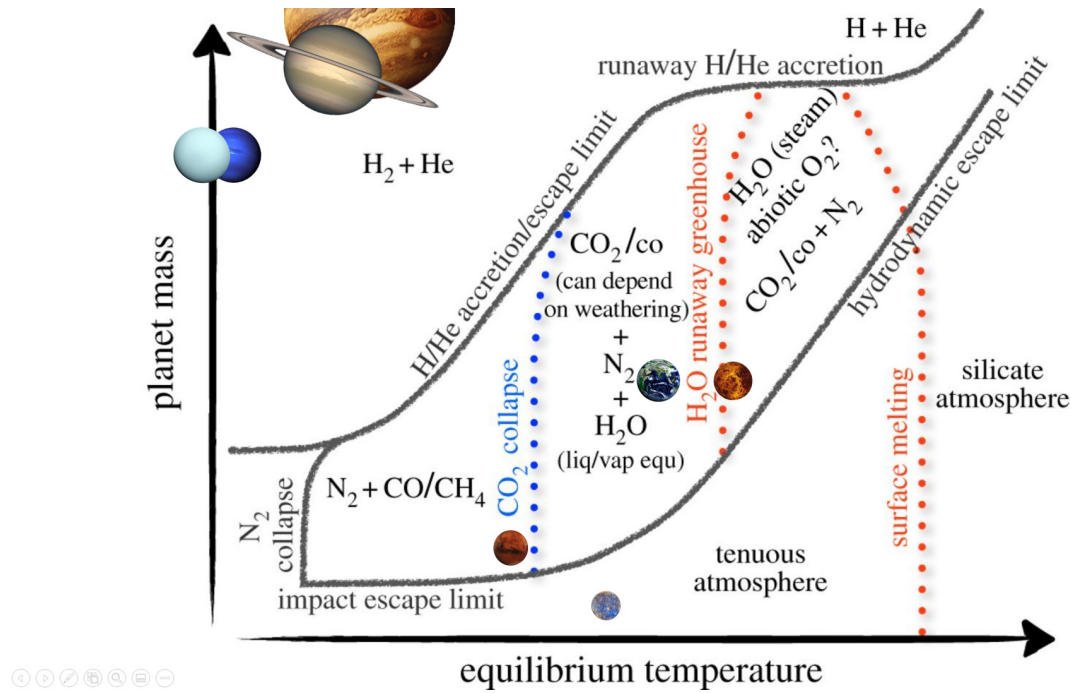


Figure 4: Model describing main atmospheric species as a function of equilibrium temperature and mass of the planet, all 8 planets of our solar system are mapped in this model. Figure taken and modified from F. Forget and J. Leconte 2014 and Tinetti et al. 2018.⁵¹

The main factors driving the equilibrium compositions of atmospheres are the following:

- i) The elemental abundances when the planet is formed (usually outgassing takes place after accretion).
- ii) Temperature of the atmosphere depending on the type of the host star, the distance of a planet from the hosting star, planetary albedo and greenhouse effect and internal energy of the planet given by tidal forces, radioactive decay, residual accretion heat etc.
- iii) Physical processes in the atmosphere such as mixing of the atmosphere, condensation, UV photolysis of atmospheric constituents etc.

The problem can be more complicated in case of non-equilibrium atmosphere. Therefore, more statistical sampling is needed and this is exactly the task for Ariel space telescope mission, dedicated to exploration of significant number of hundreds exoplanets of variable types.⁵¹

2.3 PH₃ and N₂O as false positive biosignatures

Alongside methane, nitrous oxide and phosphene are very widely discussed as a biosignature in the scientific community. While nitrous oxide can be produced by abiotic sources and it can be hardly detected by the state-of-the-art methods due to frequent overlap of its bands with absorption features of other species, its role as a biosignature can grow significantly in future with increasing resolution and detection limits of the space telescopes and improvement in computational techniques and methods.

PH₃ is also a very promising biosignature, since its abiotic sources so far discovered are not strong enough to produce detectable amounts.⁵² However, in this case, the situation will be probably changed, as discussed further in this work.

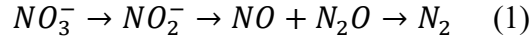
2.3.1 N₂O as a biosignature on Early planets

Nitrous oxide belongs into category of metabolic biosignatures.^{53,54} The redox metabolic reactions depend on environmental conditions such as temperature, pressure, nutrient concentration and acidity. Therefore, nitrous oxide is not considered to be unequivocal biosignature.

N₂O can be observed in UV - Vis region, but the spectral molecular band overlaps with O₂ and O₃ features, so most N₂O observations take place in IR region; 4.5 μ and 7.8 μm.^{55,56}

Nitrous oxide on Earth is produced abiotically only in negligible amounts. The most important producers are denitrifying bacteria and industrial activities (pre - industrial concentration on Earth was estimated to be 270 ppb, current concentration is 319 ppb produced biologically with negligible contribution of abiotic processes).⁵⁵⁻⁶⁰

The denitrification scheme can be summarized by Reaction 1:



Calculations suggesting stable levels of biotic N_2O as a function on O_2 mixing ratios, altitude and insolation were carried out by Segura et al. to obtain dependence of abiotically produced N_2O on oxygen levels.⁶¹ In addition, comparison to CH_4 profiles were added since presence of reduced gasses like CH_4 and N_2O in O_2 rich atmospheres is the most reliable spectroscopic biosignature so far. Results are depicted in Figure 5.

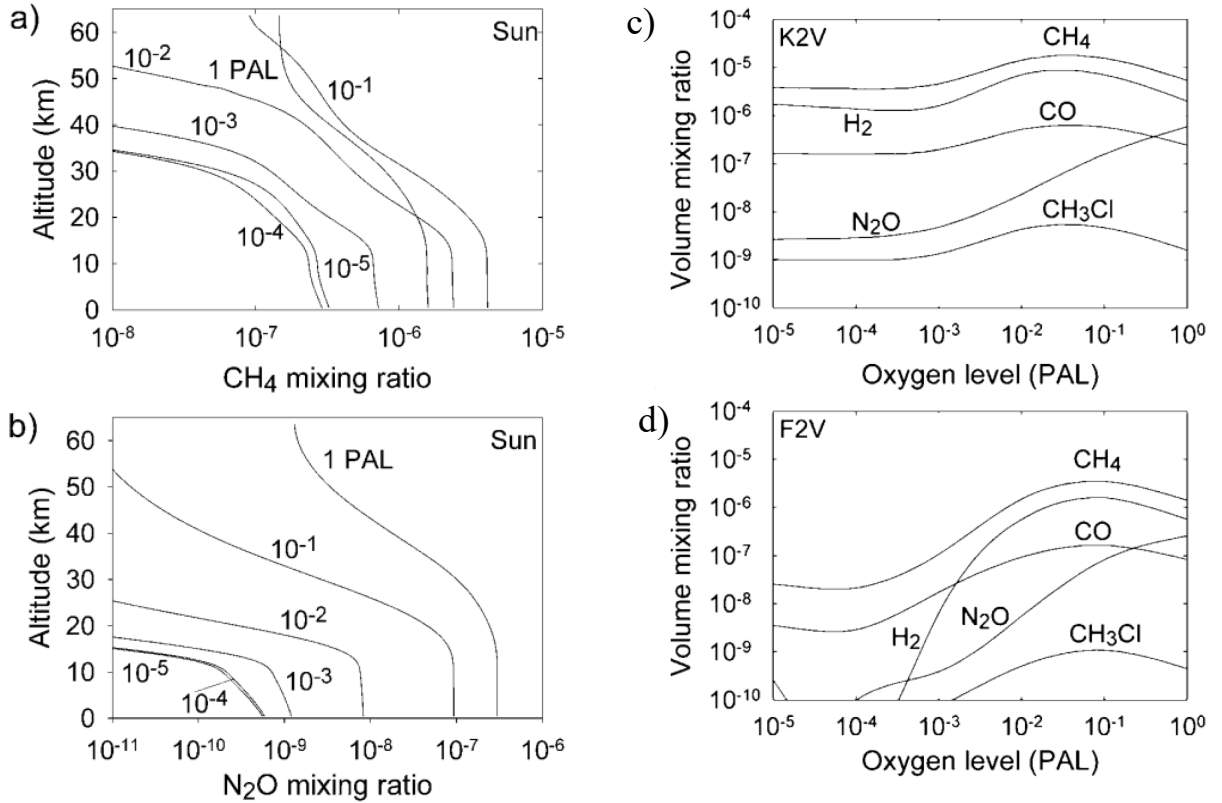
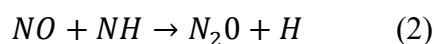


Figure 5: Vertical mixing ratio for different O_2 levels (PAL – present atmospheric level) for N_2O and CH_4 calculated with constant upward draft (a and b). Figure c shows mixing ratios of trace gasses for case of Earth-like planet orbiting K2V star dependently on oxygen levels in fractions of PAL. Figure d shows mixing ratios of trace gasses for case of Earth-like planet orbiting F2V star dependently on oxygen levels in fractions of PAL.

We can see correlation between O₂ mixing ration decrease and N₂O mixing ratio decrease. This result should be taken in account while modelling theoretical fluxes of N₂O observed on exoplanets.

It is expected that bioavailability of copper (part of enzymes participating on the last step of denitrification) was not sufficient and therefore, the N₂O equilibrium on Early Earth was actually lower than it is observed today.^{41,58,62–65}

As mentioned before, main pathway for N₂O production is denitrification. This process can also occur abiotically by chemodenitrification observed for example in Antarctica in the hypersaline ponds.⁶⁶ It should be noted that that NO₃⁻ denitrified by this process is produced using photosynthetically produced O₂.⁴¹ On the planets hosted by young stars or stars with higher magnetic activity, higher EUV fluxes are expected alongside to increase in NO and NH: production leading to abiotic synthesis of N₂O via Reaction 2:⁶⁷



N₂O can be, as mentioned above, synthesized abiotically, however, all those processes can be easily predicted in the context of the star – planet system, so N₂O could be considered as a very strong biosignature, although its detection may be difficult. Small amount of N₂O was also previously observed as a product of atmospheric lightning. However, modern atmosphere still contains only 0.002% of nitrous oxide.^{68,69}

2.3.2 PH₃ as a biosignature on Venus and other terrestrial worlds

Role of phosphine as a biosignature is currently most frequently discussed in context of Venus.⁷⁰ Discovery of phosphine on Venus was rather unexpected and left us questioning how little is actually known about Venus's chemistry. Following chapters summarize state-of-the-art knowledge about conditions on Venus, starting with general data concluded based on ground-based observations, to the results achieved by space missions such as Venera, Mariner,

and Vega series, Magellan, Galileo (Flyby), Cassini (Flyby), Venus Express, Mercury Messenger (Flyby) and Akatsuki. The conditions summarized here are implemented into a 1D atmospheric ARGO model developed in this study for an assessment of PH₃ stability and production by hypothesized photochemical reaction network similar to synthesis of methane from carbon dioxide over acidic minerals upon UV irradiation on Mars.¹³

2.3.2.1 Surface of Venus

The state-of-the-art knowledge about the surface and interior structure of Venus is not complete. The number of landing missions able to observe the conditions of Venus's surface directly is not sufficient. The prospect of rovers such as on Mars represent just a future concept due to the extreme conditions on the surface of Venus. The data are limited to the information provided by a series of Venera landers and entry probes together with Vega balloon flights, imaging performed by Pioneer and Magellan orbiters.⁷¹ We have complete lack of many important data such as seismology or a study of the heat flows.⁷²

Table 5 displayed on the next page summarizes the most general information about Venus and provided a comparison to Earth data (ESI of Venus is 0.44). Venera atmospheric and landing probes discovered that the main composition of the Venus's surface consists of pyroclastic basaltic rocks. During the Pioneer mission the global topographic map of roughly 100 km resolution was obtained, showing tectonic formations such as continental highlands with extensive belts of mountains. Along the continental highlands, islands and circular or linear valleys were observed. Hypsometry of the gained map suggested unimodal distribution of altitudes.⁷²

Missions Venera 15 and 16 then tried to gain a clearer image that would provide more information. The mission concentrated on the northern hemisphere of the planet and scanned 30% of its surface. Venera 15, 16 used 1-2 km resolution radar to observe the relief, finding out many Earth-like features.

Table 5: The general characteristics of Venus in relation to Earth.

General information		Venus		Earth
		Abs units	Relative to Earth	
Mean solar distance	10^8 km	1.082	0.723	1.496
Orbital period	days	225	0.615	365
Rotation period	days	243.025	243	0.9973
Orbital eccentricity	abs	0.0068	0.412	0.0167
Tilt of rotation axis	deg	177	7.548	23.45
Equatorial radius	km	6052	0.95	6378
Mass	10^{24} km	4.87	0.816	5.97
Mean Density	kg/m ³	5240	0.950	5500
Mean gravity constant on surface	abs	8.89	0.877	9.79

Highland regions, many of which appeared to be ancient and very deformed, similarly to the Earth's Ocean ground, as well as rift zone accompanied by volcanoes and folded mountain belts were found. On the other hand, the hypsometry of the surface still appeared significantly different compared to Earth. The planet surface appeared to have very little impact craters, suggesting the age of the surface of the planet is only in the order of a few hundred million years. This revelation gave rise to a number of questions leading to the launch of the Magellan mission.

The Magellan orbiter used radar altimetry and imaging in the course of 4 years, obtaining almost full globe image with 120-280 m resolution. Coronae that were previously thought to be impact craters are globally distributed, very often in the linear lines, leading to the idea of them originating in mantle upwelling processes. Rift zones previously observed by Venera 15, 16 missions seemed to be extending for more than thousands of kilometres, serving as a seam between broad topographical rises. Nevertheless, the extension of the rift zones never transitioned up to ocean scale basins.

While no crustal spreading was observed, the crustal shortening manifestation was observed in the form of mountain belts and ridges, even though it showed no Earth-like patterns suggesting any analogy to Earth tectonic processes.

Additionally, volcanic activity on Venus also shows significant difference from the volcanic activity on Earth. Large shield volcanoes have been observed not organised in linear lines mostly in areas of rifts, as one would presume, like they would have been in cases similar to Earth-like volcanism. Instead, the volcanoes were spread through the surface evenly, in fact volcanically originated formations cover around 40% the planet surface, even though they are mostly deformed by wrinkle ridges. Some estimations of smaller shield volcanoes exceeded the number of one million. Over 200 magma flow channels have been observed, some over thousands of kilometres long. Further study of these magma flows indicated the composition of magma not being uniform but rather diverse and complex. The volcanic plains were also studied. The estimated thickness is about 400 to 500 m. Their origin is attributed to the

decompression melting of the upper mantle layer, thus creation of volcanic plume that erupted in volcanoes distributed globally on the surface. As suggested in Figure 6:⁷³

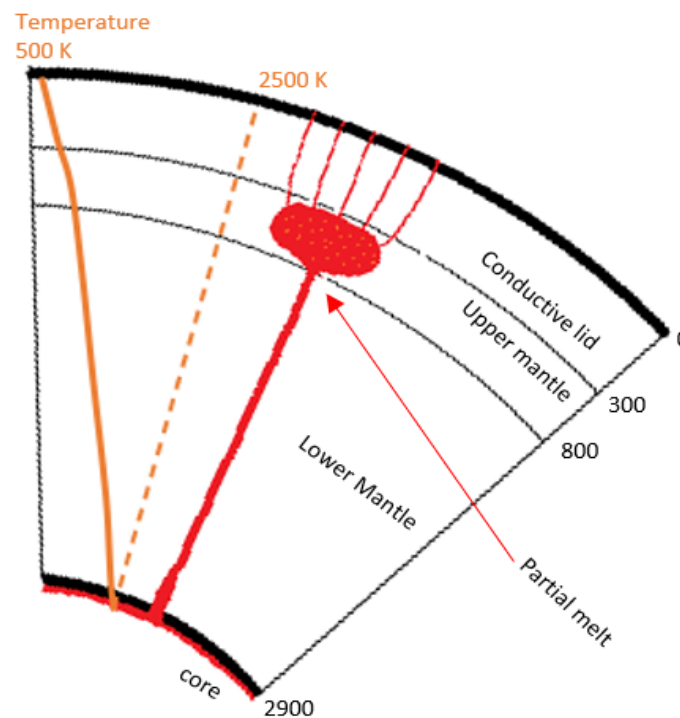


Figure 6: Scheme of interior structure of Venus, including magmatic plume and temperature profile.

In 1982, Venera 14 mission lander was able to land on the surface and obtain 1 cubic centimetre sample of soil, which was analysed by x-ray fluorescence. The surface was mainly basaltic with some silica rich compositions such as felsic – which would suggest a presence of an ocean in the past.

2.3.2.2.1 Surface/atmosphere interaction

High pressures and high temperatures of the atmosphere as well as its composition (SO_2 , CO_2 , N_2 , CO , SO_2 , OCS , H_2O , HCl etc.) suggest high gas – solid exchange to take place. Possibly, a special version of the Carbon-silica cycle can be therefore observed on Venus without the presence of liquid water. Reaction of calcium carbonate and silica leading to calcium silicate and carbon dioxide was proposed by Urey in 1952.⁷⁴ But experimental data were inconclusive.

Attempts to explain sulphur cycle and abundances of halogen gasses and water vapours also took place, but due to the lack of data only simple models can be done to explain this. Even possibilities of out of equilibria states explaining observed abundances were shown, but these would need better understanding of S-G exchange taking place. Sulphur dioxide is typically observed at 1 ppm and its lifetime in the atmosphere is believed to be around a million-year due to reactions with calcium carbonate. To outweigh this loss, the volcanoes on Venus would have to erupt more sulphur dioxide than Earth-like volcanoes. If we presume that the surface in fact has much lower calcite than previously thought at the expense of pyrites, the equilibrium would be met. Snow caps observed by radar under very specific conditions of pressure and temperature could be condensed FeS_2 , tellurium or even HgTe .⁷²

2.3.2.3 Atmosphere

The major Venus's atmospheric constituent is carbon dioxide. It makes up 95.5% and causes strong greenhouse effect sufficient to raise the surface temperatures from 230 K up to about 740 K, which makes Venus hotter than its neighbour Mercury (surface temperature of 440 K). Surprisingly, the profile of temperature corresponds to pressure in a very similar way to Earth's atmosphere (see Figure 7).⁷²

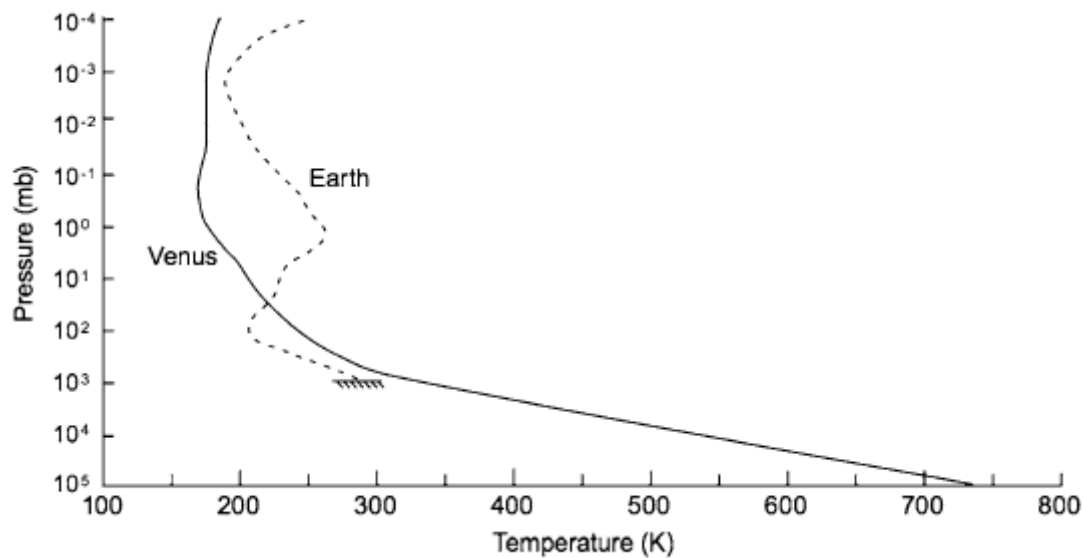


Figure 7: Comparison of Earth and Venus pT-profile

The temperature peak in the stratosphere of Earth is associated with heat absorption provided by the ozone layer. Rest of the differences are due to the different levels of CO₂ and different distance to Earth. Therefore, the atmosphere of Venus should be easily modelled by radiative transfer models.

Second most abundant compound in Venus atmosphere is N₂, making up 3.5% of the atmosphere. Its pressure is 2.7 bar, which is relatively close to the abundance on Earth. This relative similarity of the atmospheres of Venus and Earth is distorted by CO₂, but if we include CO₂ in the form of carbonates in Earth crust, we will end up with very Venus-like abundances. Venus can therefore stand as a model of Earth in case of runaway greenhouse

doomsday scenario, and it is very likely the Earth's early atmosphere was almost identical to the one on Venus. One might suggest the difference between Earth and Venus dwells in the fact that Venus is dry. But current models of planetary origins do not suggest that Earth could be wet since its origin and Venus dry, it is more likely Venus was a wet planet, with the similar amounts of water as Earth, but it lost its water in an early stage of evolution.⁷⁵

The cloud layer of Venus in the altitude of 50 km exhibits atmospheric pressure comparable to terrestrial. The clouds are not transparent in the majority of IR wavelengths. Majority of this energy is radiated back to space, since upper stratosphere, thermosphere and exosphere are transparent for IR with the exception of 15 μm CO_2 band. Planetary albedo of Venus is higher than Earth's; Venus absorbs less energy from sun than Earth does, even though the solar flux is two times greater than on Earth.⁷⁶ Greenhouse effect obviously plays a greater role in climate than on Earth. Below the cloud layer, the Temperature to pressure profile acts as dry adiabat, suggesting a gradient of 10 K per km of altitude. Since the cloud layer is 50 km in altitude and its energy suggests 235 K, the surface temperature is calculated to be 735 K. This corresponds to experimental data.⁷² The general composition is summarized in Table 6.

Table 6: The main species in Venus atmosphere, their mixing ratio on Venus and on Earth for comparison.

Species	Venus	Earth
Carbon Dioxide	0.96	0.0003
Nitrogen	0.35	0.7700.
Argon	0.00007	0.0093
Carbon Monoxide	0.00004	0.00000012
Neon	0.000005	0.000018
Sulphur dioxide	150 ppm	0.2 ppb
Water vapour	30 ppm	0.01
Carbonyl sulphide	4 ppm	0.5 ppb
HDO vapours	3 ppm	1 ppb
Hydrogen Chloride	0.5 ppm	trace
Hydrogen fluoride	0.005 ppm	trace
Atomic oxygen	Trace	trace
Hydroxyl	Trace	trace
Atomic hydrogen	Trace	trace

2.3.2.1 *The composition:*

Isotopic ratio of $^1\text{H}/^2\text{D}$ is hundred times greater than on Earth (this fact was used to assume that water ocean was indeed present on early Venus).⁷² Water vapour are present at the rate of 30 ppm, mixed in the clouds with sulphuric acid droplets.

Carbon monoxide is produced by photolysis of CO_2 in upper layers of the atmosphere where UV flux is very high, it then falls into lower atmosphere where it is mixed in the clouds for further recombination to CO_2 .⁷²

The halogen acids are probably outgassed by volcanoes, and it is assumed that the equilibrium is achieved by their reactions on planetary surface. Noble gasses should be delivered into atmosphere mainly by volcanism and that with a ratio suggesting that they could be used as a marker or a record of history after we have clearer information of their abundances and isotopic ratios.^{72,77}

2.3.2.1.1 Clouds

Clouds of Venus consist generally of sulphuric acid droplets with condensed water vapour.

Sulphuric acid is synthesized above the clouds by reaction of SO_2 with atomic oxygen produced by decomposition of CO_2 and H_2O vapour, it then condenses and descends to the cloud layer.⁷⁸

2.3.2.1.1 S- compounds

Sulphuric acid seems to be present in all altitudes above 48 km, where its evaporation conditions are met, even though its biggest contribution can be found in 52-62 km (mass loading at this altitude is around 5 mg/m^3). Mass loading of sulphuric acid is 1 to 0.1 mg/m^3 . Water mixing ratio is 1000 ppm around 50 – 60 km, 150 ppm from 53 to 26 km. SO_2 mixing ratio seem to be 50 ppm around 53 to 26 km.⁷⁹

Solid particles are also observed in clouds, we are speaking mainly of solid sulphur, S_8 mixing ratio is 3 ppm around 53 km, 15 ppm at 45 km and 3 ppm at 26 km. Sulphuric oxide has been

observed, but its abundances are incoherent among studies; it might mean SO_2 is out of equilibrium, and it takes part in chemistry and dynamics of the clouds.^{72,78,79}

2.3.2.1.2 UV absorbent

Strong absorption band in UV range indicates an existence of an unknown species being present in layer between 64 km of altitude to 47 km. It is variable during time and space, which allows us to study the dynamics of the upper cloud layer. Combinations of at least two absorbents were suggested, gaseous SO_2 with ferric chloride, molecular oxygen and water vapours depleted at the cloud tops. Furthermore, sulphuric acid condensed on FeCl_3 was suggested. Graphite grains polymerised elemental sulphur, hydrated FeCl_3 and many other substances were also recognized as a possible solution. By some, FeCl_3 is believed to be the most likely observed UV absorbent, since it has truly been detected by X-Ray fluorescence.⁷⁹ Others suggest its instability in presence of sulphuric acid. It would have to be steadily supplied presumably from the Venus's surface. As suggested lower in this study buoyancy effects are believed to be present on Venus and supplying surface particles to cloud layers.⁷²

2.3.2.1.3 Phosphorus compound:

Mass deposits (recorded by mass spectroscopy during Vega mission) of different elements are not uniform in terms of altitude, Figure 8 on the next page shows different dependency of mass loading for P, S and Cl.⁷⁹ Interestingly, from 47.5 to 51.5 km the mass deposit is dominated by phosphorus. Strong anticorrelation is observed, while their sum varies slowly in the region from 55 to 47 km, the mass deposit of sulphur and phosphorus is complementary.

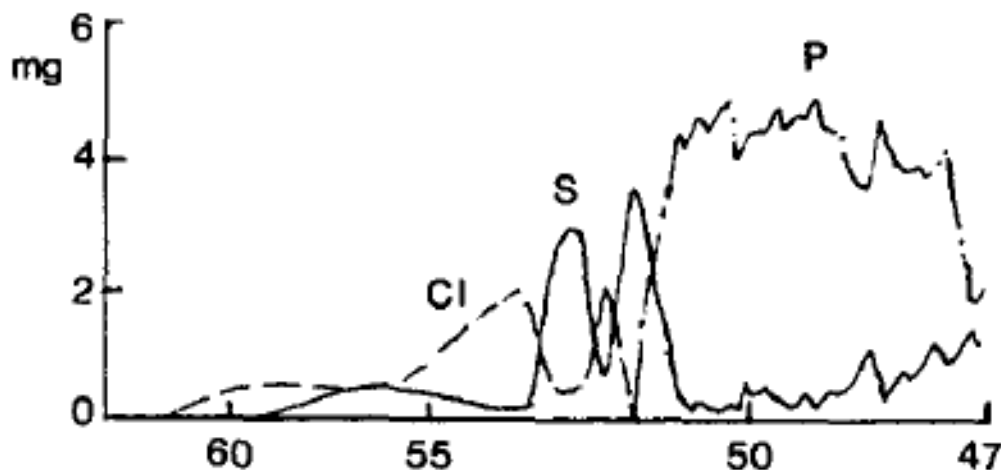
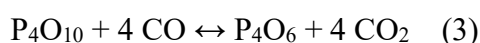
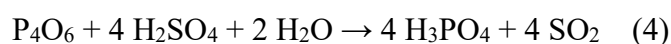


Figure 8: Mass loading of P, S and Cl in altitudes from 47 km to above 60 km.

Mass deposit of phosphorus seems to be 4 mg/m^3 in altitude of 50 km. Mixing ratio of phosphorus acid should be 2 ppm assuming phosphorous acid is the main P bearing species. Another phosphorus bearing species are dimer of most common phosphorus oxides P_4O_{10} and P_4O_6 . They are mutually convertible with reaction with carbon oxides via the reaction in Equation 3:



P_4O_6 should not condense in the atmosphere of Venus, and it exists in vapour phase due to boiling point and its vapour pressure. This is particularly important to our theory of P_4O_6 to PH_3 reaction over acidic dust in upper atmosphere. Also, it reacts with sulphuric acid in reaction expressed by the Equation 4:



This reaction is temperature dependant. That is probably the reason for different mass deposits in different altitudes for S and P.⁷⁹

Instead of phosphoric acid we should consider a $\text{P}_2\text{O}_5 - \text{H}_2\text{O}$ system. Dependence of mass loading of the main P species on altitude would then be as displayed in Figure 9:

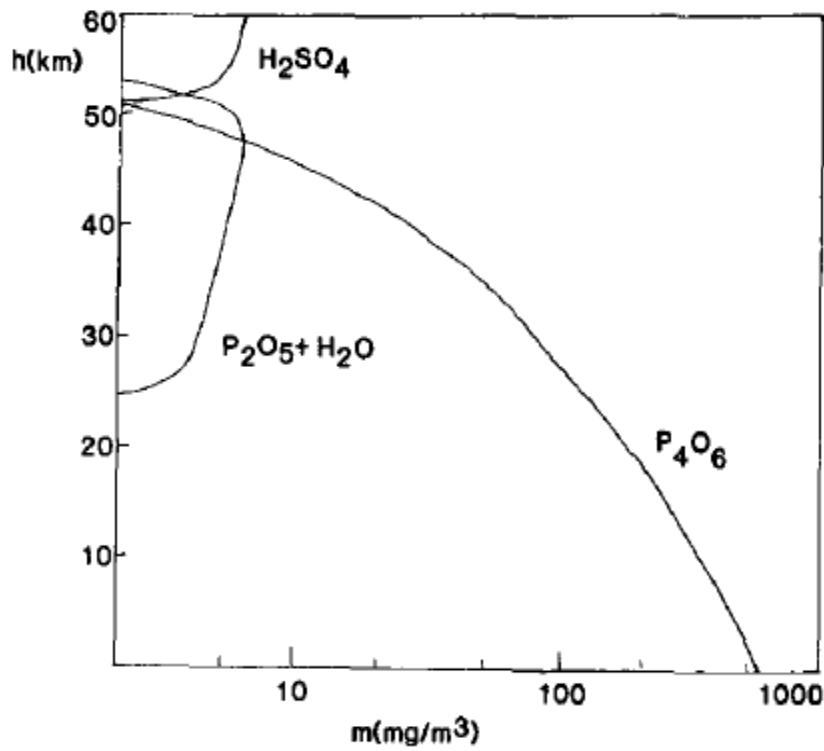


Figure 9: Mass loading of the main P species in Venus atmosphere dependently on altitude.

2.3.2.2 Phosphine

2.3.2.2.1 Detection of PH_3

The theory suggests that Earth and Venus had the same original conditions except for the factor of two differences in solar flux, making them planetary twins. It should be noted that ESI of current Venus accounts just 0.44, even lower than for most Earth-like exoplanets (max. 0.98 is estimated for KOI-4878.01) or Mars (ESI = 0.64). Taylor and Grinspoon (2009) executed models studying evolution of Venus and Earth in an alternative solar system, which is fundamentally identical to the model developed in this study, except for the fact that Earth orbits the Sun at the place Venus does and Venus swapped its place to Earth's orbit. The models suggested that after series of escape and chemical weathering events, Venus's atmosphere would predominantly comprise of nitrogen and surface temperatures and pressure would be similar to Earth tropical values.⁸⁰ Coincidentally, the same conditions were assumed by

Arrhenius on real life Venus, who studied the conditions on Venus using only albedo and other physical arguments.

Could there be life on Venus? Following question was again revived after phosphine was detected on the planet. Observation of phosphine was done previously on other celestial bodies; it was observed being synthesized abiotically in reducing the atmosphere of gas giants of our solar system.^{52,81,82} However, conditions on gas giants are thermodynamically PH_3 favourable. But on rocky planets its presence is remarkable. While on gas giants it is produced in deep layers of the atmosphere, where conditions consist of very high temperatures and pressures, and then it is dragged by upward drafts,⁸³ bare conditions on rocky planets, on the other hand, are destroying PH_3 rapidly by oxidation by surface and atmosphere. On Earth, its detection is associated with bacterial presence or anthropogenic origin. While it is not considered to be the most obvious biosignature on planets with Earth-like atmospheres,⁸⁴ its detection on rocky planets bears high biosignature potential, even though its detection is rather hard, since its spectrum is highly absorbed by our atmosphere.

Sousa-Silva et al.⁸ evaluated the possibility of false positive due to abiotic production of phosphine. They concluded whether phosphine stability in the atmosphere and its detectability are sufficient to presume that under some conditions, phosphine can be detected and assumed to be a biosignature. Her conclusion was that false positives on phosphine are highly unlikely, since all known abiotic chemistry producing phosphine are not sufficient to produce observable concentrations.^{8,52}

Abiotic sources include the synthesis from phosphate – while this itself is indeed abiotic process, phosphate is also of biological origin, production due to lightning; that was experimentally deemed possible; however, its production is very small and localized. In terms of volcanism, PH_3 was not observed to be produced volcanically on Earth, however studies

suggesting this possibility under rare conditions have been published, and exogenous delivery including meteoric and comet delivery has been proposed; both not efficient enough.

PH₃ could face some problems in detection since its absorption bands are crossed over by Earth atmosphere, but if observations were conducted by JWST, all of three strong spectra features should be observed (2.7-3.6; 4-4.48; 7.8-11 μm).⁵² Another problem is its instability in UV, higher fluxes are needed to supply enough PH₃ to be detectable. Those vary based on star type, for example in case of M dwarf those fluxes should be $10^{12} - 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ depending on the position in Habitable Zone. In cases of some stars, activation of “run-away” processes should be also feasible.

If we compare phosphine to another important biosignature listed above in biosignature section, and consider CH₃Cl and PH₃ under the same atmospheric and star type conditions, we observe that fluxes needed for CH₃Cl are $5 \cdot 10^7 - 3 \cdot 10^{11} \text{ cm}^{-2}\text{s}^{-1}$, which is lower by 4 orders of magnitude than calculated fluxes for PH₃. This is due to high reactivity of PH₃ with radicals. Thus, supplying enough PH₃ to be detectable is more difficult than CH₃Cl.⁵² On Earth, biomasses in sewage plants produce fluxes of PH₃ to $10^{14} \text{ cm}^{-2}\text{s}^{-1}$; if similar anaerobic biomass was present on some known exoplanets with easily observable atmosphere, it is very likely it would be detected by PH₃ observation.⁵²

First possible detection of PH₃ on Venus took place in June 2017 with James Clerk Maxwell Telescope (JCMT).⁸⁵ The whole planet was covered by single point spectra and 1-0 rotational transition at 1.123 mm wavelength may have been seen. Spectra faced multiple problems:

The absorption line was detected in a quasi-continuum created by broad emission of deeper opaque atmosphere, and after fitting and subtracting signatures of reflected light, ripples of 8.16

periods across 250 MHz appeared. Another fitting of spectra was needed to smoothen out the ripples.

Spectra were binned to the velocity of 2.2 km/s, which is consistent with Venus's velocity, but it was not precisely characterized.

After all this manipulation with spectra was done, a spectral line with signal-noise ratio of 3-7 was gained. Due to the lack of actual velocity which should have been used to fit spectra, it was possible that the observed line was a residual artefact, or nearby transition line of other molecules that has shifted due to Doppler effect.

This observation was done with inconclusive results and second confirmation is needed. Spectra from Atacama Large Millimetre/Submillimetre Array (ALMA) were used (2019). Calibration on Callisto moon spectra was done, second check was done on HDO $2_{2,0} - 3_{1,3}$ line of 1.126mm was done also performed. Line was well fitted by a radiative transfer model – normal Venus water abundance was observed. PH₃ 1-0 line was observed again, the same problem with spectral ripple appeared on a bigger scale, but the PH₃ line was recovered anyway.

While PH₃ detection on Venus is quite unexpected and controversial, Graves J. et.al believe they have truly detected PH₃ based on the following arguments:⁸⁵ Absorption has been observed by both ALMA and JCMT. Different methods of processing were used on both measurements and results are still consistent. There have been no other candidates explaining the observed line well. Altitude in which PH₃ was observed must be higher than 53-61 km, which is where the continuum used to measure PH₃ line arises. But it could be formed in lower altitudes where pressure is higher and temperatures also (in comparison to 30°C and 0.5 bar presumed in the altitude where it was observed). Latitudes at which it was observed are mainly mid latitudes, it was also observed near equatorial, but on a much lower scale, it was not detected on poles; but

since manipulation was done to gain better signal, it is possible observed data do not actually fit real physical data.

PH₃ abundance was estimated from JCMT spectra since it had lower signal losses. Abundance was calculated to be 20-30 ppb.

3 Modelling part

3.1 ARGO 1D Lagrangian High Energy Chemistry/Diffusion Code for Planetary Atmospheres

ARGO 1D atmospheric model is a Lagrangian equation-based model. This model, as well as every atmospheric model, is based on a set of conservation principles that need to be satisfied for the model to work; these principles are represented by the states that cannot be changed when particles are entering and exiting an infinitesimal box, except for the upper and lower boundary conditions, where surface fluxes or atmospheric escape will provide a source or a sink of mass.

Those principles are conservation of mass, conservation of heat, conservation of motion, conservation of water - for this particular principal models need to take in account the changes of phase and the movement throughout the atmosphere, and finally the conservation of gaseous and aerosol materials, which are possible to be transformed one to the other within an atmospheric box.⁸⁶

In order to satisfy all the principles of conservation while integrating forward in time, the system that is able to solve a set of partial differential equations (PDE) in a vector form is needed.

This set can be summarized by Equation 5:

$$\frac{\partial \psi}{\partial t} + u \times \nabla \psi = R \quad (5)$$

Ψ is a vector consisting of state variables such as velocity, density, potential temperature, concentration of each species, u is the vector representing 2- or 3-dimensional velocity and R is the vector of forces and sources including eddy diffusion, Brownian movement and chemical production or destruction of species.

The system able to reduce and solve this PDE set is a Lagrangian framework, computing reduced PDE in the form of Equation 6:⁸⁷

$$\frac{\partial \psi}{\partial t} = R \quad (6)$$

ARGO solves previous equation using various inputs.⁸⁸

This simplification can be done in 1D framework once the vertical velocity flow is parametrised by eddy diffusion.

Various profiles of the atmosphere; those are experimentally measured in terms of Earth, Venus and Mars via atmospheric balloons and landers, or spectroscopically obtained and calculated in case of more remote atmospheres.

The important parameters are pT profile (dependence of pressure and temperature), density profile and vertical eddy diffusion K_{zz} [cm^2s^{-1}].

The atmospheric elemental abundances and initial chemical composition need to be introduced to the model, these can be obtained spectroscopically, or via various methods remotely, in situ or assumed from the first principals. Chemical composition is introduced with the information of ultraviolet photodissociation and photoionization cross sections of each species, so that photochemistry can be computed.

Boundary conditions at the top and the bottom of the model vertical domain need to be known or can be assumed.

Actinic flux at the top of the atmosphere, meaning that radiant flux through the unit sphere expressed as the integration of radiance over all angles is needed.

These inputs are measurable for atmospheres of many cases but can also be estimated from Eulerien models or assumed.

Final input needed to run the model is Chemical Network.

Chemical network used in this study was the STAND March 2021 network designed for general planetary atmosphere studies.⁸⁹ It is a H/C/N/O network, including reactions producing or destroying phosphine. Whole phosphorus chemistry is not included in STAND March 2021

network, implementing complete phosphorus chemistry into the model is the question of future research. STAND network however computes with all known reactions occurring in the atmospheres of various planets, from Earth-like planets to hot Jupiter planets, including species containing up to 6 hydrogen atoms, 2 carbon, 2 nitrogen and 3 oxygen, for which rate constants are well-known or estimated, since the reaction is too important to not be included in the network. More complicated chemistry is included in a less complete manner. Some of the reactions of phosphorus chemistry and N₂O chemistry introduced in the STAND network relevant to this study are summarized in the Table 7 on the next page:

Table 7: Destruction or production of phosphine and some of nitrous oxides. Constants characterizing the Kooij⁹⁰ form rate constants α , β and γ are tabled. Reactions are high indexed $a - g$ depending on the type of reaction, with a being low pressure thermal decomposition reaction, b being high pressure thermal decomposition reaction, c is neutral bimolecular reaction, d is the same neutral bimolecular reaction but in reverse direction and in high pressures, e is photochemical reaction, f is low pressure three body recombination reaction and g is high pressure three body recombination reaction. Low r index means reversed reaction. M species means third body. Units in third fourth and fifth column are: α in s^{-1} , $cm^3 s^{-1}$, or $cm^6 s^{-1}$ for 1-body, 2-body, and 3-body reactions. γ is in K . β is dimensionless.

	Reaction	α	β	γ
PH ₃ Production	PH ₂ + H $\rightarrow$ PH ₃ ^a _r	3.40×10^{-8}	0.00	3.56×10^4
	PH ₂ + H $\rightarrow$ PH ₃ ^b _r	1.91×10^{18}	0.00	4.01×10^4
	PH ₂ + H ₂ $\rightarrow$ PH ₃ + H ^c _r	7.22×10^{-11}	0.00	8.44×10^2
	PH ₂ + H ₂ $\rightarrow$ PH ₃ + H ^d	1.59×10^{-12}	0.00	0.00
	PH ₂ + HO $\rightarrow$ PH ₃ + O ^c _r	4.75×10^{-11}	0.00	0.00
	PH ₂ + HO $\rightarrow$ PH ₃ + O ^d	4.75×10^{-11}	0.00	0.00
	PH ₂ + H ₂ O $\rightarrow$ PH ₃ + HO ^c _r	1.61×10^{-11}	0.00	0.00
	PH ₂ + H ₂ O $\rightarrow$ PH ₃ + HO ^d	1.61×10^{-11}	0.00	0.00
	PH ₂ + HCl $\rightarrow$ PH ₃ + Cl ^c _r	2.40×10^{-11}	0.00	0.00
PH ₃ Destruction	PH ₃ $\rightarrow$ PH ₂ + H ^a	3.40×10^{-08}	0.00	3.56×10^4
	PH ₃ $\rightarrow$ PH ₂ + H ^b	1.91×10^{18}	0.00	4.01×10^4
	PH ₃ + H $\rightarrow$ PH ₂ + H ₂ ^c	7.22×10^{-11}	0.00	8.44×10^2
	PH ₃ + O $\rightarrow$ PH ₂ + HO ^c	4.75×10^{-11}	0.00	0.00
	PH ₃ + HO $\rightarrow$ PH ₂ + H ₂ O ^c	1.61×10^{-11}	0.00	0.00
	PH ₃ + Cl $\rightarrow$ PH ₂ + HCl ^c	2.40×10^{-10}	0.00	0.00
	PH ₃ $\rightarrow$ PH ₂ + H ^e	---	---	---

	Reaction	α	β	γ
N ₂ O Production	N ₂ + O (¹ D) + M → N ₂ O ^a	2.80×10^{-36}	-0.90	0.00
	N ₂ + O (¹ D) + M → N ₂ O ^b	6.76×10^{-17}	-1.90	0.00
	N ₂ + O → N ₂ O ^a _r	9.51×10^{-10}	0.00	2.90×10^4
	N ₂ + O → N ₂ O ^b _r	2.30×10^{-10}	-1.00	2.90×10^4
	N ₂ O → N ₂ O ⁺ + e ⁻ _r ^f	2.13×10^{-21}	-2.50	0.00
	N ₂ O → N ₂ O ⁺ + e ⁻ _r ^g	5.14×10^{-2}	-3.50	0.00
	O + HN ₂ → N ₂ O + H ^c	5.27×10^{-11}	-0.40	0.00
	NO + HN → N ₂ O + H ^c	1.07×10^{-12}	0.75	0.00
	N + NO ₂ → N ₂ O + O _r ^c	5.80×10^{-12}	0.00	0.00
	CN + NO ₂ → N ₂ O + CO ^c	7.11×10^{-12}	0.00	0.00
N ₂ O Destruction	N ₂ O → N ₂ + O ^a	9.51×10^{-10}	0.00	2.90×10^4
	N ₂ O → N ₂ + O ^b	2.30×10^{10}	-1.00	2.90×10^4
	N ₂ O → N ₂ + O (¹ D) ^b _r	6.76×10^{-17}	-1.90	0.00
	N ₂ O ⁺ + e ⁻ → N ₂ O ^g	5.14×10^{-02}	-3.50	0.00
	N ₂ O + H → HO + NO ^c _r	1.60×10^{-10}	0.00	7.60×10^3
	N ₂ O + N → N ₂ + NO ^c	1.50×10^{-11}	0.00	5.09×10^2
	O + N ₂ O → 2 NO ^c	1.52×10^{-10}	0.00	1.40×10^4
	O + N ₂ O → N ₂ + O ₂ ^c	6.13×10^{-12}	0.00	8.02×10^3
	CH + N ₂ O → HCN + NO ^c	7.82×10^{-11}	0.00	0.00
	CH + N ₂ O → CO + N ₂ + H ^c	3.09×10^{-11}	0.00	0.00
	CN + N ₂ O → NCO + N ₂ ^c	2.01×10^{-12}	0.00	0.00
	CN + N ₂ O → CNN + NO ^c	1.73×10^{-14}	2.60	1.86×10^3
	N ₂ O + CO → CO ₂ + N ₂ ^c	5.30×10^{-13}	0.00	1.02×10^4

As presented above, STAND network is basically a list of chemical reactions, the rate constants and the constants α , β and γ , that can be used to extrapolate rate constants for low pressure k_0 , high pressure k_∞ (Equations 7 and 8) and their linear combinations for any pressure in between.⁸⁸

$$k_0 = \alpha_0 \left(\frac{T}{300K} \right)^{\beta_0} e^{-\gamma_0/T} \quad (7)$$

$$k_\infty = \alpha_\infty \left(\frac{T}{300K} \right)^{\beta_\infty} e^{-\gamma_\infty/T} \quad (8)$$

T is a gas phase temperature, α , β and γ are constants characteristic to each reaction.

These have been obtained from multiple databases such as NIST Chemical Kinetics Database, Ikezoe et al. Gas phase ion - molecule reaction rate constants database, Sander et. al Chemical Kinetics and photokinetic Data for use in atmospheric studies, the KIDA database and OSU chemical network database and other.

The STAND chemical network includes various types of reactions.

Two body neutral reactions described by the general reaction $A + B \rightarrow C + D$. The two body reactions are included in STAND as a reversed reaction. Reaction rates are temperature dependant as follows:

$$k_2 = \alpha \left(\frac{T}{300K} \right)^{\beta} e^{-\frac{\gamma}{T}} \quad (9)$$

Using the same constants as described in reactions above (Equations 7 and 8).

Ion neutral reactions expressed by $A^+ + B \rightarrow C^+ + D$ (or in case of charge exchange reactions $A^+ + B \rightarrow A + B^+$) are mostly temperature independent with the exception of charge exchange reactions. Reversed reactions are also included in STAND.

Three body neutral reactions described as $A + B + M \rightarrow AB + M$ or in case of three body dissociation $AB + M \rightarrow A + B + M$ are temperature and pressure dependent; their reaction rate can however be reduced to two body reaction rate via Equation (10):

$$k_2 = \frac{k_\infty p_r}{1+p_r} \quad (10)$$

k_∞ is a reaction rate in a high pressure calculated via Equation (8) p_r is a reduced pressure related to the third body number density $[M]$ $[\text{cm}^{-3}]$ via Equation (11):

$$p_r = \frac{k_0[M]}{k_\infty} \quad (11)$$

Thermal decomposition is the majority of three body dissociations reactions. These are very well studied in high temperature, we however lack the knowledge of their behaviour in lower temperature, rates of dissociative reactions in low temperatures are calculated as a reverse three body neutral reactions.

Radiative associations $A + B \rightarrow C + \gamma$ are reactions characteristic by irradiation of photons after recombination of the reactants. Reaction rate can again be modified into two body reactions by multiplication of dimensionless transitional function, which better approximates the transitions between high and low pressures.

Photodissociation reactions are represented not by reaction rates, instead cross sections σ_i of each photo dissociative reaction are implemented into ARGO. These were obtained using the PHIDRATES database and have a unit of $[\text{cm}^2]$ and are a function of wavelength λ $[\text{nm}]$ (for calculations of kinetics of these reactions the model ranges from 0.1 nm to 1000 nm).

Kinetics of the reaction are calculated via integration (Equation 12) of cross section combined with actinic flux $F(\lambda, z)$ $[\text{photon cm}^{-2}\text{s}^{-1}\text{nm}^{-1}]$ over wavelength ranging from 0.1 nm to 1000 nm:

$$k_{ph,i}(z) = \tau_f \int_{0.1\text{nm}}^{1000\text{nm}} \sigma_i F(\lambda, z) d\lambda \quad (12)$$

z is the altitude in terms of cm. τ_f is a fraction of time for which the atmosphere is irradiated, represented by a dimensionless factor.

Cross sections relevant to this study are depicted in: Figure 10 - PH_3 ; cross section and Figure 11 - N_2O photodissociation into $\text{N}_2(^1\Sigma) + \text{O}(^1\text{S})$ and N_2O photodissociation into $\text{N}_2(^1\Sigma) + \text{O}(^1\text{D})$.

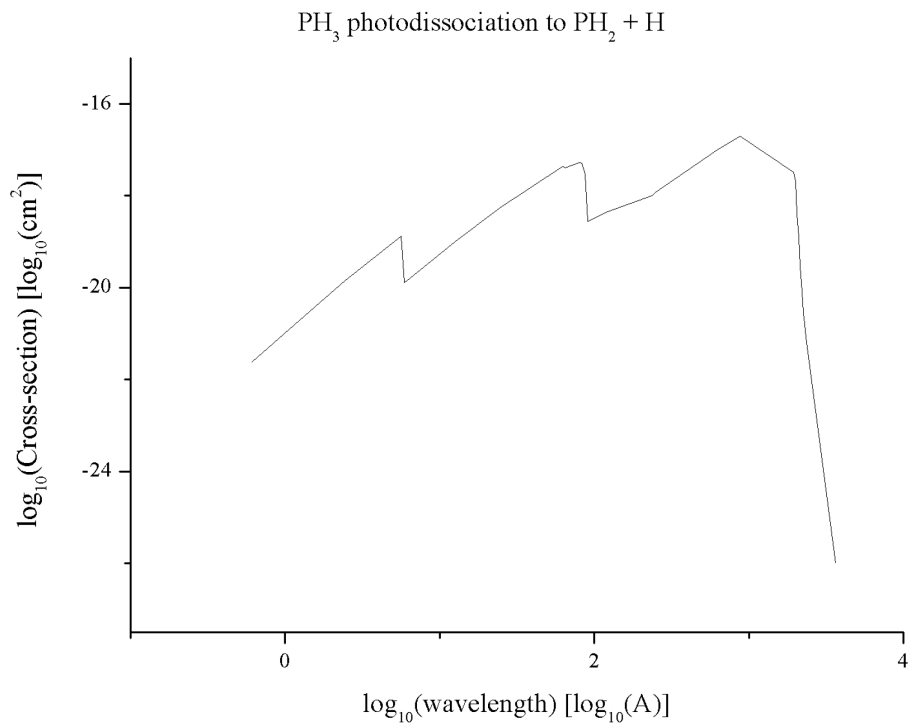


Figure 10: Cross section of PH_3 , obtained from the PHIDRATES database.

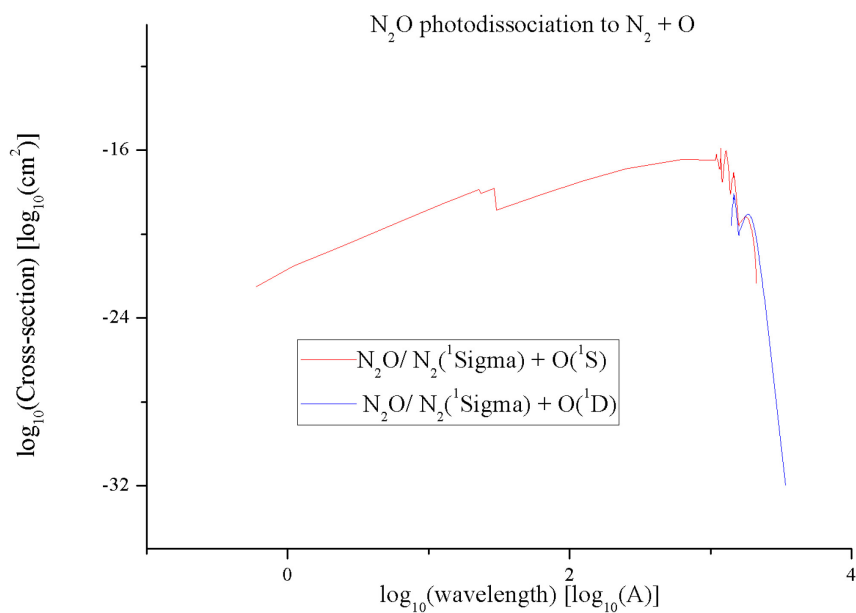


Figure 11: Cross section of N_2O photodissociation into $\text{N}_2(^1\Sigma) + \text{O}(^1\text{S})$ and N_2O photodissociation into $\text{N}_2(^1\Sigma) + \text{O}(^1\text{D})$.

STAND March 2021 also includes various thermal ionisation reactions, recombination reactions and cosmic-ray chemistry, for further information on these see Rimmer Helling 2016.⁸⁸

Using these inputs, as described above, ARGO solves the continuity Lagrange Equations. In case of 1D model, the continuity equation from the Equation 5 can be described for each species by as follows:

$$\frac{\partial n_i}{\partial t} = P_i - L_i - \frac{\partial \phi_i}{\partial z} \quad (13)$$

Where n_i is a number density of each species [cm^{-3}] and P_i and L_i are production and destruction rates of each species. These can be calculated knowing n_i as well as n_j , n_k or $[M]$; density numbers of all species taking place in production or destruction of a species i depending on the order of the reaction and kinetic constants, calculated by Kooij manner (Equations 7 and 8) from STAND chemical network input: (Equations 14 and 15):

$$P_i = S_i + \sum k_1 n_j + \sum k_2 n_j n_k + \sum K_3 [M] n_j n_k \quad (14)$$

$$L_i = \sum k_1 n_i + \sum K_2 n_j n_i + \sum k_3 [M] n_j n_k \quad (15)$$

$\frac{\partial \phi_i}{\partial z}$ is a derivation of a change of flux with height; ϕ_i is a combination of K_{ZZ} and D – eddy diffusion and Brown movement.

To solve this set of equations, the simplification of Equation 13 in the Alam and Lin manner (Equation 4)⁸⁷ is needed, resulting in Equation 16:

$$\frac{\partial n_i}{\partial t} = - \frac{\partial \phi_i}{\partial z} \quad (16)$$

This represents the eddy diffusion movement of an infinitesimal cube in the direction up into the atmosphere; when the boundary conditions of p and T profiles are met (top of the modelled atmosphere), eddy diffusion takes the cube down in the atmosphere. In case of the Venus's

atmosphere modelled here the model vertical grid is 1 km in range of 0-60 km, then 2 km in range of 60-100 km, then one step was of magnitude of 5 km until the maximal altitude of 115 was reached. The movement of the infinitesimal cube was tracked and the differential diffusion of molecules of species i $\frac{\partial n_{i,j}}{\partial t}$ into and out of the cube j , including the source terms such as production and destruction, was then tracked using the formula first used by Hu et al. (Equation 17):⁹¹

$$\frac{\partial n_{i,j}}{\partial t} = P_{i,j} - L_{i,j} - d_{j+1/2} \frac{n_{g,j+1/2}}{n_{g,j+1}} n_{i,j+1} + \left(-d_{j+1/2} \frac{n_{g,j+1/2}}{n_{g,j}} + d_{j-1/2} \frac{n_{g,j-1/2}}{n_{g,j}} \right) n_{i,j} + d_{j-1/2} \frac{n_{g,j-1/2}}{n_{g,j-1}} n_{i,j-1} \quad (17)$$

The $P_{i,j}$ is the production rate as calculated by equation X using reaction rates corresponding to the pressure, temperature, and insolence of the right altitude z . $L_{i,j}$ is the corresponding destruction rate from equation Y. Index j therefore represents the cube we are currently interested in, index $j-1$ is the cube placed below it. Index $j+1$ is the cube placed above. Index $j + \frac{1}{2}$ is the average of the cube j and $j+1$ and $j - \frac{1}{2}$ is analogically the mean of j and $j-1$.

$-d_{j+1/2} \frac{n_{g,j+1/2}}{n_{g,j+1}} n_{i,j+1}$ represents loss of particles due to the diffusion into box $j+1$ above currently calculated infinitesimal cube j . $+ \left(-d_{j+1/2} \frac{n_{g,j+1/2}}{n_{g,j}} + d_{j-1/2} \frac{n_{g,j-1/2}}{n_{g,j}} \right) n_{i,j}$ stands for molecules re-entering their original cubes. $+ d_{j-1/2} \frac{n_{g,j-1/2}}{n_{g,j-1}} n_{i,j-1}$ is the term representing molecules entering cube j from the cube below it $j-1$.

Equation 17 is solved using NAHOON public code written in Fortran 77 and DLSODES double precision solver used to solve coupled stiff differential equations.⁹²

This sort of evolvment of the atmosphere is run repeatedly, until one set of the movement of the cube up the atmosphere sets the same values as the run of the cube down to the atmosphere

within 0.1% error of convergence. The following scheme (Figure 12) represents the flow chart of 1D Photochemistry / Diffusion code.

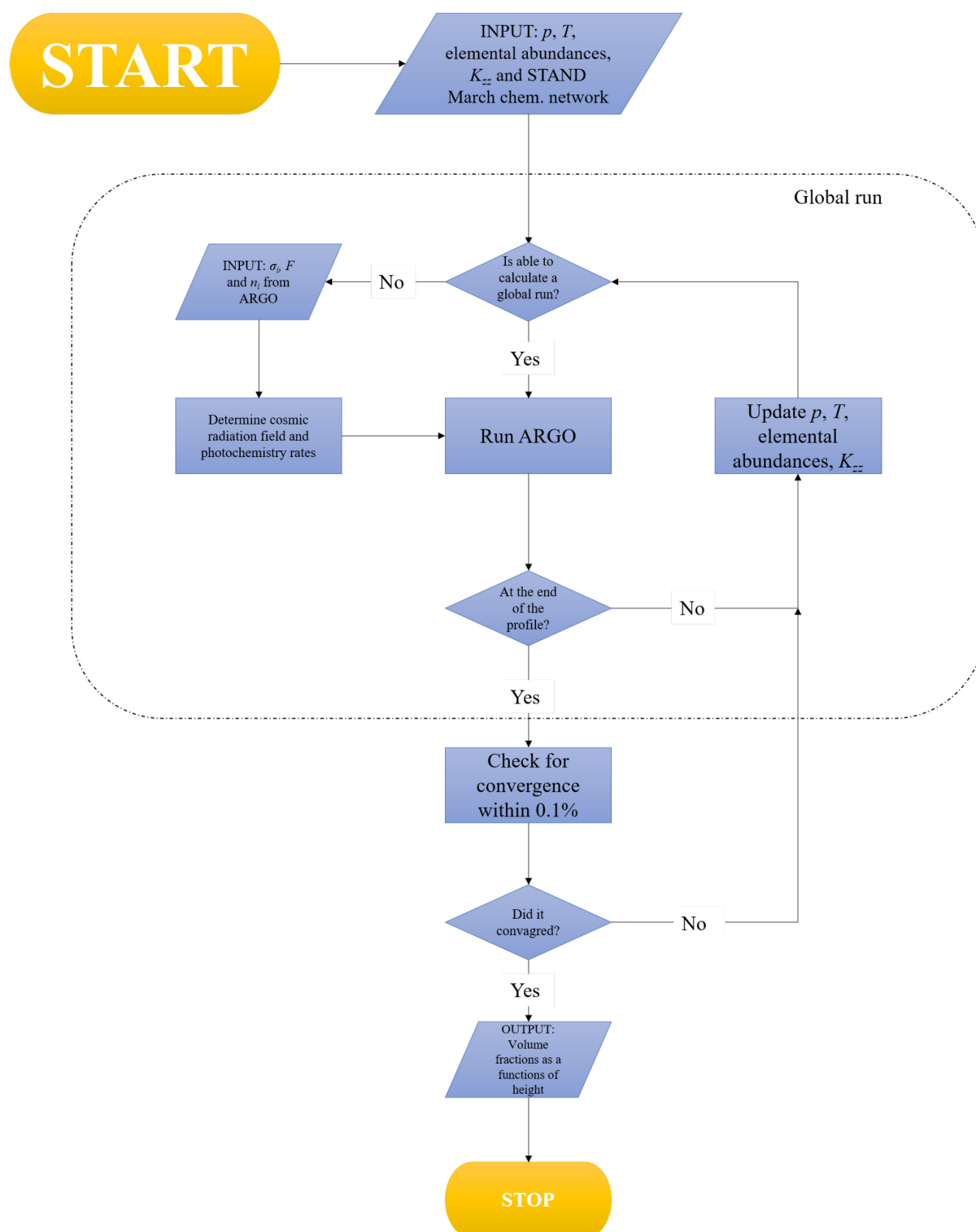


Figure 12: Flow chart of the program. Modified from Rimmer and Helling 2016.⁸⁸

The advantages of Lagrangian models are the higher stability, lower diffusion and dispersion errors and twice as fast computational time in comparison to Eulerian models. They are also 20 times faster to compute than semi-Lagrangian models and can solve both dynamical and tracer equations simultaneously.⁸⁷

3.2 Photocatalytic reduction of phosphorus oxides to phosphine

For evaluation of acid hydrogen enhanced photocatalytic reduction of phosphorus oxides to phosphine, the modelling was based on previously tested synthesis of methane from carbon dioxide over acidic minerals. The methane photocatalytic production described by Knížek et al.^{13,14} was observed in the experiment performed as described below:

Reactivity of mixtures of 0.5 g of solid catalyst, 6 Torr of HCl vapours and 6 Torr of CO₂ were studied on 18 finely grained minerals: Al₂O₃, kaolinite, MgO, CaCO₃, TiO₂, montmorillonite, natural clay, natural rutile, basalt, clay with montmorillonite, ilmenite, clay with kaolinite. Part of the cuvette made from quartz was filled with finely grained mineral and left in 155°C and 10⁻³ Torrs for two days so the mineral was degassed and dried after the end of this two days period. Cuvette was evacuated and connected to the reservoir cooled by liquid nitrogen filled with 37% aqueous solution of HCl. After HCl melted, its vapours filled the cuvette. Vapour pressure of the HCl at this temperature was 6 Torr. Before the cuvette was finally sealed, 6 Torr of CO₂ were added. Sealed cuvette was irradiated via the quartz part of the cuvette by UV using 160 W Hg broad lamp with maximum absorbance wavelength of 350 nm for 3500 h. The IR spectra of the gas mixture were measured during certain moments of irradiation using the borosilicate part of the cuvette.

Knížek et al. measured changing concentrations of CO₂ and CH₄ in time to calculate the first order kinetics rates. Conversion from CO₂ to CH₄ has been observed in many cases depending on the type of catalyst used in the mixture. Highest achieved kinetics was achieved in the case

of ilmenite; kinetic constant of production of CH_4 was $(5.0 \pm 19.6) \times 10^{-3} \text{ h}^{-1}$. This order of magnitude of production kinetics was achieved multiple times.¹³ We presume that this mechanism could work generally as photocatalysis of production of hydrides from oxides of a range of species, therefore we assume also PH_3 production is possible in upper atmosphere over dust upon UV radiation from P_4O_6 existing in here in a gas phase. For further estimations of PH_3 production effectivity in this study, we adopted *ad hoc* experimental rate constant of P_4O_6 to PH_3 reaction $k = 5.0 \times 10^{-3} \text{ h}^{-1}$ similar to the reaction estimated previously for analogical process of CO_2 to CH_4 reaction.

3.2.1 Model conditions

To evaluate efficiency of H^+ enhanced photocatalytic production of phosphine, we need to determine stability of phosphine in Venus's atmosphere; the mixing ratios and reaction rates producing and destroying PH_3 at any altitude needed to be known. For this reason, ARGO has been run as described in the previous chapter. Input files have been modified to best copy the conditions on Venus. Density profile is shown in Figure 13:

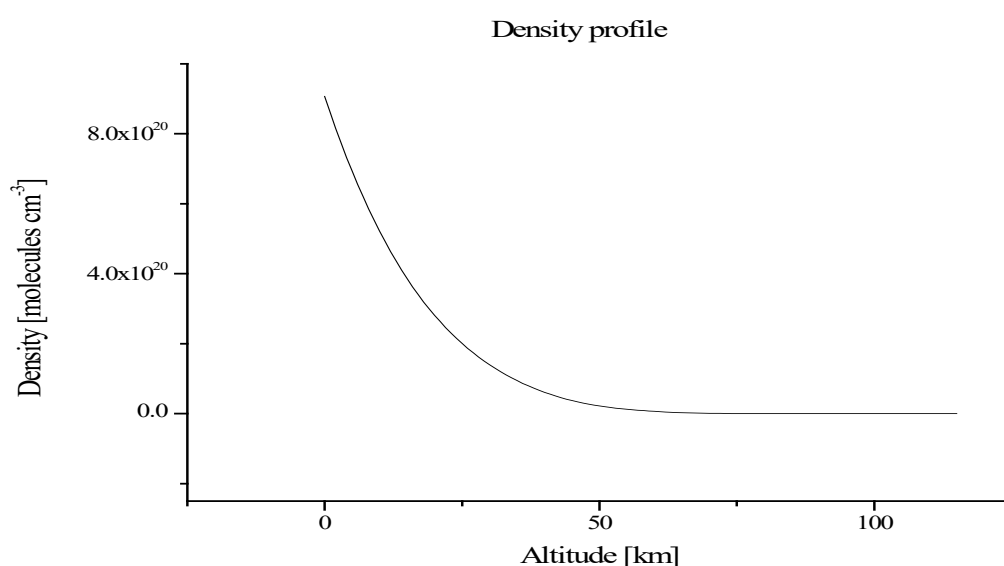


Figure 13: Density profile of Venus atmosphere.

Temperature and pressure profile implemented into ARGO is shown in Figure 14:

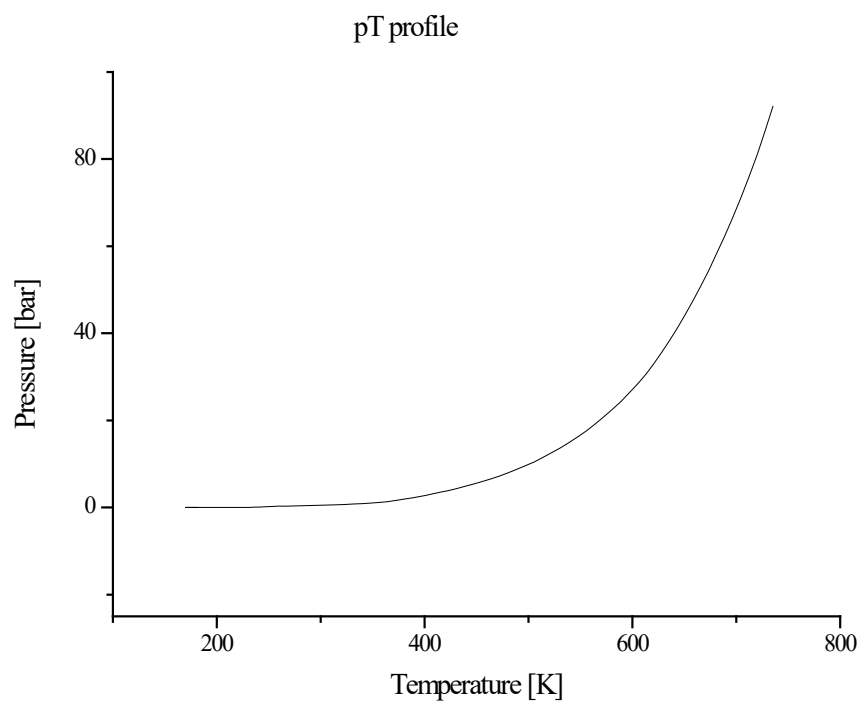


Figure 14: pT profile adopted for Venus by the model presented in this study.

The vertical profile of the assumed model eddy-diffusion coefficient is shown in Figure 15:

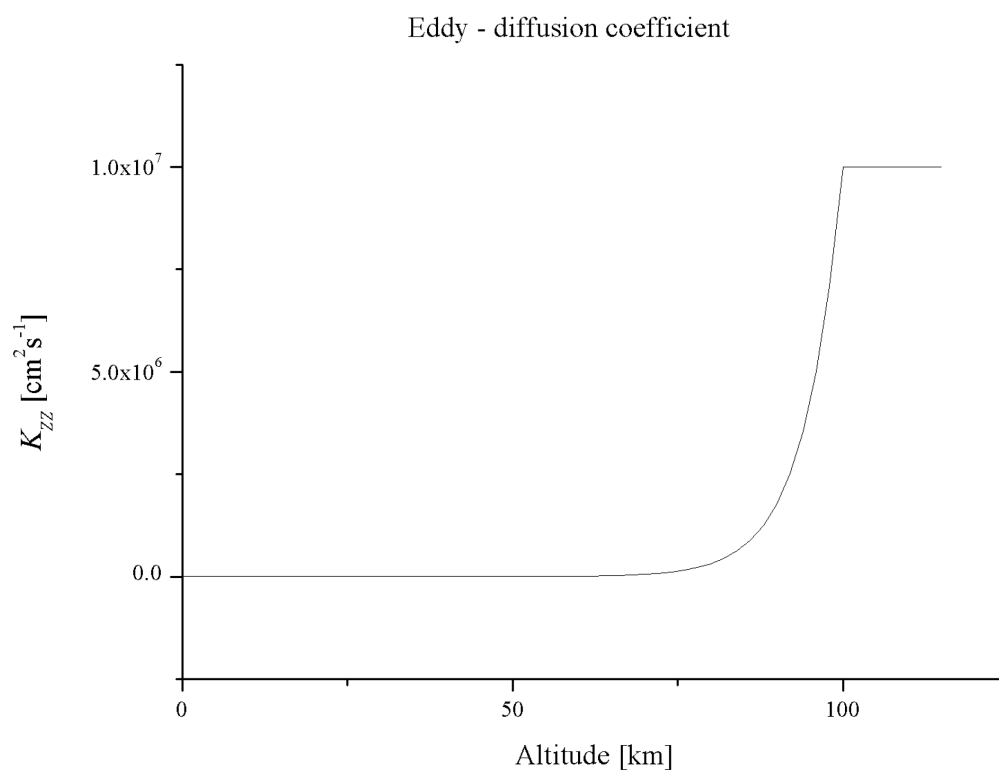


Figure 15: Eddy diffusion as a function of height.

Elemental abundances were set to zero, except for those species summarized in Table 8:

Table 8: Species implemented into ARGO and their mixing ratios at the surface. Compare with Table 6.

Species	Mixing ratio
CO ₂	0.96
N ₂	0.3
SO ₂	1.5×10^{-4}
H ₂ O	3×10^{-5}
CO	2×10^{-5}
OCS	5×10^{-6}
HCl	5×10^{-7}
NO	5.5×10^{-9}
H ₂	3×10^{-9}
PH ₃	2×10^{-8}
H ₂ S	1×10^{-9}

Using these inputs and some of the other inputs from the previous chapter the program calculated Volume fractions as a function of altitude.

3.3 N₂O steady state model

In my previous work, I have introduced the experiment focused on laser-based simulation of the asteroid atmospheric entry and impact to N₂O production on Early Earth and planets with Earth-like atmospheres undergoing the age of heavy bombardment. Mixtures simulating Early Earth atmosphere or atmospheres possible on terrestrial planets in the Habitable Zone, containing liquid phase presumed to be present on the surface of planet in Habitable Zone and in some cases catalyst in the form of minerals present on the terrestrial planets have been irradiated multiple time by 500 J per shot terawatt laser. The results of laser induced dielectric breakdown have been measured spectroscopically and quantified.

Production in terms of molecules per Joule have ranged variously from 8×10^{14} to 5.5×10^{16} molecules J⁻¹. Models simulating destruction of N₂O to determine its destruction rates and producing the stable state concentrations of N₂O throughout the atmosphere and its mixing ratios and density profiles have been run on atmospheres with N₂/CO₂ mixing ratio of 0.8/0.2. The results of experimental mixtures simulating these ratios are summarized in Table 9:

Table 9: Summary of the N_2O production in experiments using 600 Torr of N_2 and 150 Torr of CO_2 as a main component of the experimental mixture. Added composition and yield of molecules per joule are included.

Added composition	χ [molecules J^{-1}]
600 Torr of N_2 and 150 Torr of CO_2	2.1×10^{15}
HCN (<i>l</i>)	5.5×10^{16}
H_2O (<i>l</i>)	3×10^{14}
H_2O (<i>l</i>); Clay (<i>s</i>)	9×10^{14}
HCl (<i>l</i>); Montmorillonite (<i>s</i>)	5.8×10^{15}
HCl (<i>l</i>); A200 (<i>s</i>)	3×10^{15}
H_2SO_4 (<i>l</i>); A200 (<i>s</i>); Clay (<i>s</i>)	6×10^{15}
H_2SO_4 (<i>l</i>); A200 (<i>s</i>)	3×10^{14}
A200 (<i>s</i>)	2×10^{15}

Average yield of molecules produced by one Joule of energy is 8×10^{15} molecules J^{-1} .

Production rate in terms of surface flux was previously calculated in the bachelor thesis of the author of this study and will be again published in a paper submitted to JGR: Planets (see attached submitted revision of the paper). The energy fluxes of LHB were used in calculating the surface flux via Equation 18:

$$\Phi = \frac{\chi E_T}{4\pi R^2} \quad (18)$$

Surface flux multiplied by lifetime τ of the N_2O is equal to column density (Equation 19).

$$d_{c,i} = \phi \times \tau \quad (19)$$

Lifetime τ can be calculated via Equation 20:

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots + \frac{1}{\tau_n} \quad (20)$$

τ is total lifetime, τ_i is lifetime of the same molecule destroyed only by the reaction i . Using comparison of column density of N_2O and overall column density we are able to obtain a mixing ratio of N_2O .

$$c = \frac{d_{c,i}}{d_c} \quad (21)$$

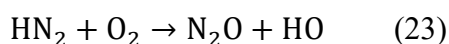
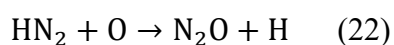
3.3.1 Modelling of Early Earth atmosphere

To calculate stable concentrations of N_2O produced by our mechanism we need to know destruction and production rates of N_2O .

Calculation was performed using conditions expected to be similar to Early Earth.

STAND March 2021 contains a complete nitrogen atmospheric chemistry. Table 7 in the modelling section presents only a few selected nitrous oxide producing or destroying reactions. Proper description of the nitrogen network itself would be the topic of a very excessive study worthy of a dissertation project. For the sake of this study, only a few main reactions dominating the destruction rate on N_2O are important.

The reactions most significantly attributing to destruction or production of N_2O are following (Equations 22-30):



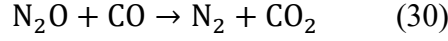
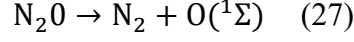
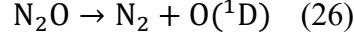
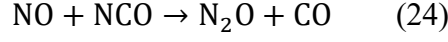


Table of various inputs dependence on height is presented below (Table 10):

Table 10: Density, pressure, temperature, and eddy diffusion dependence on height

Height [Km]	Density [cm^{-3}]	Pressure [Bar]	Temperature [K]	Eddy diffusion K_{zz} [$\text{cm}^2 \text{s}^{-1}$]
0	4.95×10^{08}	1.04×10^0	272.1	1.00×10^{05}
2	5.17×10^{08}	8.05×10^{-01}	263.6	1.00×10^{05}
4	5.90×10^{08}	6.17×10^{-01}	249.6	1.00×10^{05}
6	6.74×10^{08}	4.66×10^{-01}	234.8	1.00×10^{05}
8	2.28×10^{09}	3.45×10^{-01}	222.6	1.00×10^{05}
10	3.17×10^{09}	2.53×10^{-01}	214.9	8.10×10^{04}
12	3.98×10^{09}	1.84×10^{-01}	212.4	1.80×10^{04}
14	4.75×10^{09}	1.33×10^{-01}	212.4	5.80×10^{03}
16	5.70×10^{09}	9.67×10^{-02}	211.5	3.90×10^{03}
18	6.45×10^{09}	7.00×10^{-02}	209.1	3.90×10^{03}
20	7.33×10^{09}	5.05×10^{-02}	206.7	4.50×10^{03}
22	8.36×10^{09}	3.63×10^{-02}	205.8	5.80×10^{03}
24	1.71×10^{10}	2.61×10^{-02}	206.3	7.40×10^{03}
26	1.85×10^{10}	1.88×10^{-02}	208.4	9.50×10^{03}
28	2.82×10^{10}	1.36×10^{-02}	211.7	1.20×10^{04}
30	4.08×10^{10}	9.94×10^{-03}	216.5	1.40×10^{04}
32	5.00×10^{10}	7.30×10^{-03}	222.7	1.80×10^{04}
34	5.55×10^{10}	5.41×10^{-03}	229.9	2.10×10^{04}
36	6.94×10^{10}	4.05×10^{-03}	237.3	2.60×10^{04}
38	8.82×10^{10}	3.06×10^{-03}	244.4	3.20×10^{04}
40	1.00×10^{11}	2.33×10^{-03}	250.7	4.00×10^{04}
42	1.14×10^{11}	1.79×10^{-03}	255.9	5.10×10^{04}
44	1.32×10^{11}	1.38×10^{-03}	259.5	6.10×10^{04}
46	3.81×10^{11}	1.06×10^{-03}	260.9	7.50×10^{04}

Table 10 continuation

48	9.15×10^{11}	8.20×10^{-04}	260.2	9.20×10^{04}
50	1.28×10^{12}	6.32×10^{-04}	257.9	1.12×10^{05}
52	1.80×10^{12}	4.86×10^{-04}	254.6	1.12×10^{05}
54	2.56×10^{12}	3.73×10^{-04}	250.9	1.12×10^{05}
56	3.67×10^{12}	2.85×10^{-04}	247.2	1.12×10^{05}
58	5.29×10^{12}	2.16×10^{-04}	243.7	1.12×10^{05}
60	7.65×10^{12}	1.64×10^{-04}	240.6	1.12×10^{05}
62	1.11×10^{13}	1.24×10^{-04}	237.7	1.12×10^{05}
64	1.59×10^{13}	9.33×10^{-05}	235.0	1.12×10^{05}
66	2.28×10^{13}	7.01×10^{-05}	232.7	1.12×10^{05}
68	3.23×10^{13}	5.25×10^{-05}	230.6	1.12×10^{05}
70	4.55×10^{13}	3.92×10^{-05}	228.7	1.12×10^{05}
72	6.36×10^{13}	2.92×10^{-05}	227.1	1.12×10^{05}
74	8.80×10^{13}	2.18×10^{-05}	225.3	1.12×10^{05}
76	1.21×10^{14}	1.62×10^{-05}	222.3	1.12×10^{05}
78	1.64×10^{14}	1.19×10^{-05}	218.4	1.12×10^{05}
80	2.21×10^{14}	8.77×10^{-06}	213.9	1.12×10^{05}
82	2.97×10^{14}	6.39×10^{-06}	209.1	2.00×10^{05}
84	3.96×10^{14}	4.63×10^{-06}	204.4	4.00×10^{05}
86	5.27×10^{14}	3.33×10^{-06}	199.8	6.00×10^{05}
88	7.00×10^{14}	2.38×10^{-06}	195.7	8.00×10^{05}
90	9.32×10^{14}	1.69×10^{-06}	192.1	1.00×10^{06}
92	1.24×10^{15}	1.19×10^{-06}	189.3	1.20×10^{06}
94	1.65×10^{15}	8.37×10^{-07}	187.4	1.40×10^{06}
96	2.18×10^{15}	5.87×10^{-07}	186.7	1.60×10^{06}
98	2.88×10^{15}	4.12×10^{-07}	187.5	1.80×10^{06}
100	3.78×10^{15}	2.90×10^{-07}	190.3	2.00×10^{06}

The elemental abundances at the surface inputted into the model were corresponding with the Table 11:

Table 11: Elemental abundances of species inputted into model of Early Earth atmosphere.

Species	Mixing ratio
N ₂	0.80
CO ₂	0.20
H ₂ O	0.01
H ₂	0.001
CO	10 ⁻⁵
CH ₄	2 × 10 ⁻⁶
N ₂ O	2 × 10 ⁻⁷
CH ₄ O ₂	2 × 10 ⁻⁹
CH ₂ O	10 ⁻⁹
HCN	2 × 10 ⁻¹⁰
HNO ₃	10 ⁻¹⁰
NO ₂	6 × 10 ⁻¹¹
CH ₃ O ₂	1.45 × 10 ⁻¹¹
HO ₂	10 ⁻¹³
HO	10 ⁻¹⁴

We note that Table 11 displays the N₂O concentration of 200 ppb; this is an anticipation of the equilibrium N₂O abundance produced by our mechanism.

4. Results

4.1 Photocatalytic reduction of phosphorus oxide to phosphine.

Mixing ratios calculated by ARGO of selected species are depicted in Figure 16. These species were selected in order to verify the result of calculated mixing ratios with previously calculated by Rimmer in Bains et. al.⁷

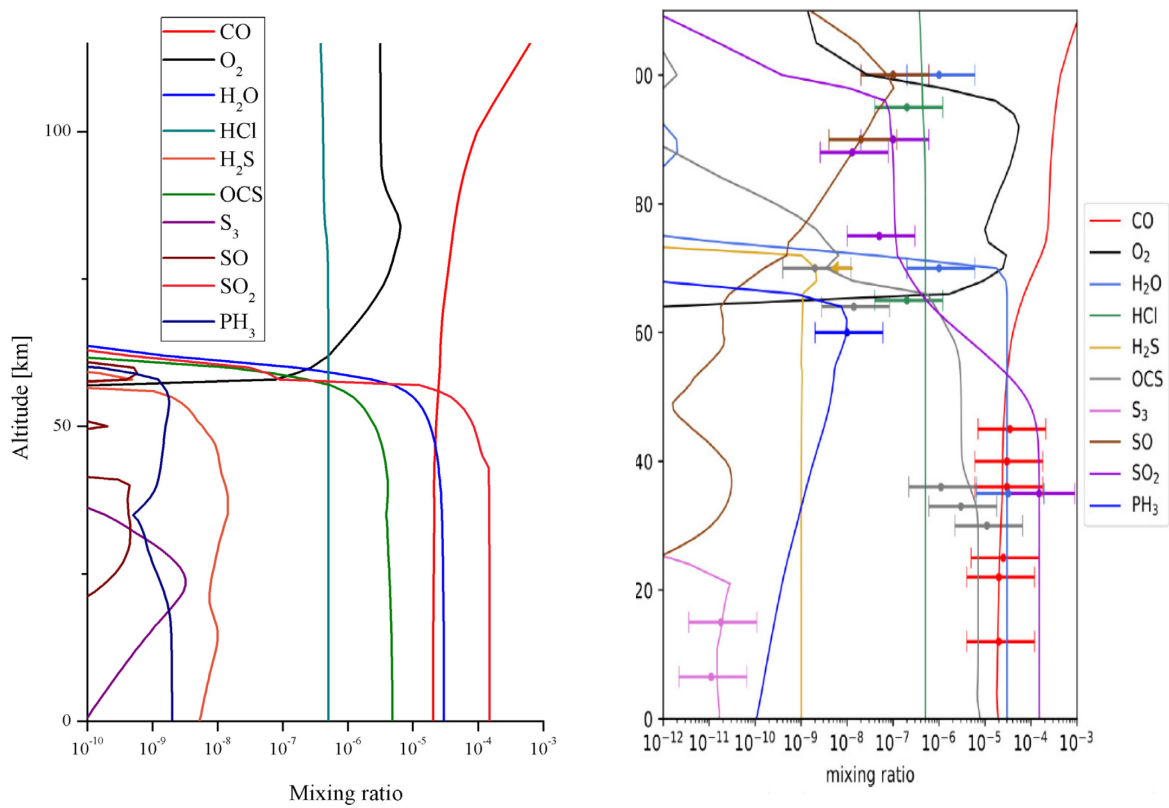


Figure 16: Mixing ratio of some of the species of Venus's atmosphere; the right panel was calculated by Rimmer in Bains et. al (2020), the left panel are results of ARGO with the STAND 2021 network.

The observable difference in the results may be due to slightly variable initial conditions and the fact that the chemical network used in this study was slightly different. PH_3 abundance seems to be in reasonable agreement. The mixing ratios of species relevant to the PH_3 production or destruction are as follows (Figure 17 on the next page):

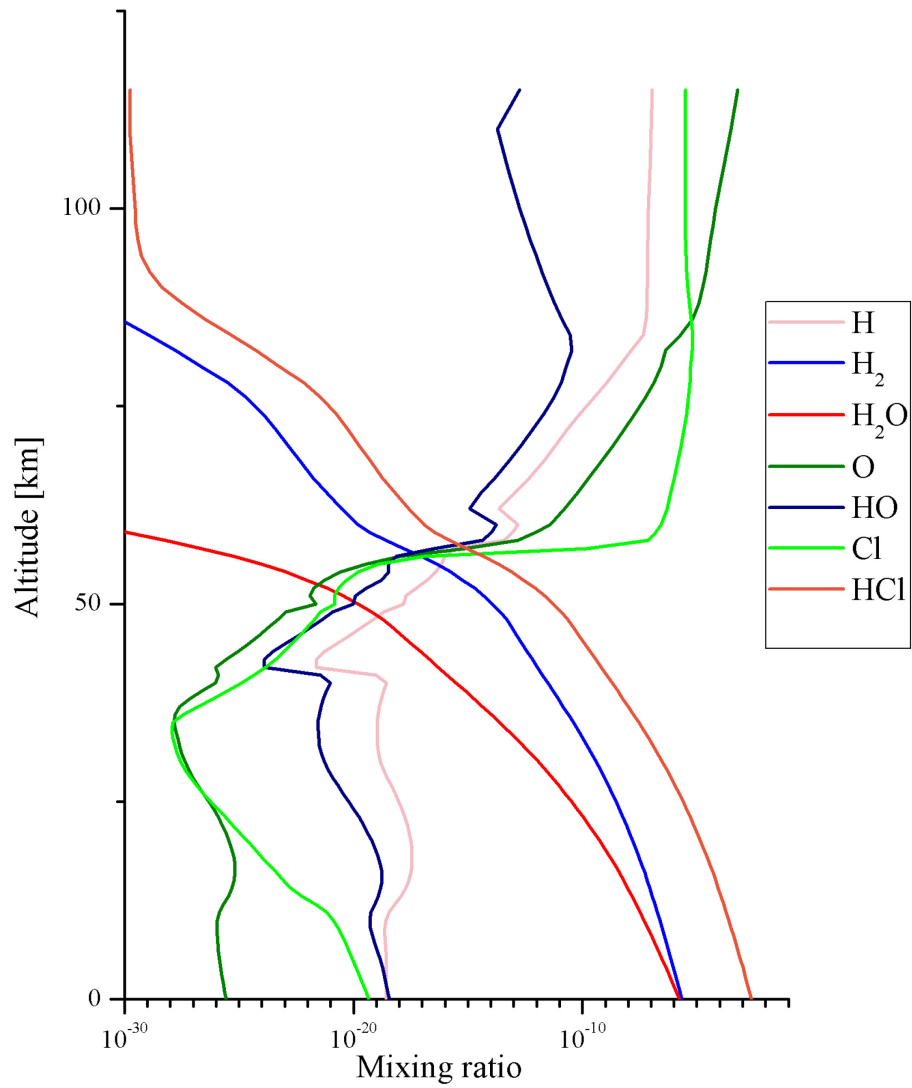
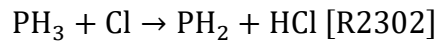
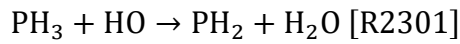
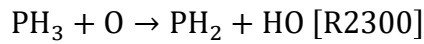
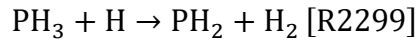
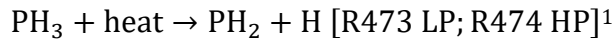
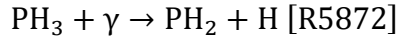


Figure 17: Mixing ratio of species playing role in PH_3 production or destruction. As the figure presents, lines that have red to orange and yellow colour are representing mixing ratios of species playing a role in production. Blue lines are mixing ratios of second species in two body reactions leading to both destruction and production of PH_3 and green lines are representing species whose reactions lead only to destruction.

The program also provides reaction rates of each reaction for each altitude. Reactions relevant for destruction are following; the number corresponding to the reaction in Tables in the appendix can be found in the brackets at the end of each equation:



γ stands for a photon. Table of reaction rates of each reaction can be found in the appendix as well as the Table of mixing ratios.

One body reaction rate k_1 (R5872, R473, R474) are expressed in $[\text{s}^{-1}]$, two body reaction rates k_2 (R2299, R2300, R2301, R2302) in $[\text{cm}^3 \text{ s}^{-1}]$. Calculation of destruction rate is performed using Equation 31:

$$L_i = \sum (k_1 [\text{s}^{-1}] \times d_{\text{PH}_3} [\text{cm}^{-3}]) + \sum (k_2 [\text{cm}^3 \times \text{s}^{-1}] \times d_j [\text{cm}^{-3}] d_{\text{PH}_3} [\text{cm}^{-3}]). \text{ (31)}$$

Unit density d $[\text{cm}^{-3}]$ of each species must have been calculated in order to solve the previous equation correctly. Gas density D of Venus atmosphere was however one of the inputs involved into the program, unit density d_i expressed by Equation 32:

$$d_i = D \times x_i \text{ (32)}$$

¹ LP – low pressure; HP – high pressure

x_i is the mixing ratio of given species. Unit density of species playing a role in destruction of PH_3 are listed in the Table A1 in appendix. For this calculation, mixing ratio of phosphine corresponded to 20 ppb in any altitude of the atmosphere.

Every variable in Equation 31 has been plotted in the following graphs for one body reactions, two body reaction and finally for their summation (Figures 18, 19). Plots are on a logarithmic scale.

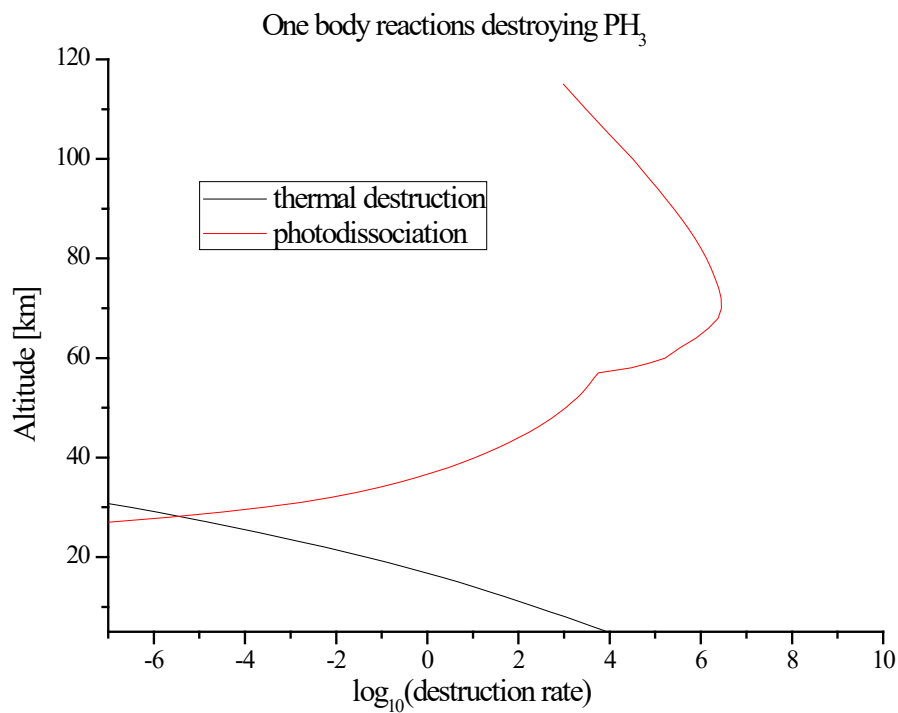


Figure 18: Destruction rates of photodissociation (R5872) and thermal decomposition (R473 + R474); destruction rates are in units of $\text{s}^{-1} \text{cm}^{-3}$.

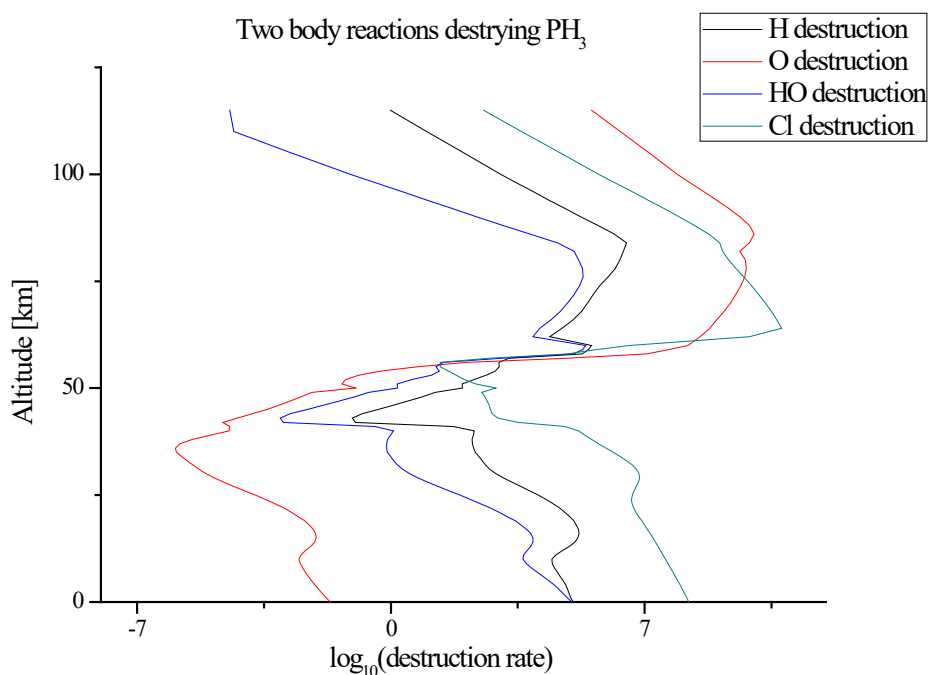


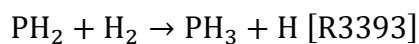
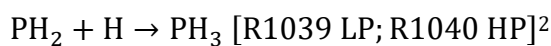
Figure 19: Destruction rates of two body reactions with H (R2299), O (R2300), HO (R2301), Cl (R2302); destruction rates are in units of $s^{-1} cm^{-3}$.

Total destruction rate will be presented later, where the comparison to our production rate and other known abiotic pathways producing PH_3 are compared.

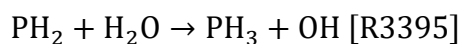
Table of destruction rates is presented in the appendix.

4.1.1 Abiotic production (excluding our mechanism):

Reactions producing PH_3 are summarized below (again with the corresponding reaction name in STAND file):



² LP – low pressure; HP – high pressure



Reaction rates of these reactions are in the appendix.

In order to calculate production rates of PH_3 , the concentrations of PH_2 must be known. However, the network producing PH_2 from other P species is not thermodynamically known and would require further deep experimental investigation. Even so, less accurate calculation of PH_3 production rate by abiotic processes (excluding our mechanism) is possible; the kinetic network leading to PH_2 and PH_3 production is not known in the same terms as rest of the STAND chemical network – in the Kooij manner, but the ratio of forward and destruction reactions are well known, therefore simple kinetic network using effective constants with the correct ratios can be constructed.

The ARGO 1D Lagrangian High Energy Chemistry/Diffusion Code for Planet Atmospheres computes also with diffusion. Since the ratio of the speed of those reactions and diffusion are not known, the fake reaction rates for these reactions are set relatively high, so the model can iterate faster to steady state mixing ratios of said species without destruction of steady states by diffusion. The calculated atmospheric profiles will be favouring lower altitudes. The Diffusion part of ARGO can be later run separately once the mixing ratios of P species are known.

The network in question is expressed on Figure 20:⁷

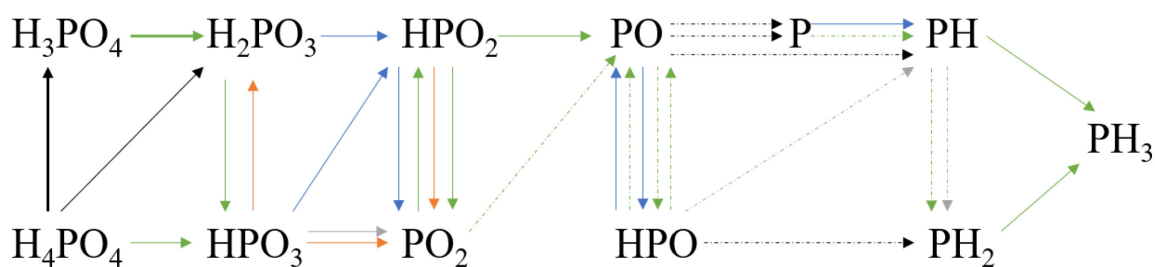


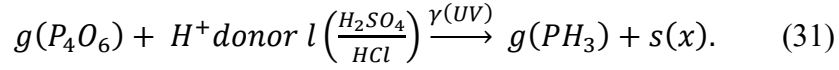
Figure 20: Chemical network of P leading to production of PH_3 . The dotted lines are unknown, and their ratio of forward rate and destruction rate was estimated by N species analogue. Each colour of the line representing a reaction represents the ratio of forward and destruction reaction: green lines are 10^3 , blue 10^{-2} , orange 10^{-4} , grey are 10^{-7} and black are 10^{-9} .

The network on Figure 20 is biased towards production of phosphine, since no oxidation reactions are included, even though they are highly probable. Depending on altitude, the main species of P may change, but generally one may say the dominant species is H_3PO_4 . From the Figure 20, it should be obvious that the indirect production of phosphine from H_3PO_4 is not favourable since there is no pathway with a limiting step ratio higher than one.

Using this kinetic network rates, stable state concentration of PH_2 was calculated. Then the production rate of PH_3 was calculated analogically to the destruction rate. Comparison of both abiotic production and destruction rates is in Figure 22 alongside with the theoretical production rate of our proposed mechanism.

4.1.2 Comparison to our production rate

As presented in Figure 22, reactions producing the PH_3 implemented in the STAND network are not sufficient to result in stable concentrations of 20 ppb. However, we can include the mechanism producing PH_3 from P_4O_6 via reaction in Equation 31:



To calculate the efficiency of this mechanism the pseudo-first order reaction was used, since the P_4O_6 will be the rate controlling agent. The supply of the other reactants will not change in time due to the effect of this reaction. Following equation (32) was used to calculate the production rate:

$$P_i = d_{P_4O_6} \times k. \quad (32)$$

The density of P_4O_6 was previously calculated by Krasnopolsky. The profile of density of P_4O_6 throughout the atmosphere is depicted in the following Figure (21):

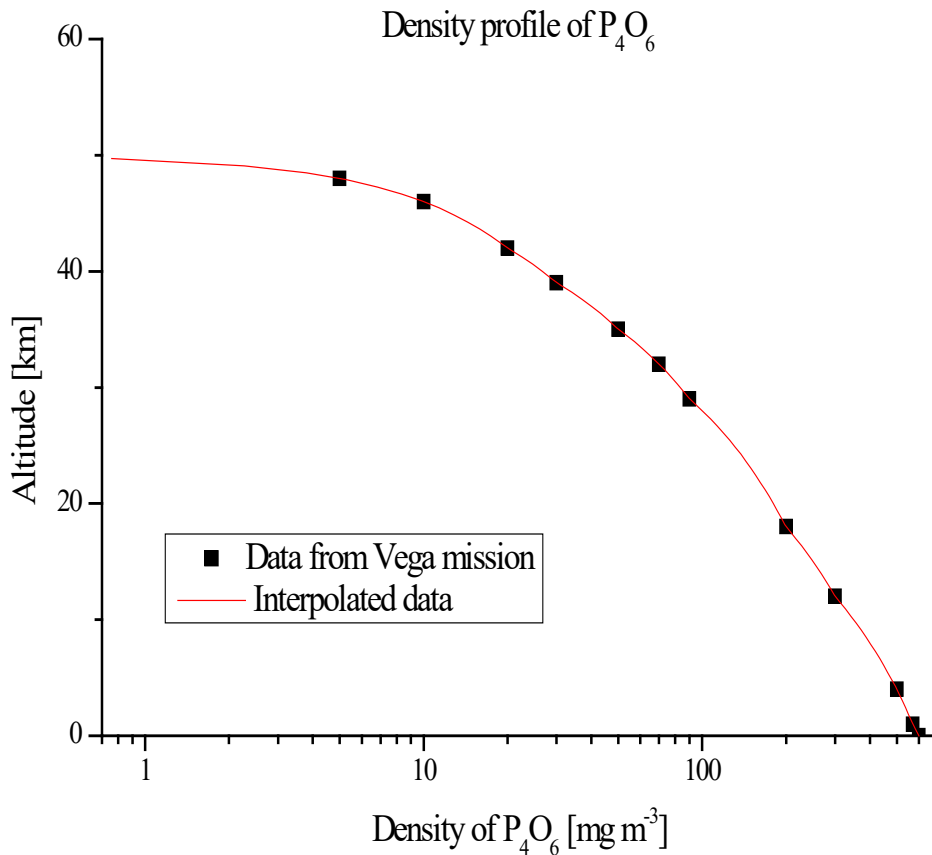


Figure 21: The density profile of P_4O_6 , blue dots are data read from the graph in Figure 9,⁷⁹ dotted line are fitted data.

The density profile was recalculated to the units corresponding to ARGO units as so

(Equation 33):

$$\frac{d_k N_A}{1000 \times M} 10^{-6} \quad (33)$$

Where d_k is a density profile as presented by Krasnopolsky, N_A is a Avogadro's number, M is a molar mass of $P_4O_6 = 219.88$ g/mol.

The gained density profile is presented in Table 12.

Table 12: Densities of P_4O_6 and their dependence on altitude.

h [km]	density [molecules/cm ³]	h [km]	density [molecules/cm ³]
0	0	26	0.000026
1	0.000001	27	0.000027
2	0.000002	28	0.000028
3	0.000003	29	0.000029
4	0.000004	30	0.00003
5	0.000005	31	0.000031
6	0.000006	32	0.000032
7	0.000007	33	0.000033
8	0.000008	34	0.000034
9	0.000009	35	0.000035
10	0.00001	36	0.000036
11	0.000011	37	0.000037
12	0.000012	38	0.000038
13	0.000013	39	0.000039
14	0.000014	40	0.00004
15	0.000015	41	0.000041
16	0.000016	42	0.000042
17	0.000017	43	0.000043
18	0.000018	44	0.000044
19	0.000019	45	0.000045
20	0.00002	46	0.000046
21	0.000021	47	0.000047
22	0.000022	48	0.000048
23	0.000023	49	0.000049
24	0.000024	50	0.00005
25	0.000025		

This profile was then multiplied by Knížek reaction rate, to obtain following production rate¹³

(Table 13):

Table 13: Dependence on production rates of phosphine by our mechanism and altitude. Production rate is in units of $s^{-1} cm^{-3}$.

h [km]	Production rate	h [km]	Production rate	h [km]	Production rate	h [km]	Production rate	h [km]	Production rate
0	1.46×10^{11}	10	8.88×10^{10}	20	4.63×10^{10}	30	1.83×10^{10}	40	4.80×10^9
1	1.40×10^{11}	11	8.39×10^{10}	21	4.28×10^{10}	31	1.63×10^{10}	41	4.25×10^9
2	1.33×10^{11}	12	7.91×10^{10}	22	3.95×10^{10}	32	1.44×10^{10}	42	3.85×10^9
3	1.27×10^{11}	13	7.45×10^{10}	23	3.64×10^{10}	33	1.27×10^{10}	43	3.59×10^9
4	1.21×10^{11}	14	7.01×10^{10}	24	3.33×10^{10}	34	1.12×10^{10}	44	3.47×10^9
5	1.16×10^{11}	15	6.57×10^{10}	25	3.05×10^{10}	35	9.73×10^9	45	3.51×10^9
6	1.10×10^{11}	16	6.16×10^{10}	26	2.77×10^{10}	36	8.45×10^9	46	2.21×10^9
7	1.04×10^{11}	17	5.75×10^{10}	27	2.52×10^{10}	37	7.32×10^9	47	1.48×10^9
8	9.91×10^{10}	18	5.36×10^{10}	28	2.27×10^{10}	38	6.34×10^9	48	1.23×10^9
9	9.39×10^{10}	19	4.99×10^{10}	29	2.04×10^{10}	39	5.50×10^9	49	6.15×10^8

Following production rate was added to graph of production and destruction of PH_3 :

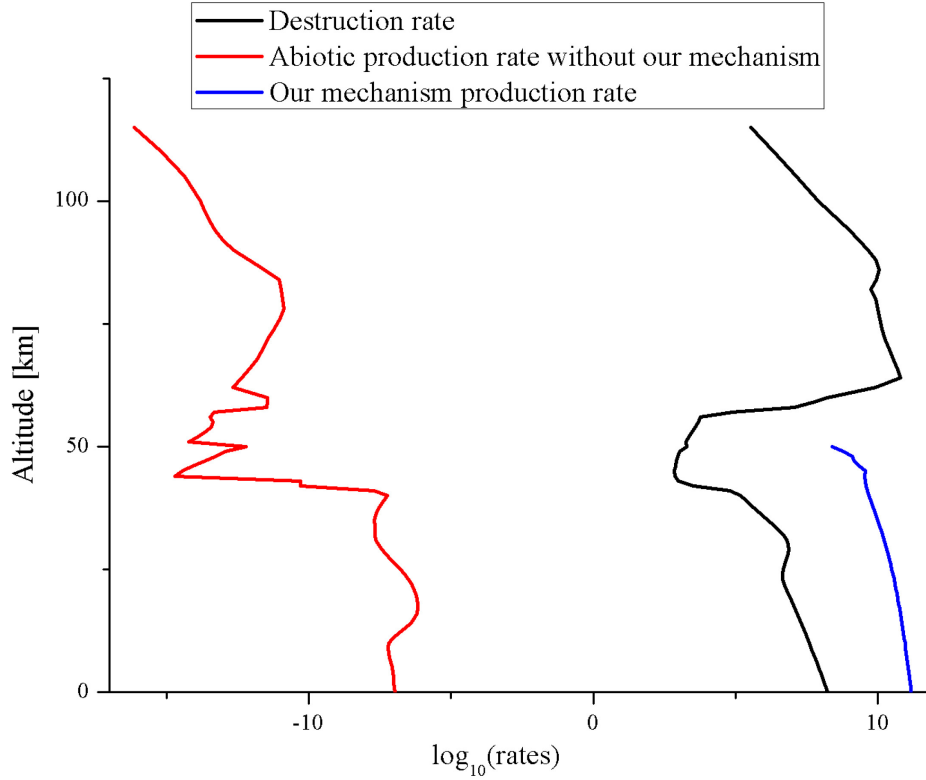


Figure 22: Comparison of production rates; orange line is the production needed to sustain 20 ppb in any part of the atmosphere, grey line represents production rates as calculated by ARGO, blue dotted line is production if we include our mechanism, green line is the production solely by our mechanism. Rates are in units of $s^{-1} cm^{-3}$.

Presuming that PH_3 photocatalytic production is indeed of the same effectiveness as methane production, this mechanism significantly overproduces observed concentrations of PH_3 .

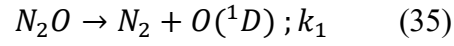
Using the equation for stable state of PH_3 (Equation 34)

$$P_i - L_i = 0 \quad (34)$$

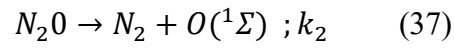
and Equation 31 for destruction rate, we obtain the stable state concentration of PH_3 between altitudes 0-50 km was calculated as 9 ppm.

4.2 N₂O stable state model:

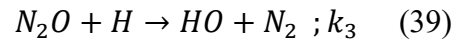
Using results of ARGO, the lifetimes of N₂O destroyed only by the dominant reactions (35, 37, 39, 41, 43) can be calculated accordingly (Equations 36, 38, 40, 42, 44):



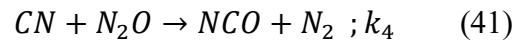
$$\tau_1 = \frac{1}{k_1} \quad (36)$$



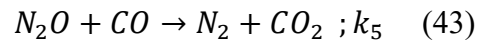
$$\tau_2 = \frac{1}{k_2} \quad (38)$$



$$\tau_3 = \frac{1}{k_3[H]} \quad (40)$$



$$\tau_4 = \frac{1}{k_4[CN]} \quad (42)$$



$$\tau_5 = \frac{1}{k_5[CO_2]} \quad (44)$$

Calculated dependence of the lifetimes to the altitude is depicted in Figure 23:

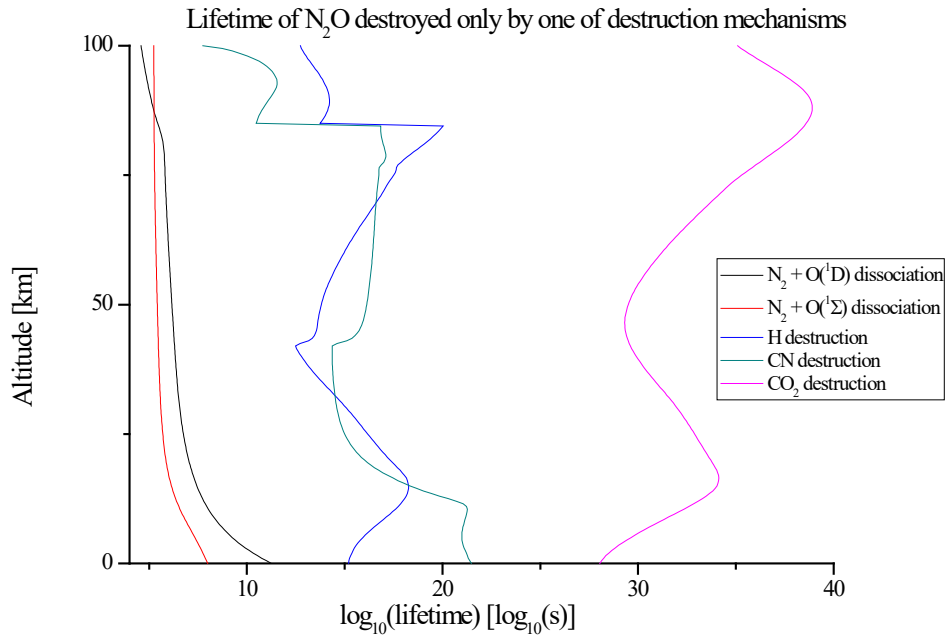


Figure 23: Lifetime of N_2O , if it was destroyed by only one of the strongest reactions. This Figure features 5 strongest destruction reactions.

Total lifetime calculated like so $\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots + \frac{1}{\tau_n}$, is introduced in the next Figure (24):

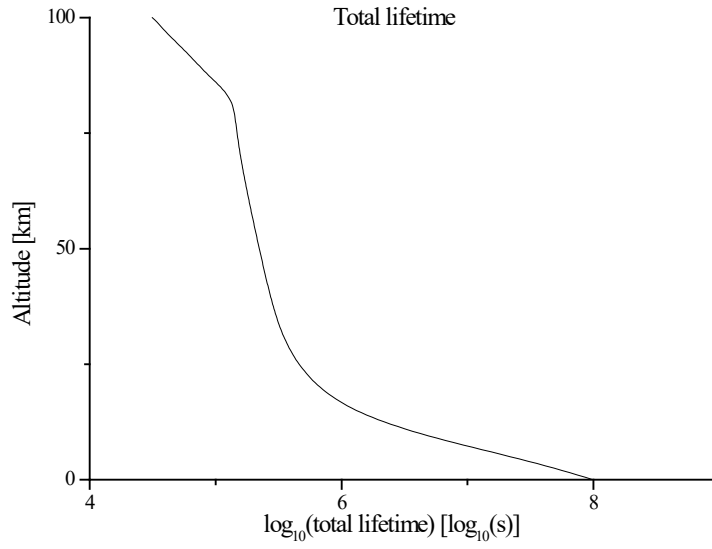


Figure 24: Total lifetime of N_2O .

Surface flux is calculated via Equation 18:

$$\Phi = \frac{\chi \dot{E}_T}{4\pi R^2} \quad (18)$$

χ being the energy yield in [molecules $Joule^{-1}$]. $\dot{E}_T$ is energy deposition rate of LHB meteoric activity - for this calculation $1.3 \times 10^{13} J s^{-1}$ was used.²⁷ And R^2 represents the radius of a planet – in this case Earth.

Using the value for N_2O yield 8×10^{15} molecules J^{-1} the surface flux is calculated to be $2 \times 10^{10} molecules cm^{-2} s^{-1}$.

The Equation 18 uses surface flux which cannot be properly compared to total lifetime as a function. For this reason, simple estimation supplementing average lifetime τ_M for the total lifetime function must be made. Following calculation need to be carried out (45).

$$\frac{1}{\tau_M} = \frac{\int \frac{1}{\tau} \times d}{\int d} \quad (45)$$

Equation 19 and 45 can be carried out to obtain the mixing ratio of 230 ppb.

5. Discussion

Two new sources of phosphine and nitrous oxide are proposed based on my calculations. Their effect on the atmosphere of Venus and Early Earth is modelled. Significance of this result shall be further discussed in the terms of detectability. Furthermore, our result is compared to other proposed possible sources of phosphine on Venus, and N_2O on Earth-like planets. Question of life on Venus is also discussed. Both production of N_2O and PH_3 are compared with the mass of the biomass able to produce the same concentrations of both biosignature gases. The parallel between C and P in terms of presented reaction will be discussed further.

5.1 Detectability

Ariel space telescope detection limit varies from 10 – 100 ppm for most common exoplanetary atmospheric constituents (mostly H_2O , NO , HCN , NH_3 , CH_4 , CO , AlO , TiO , O_2 , Na , K , FeO , Fe , Mg , MgO , VO , MgH , TiH , FeH , HF , H_2S , SO_2 , NaH , HCl , HBr , KCl , PH_3 , C_2H_2 , C_2H_4 , C_2H_6). In the case of PH_3 , the production by our new abiotic mechanism just reaches the lower detection limit. Of course, the mixing ratio estimated in this study is theoretical, based on similarity of PH_3 synthesis from P_4O_6 *via* reaction exhibiting rate constant estimated for CH_4 origin from CO_2 , i.e. on its “carbon” parallel. Modelling was done for a planet with Venus-like conditions, which is a rather hostile environment for significant PH_3 build up. Possibly, the planet with less oxidizing conditions would yield better mixing ratios of phosphine, which would allow easier detection. Lastly, better evaluation of C-P parallel in the question of photocatalytic H^+ enhanced reduction of oxides to hydrides is needed. The production of N_2O via asteroid impact is not productive enough to yield in significant amounts of N_2O detectable by Ariel; the possibility of better detection limits is in the distant future. In systems undergoing a more cataclysmic scenario than LHB in Earth’s history, N_2O concentrations could build up to the higher levels, however the energy yield from the heavy bombardment would need to be 45 times higher than it has been expected for Early Earth. N_2O may however not be observable

even when produced by biological denitrification processes, which seems to be the main source of N_2O in Earth atmosphere, excluding anthropogenic sources, yet the present atmospheric level of N_2O is 319 ppb.⁹³ N_2O production is only an intermediate in the denitrification pathway and even though N_2O is created by denitrifying bacteria, big part of it is later destroyed by the same biomass.⁹⁴

5.2 Could discovery of PH_3 mean life on Venus?

Propositions suggesting that life could be present in cloud layers on Venus have been made by Morowitz and Sagan in 1967⁹⁵ and the again at the end of last century by Grinspoon,⁹⁶ Cockwell⁹⁷ and the others. The cloud layers at the altitude of 48 – 50 km ($T = 60^\circ\text{C}$, $p = 1$ bar.) could possibly bear conditions similar to environment in which some type of extremophiles live on Earth. Furthermore, UV flux is comparable to the one on Earth during the time of Archean (Photosynthesis organisms present),⁹⁸ water is present in 40-200 ppm, depending on latitude. While this supply of water is low, it could be concentrated in sulphuric acid droplets, where the water supply could be locally sufficient. The clouds are CO_2 dominated, sulphur acid enriched and containing iron.

Thus, life on Venus would probably use phototropic reduction of CO_2 to gain energy. Both phosphorus ($\text{P}_2\text{O}_5 + \text{H}_3\text{PO}_4$) and sulphur are in great supply in Venus clouds, which is convenient for Earth-like forms of life. On the other hand, pH is considered to be 1.5 – 0.5 bar in the altitude of 48-65 km, but some eukaryotes living on Earth are known to grow under pH of less than 1. Bacteria and Archaea are known to live under corresponding conditions, some of which even produce sulphuric acid as a metabolite using Fe^{3+} as an electron acceptor.¹⁶

This iron-sulphur-based metabolism would bring better clarity to the sulphur cycle on Venus.

On Earth there is no evidence suggesting that airborne microorganisms stay afloat, they all descend back to surface.¹⁶ If we believe this mechanism applies for Venus, to contra surface to

clouds transportation is needed, since the surface of Venus is inhabitable. Very strong updraft had been observed by Vega mission balloons. If microorganism actually lived in clouds of Venus, it would explain the fluctuations in albedo and opacity of cloud layers.¹⁶

5.3 Comparison to biomass

Amato et al (2007) suggested that considering the particle sizes in clouds of Venus the possible biomass in lower clouds could be around $44 \text{ mg} \times \text{m}^{-3}$. This number is consistent with upper biomass value for terrestrial biological aerosols.⁹⁹ However, later studies suggest upper limit of Venusian biomass to be lower.¹⁰⁰ If Venus did really contain living organisms, they would be hard to detect by a spectroscopic measurement, since their spectral signatures could be very close or overlapping with bulk planetary spectra of Venus.

Considering recent revival of discussion about possibility of life on Venus, Izenberg et al. used Drake equation in order to estimate probability of life on Venus; they obtained $\approx 10\%$ probability.¹⁰¹

Further evaluation of feasibility of life on Venus was performed also by M. Lingam and A. Loeb, who came up with the conclusion that biomass producing 20 ppb of PH_3 would have to weight $M_{\text{biomass}} \approx 4 \times 10^7 \text{ kg}$ and exhibit a density of $\rho_{\text{biomass}} \approx 10^{-4} \text{ mg m}^{-3}$.¹⁰⁰

Since the mixing ratio of N_2O in Earth's atmosphere was 319 ppb in 2005 and part of its production is due to human activity, the biomass producing 230 ppb would be less than 72% of today's denitrifying biomass.

To evaluate the biomass using N_2O from metabolism and therefore destroying fluxes of N_2O comparable with our experimental and modelling data, Figure 3 from paper by Qi-Wu Hu et al.⁹⁴ where the dependence on N_2O fluxes and density of biomass (dry weight) was used. The linear dependence of N_2O destruction to biomass is according to Qi-Wu Hu (Equation 46):

$$\rho = \frac{51.52 - \phi}{0.0073} \quad (46)$$

ρ is biomass density [$\text{g}_{\text{d.w.}} \text{m}^{-2}$] and ϕ is the flux of N_2O [$\mu\text{g m}^{-2} \text{h}^{-1}$]. Calculated flux of N_2O created during cataclysmic events comparable to LHB on early planets was 2×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$. Biomass needed to eat up 230 ppb has the density of 7057 $\text{g}_{\text{d.w.}} \text{m}^{-2}$.

5.4 Other possible sources of phosphine in Venus atmosphere

Before considering the biological possibility of PH_3 origin, we must consider numerous other sources. There must be a source of phosphorus in the atmosphere, surface or subsurface, or it must be delivered by interplanetary matter like meteorites.

Dieter Wolf and Herbert Palme¹⁰² have been determining the composition of various meteorites, using XRF method with error in order of units of ppm. First analysis of Allende meteorite showed consistency with previously written literature on chondrite meteorite composition.

Results are summarized in Table 14:

*Table 14: minerals contained in the chondrite meteorite and their weight percentage as measured by Wolf and Palme and comparison to other literature.*¹⁰²

Species	Average weight percentage	Literature obtained weight percentage
SiO_2	34.67	34.28
FeO	30.20	30.32
MgO	24.49	24.59
CaO	2.62	2.58
Al_2O_3	3.24	3.28
Cr_2O_3	0.512	0.53
P_2O_5	0.24	0.24
MnO	0.19	0.19
TiO_2	0.15	0.15

The experiment was carried out on other chondrites. Abundance of phosphorus varied from 760-1080 ppm. Phosphorus is mainly in the form of phosphorus oxide, production of PH_3 may be possible even on the surface of meteorites flying through down the atmosphere. However, production occurring only on the surface of meteorites is not sufficient.

Phosphorus has also been detected by Vega balloons.⁷⁹ Since the conditions on Venus are oxidizing, it is no surprise Vega balloons discovered only oxides of phosphorus and hydrated phosphorus oxides. Even if we consider rather extreme conditions such as temperatures of 1500 K and pressure of 10 000 bar, the formation of PH_3 from P_xO_y is just not favoured in levels to achieve equilibrium according to thermodynamic calculations conducted by Greaves et al. (2020).¹⁷

As calculated above, flux of PH_3 would have to be $10^6 - 10^7$ molecules $\text{cm}^{-2} \text{s}^{-1}$.

Thermolysis of H_3PO_3 is a possible pathway to PH_3 , but in Venusian conditions, hydration of P_xO_y leads to H_3PO_4 . The pathway from H_3PO_4 has been evaluated in this study and also by Bains, in both cases this pathway was several orders of magnitude inefficient.⁷

Photochemical reactions are also out of option to produce such a high flux of PH_3 molecules since the atmosphere consists mainly of O and OH radicals. As discussed above, on terrestrial rocky planets which are usually surrounded by secondary atmosphere or have no atmosphere at all, the pressure of hydrogen is very low - for instance 0.55 ppm on Earth, 4 ppb on Venus.⁷

Energetic events such as lightning and impacts are also not sufficient.⁷

As comets are one of the primary sources of carbon and prebiotic chemistry on Early Earth, comets should be also considered as a possible source for phosphine on Venus. Phosphine has been observed on Hale-Bopp comet, its abundance being 0.13% of the abundance of water. It has not been detected on any other comets than Hale-Bopp (to date of 2005) but that is a case of many other significant prebiotic molecules that are believed to be dragged to Earth by

comets. Comet composition is believed to be universal, even though the gas/dust ratio varies, this is a very simple first approximation, with growing ability to perform spectroscopy more precisely more information on that matter shall be gained.¹⁰³

5.5 N₂O other abiotic productions

N₂O has many other abiotic productions. We are however able to foresee them model their effects on the atmospheres very well. Those abiotic productions of N₂O were previously discussed in Section 2 of this study, furthermore, brief summery on some of the N₂O production was presented also in bachelor thesis of the author of this study, another summery will be published in paper revised now for JGR: Planets (see attachment).²⁷

1D vs 3D models.

Very strong cloud dynamics have been observed on Venus.⁷² Cloud behaviour and properties in lower levels of altitude are not quite clear. Last in situ obtained data suggest that the lowest part of clouds have the biggest density and particles sizes, certain observations suggest non spherical shape of particles.

Circumstantial evidence of the presence of another solid phase species were observed. The near infrared window allows us to take photographs of deepest clouds, where these particles have been observed, as well as UV contrasts suggesting the same. These “large” particles have 2-8 μm . It is possible that buoyancy effects could be the source of these particles; their origin then would be wind-blow dust or solid parts ejected by volcanic activity, which would suggest these particles should be covered in sulphuric acid condensations. This has amazing solid phase catalysis potential.^{72,104} While layer of these large particles is only 1-2 km long, it is accounting for most of the total column optical depth, since it is the densest (50 - 800 particles in cubic centimetre) part of the atmosphere.⁷²

Dynamics of the cloud layer is determined by 3 main functions:

- Super rotation of zones – winds circle at high speed in direction parallel to the equator. Rotation of the cloud layer is 50 times faster than the rotation of Venus around its planetary axes. The gradient of speed is present, lowest winds are expected near the surface; from surface to cloud layer winds are gaining speed, which then declines with increasing altitudes. In 90 km of altitude zonal super rotations are arrested.
- Hadley circulations – slow exchange between atmosphere in low latitudes and high latitudes in perpendicular direction to equator.
- Polar vortexes – they fill up a third of each hemisphere with the centre on poles.

Graphical representation of these processes is summarized in Figure 24 on the next page.⁸⁰

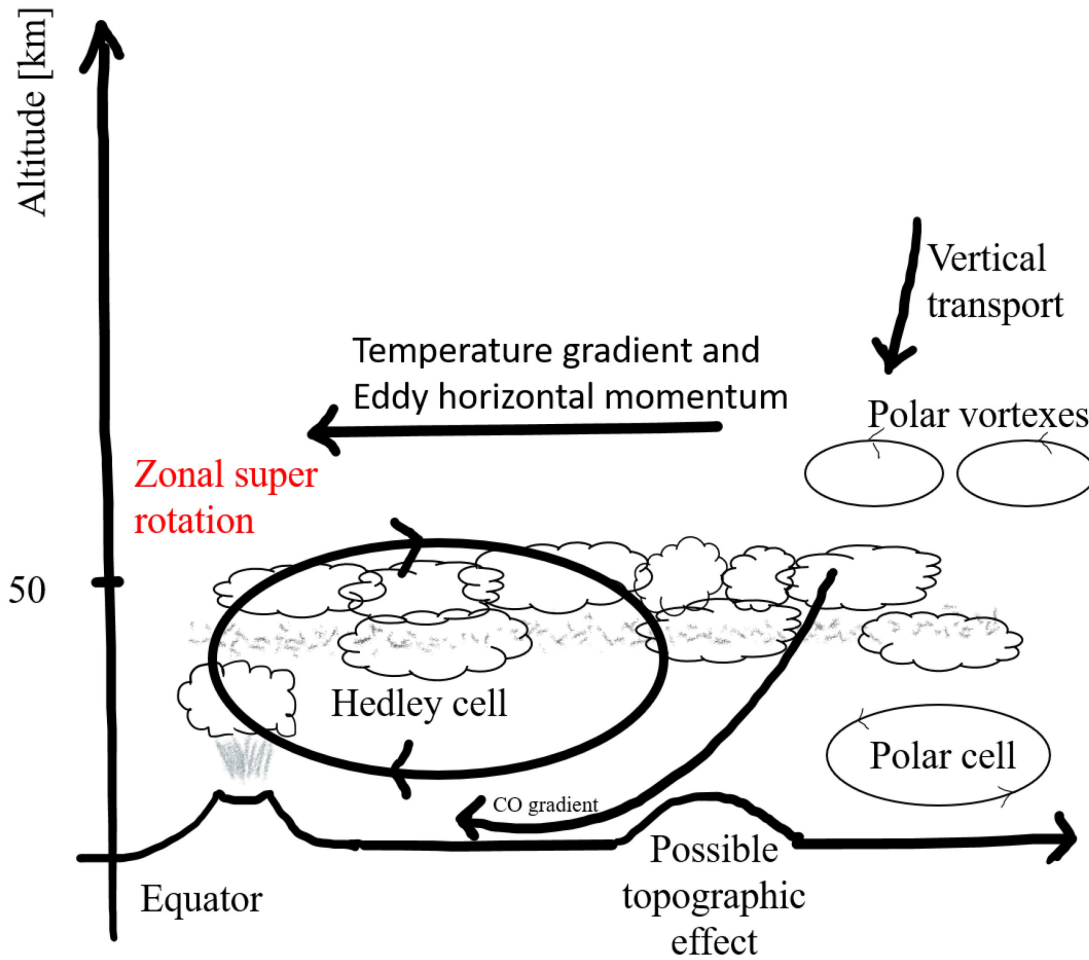


Figure 24: Graphical representation of the cloud dynamics on Venus, modified from Taylor and Grinspoon 2009.⁸⁰

These processes allow transportation of mass from polar caps to equator and vice versa. They help to maintain low gradients of surface temperatures and gradients of temperatures in cloud layers, which are mainly dominated by altitude, not latitude. The temperatures vary on a scale of 2 K, except for regions of 65° latitudes, where the cloud tops are located on lower levels. This has been studied via IR imaging.

1D model absolutely ignores these processes, it also does not include the gradients of temperature and horizontal eddy diffusion, for this reason the PH_3 produced by our model is not latitude dependent. The PH_3 was mainly observed in mid latitude and less significantly in the equatorial levels; this observation may be due to the two major rotation cells meeting in the

mid latitude region, both of those cells drag the material in. 3D models are computationally very complicated even for cases like Earth, 3D model for Venus would need better knowledge of the processes mixing Venusian atmosphere and better computational power.

5.7 PH₃ and CH₄ parallel

Could this mechanism truly work on Venus? First problem our model faces is the question of solar flux needed for photocatalysis. Our prediction is based on the experiment build for evaluation of abiotic production of methane on Mars. In this experiment, 160 W lamp was used.¹³ Solar flux levels were measured throughout the atmosphere by Pioneer LSFR experiment and by spectrophotometry by Venera landers. Solar fluxes of those missions varied, but the general trend was consistent in both measurements. The data measured by Pioneer and Venera landers are shown in Figure 25.¹⁰⁵

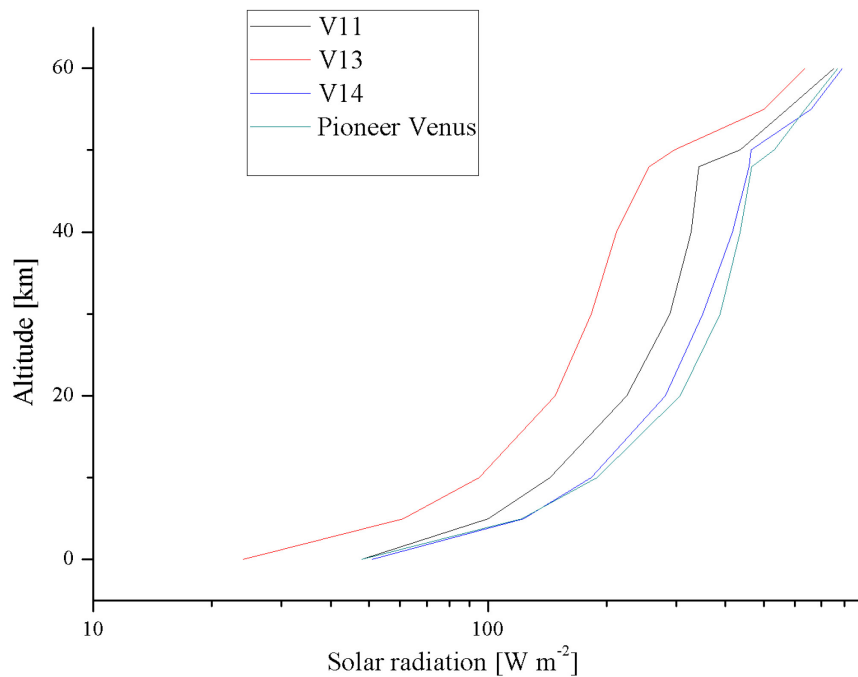


Figure 25: Measured solar fluxes of Venus dependently on the altitude. Data were obtained by Venera 11, 13 and 14 landers and by Pioneer Venus.

The surface solar flux measured by those 4 missions is on average 43 W/m^2 . Better assessment of feasibility of this process taking place directly on surface needs to be done in future research. If linearity would apply; in this case three times lower solar flux equals three times lower production rate. However, even under such conditions, our mechanism still would be sufficient enough to supply measured concentrations. Furthermore, as discussed before, lower part of clouds consists of layer of aerosol of solid parts presumed to have strong catalytic potential and acid droplets, which is convenient to our mechanism, P_4O_6 is less abundant than on surface, but its density profile is still high enough to produce sufficient amounts of PH_3 . Solar flux in this altitude is higher than 300 W/m^2 . Production could possibly occur also in this area.

Most fundamental question is however whether this production occurs even under ideal conditions since it has not been experimentally tested. For this reason, experiment has been proposed.

P_4O_6 can be produced from red phosphorous by burning under controlled conditions in 20 Torrs of oxygen and 740 Torr of nitrogen and 130°C to 150°C in the flow aperture. Under these conditions P_4O_6 is liquid, but its vapour pressure is 37 Torr.¹⁰⁶ Flow aperture can be joined with ice bath used to capture pure P_4O_6 which solidifies in 23.8°C . During experiment producing phosphine ice bath can be removed and heated back to temperatures allowing us to work with gaseous P_4O_6 . This part of apparatus would be made from borosilicate glass to hold during those temperature changes.

Rest of the experiment could be analogous to experiment done by Knížek et al.¹³

Many dangerous substances will be used or produced during this experiment, for this reason proper procedure and control should be used and this is also the reason, why the mechanism has been first explored theoretically in this thesis.

6. Conclusion

In the modelling section of this study, CO₂ rich and N₂ rich atmospheres were simulated in order to evaluate the importance and stability of two biosignature molecules: PH₃ and N₂O. These models can be applied to any terrestrial planet undergoing a runaway greenhouse scenario (in the case on CO₂ rich atmospheres) such as Venus, or to any other planet with sufficient solar flux and an atmosphere dominated by CO₂ or N₂.

New arguments for suspecting these biosignatures to be false positive are presented: Synthesis of N₂O by impact plasma (previously experimentally verified in my bachelor thesis) is now fully evaluated as a plausible source of abiotic N₂O synthesis. This means that false positivity needs to be taken into account when assessing the biotic origin of N₂O on young terrestrial exoplanet.

A new theoretical pathway of PH₃ synthesis from P₄O₆ was introduced and its effectiveness is calculated by Venus atmosphere model. Computation of PH₃ yield suggests that its synthesis from P₄O₆ upon UV radiation on acidic surface of atmospheric dust is potentially very effective and could stand for source of phosphine recently tentatively detected on Venus. Furthermore, this pathway seems to be able to produce abiotic PH₃ at concentration of 1 ppm lower than the detection limit of Ariel for some classes of exoplanets. An experimental verification of this result is proposed and will be part of candidate's future research.

Thus, I suggest novel abiotic sources of so far positively evaluated biosignatures. These results should be taken into account during the analysis of data from the Ariel mission and any further space exploration, keeping in mind that:

A biosignature means the possible detection of life only after all abiotic scenarios have been deemed inefficient to produce the detected signal.

In case of N₂O and PH₃, abiotic scenario cannot be excluded and both molecules therefore represent potential false positive biosignatures.

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Appendix

Table A1: Density profiles of species destroying PH_3

Altitude [km]	H [molecules cm^{-3}]	O [molecules cm^{-3}]	HO [molecules cm^{-3}]	Cl [molecules cm^{-3}]
0	2.59×10^2	2.46×10^{-5}	3.41×10^2	3.86×10^2
1	2.36×10^2	2.01×10^{-5}	2.63×10^2	3.54×10^2
2	2.28×10^2	1.66×10^{-5}	2.14×10^2	3.25×10^2
3	2.21×10^2	1.38×10^{-5}	1.74×10^2	2.97×10^2
4	2.08×10^2	1.15×10^{-5}	1.36×10^2	2.71×10^2
5	1.89×10^2	9.81×10^{-6}	1.02×10^2	2.47×10^2
6	1.67×10^2	8.42×10^{-6}	7.41×10^1	2.24×10^1
7	1.49×10^2	7.38×10^{-6}	5.42×10^1	2.03×10^1
8	1.34×10^2	6.59×10^{-6}	4.03×10^1	1.85×10^1
9	1.25×10^2	6.00×10^{-6}	3.05×10^1	1.67×10^1
10	1.34×10^2	5.91×10^{-6}	2.64×10^1	1.52×10^1
11	1.82×10^2	6.98×10^{-6}	2.90×10^1	1.37×10^1
12	3.00×10^2	9.92×10^{-6}	3.84×10^1	1.24×10^1
13	5.05×10^2	1.49×10^{-5}	5.18×10^1	1.12×10^1
14	7.60×10^2	2.01×10^{-5}	6.26×10^1	1.01×10^1
15	1.00×10^3	2.36×10^{-5}	6.64×10^1	9.16×10^1
16	1.17×10^3	2.44×10^{-5}	6.21×10^1	8.26×10^1
17	1.22×10^3	2.23×10^{-5}	5.09×10^1	7.36×10^1
18	1.17×10^3	1.85×10^{-5}	3.82×10^1	6.53×10^1
19	1.08×10^3	1.46×10^{-5}	2.76×10^1	5.82×10^1
20	8.98×10^2	1.04×10^{-5}	1.78×10^1	5.11×10^1
21	7.25×10^2	7.13×10^{-6}	1.12×10^1	4.56×10^1
22	5.62×10^2	4.70×10^{-6}	6.91×10^0	4.21×10^0
23	4.12×10^2	2.91×10^{-6}	4.04×10^0	4.07×10^0
24	2.86×10^2	1.69×10^{-6}	2.25×10^0	4.22×10^0
25	1.93×10^2	9.62×10^{-7}	1.25×10^0	4.75×10^0
26	1.24×10^2	5.25×10^{-7}	6.74×10^{-1}	5.65×10^{-1}
27	7.83×10^1	2.86×10^{-7}	3.66×10^{-1}	7.05×10^{-1}
28	4.88×10^1	1.60×10^{-7}	2.02×10^{-1}	8.66×10^{-1}
29	3.19×10^1	9.71×10^{-8}	1.19×10^{-1}	1.01×10^{-1}
30	2.16×10^1	6.12×10^{-8}	7.36×10^{-2}	1.05×10^{-2}
31	1.63×10^1	4.19×10^{-8}	5.09×10^{-2}	9.70×10^{-2}
32	1.38×10^1	3.06×10^{-8}	3.98×10^{-2}	8.06×10^{-2}
33	1.25×10^1	2.31×10^{-8}	3.40×10^{-2}	6.11×10^{-2}
34	1.14×10^1	1.74×10^{-8}	3.00×10^{-2}	4.36×10^{-2}
35	9.97	1.34×10^{-8}	2.63×10^{-2}	2.99×10^{-2}
36	1.02×10^1	1.39×10^{-8}	2.74×10^{-2}	2.06×10^{-2}
37	1.06×10^1	2.04×10^{-8}	2.96×10^{-2}	1.41×10^{-2}
38	1.18×10^1	4.88×10^{-8}	3.49×10^{-2}	9.82×10^{-2}
39	1.43×10^1	1.62×10^{-7}	4.53×10^{-2}	7.11×10^{-2}

40	1.72×10	¹	5.95×10	⁻⁷	5.98×10	⁻²	5.13×10	⁻²
41	5.22		6.82×10	⁻⁷	2.04×10	⁻²	2.39×10	⁻²
42	1.18×10	⁻²	4.82×10	⁻⁷	6.63×10	⁻⁵	1.39×10	⁻⁵
43	1.11×10	⁻²	1.35×10	⁻⁶	6.03×10	⁻⁵	4.07×10	⁻⁵
44	2.40×10	⁻²	3.86×10	⁻⁶	1.26×10	⁻⁴	3.13×10	⁻⁴
45	7.21×10	⁻²	1.04×10	⁻⁵	3.95×10	⁻⁴	3.11×10	⁻⁴
46	2.24×10	⁻¹	2.56×10	⁻⁵	1.27×10	⁻³	3.22×10	⁻³
47	6.81×10	⁻¹	5.92×10	⁻⁵	4.00×10	⁻³	3.14×10	⁻³
48	1.93		1.31×10	⁻⁴	1.15×10	⁻²	3.02×10	⁻²
49	5.01		2.85×10	⁻⁴	3.06×10	⁻²	2.74×10	⁻²
50	3.32×10	¹	5.01×10	⁻³	2.17×10	⁻¹	7.53×10	⁻¹
51	3.86×10	¹	2.42×10	⁻³	2.35×10	⁻¹	2.34×10	⁻¹
52	9.79×10	¹	3.32×10	⁻³	6.60×10	⁻¹	1.25×10	⁻¹
53	2.55×10	²	8.64×10	⁻³	2.58×10	⁰	8.32×10	⁰
54	5.48×10	²	3.85×10	⁻²	4.76×10	⁰	5.85×10	⁰
55	8.74×10	²	4.51×10	⁻¹	4.32×10	⁰	3.83×10	⁰
56	1.09×10	³	1.17×10	¹	7.83×10	⁰	4.28×10	⁰
57	2.59×10	³	7.15×10	³	3.28×10	²	1.01×10	²
58	3.54×10	⁵	1.34×10	⁶	3.78×10	⁴	1.69×10	⁴
59	6.71×10	⁵	6.40×10	⁶	8.06×10	⁴	1.32×10	⁴
60	1.01×10	⁶	2.54×10	⁷	1.12×10	⁵	1.21×10	⁵
62	1.10×10	⁵	7.69×10	⁷	5.50×10	³	3.49×10	³
64	3.70×10	⁵	2.01×10	⁸	1.21×10	⁴	3.76×10	⁴
66	1.16×10	⁶	4.49×10	⁸	3.52×10	⁴	4.03×10	⁴
68	3.12×10	⁶	1.06×10	⁹	9.38×10	⁴	4.09×10	⁴
70	6.99×10	⁶	2.29×10	⁹	2.18×10	⁵	4.06×10	⁵
72	1.54×10	⁷	4.73×10	⁹	4.83×10	⁵	3.90×10	⁵
74	3.72×10	⁷	9.59×10	⁹	1.01×10	⁶	3.66×10	⁶
76	9.96×10	⁷	1.81×10	¹⁰	1.85×10	⁶	3.35×10	⁶
78	2.62×10	⁸	2.96×10	¹⁰	2.65×10	⁶	3.05×10	⁶
80	6.11×10	⁸	4.16×10	¹⁰	3.02×10	⁶	2.84×10	⁶
82	1.34×10	⁹	4.39×10	¹⁰	3.49×10	⁶	2.91×10	⁶
84	2.98×10	⁹	1.25×10	¹¹	1.89×10	⁶	3.78×10	⁶
86	2.52×10	⁹	2.65×10	¹¹	5.18×10	⁵	2.94×10	⁵
88	1.70×10	⁹	3.21×10	¹¹	1.54×10	⁵	1.95×10	⁵
90	1.08×10	⁹	2.92×10	¹¹	4.91×10	⁴	1.23×10	⁴
92	6.62×10	⁸	2.34×10	¹¹	1.59×10	⁴	7.50×10	⁴
94	4.02×10	⁸	1.78×10	¹¹	5.31×10	³	4.54×10	³
96	2.42×10	⁸	1.33×10	¹¹	1.78×10	³	2.73×10	³
98	1.46×10	⁸	9.85×10	¹⁰	6.05×10	²	1.64×10	²
100	8.77×10	⁷	7.30×10	¹⁰	2.09×10	²	9.83×10	²
105	2.81×10	⁷	4.46×10	¹⁰	1.75×10	¹	3.09×10	¹
110	8.86×10	⁶	2.60×10	¹⁰	1.66×10	⁰	9.64×10	⁰
115	2.83×10	⁶	1.48×10	¹⁰	4.47×10	⁰	3.04×10	⁰

Table A2: Rate constants of reactions destroying PH_3 with corresponding names. Reaction rate constants of reactions R473 and R5872 are in terms of s^{-1} the rest of the reactions is in terms of $\text{cm}^3 \text{s}^{-1}$.

Altitude [km]	R473	R2299	R2300	R2301	R2302	R5872	
0	1.27×10^{-8}	2.29×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
1	7.22×10^{-9}	2.26×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
2	4.08×10^{-9}	2.24×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
3	2.23×10^{-9}	2.21×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
4	1.20×10^{-9}	2.18×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
5	6.40×10^{-10}	2.15×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
6	3.31×10^{-10}	2.12×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
7	1.73×10^{-10}	2.09×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
8	9.03×10^{-11}	2.06×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
9	4.54×10^{-11}	2.03×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
10	2.29×10^{-11}	2.00×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	0.00	
11	1.13×10^{-11}	1.97×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.12×10^{-49}	-49
12	5.63×10^{-12}	1.94×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.03×10^{-46}	-46
13	2.68×10^{-12}	1.91×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.53×10^{-44}	-44
14	1.29×10^{-12}	1.88×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	8.67×10^{-42}	-42
15	6.15×10^{-13}	1.85×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.55×10^{-39}	-39
16	2.83×10^{-13}	1.82×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.03×10^{-37}	-37
17	1.21×10^{-13}	1.79×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.00×10^{-35}	-35
18	5.03×10^{-14}	1.76×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.50×10^{-33}	-33
19	2.11×10^{-14}	1.72×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	8.75×10^{-32}	-32
20	7.98×10^{-15}	1.69×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.98×10^{-30}	-30
21	3.02×10^{-15}	1.65×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.44×10^{-28}	-28
22	1.14×10^{-15}	1.62×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	4.18×10^{-27}	-27
23	4.09×10^{-16}	1.58×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	9.86×10^{-26}	-26
24	1.39×10^{-16}	1.55×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.95×10^{-24}	-24
25	4.68×10^{-17}	1.51×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.69×10^{-23}	-23
26	1.49×10^{-17}	1.47×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	9.29×10^{-22}	-22
27	4.62×10^{-18}	1.44×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.86×10^{-20}	-20
28	1.36×10^{-18}	1.40×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	6.70×10^{-19}	-19
29	4.03×10^{-19}	1.36×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	9.93×10^{-18}	-18
30	1.07×10^{-19}	1.32×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	9.59×10^{-17}	-17
31	2.74×10^{-20}	1.28×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	6.38×10^{-16}	-16
32	6.91×10^{-21}	1.24×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.18×10^{-15}	-15
33	1.72×10^{-21}	1.21×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.27×10^{-14}	-14
34	4.00×10^{-22}	1.17×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	4.29×10^{-14}	-14
35	8.68×10^{-23}	1.13×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.28×10^{-13}	-13
36	1.85×10^{-23}	1.09×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.44×10^{-13}	-13
37	3.72×10^{-24}	1.05×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	8.52×10^{-13}	-13
38	7.62×10^{-25}	1.02×10^{-11}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.98×10^{-12}	-12
39	1.57×10^{-25}	9.83×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	4.34×10^{-12}	-12

40	2.86×10^{-26}	9.47×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	9.11×10^{-12}
41	5.33×10^{-27}	9.13×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.84×10^{-11}
42	1.15×10^{-27}	8.83×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.59×10^{-11}
43	2.29×10^{-28}	8.52×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	6.75×10^{-11}
44	4.23×10^{-29}	8.21×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.23×10^{-10}
45	6.13×10^{-30}	7.92×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.18×10^{-10}
46	1.04×10^{-30}	7.66×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.74×10^{-10}
47	1.58×10^{-31}	7.39×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	6.25×10^{-10}
48	2.47×10^{-32}	7.13×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.01×10^{-9}
49	2.24×10^{-33}	6.81×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.60×10^{-9}
50	1.45×10^{-34}	6.46×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.46×10^{-9}
51	6.22×10^{-36}	6.08×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.70×10^{-9}
52	2.25×10^{-37}	5.70×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	5.43×10^{-9}
53	3.01×10^{-39}	5.25×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	7.79×10^{-9}
54	4.57×10^{-41}	4.84×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.09×10^{-8}
55	2.81×10^{-43}	4.39×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.50×10^{-8}
56	9.72×10^{-46}	3.94×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.03×10^{-8}
57	1.35×10^{-48}	3.48×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.83×10^{-8}
58	0.00	3.07×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.67×10^{-7}
59	0.00	2.77×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	4.75×10^{-7}
60	0.00	2.58×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.25×10^{-6}
62	0.00	2.34×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.65×10^{-6}
64	0.00	2.17×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.19×10^{-5}
66	0.00	2.01×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.26×10^{-5}
68	0.00	1.90×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	7.54×10^{-5}
70	0.00	1.79×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.31×10^{-4}
72	0.00	1.69×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.88×10^{-4}
74	0.00	1.59×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	2.45×10^{-4}
76	0.00	1.46×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.04×10^{-4}
78	0.00	1.31×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	3.67×10^{-4}
80	0.00	1.12×10^{-12}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	4.33×10^{-4}
82	0.00	9.63×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	5.01×10^{-4}
84	0.00	8.22×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	5.71×10^{-4}
86	0.00	6.96×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	6.43×10^{-4}
88	0.00	6.07×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	7.19×10^{-4}
90	0.00	5.39×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	8.04×10^{-4}
92	0.00	5.10×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	9.01×10^{-4}
94	0.00	4.97×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.01×10^{-3}
96	0.00	5.04×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.13×10^{-3}
98	0.00	5.17×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.26×10^{-3}
100	0.00	5.37×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.40×10^{-3}
105	0.00	5.81×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.55×10^{-3}
110	0.00	6.30×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.74×10^{-3}
115	0.00	6.99×10^{-13}	4.75×10^{-11}	1.61×10^{-11}	2.40×10^{-10}	1.97×10^{-3}

Table A3: Calculated decadic logarithm of destruction rates of PH_3 and their dependence on altitude. Rates are in the units of $\text{s}^{-1} \text{cm}^{-3}$.

Altitude [km]	H destruction	O destruction	HO destruction	Cl destruction	R473	R5872	Total:
0	5.03	-1.67	5.00	8.23	5.36	--	8.23
1	4.96	-1.78	4.86	8.17	5.09	--	8.17
2	4.92	-1.89	4.75	8.10	4.82	--	8.11
3	4.88	-2.00	4.64	8.04	4.54	--	8.04
4	4.82	-2.10	4.51	7.98	4.25	--	7.98
5	4.75	-2.19	4.36	7.91	3.95	--	7.91
6	4.67	-2.28	4.19	7.85	3.64	--	7.85
7	4.59	-2.36	4.03	7.78	3.33	--	7.78
8	4.51	-2.44	3.88	7.72	3.02	--	7.72
9	4.45	-2.50	3.74	7.65	2.70	--	7.65
10	4.45	-2.53	3.65	7.58	2.38	--	7.58
11	4.55	-2.49	3.66	7.51	2.05	-35.68	7.51
12	4.73	-2.36	3.76	7.44	1.72	-33.02	7.44
13	4.93	-2.21	3.86	7.37	1.37	-30.51	7.37
14	5.07	-2.11	3.92	7.30	1.02	-28.15	7.30
15	5.16	-2.06	3.92	7.23	0.68	-25.92	7.23
16	5.19	-2.08	3.86	7.16	0.31	-23.83	7.16
17	5.17	-2.14	3.75	7.08	-0.09	-21.87	7.09
18	5.12	-2.25	3.59	7.00	-0.49	-20.02	7.01
19	5.05	-2.38	3.43	6.92	-0.90	-18.28	6.93
20	4.93	-2.56	3.21	6.84	-1.35	-16.65	6.84
21	4.80	-2.75	2.98	6.76	-1.80	-15.12	6.77
22	4.65	-2.96	2.74	6.70	-2.25	-13.69	6.70
23	4.48	-3.20	2.48	6.65	-2.73	-12.34	6.66
24	4.28	-3.46	2.19	6.64	-3.22	-11.08	6.64
25	4.07	-3.74	1.91	6.66	-3.73	-9.83	6.66
26	3.83	-4.03	1.61	6.71	-4.25	-8.46	6.71
27	3.59	-4.32	1.31	6.77	-4.79	-7.00	6.77
28	3.34	-4.61	1.02	6.83	-5.35	-5.66	6.83
29	3.12	-4.86	0.76	6.86	-5.92	-4.52	6.86
30	2.90	-5.09	0.52	6.85	-6.53	-3.57	6.85
31	2.73	-5.29	0.33	6.78	-7.15	-2.78	6.78
32	2.61	-5.46	0.19	6.67	-7.78	-2.12	6.67
33	2.52	-5.61	0.08	6.51	-8.42	-1.55	6.51
34	2.43	-5.77	-0.01	6.33	-9.09	-1.06	6.33
35	2.33	-5.92	-0.10	6.13	-9.79	-0.62	6.13
36	2.29	-5.94	-0.12	5.93	-10.4	-0.22	5.93
37	2.25	-5.81	-0.12	5.73	-11.2	0.13	5.73
38	2.24	-5.47	-0.09	5.54	-11.9	0.46	5.54
39	2.27	-4.99	-0.01	5.36	-12.6	0.76	5.36
40	2.30	-4.46	0.07	5.18	-13.4	1.05	5.18
41	1.72	-4.44	-0.44	4.80	-14.2	1.31	4.80

42	-0.98	-4.64	-2.97	3.53	-14.9	1.56	3.53
43	-1.06	-4.23	-3.05	2.95	-15.6	1.79	2.98
44	-0.79	-3.82	-2.77	2.79	-16.4	2.01	2.86
45	-0.37	-3.43	-2.32	2.75	-17.3	2.21	2.86
46	0.06	-3.09	-1.86	2.72	-18.1	2.40	2.89
47	0.48	-2.77	-1.41	2.66	-19.0	2.58	2.92
48	0.87	-2.47	-1.00	2.59	-19.8	2.74	2.98
49	1.22	-2.18	-0.62	2.51	-20.9	2.89	3.05
50	1.97	-0.98	0.18	2.90	-22.2	3.03	3.29
51	1.97	-1.35	0.17	2.34	-23.6	3.16	3.25
52	2.29	-1.26	0.57	2.02	-25.1	3.28	3.35
53	2.63	-0.89	1.12	1.80	-27.0	3.39	3.47
54	2.88	-0.29	1.34	1.60	-28.8	3.49	3.59
55	2.99	0.73	1.25	1.37	-31.1	3.58	3.68
56	2.98	2.10	1.45	1.36	-33.6	3.66	3.76
57	3.26	4.83	3.02	2.68	-36.5	3.75	4.89
58	5.28	7.05	5.03	4.85	--	4.47	7.06
59	5.45	7.67	5.30	5.69	--	4.86	7.68
60	5.53	8.20	5.37	6.58	--	5.21	8.21
62	4.38	8.53	3.92	9.89	--	5.53	9.91
64	4.72	8.80	4.11	10.77	--	5.90	10.78
66	5.03	8.99	4.42	10.65	--	6.18	10.66
68	5.27	9.21	4.68	10.49	--	6.38	10.52
70	5.43	9.38	4.88	10.33	--	6.45	10.37
72	5.59	9.52	5.06	10.14	--	6.44	10.24
74	5.77	9.66	5.21	9.94	--	6.39	10.13
76	5.99	9.77	5.30	9.74	--	6.31	10.05
78	6.19	9.81	5.29	9.52	--	6.22	9.99
80	6.32	9.78	5.17	9.32	--	6.12	9.91
82	6.41	9.62	5.05	9.15	--	6.00	9.75
84	6.50	9.89	4.60	9.07	--	5.87	9.95
86	6.16	10.02	3.84	8.77	--	5.73	10.04
88	5.73	9.90	3.11	8.38	--	5.57	9.91
90	5.27	9.64	2.40	7.97	--	5.41	9.65
92	4.81	9.32	1.69	7.53	--	5.23	9.33
94	4.35	8.98	0.98	7.09	--	5.06	8.98
96	3.91	8.62	0.28	6.64	--	4.87	8.63
98	3.47	8.26	-0.42	6.18	--	4.69	8.26
100	3.03	7.90	-1.11	5.73	--	4.51	7.90
105	2.01	7.12	-2.75	4.67	--	3.99	7.12
110	0.99	6.33	-4.33	3.60	--	3.48	6.33
115	-0.01	5.54	-4.45	2.56	--	2.99	5.54

Production was calculated in analogous manner.

Table A4: Lifetimes of N_2O if it were destroyed only by one of each reaction, corresponding reactions can be found in the result section of this study.

Altitude [km]	τ_2		τ_1		τ_3		τ_4		τ_5	
0.0	1.76×10	¹¹	9.90×10	⁷	1.58×10	¹⁵	2.94×10	²¹	1.10×10	²⁸
0.5	9.91×10	¹⁰	8.61×10	⁷	1.66×10	¹⁵	2.49×10	²¹	1.34×10	²⁸
1.0	5.73×10	¹⁰	7.49×10	⁷	1.79×10	¹⁵	2.11×10	²¹	1.72×10	²⁸
1.5	3.40×10	¹⁰	6.50×10	⁷	2.03×10	¹⁵	1.88×10	²¹	2.28×10	²⁸
2.0	1.30×10	¹⁰	5.63×10	⁷	2.35×10	¹⁵	1.65×10	²¹	3.19×10	²⁸
2.5	8.30×10	⁹	4.86×10	⁷	2.70×10	¹⁵	1.44×10	²¹	4.55×10	²⁸
3.0	5.45×10	⁹	4.18×10	⁷	3.16×10	¹⁵	1.27×10	²¹	6.70×10	²⁸
3.5	3.66×10	⁹	3.58×10	⁷	3.81×10	¹⁵	1.14×10	²¹	1.02×10	²⁹
4.0	2.52×10	⁹	3.06×10	⁷	4.78×10	¹⁵	1.04×10	²¹	1.60×10	²⁹
4.5	1.78×10	⁹	2.60×10	⁷	6.29×10	¹⁵	9.92×10	²⁰	2.59×10	²⁹
5.0	1.28×10	⁹	2.20×10	⁷	8.42×10	¹⁵	9.70×10	²⁰	4.26×10	²⁹
5.5	9.35×10	⁸	1.86×10	⁷	1.15×10	¹⁶	9.73×10	²⁰	7.10×10	²⁹
6.0	6.96×10	⁸	1.57×10	⁷	1.60×10	¹⁶	1.00×10	²¹	1.22×10	³⁰
6.5	5.27×10	⁸	1.33×10	⁷	2.23×10	¹⁶	1.05×10	²¹	2.09×10	³⁰
7.0	4.04×10	⁸	1.12×10	⁷	3.21×10	¹⁶	1.11×10	²¹	3.70×10	³⁰
7.5	3.14×10	⁸	9.48×10	⁶	4.60×10	¹⁶	1.20×10	²¹	6.55×10	³⁰
8.0	2.47×10	⁸	8.05×10	⁶	6.66×10	¹⁶	1.30×10	²¹	1.18×10	³¹
8.5	1.97×10	⁸	6.85×10	⁶	9.62×10	¹⁶	1.42×10	²¹	2.12×10	³¹
9.0	1.59×10	⁸	5.86×10	⁶	1.38×10	¹⁷	1.56×10	²¹	3.81×10	³¹
9.5	1.30×10	⁸	5.04×10	⁶	2.00×10	¹⁷	1.70×10	²¹	6.95×10	³¹
10.0	1.07×10	⁸	4.35×10	⁶	2.81×10	¹⁷	1.82×10	²¹	1.24×10	³²
10.5	8.87×10	⁷	3.78×10	⁶	3.96×10	¹⁷	1.88×10	²¹	2.26×10	³²
11.0	7.45×10	⁷	3.30×10	⁶	5.42×10	¹⁷	1.69×10	²¹	4.01×10	³²
11.5	6.31×10	⁷	2.90×10	⁶	7.19×10	¹⁷	1.13×10	²¹	6.93×10	³²
12.0	5.39×10	⁷	2.56×10	⁶	9.22×10	¹⁷	5.21×10	²⁰	1.16×10	³³
12.5	4.64×10	⁷	2.28×10	⁶	1.16×10	¹⁸	1.96×10	²⁰	1.94×10	³³
13.0	4.02×10	⁷	2.04×10	⁶	1.38×10	¹⁸	7.13×10	¹⁹	3.05×10	³³
13.5	3.51×10	⁷	1.83×10	⁶	1.58×10	¹⁸	2.69×10	¹⁹	4.53×10	³³
14.0	3.09×10	⁷	1.66×10	⁶	1.74×10	¹⁸	1.08×10	¹⁹	6.49×10	³³
14.5	2.74×10	⁷	1.51×10	⁶	1.83×10	¹⁸	4.60×10	¹⁸	8.72×10	³³
15.0	2.44×10	⁷	1.38×10	⁶	1.83×10	¹⁸	2.11×10	¹⁸	1.07×10	³⁴
15.5	2.18×10	⁷	1.27×10	⁶	1.74×10	¹⁸	1.03×10	¹⁸	1.23×10	³⁴
16.0	1.96×10	⁷	1.17×10	⁶	1.59×10	¹⁸	5.35×10	¹⁷	1.32×10	³⁴
16.5	1.78×10	⁷	1.09×10	⁶	1.42×10	¹⁸	2.95×10	¹⁷	1.35×10	³⁴
17.0	1.61×10	⁷	1.01×10	⁶	1.13×10	¹⁸	1.59×10	¹⁷	1.29×10	³⁴
17.5	1.47×10	⁷	9.50×10	⁵	8.72×10	¹⁷	9.01×10	¹⁶	1.18×10	³⁴
18.0	1.35×10	⁷	8.93×10	⁵	6.69×10	¹⁷	5.35×10	¹⁶	1.05×10	³⁴
18.5	1.24×10	⁷	8.42×10	⁵	5.01×10	¹⁷	3.32×10	¹⁶	8.92×10	³³
19.0	1.15×10	⁷	7.97×10	⁵	3.71×10	¹⁷	2.15×10	¹⁶	7.44×10	³³
19.5	1.06×10	⁷	7.58×10	⁵	2.77×10	¹⁷	1.44×10	¹⁶	6.21×10	³³
20.0	9.85×10	⁶	7.22×10	⁵	2.06×10	¹⁷	9.99×10	¹⁵	5.07×10	³³
20.5	9.17×10	⁶	6.90×10	⁵	1.53×10	¹⁷	7.15×10	¹⁵	4.15×10	³³

21.0	8.56×10	⁶	6.61×10	⁵	1.17×10	¹⁷	5.26×10	¹⁵	3.48×10	³³
21.5	8.01×10	⁶	6.34×10	⁵	8.88×10	¹⁶	3.97×10	¹⁵	2.86×10	³³
22.0	7.52×10	⁶	6.10×10	⁵	6.76×10	¹⁶	3.07×10	¹⁵	2.35×10	³³
22.5	7.07×10	⁶	5.88×10	⁵	5.27×10	¹⁶	2.43×10	¹⁵	1.98×10	³³
23.0	6.66×10	⁶	5.68×10	⁵	4.06×10	¹⁶	1.96×10	¹⁵	1.63×10	³³
23.5	6.29×10	⁶	5.49×10	⁵	3.15×10	¹⁶	1.62×10	¹⁵	1.35×10	³³
24.0	5.96×10	⁶	5.32×10	⁵	2.45×10	¹⁶	1.35×10	¹⁵	1.12×10	³³
24.5	5.65×10	⁶	5.16×10	⁵	1.91×10	¹⁶	1.15×10	¹⁵	9.25×10	³²
25.0	5.37×10	⁶	5.01×10	⁵	1.50×10	¹⁶	9.94×10	¹⁴	7.68×10	³²
25.5	5.12×10	⁶	4.88×10	⁵	1.18×10	¹⁶	8.69×10	¹⁴	6.38×10	³²
26.0	4.88×10	⁶	4.75×10	⁵	9.17×10	¹⁵	7.70×10	¹⁴	5.21×10	³²
26.5	4.67×10	⁶	4.63×10	⁵	7.27×10	¹⁵	6.89×10	¹⁴	4.34×10	³²
27.0	4.47×10	⁶	4.52×10	⁵	5.68×10	¹⁵	6.22×10	¹⁴	3.56×10	³²
27.5	4.29×10	⁶	4.42×10	⁵	4.45×10	¹⁵	5.67×10	¹⁴	2.92×10	³²
28.0	4.12×10	⁶	4.32×10	⁵	3.43×10	¹⁵	5.21×10	¹⁴	2.35×10	³²
28.5	3.96×10	⁶	4.23×10	⁵	2.70×10	¹⁵	4.83×10	¹⁴	1.93×10	³²
29.0	3.82×10	⁶	4.15×10	⁵	2.10×10	¹⁵	4.50×10	¹⁴	1.56×10	³²
29.5	3.68×10	⁶	4.07×10	⁵	1.60×10	¹⁵	4.21×10	¹⁴	1.24×10	³²
30.0	3.56×10	⁶	4.00×10	⁵	1.23×10	¹⁵	3.97×10	¹⁴	9.91×10	³¹
30.5	3.44×10	⁶	3.93×10	⁵	9.43×10	¹⁴	3.76×10	¹⁴	7.92×10	³¹
31.0	3.33×10	⁶	3.86×10	⁵	7.27×10	¹⁴	3.57×10	¹⁴	6.34×10	³¹
31.5	3.23×10	⁶	3.80×10	⁵	5.43×10	¹⁴	3.41×10	¹⁴	4.91×10	³¹
32.0	3.13×10	⁶	3.74×10	⁵	4.14×10	¹⁴	3.27×10	¹⁴	3.88×10	³¹
32.5	3.04×10	⁶	3.69×10	⁵	3.06×10	¹⁴	3.14×10	¹⁴	2.97×10	³¹
33.0	2.96×10	⁶	3.63×10	⁵	2.31×10	¹⁴	3.02×10	¹⁴	2.32×10	³¹
33.5	2.88×10	⁶	3.58×10	⁵	1.73×10	¹⁴	2.92×10	¹⁴	1.78×10	³¹
34.0	2.80×10	⁶	3.53×10	⁵	1.27×10	¹⁴	2.82×10	¹⁴	1.35×10	³¹
34.5	2.73×10	⁶	3.49×10	⁵	9.59×10	¹³	2.74×10	¹⁴	1.05×10	³¹
35.0	2.66×10	⁶	3.45×10	⁵	7.26×10	¹³	2.67×10	¹⁴	8.14×10	³⁰
35.5	2.60×10	⁶	3.40×10	⁵	5.44×10	¹³	2.60×10	¹⁴	6.24×10	³⁰
36.0	2.53×10	⁶	3.36×10	⁵	4.15×10	¹³	2.54×10	¹⁴	4.88×10	³⁰
36.5	2.48×10	⁶	3.33×10	⁵	3.19×10	¹³	2.49×10	¹⁴	3.83×10	³⁰
37.0	2.42×10	⁶	3.29×10	⁵	2.42×10	¹³	2.44×10	¹⁴	2.96×10	³⁰
37.5	2.37×10	⁶	3.26×10	⁵	1.88×10	¹³	2.40×10	¹⁴	2.33×10	³⁰
38.0	2.31×10	⁶	3.22×10	⁵	1.46×10	¹³	2.37×10	¹⁴	1.85×10	³⁰
38.5	2.26×10	⁶	3.19×10	⁵	1.16×10	¹³	2.34×10	¹⁴	1.49×10	³⁰
39.0	2.22×10	⁶	3.16×10	⁵	9.27×10	¹²	2.32×10	¹⁴	1.20×10	³⁰
39.5	2.17×10	⁶	3.13×10	⁵	7.42×10	¹²	2.30×10	¹⁴	9.72×10	²⁹
40.0	2.12×10	⁶	3.10×10	⁵	6.06×10	¹²	2.29×10	¹⁴	8.00×10	²⁹
40.5	2.08×10	⁶	3.07×10	⁵	4.97×10	¹²	2.29×10	¹⁴	6.60×10	²⁹
41.0	2.04×10	⁶	3.04×10	⁵	4.16×10	¹²	2.29×10	¹⁴	5.53×10	²⁹
41.5	2.00×10	⁶	3.01×10	⁵	3.49×10	¹²	2.30×10	¹⁴	4.64×10	²⁹
42.0	1.96×10	⁶	2.99×10	⁵	3.06×10	¹²	2.33×10	¹⁴	4.02×10	²⁹
42.5	1.92×10	⁶	2.96×10	⁵	5.22×10	¹²	4.02×10	¹⁴	3.49×10	²⁹
43.0	1.88×10	⁶	2.94×10	⁵	1.42×10	¹³	1.29×10	¹⁵	3.11×10	²⁹

43.5	1.85×10^6	6	2.91×10^5	5	2.21×10^{13}	2.34×10^{15}	2.78×10^{29}
44.0	1.81×10^6	6	2.89×10^5	5	2.77×10^{13}	3.38×10^{15}	2.52×10^{29}
44.5	1.77×10^6	6	2.86×10^5	5	3.24×10^{13}	4.43×10^{15}	2.35×10^{29}
45.0	1.74×10^6	6	2.84×10^5	5	3.62×10^{13}	5.51×10^{15}	2.22×10^{29}
45.5	1.71×10^6	6	2.81×10^5	5	3.86×10^{13}	6.47×10^{15}	2.13×10^{29}
46.0	1.68×10^6	6	2.79×10^5	5	4.07×10^{13}	7.33×10^{15}	2.10×10^{29}
46.5	1.64×10^6	6	2.77×10^5	5	4.20×10^{13}	8.14×10^{15}	2.07×10^{29}
47.0	1.61×10^6	6	2.75×10^5	5	4.39×10^{13}	8.95×10^{15}	2.10×10^{29}
47.5	1.58×10^6	6	2.72×10^5	5	4.58×10^{13}	9.71×10^{15}	2.16×10^{29}
48.0	1.55×10^6	6	2.70×10^5	5	4.81×10^{13}	1.05×10^{16}	2.25×10^{29}
48.5	1.52×10^6	6	2.68×10^5	5	5.16×10^{13}	1.12×10^{16}	2.42×10^{29}
49.0	1.49×10^6	6	2.66×10^5	5	5.49×10^{13}	1.20×10^{16}	2.59×10^{29}
49.5	1.47×10^6	6	2.64×10^5	5	5.88×10^{13}	1.27×10^{16}	2.82×10^{29}
50.0	1.44×10^6	6	2.62×10^5	5	6.33×10^{13}	1.34×10^{16}	3.12×10^{29}
50.5	1.41×10^6	6	2.60×10^5	5	6.88×10^{13}	1.41×10^{16}	3.49×10^{29}
51.0	1.39×10^6	6	2.58×10^5	5	7.53×10^{13}	1.47×10^{16}	3.97×10^{29}
51.5	1.36×10^6	6	2.56×10^5	5	8.26×10^{13}	1.54×10^{16}	4.52×10^{29}
52.0	1.34×10^6	6	2.54×10^5	5	9.16×10^{13}	1.61×10^{16}	5.23×10^{29}
52.5	1.31×10^6	6	2.52×10^5	5	1.03×10^{14}	1.68×10^{16}	6.15×10^{29}
53.0	1.29×10^6	6	2.50×10^5	5	1.15×10^{14}	1.74×10^{16}	7.23×10^{29}
53.5	1.27×10^6	6	2.48×10^5	5	1.30×10^{14}	1.81×10^{16}	8.65×10^{29}
54.0	1.24×10^6	6	2.46×10^5	5	1.47×10^{14}	1.88×10^{16}	1.04×10^{30}
54.5	1.22×10^6	6	2.45×10^5	5	1.69×10^{14}	1.95×10^{16}	1.26×10^{30}
55.0	1.20×10^6	6	2.43×10^5	5	1.94×10^{14}	2.02×10^{16}	1.54×10^{30}
55.5	1.18×10^6	6	2.41×10^5	5	2.22×10^{14}	2.09×10^{16}	1.89×10^{30}
56.0	1.16×10^6	6	2.39×10^5	5	2.57×10^{14}	2.15×10^{16}	2.35×10^{30}
56.5	1.14×10^6	6	2.38×10^5	5	2.99×10^{14}	2.22×10^{16}	2.93×10^{30}
57.0	1.12×10^6	6	2.36×10^5	5	3.47×10^{14}	2.29×10^{16}	3.67×10^{30}
57.5	1.10×10^6	6	2.34×10^5	5	4.04×10^{14}	2.36×10^{16}	4.60×10^{30}
58.0	1.08×10^6	6	2.33×10^5	5	4.70×10^{14}	2.43×10^{16}	5.79×10^{30}
58.5	1.06×10^6	6	2.31×10^5	5	5.55×10^{14}	2.50×10^{16}	7.43×10^{30}
59.0	1.04×10^6	6	2.29×10^5	5	6.55×10^{14}	2.56×10^{16}	9.55×10^{30}
59.5	1.03×10^6	6	2.28×10^5	5	7.74×10^{14}	2.63×10^{16}	1.23×10^{31}
60.0	1.01×10^6	6	2.26×10^5	5	9.17×10^{14}	2.69×10^{16}	1.60×10^{31}
60.5	9.91×10^5	5	2.25×10^5	5	1.09×10^{15}	2.75×10^{16}	2.07×10^{31}
61.0	9.75×10^5	5	2.23×10^5	5	1.29×10^{15}	2.82×10^{16}	2.70×10^{31}
61.5	9.59×10^5	5	2.22×10^5	5	1.54×10^{15}	2.88×10^{16}	3.53×10^{31}
62.0	9.43×10^5	5	2.20×10^5	5	1.84×10^{15}	2.94×10^{16}	4.63×10^{31}
62.5	9.27×10^5	5	2.19×10^5	5	2.23×10^{15}	3.00×10^{16}	6.21×10^{31}
63.0	9.12×10^5	5	2.17×10^5	5	2.68×10^{15}	3.06×10^{16}	8.20×10^{31}
63.5	8.97×10^5	5	2.16×10^5	5	3.22×10^{15}	3.11×10^{16}	1.09×10^{32}
64.0	8.83×10^5	5	2.15×10^5	5	3.94×10^{15}	3.17×10^{16}	1.48×10^{32}
64.5	8.69×10^5	5	2.13×10^5	5	4.77×10^{15}	3.23×10^{16}	1.97×10^{32}
65.0	8.55×10^5	5	2.12×10^5	5	5.78×10^{15}	3.29×10^{16}	2.65×10^{32}
65.5	8.42×10^5	5	2.11×10^5	5	7.04×10^{15}	3.35×10^{16}	3.56×10^{32}

66.0	8.29×10 ⁵	2.09×10 ⁵	8.75×10 ¹⁵	3.41×10 ¹⁶	4.91×10 ³²
66.5	8.16×10 ⁵	2.08×10 ⁵	1.07×10 ¹⁶	3.47×10 ¹⁶	6.68×10 ³²
67.0	8.03×10 ⁵	2.07×10 ⁵	1.33×10 ¹⁶	3.54×10 ¹⁶	9.10×10 ³²
67.5	7.91×10 ⁵	2.06×10 ⁵	1.64×10 ¹⁶	3.61×10 ¹⁶	1.25×10 ³³
68.0	7.80×10 ⁵	2.04×10 ⁵	2.01×10 ¹⁶	3.69×10 ¹⁶	1.68×10 ³³
68.5	7.69×10 ⁵	2.03×10 ⁵	2.49×10 ¹⁶	3.77×10 ¹⁶	2.32×10 ³³
69.0	7.58×10 ⁵	2.02×10 ⁵	3.09×10 ¹⁶	3.86×10 ¹⁶	3.22×10 ³³
69.5	7.47×10 ⁵	2.01×10 ⁵	3.77×10 ¹⁶	3.96×10 ¹⁶	4.39×10 ³³
70.0	7.37×10 ⁵	2.00×10 ⁵	4.58×10 ¹⁶	4.06×10 ¹⁶	6.01×10 ³³
70.5	7.27×10 ⁵	1.99×10 ⁵	5.64×10 ¹⁶	4.17×10 ¹⁶	8.44×10 ³³
71.0	7.18×10 ⁵	1.98×10 ⁵	6.85×10 ¹⁶	4.30×10 ¹⁶	1.17×10 ³⁴
71.5	7.09×10 ⁵	1.97×10 ⁵	8.30×10 ¹⁶	4.44×10 ¹⁶	1.62×10 ³⁴
72.0	7.00×10 ⁵	1.96×10 ⁵	9.80×10 ¹⁶	4.58×10 ¹⁶	2.20×10 ³⁴
72.5	6.92×10 ⁵	1.95×10 ⁵	1.19×10 ¹⁷	4.74×10 ¹⁶	3.08×10 ³⁴
73.0	6.84×10 ⁵	1.94×10 ⁵	1.42×10 ¹⁷	4.91×10 ¹⁶	4.32×10 ³⁴
73.5	6.75×10 ⁵	1.93×10 ⁵	1.71×10 ¹⁷	5.10×10 ¹⁶	6.11×10 ³⁴
74.0	6.68×10 ⁵	1.92×10 ⁵	2.10×10 ¹⁷	5.30×10 ¹⁶	8.88×10 ³⁴
74.5	6.61×10 ⁵	1.92×10 ⁵	2.58×10 ¹⁷	5.49×10 ¹⁶	1.30×10 ³⁵
75.0	6.53×10 ⁵	1.91×10 ⁵	3.21×10 ¹⁷	5.60×10 ¹⁶	1.96×10 ³⁵
75.5	6.46×10 ⁵	1.90×10 ⁵	3.82×10 ¹⁷	5.59×10 ¹⁶	2.98×10 ³⁵
76.0	6.39×10 ⁵	1.89×10 ⁵	4.24×10 ¹⁷	5.52×10 ¹⁶	4.56×10 ³⁵
76.5	6.31×10 ⁵	1.89×10 ⁵	4.42×10 ¹⁷	5.83×10 ¹⁶	7.04×10 ³⁵
77.0	6.24×10 ⁵	1.88×10 ⁵	5.38×10 ¹⁷	7.57×10 ¹⁶	1.06×10 ³⁶
77.5	6.15×10 ⁵	1.87×10 ⁵	7.45×10 ¹⁷	9.81×10 ¹⁶	1.66×10 ³⁶
78.0	6.06×10 ⁵	1.87×10 ⁵	1.06×10 ¹⁸	1.16×10 ¹⁷	2.54×10 ³⁶
78.5	5.96×10 ⁵	1.86×10 ⁵	1.55×10 ¹⁸	1.26×10 ¹⁷	3.92×10 ³⁶
79.0	5.84×10 ⁵	1.85×10 ⁵	2.31×10 ¹⁸	1.26×10 ¹⁷	6.08×10 ³⁶
79.5	5.69×10 ⁵	1.85×10 ⁵	3.41×10 ¹⁸	1.19×10 ¹⁷	9.23×10 ³⁶
80.0	5.50×10 ⁵	1.84×10 ⁵	5.13×10 ¹⁸	1.11×10 ¹⁷	1.41×10 ³⁷
80.5	5.28×10 ⁵	1.84×10 ⁵	7.77×10 ¹⁸	1.03×10 ¹⁷	2.16×10 ³⁷
81.0	5.02×10 ⁵	1.83×10 ⁵	1.13×10 ¹⁹	9.39×10 ¹⁶	3.14×10 ³⁷
81.5	4.72×10 ⁵	1.83×10 ⁵	1.68×10 ¹⁹	8.62×10 ¹⁶	4.73×10 ³⁷
82.0	4.39×10 ⁵	1.82×10 ⁵	2.38×10 ¹⁹	7.96×10 ¹⁶	6.73×10 ³⁷
82.5	4.05×10 ⁵	1.82×10 ⁵	3.37×10 ¹⁹	7.46×10 ¹⁶	9.60×10 ³⁷
83.0	3.71×10 ⁵	1.81×10 ⁵	4.64×10 ¹⁹	7.09×10 ¹⁶	1.33×10 ³⁸
83.5	3.37×10 ⁵	1.81×10 ⁵	6.24×10 ¹⁹	6.90×10 ¹⁶	1.80×10 ³⁸
84.0	3.06×10 ⁵	1.81×10 ⁵	8.36×10 ¹⁹	6.88×10 ¹⁶	2.43×10 ³⁸
84.5	2.77×10 ⁵	1.80×10 ⁵	1.09×10 ²⁰	7.07×10 ¹⁶	3.19×10 ³⁸
85.0	2.51×10 ⁵	1.80×10 ⁵	5.54×10 ¹³	3.02×10 ¹⁰	3.91×10 ³⁸
85.5	2.28×10 ⁵	1.80×10 ⁵	6.96×10 ¹³	3.27×10 ¹⁰	4.82×10 ³⁸
86.0	2.07×10 ⁵	1.80×10 ⁵	8.52×10 ¹³	3.66×10 ¹⁰	5.73×10 ³⁸
86.5	1.90×10 ⁵	1.79×10 ⁵	1.02×10 ¹⁴	4.14×10 ¹⁰	6.60×10 ³⁸
87.0	1.74×10 ⁵	1.79×10 ⁵	1.19×10 ¹⁴	4.83×10 ¹⁰	7.35×10 ³⁸
87.5	1.60×10 ⁵	1.79×10 ⁵	1.35×10 ¹⁴	5.74×10 ¹⁰	7.90×10 ³⁸
88.0	1.48×10 ⁵	1.79×10 ⁵	1.46×10 ¹⁴	6.94×10 ¹⁰	7.92×10 ³⁸

88.5	1.38×10	⁵	1.79×10	⁵	1.59×10	¹⁴	8.46×10	¹⁰	7.95×10	³⁸
89.0	1.28×10	⁵	1.79×10	⁵	1.65×10	¹⁴	1.04×10	¹¹	7.44×10	³⁸
89.5	1.20×10	⁵	1.78×10	⁵	1.68×10	¹⁴	1.28×10	¹¹	6.73×10	³⁸
90.0	1.12×10	⁵	1.78×10	⁵	1.63×10	¹⁴	1.61×10	¹¹	5.68×10	³⁸
90.5	1.05×10	⁵	1.78×10	⁵	1.55×10	¹⁴	1.98×10	¹¹	4.64×10	³⁸
91.0	9.88×10	⁴	1.78×10	⁵	1.46×10	¹⁴	2.39×10	¹¹	3.67×10	³⁸
91.5	9.29×10	⁴	1.78×10	⁵	1.31×10	¹⁴	2.82×10	¹¹	2.72×10	³⁸
92.0	8.73×10	⁴	1.78×10	⁵	1.16×10	¹⁴	3.20×10	¹¹	1.96×10	³⁸
92.5	8.22×10	⁴	1.77×10	⁵	9.93×10	¹³	3.47×10	¹¹	1.32×10	³⁸
93.0	7.73×10	⁴	1.77×10	⁵	8.56×10	¹³	3.52×10	¹¹	8.98×10	³⁷
93.5	7.28×10	⁴	1.77×10	⁵	7.25×10	¹³	3.32×10	¹¹	5.94×10	³⁷
94.0	6.86×10	⁴	1.77×10	⁵	6.05×10	¹³	2.93×10	¹¹	3.84×10	³⁷
94.5	6.47×10	⁴	1.76×10	⁵	4.95×10	¹³	2.47×10	¹¹	2.42×10	³⁷
95.0	6.11×10	⁴	1.76×10	⁵	3.99×10	¹³	1.96×10	¹¹	1.49×10	³⁷
95.5	5.77×10	⁴	1.76×10	⁵	3.17×10	¹³	1.47×10	¹¹	8.96×10	³⁶
96.0	5.46×10	⁴	1.76×10	⁵	2.53×10	¹³	1.04×10	¹¹	5.45×10	³⁶
96.5	5.19×10	⁴	1.75×10	⁵	2.04×10	¹³	6.92×10	¹⁰	3.34×10	³⁶
97.0	4.93×10	⁴	1.75×10	⁵	1.62×10	¹³	4.19×10	¹⁰	2.01×10	³⁶
97.5	4.70×10	⁴	1.75×10	⁵	1.30×10	¹³	2.24×10	¹⁰	1.22×10	³⁶
98.0	4.48×10	⁴	1.75×10	⁵	1.06×10	¹³	1.07×10	¹⁰	7.45×10	³⁵
98.5	4.28×10	⁴	1.74×10	⁵	8.67×10	¹²	4.64×10	⁹	4.60×10	³⁵
99.0	4.08×10	⁴	1.74×10	⁵	7.31×10	¹²	1.80×10	⁹	2.94×10	³⁵
99.5	3.83×10	⁴	1.74×10	⁵	6.11×10	¹²	5.42×10	⁸	1.84×10	³⁵
100.0	1.76×10	¹¹	1.73×10	⁵	5.39×10	¹²	5.53×10	⁷	1.22×10	³⁵

Impact production of nitrogen oxides in the Hadean atmosphere

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Impact production of nitrogen oxides in the Hadean atmosphere

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Key Points:

- A laboratory model of N_xO_y formation by impacts finds a large yield of N_2O .
- The steady-state abundance of N_2O in a one-dimensional atmospheric model shows that impact-production is still insufficient to significantly warm the Hadean Earth.

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Abstract

We investigate the impact formation of nitrogen oxides in the model Hadean atmosphere and the potential for greenhouse warming due to the production of nitrous oxide (N_2O). N_2O has been considered to be a relatively stable greenhouse gas produced by impact plasma. However, its warming potential strongly depends on its production rate and its stability in the early atmosphere. The high-energy-density synthesis efficiencies of NO, N_2O , and NO_2 are evaluated for gas mixtures representing an early Earth atmosphere by simulating an impact plasma with terawatt-class laser-induced dielectric breakdown (TC-LIDB) using the terawatt-scale Prague Asterix Laser System. Manifestations of laser induced high-energy-density plasma, such as a plasma temperature exceeding 10 000 K, high electron densities and large interaction volume, make this one of the best available laboratory models for simulating the chemical consequences of a meteoroid atmospheric entry. The measured yields of NO, N_2O , and NO_2 have been found to reach 6×10^{16} , 2×10^{16} , and 2×10^{15} molec J^{-1} , respectively. The N_2O yield is far above an upper limit determined from a previous tabletop LIDB experiment, while the NO and NO_2 yields are in broad agreement with a range of LIDB and electric-discharge experiments. Using the yield estimated for TC-LIDB plasma simulating an asteroid impact and a one-dimensional photochemical model of the Hadean atmosphere undergoing heavy bombardment, we find a large source flux of N_2O , but its steady-state partial pressure is still insufficient to warm the climate. These findings support a scenario of early Earth warming by other greenhouse gases, a significant source of N_2O other than impacts, or a relatively cold climate during part of the Hadean eon plausible for lower global temperatures due to anticipated lack of solar flux or depletion of greenhouse gases such as CO_2 on young early Earth.

Plain language summary

The climate of the Earth 4.5 to 4 billion years ago is not well known but geological evidence suggests the presence of liquid water. Although subglacial occurrence of liquid water cannot be excluded, some theories assume that this is at odds with the possibility of a very cold, and perhaps completely frozen, early Earth implied by the less-bright Sun at that time. Extra greenhouse warming of the Earth by atmospheric gases is then thought necessary to keep the surface temperature high enough for liquid water. Meteorites impacted the early Earth at a greater rate than today and provided a source of energy for forming possible greenhouse-gas molecules. In this paper, we mimic the impact-triggered formation of nitrogen oxide molecules (NO, NO_2 , N_2O) in the laboratory using a laser-created high energy plasma. We then compute the stable amount of N_2O that might have existed 4.5 billion years ago and find this to be too small to contribute to greenhouse warming. However, the effect of large amounts of impact-formed nitrogen oxides may be significant for detailed studies of the short-time consequences of a large impact on the early-Earth atmosphere, or as chemical inputs to the first stages of biochemistry, or for models of the atmospheres of exoplanets in young star systems encountering heavy bombardment.

1 Introduction

The geological record of well-preserved rocks from the Hadean eon preceding 4 Ga is lacking and the physical and chemical environment at that time is obscured. This uncertainty encompasses the important transition from a hot and hostile world following the Moon-forming event between 4.51 and 4.47 Ga (Bottke et al., 2015; Lock et al., 2020) and heavy bombardment and late veneer occurring before 3.5 Ga (Genda et al., 2017; Bottke & Norman, 2017) to the hot but life supporting Archean ocean planet established by around 4 Ga (Catling & Zahnle, 2020).

Extra-terrestrial impacts certainly influenced the Earth over this period, and the remnant lunar surface (Koeberl, 2006; Ryder, 2002) implies a decreasing number of impactors with solar system age, with the median estimate for a final impact capable of global ocean vaporisation of 4.3 Ga (Marchi et al., 2014). Lunar studies (Bottke & Norman, 2017) also suggest Earth experienced a late-heavy bombardment (LHB) with increased impact frequency between 4.2 and 3.5 Ga and peaking at (3.85 ± 0.05) Ga (Koeberl et al., 2000), but its occurrence and timing are not agreed upon (Wetherill, 1975; Boehnke & Harrison, 2016; Morbidelli et al., 2018; Mojzsis et al., 2019).

Analysis of Ce-anomalies in igneous zircons of crustal origin preceding 4 Ga reveal a significantly more reduced Hadean continental crust than today, and a progressive oxidation between 4 and 3.6 Ga (Yang et al., 2014). This could be the result of massive impact delivery and impact-induced degassing of reduced material (Kuwahara & Sugita, 2015), that is, CO- and H₂-rich volcanic species (Yang et al., 2014) with the probable addition of CH₄-rich fluids, along with a possible contribution to transient highly-reducing atmospheric states through the reduction of seawater to hydrogen by iron-cored impactors (Genda et al., 2017; Zahnle et al., 2020). Overall, the degree to which the atmosphere was reducing and its precise composition remain unknown, and theorising on the evolution of these parameters over geological time is an active field of research (e.g., Shaw (2008); Lammer et al. (2018); Zahnle et al. (2020)).

Stellar-evolution models maintain that total solar intensity has steadily increased, with approximately 30% more radiative-energy output today than 4.6 Ga (Feulner, 2012; Charnay et al., 2020). One dimensional models of radiative transfer in the Archean and Hadean atmosphere find a lower surface temperature than today to the extent where no liquid water is expected on the surface (Sagan & Mullen, 1972; Feulner, 2012), in contradiction to analyses of 4 Ga igneous zircons presenting strong evidence for the presence of liquid water and supracrustal rocks around 4.2 Ga, or possibly as early as 4.325 Ga (Wilde et al., 2001; Cavosie et al., 2005).

Some proposed sources for the extra warming needed to prevent a frozen Hadean, and subsequent Archean eon, are reviewed by Kasting and Catling (2003), Feulner (2012), and Charnay et al. (2020), and include Solar mass-change, alteration of the Earth's albedo by clouds or continental configuration, an enhanced Solar wind flux, or rotation and obliquity variations. The leading hypothesis is enhanced greenhouse warming due to infrared-active atmospheric molecules, with arguments set forth proposing CO₂ (Kuhn & Kasting, 1983; Kasting & Catling, 2003; Kasting, 2014), NH₃ (Sagan & Mullen, 1972; Kuhn & Kasting, 1983), and CH₄ (Kiehl & Dickinson, 1987; Haqq-Misra et al., 2008). Investigators of greenhouse effects in the more-recent Proterozoic atmosphere predict possible climate forcing due to N₂O (Buick, 2007; Roberson et al., 2011; Stanton et al., 2018) but require a biologically-mediated source or reasonable O₂ co-abundance that are unlikely to apply to the Hadean. Alternatively, Airapetian et al. (2016) proposed an enhanced Solar wind flux could have increased the abiotic nitrogen N-fixation rate and lead to an abundance of N₂O. The importance of the species mentioned above to greenhouse warming hinges on their potential for radiative forcing, source magnitude, and stability against photolysis, chemistry, surface deposition, and atmospheric escape. Recently, three-dimensional global climate models including atmosphere-surface feedback, as reviewed by Charnay et al. (2020), find warming of the Archean by an abundance of CO₂ within geological constraints can be sufficient to prevent a global ice age.

Another motivation for estimating the early-Earth abundance of N_xO_y species is to constrain their potential influence on the development of life. The fixation of N₂ makes available a huge amount of energy following the reaction of NO_x species (NO and NO₂) with simple prebiotic precursors like cyanate or the derivatives of urea, with the provision of several hundreds kJ mol⁻¹ estimated from thermodynamic data (Amend & Shock, 2001). In this context, nitric oxide can drive the abiotic formation of peptide biopolymers from amino acid derivatives (Taillades et al., 1999). Nitric oxide is also a proposed elec-

tron acceptor during the evolution of the biochemical metabolisms of aerobic respiration and oxygenic photosynthesis before atmospheric oxygenation (Ducluzeau et al., 2009; Gribaldo et al., 2009; Wong et al., 2017).

The formation of NO_x by lightning has been well-studied in the laboratory and environment (e.g., Chameides et al. (1977); Levine et al. (1981); Navarro-González et al. (2001)). Modern-day lightning produces NO_x at a rate of $2 \times 10^{11} \text{ mol y}^{-1}$ (Schumann & Huntrieser, 2007) out of a total natural and anthropogenic source of $1.4 \times 10^{12} \text{ mol y}^{-1}$ (Müller & Stavrakou, 2004). For comparison, the amount of NO_x generated by the energy deposited in a single impact with a large extraplanetary body can also be significant, or overwhelming, with an estimated $1.25 \times 10^{10} \text{ mol}$ produced by the 1908 Tunguska event (Curci et al., 2004) and $1.5 \times 10^{14} \text{ mol}$ by the Chicxulub impact 66 Ma (Parkos et al., 2015).

In this work, we present new experimental data simulating high-velocity impact shocks by laser-induced dielectric breakdown (LIDB) and probe the production of nitrogen oxides. The measured production efficiency (or yield) of N_2O is applied to a photochemical model of the Hadean atmosphere and the resultant steady-state abundance and greenhouse warming estimated.

2 Experimental yield of nitrogen oxides

2.1 Method

Terawatt-class laser-induced dielectric breakdown (TC-LIDB) of gas mixtures simulating possible early-Earth atmospheric compositions was induced by the focused beam of the Prague Asterix Laser System (PALS) (Jungwirth et al., 2001) in a similar layout as used during previous studies performed in our laboratory, e.g., Civiš et al. (2004); Ferus et al. (2017); Ferus, Pietrucci, et al. (2019). The TW-class iodine photodissociation laser generates 350 ps pulses of 1315.2 nm near-infrared radiation and provides one pulse every 25 minutes. Each pulse can carry up to 1000 J of radiation energy. The laser beam was focused by a 15-cm-in-diameter CaF_2 plano-convex lens with a focal length of 25 cm through a 10 cm-diameter Pyrex window into a glass cell filled with the atmosphere analogue.

In multiphase experiments, the 800 cm^3 sample cell contains not only the gas mixture but also a liquid sample and/or catalytic solids representing planetary and meteoritic materials. The height of the laser beam focus above this material is adjusted to avoid any direct interaction of the focused laser beam with solids and liquids (that is, the LIDB occurs in gas only) but to secure effective contact between the expanding LIDB plasma and condensed material.

During the experiments described here, a mixture of gases was typically subjected to between 11 and 25 pulses with 25 min pauses between subsequent pulses. The pulse energy was kept constant at 150 J, and the total accumulated energy varied between 1650 to 3750 J. Each pulse interaction results in an expanding plasma mimicking the conditions surrounding a high-velocity extraterrestrial body as it enters the atmosphere, explodes, or generates an impact plume. The analysis of atomic and molecular emission lines during our previous PALS TC-LIDB investigations revealed vibrational, rotational, and electronic excitation temperatures ranging from 4200 to 9300 K, depending on the sample composition and pressure and irradiation conditions (Babánková et al., 2006). In this study, the electron density has been estimated to reach 10^{17} cm^{-3} .

After each laser irradiation series, the gas-phase contents of the irradiation cell are transferred to a Bruker IFS 125HR high-resolution infrared Fourier-transform spectrometer for constituent analysis. The spectrometer was operated in the mid-infrared between 600 and 4000 cm^{-1} using a KBr beamsplitter and HgCdTe liquid- N_2 -cooled detector. The

Table 1. Formation efficiencies and upper limits in laboratory LIDB experiments (molecules J⁻¹).

Sample composition ^a	NO	N ₂ O	NO ₂
N₂(80%), CO₂(20%)			
–	3.0×10^{16}	3.7×10^{16}	2.1×10^{15}
<i>v</i> (H ₂ O)	2.3×10^{16}	4.2×10^{14}	$< 3 \times 10^{14}$
<i>s</i> (anatase)	2.4×10^{16}	1.8×10^{16}	5.4×10^{14}
<i>v</i> (H ₂ O) <i>s</i> (clay)	1.8×10^{17}	4.2×10^{15}	8.8×10^{14}
<i>v</i> (HCl) <i>s</i> (clay)	8.6×10^{16}	2.0×10^{16}	5.8×10^{15}
<i>v</i> (HCl), <i>s</i> (anatase)	1.4×10^{16}	2.1×10^{16}	$< 3 \times 10^{15}$
<i>v</i> (H ₂ SO ₄), <i>s</i> (anatase)	8.8×10^{15}	3.6×10^{14}	$< 3 \times 10^{14}$
<i>v</i> (H ₂ SO ₄), <i>s</i> (anatase), <i>s</i> (clay)	5.0×10^{16}	$< 6 \times 10^{15}$	$< 6 \times 10^{15}$
<i>s</i> (anatase)	6.8×10^{16}	4.5×10^{15}	$< 6 \times 10^{14}$
<i>s</i> (anatase)	8.6×10^{16}	6.0×10^{15}	$< 2 \times 10^{15}$
CO(50%), NH₃(50%)			
–	2.3×10^{16}	2.8×10^{16}	$< 3 \times 10^{16}$
<i>v</i> (H ₂ O), <i>s</i> (clay)	2.6×10^{16}	1.9×10^{16}	$< 3 \times 10^{16}$
<i>v</i> (H ₂ O)	3.2×10^{16}	5.1×10^{16}	$< 2 \times 10^{15}$
<i>v</i> (H ₂ O), <i>s</i> (anatase)	1.2×10^{17}	1.2×10^{16}	$< 2 \times 10^{15}$
Mean yield	6×10^{16}	2×10^{16}	2×10^{15}

^a The gas-phase composition is given in bold along with liquid / solution (*v*) and surface (*s*) samples present in the interaction chamber.

resulting spectra are averages of 200 measurements, apodised with a Blackman-Harris function, and with a spectral resolution of 0.02 cm⁻¹. The concentrations of NO, NO₂ and N₂O were determined by comparison with calibration measurements over a wide range of partial pressures using standard gases: nitrous oxide ($\geq 99.998\%$ purity, Sigma Aldrich), nitric oxide (98.5%, Sigma Aldrich), nitrogen dioxide ($\geq 99.5\%$, Sigma Aldrich). A verification of this analysis was made by comparing the observed absorption band profiles with simulations profiles computed from linelists taken from the HITRAN database (Gordon et al., 2017). We analysed the NO fundamental band at 1875 cm⁻¹, NO₂ ν_3 band at 1618 cm⁻¹, and N₂O ν_3 band at 2224 cm⁻¹. The measured concentrations are converted into production efficiencies, that is the amount of product formed per unit of input energy (molecules J⁻¹), that can be used to scale our laser experiment to an impacted atmosphere.

The PALS laser deposits significantly greater energy than do tabletop LIDB facilities, and generates a greater volume of hotter plasma, with measured electronic and vibrational temperatures $T_{\text{exc}} = 8000 - 10\,000$ K and $T_{\text{vib}} = 4200 - 6500$ K. The chemically active plasma has a diameter of about 4 cm and the resulting fireball expands at a velocity on the order of 300 km s⁻¹ (Babánková et al., 2006; Ferus, Kubelík, et al., 2019). The principal limitation of the PALS laser is its long 25 min duty cycle that precludes the study of a wider range of sample compositions.

2.2 Results

The measured formation efficiencies for several models of the early Earth atmosphere are listed in Table 1 with NO and N₂O consistently detected and synthesised nitrogen oxide (NO₂) measured in several cases. All results are for 1 atm sample pressure with gas-phase composition corresponding to a redox-neutral atmosphere (N₂:CO₂ = 80:20) or reduced state (CO:NH₃ = 50:50). The elemental-nitrogen density is about three times greater in the former case, while the oxygen densities are similar. Additional experiments were conducted with each gas mixture including either liquid/solvent reservoirs (H₂O, HCl, H₂SO₄) or catalysing substrates (mineral anatase and montmorillonite clay). We have also reanalysed spectra taken from experimental campaigns conducted for various objectives (Civiš et al., 2004; Babánková et al., 2006; Civiš et al., 2008; Ferus et al., 2011; Ferus et al., 2014; Ferus et al., 2015; Civiš et al., 2016; Ferus et al., 2017; Ferus et al., 2017; Ferus, Pietrucci, et al., 2019). Regarding differences in yields of N₂O in particular mixtures with different gas phase and solid phase composition, we adopt for the model of planetary chemistry the mean production yield of each species.

The full range of measured NO production yields spans a factor of 20 with a mean of 6×10^{16} molec J⁻¹. The mean N₂O yield is 2×10^{16} molec J⁻¹ and varies by more than a factor of 100 between experiments, which reduces to a factor of 10 when neglecting two measurements with anomalously low N₂O yields below 10^{15} molec J⁻¹. A factor of 20 variation encompasses all measured NO₂ yields and upper limits, with a mean of 2×10^{15} molec J⁻¹. Only upper limits for NO₂ are available for the reducing-atmosphere CO:NH₃ experiments because of a strong overlap of NH₃ absorption with the NO₂ ν_3 band.

2.3 Discussion

A comparison of newly-measured yields with previous shock-chemistry experiments producing nitrogen oxides is given in Table 2 (see also the data reviewed in Lawrence et al. (1995) and Rahman and Cooray (2008)). Most existing data is collected in the interests of quantifying lightning-initiated nitrogen fixation in modern-Earth air, but some data exists for exotic gas mixtures and energy sources.

The NO yields in Table 2, or NO_x yields when NO is not discriminated from NO₂ but likely to be the dominant product, are generally consistent within a factor of ten and our measurement falls near the middle of their distribution. Significantly lower NO yields are measured when generated in a coronal discharge, which may be due to a higher degree of ionisation and lower temperature generated in these experiments relative to spark discharges and LIDB (Nna Mvondo et al., 2001). The measured 10^{16} to 5×10^{17} molec J⁻¹ NO yields are well-modelled by their thermochemical equilibrium abundance assuming a freeze-out temperature between 2000 to 5000 K in the rapidly cooling experimental plasmas and shocks (Chameides, 1979; Chameides & Walker, 1981; Mancinelli & McKay, 1988; Navarro-González et al., 2001). Their consistency persists over a large range of deposited energies (e.g., Table 1 of Cooray et al. (2009)); when generated by LIDB (e.g., Nna Mvondo et al. (2001); Navarro-González et al. (2001); Rahman and Cooray (2003)), pulsed lightning or coronal electric discharges (e.g., Levine et al. (1981); Stark et al. (1996); Nna Mvondo et al. (2001)), continuous plasma (Hill et al., 1988; Kim et al., 2010) or particle beams (Rahman et al., 2006). The NO yield is maximised for an approximately even N₂:CO₂ mixing ratio in the measurements of Nna Mvondo et al. (2001), which is also consistent with a low yield in the nitrogen-depleted Venus-analogue probed by Levine et al. (1982).

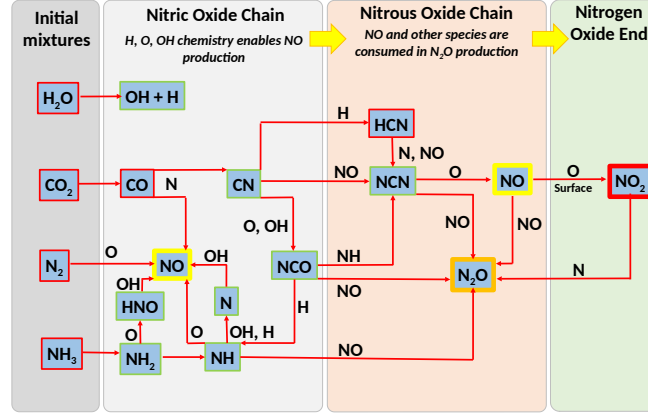
In experiments where the relative yield of NO and NO₂ is estimated, the production of the former is dominant. This is consistent with the 30:1 mean NO:NO₂ production ratio measured by us. In electric discharges, NO₂ may form after high-temperature shock conditions have dissipated from the NO primary-product (Chameides et al., 1977; Stark et al., 1996; Kim et al., 2010), and its abundance is enhanced by environmental

Table 2. Comparison of measured N_xO_y yields.

Simulated atmosphere	NO_x ^a	Yield (molec. J ⁻¹)		N_2O	Reference
Experimental method: LIDB					
Early Earth ^b		6×10^{16}	2×10^{15}	2×10^{16}	This work ^c
Modern Earth		3×10^{14}			Navarro-González et al. (2001) ^d
Modern Earth		1.5×10^{17}			Navarro-González et al. (2001) ^e
Modern Earth	$(6.7 \pm 0.5) \times 10^{16}$	$(4.6 \pm 0.5) \times 10^{16}$			Rahman and Cooray (2003)
Early Mars ^f		4.1×10^{16}			Navarro-González et al. (2019)
Venus ^g		1.3×10^{16}			Nna Mvondo et al. (2001)
Experimental method: spark electric discharge					
Modern Earth	$(1.1 \pm 0.2) \times 10^{16}$				Cook et al. (2000)
Modern Earth		4.6×10^{17}			Wang et al. (1998)
Modern Earth	5×10^{15}				Stark et al. (1996)
Modern Earth	$1\text{--}2 \times 10^{16}$				Cooray and Rahman (2005) ^h
Modern Earth	$(6 \pm 1) \times 10^{16}$				Chameides et al. (1977)
Modern Earth	$(3.0 \pm 0.2) \times 10^{16}$	$(2.8 \pm 0.2) \times 10^{16}$			Rehbein and Cooray (2001)
Modern Earth				4×10^{12}	Levine et al. (1979)
Modern Earth		$(5 \pm 2) \times 10^{16}$			Levine et al. (1981)
Venus ⁱ		$(3.7 \pm 0.7) \times 10^{15}$			Levine et al. (1982)
Experimental method: coronal electric discharge					
Modern Earth	$3.6\text{--}5.7 \times 10^{14}$				Rehbein and Cooray (2001)
Early Earth ^j		1.3×10^{14}		1.2×10^{13}	Nna Mvondo et al. (2001)
Modern Earth		$(1.4 \pm 0.7) \times 10^{16}$		$(1.0 \pm 0.5) \times 10^{17}$	Hill et al. (1988) ^k
Experimental method: Sample flowed through a continuous microwave plasma					
Modern Earth		$0.5\text{--}0.8 \times 10^{16}$	$9\text{--}14 \times 10^{16}$		Kim et al. (2010)
Experimental method: Flowing sample subjected to α -particle irradiation					
Modern Earth	2×10^{17}				Rahman et al. (2006)

^a Odd-nitrogen species are not discriminated.^b $N_2 : CO_2 = 80 : 20$ or $CO : NH_3 = 50 : 50$ ^c The estimated uncertainty is a factor of 10.^d This is a partial yield measured in an expanding shock wave surrounding the laser-generated plasma.^e This is a partial yield measured in the core of laser-generated plasma.^f $CO_2 : N_2 : H_2 = 40 : 40 : 20$ ^g $N_2 : CO_2 = 20 : 80$ ^h In a positive-streamer discharge.ⁱ $N_2 : CO_2 = 4 : 96$ ^j Measured for a range of $N_2:CO_2$ mixing ratios, with the listed peak yields for a 1:1 mixture.^k Pulsed discharge in a flowing cell.

Figure 1. Simplified network of N_xO_y high temperature and pressure chemistry derived from Glarborg et al. (2018).



ozone (Levine et al., 1981; Stark et al., 1996; Hill et al., 1988), which is absent in our anoxic experiments related to Hadean atmosphere lacking molecular oxygen.

Only a few measurements of N_2O yield exist and their multiple-order-of-magnitude disparity suggests that N_2O is not a thermochemical primary product in the laboratory-generated plasma and shock waves. Instead, it likely forms during the equilibration of heated and dissociated matter and is sensitive to the experiment-specific details of this cool down (Donohoe et al., 1977; Hill et al., 1988). A large-scale lightning simulator is used by Levine et al. (1979) to subject air to 17.5 kJ of electrical energy and produced a low $4 \times 10^{12} \text{ molec J}^{-1}$ yield of N_2O , while Nna Mvondo et al. (2001) produced a similar yield, $1.16 \times 10^{13} \text{ molec J}^{-1}$, in a table top coronal discharge in a 1:1 mixture of N_2 and CO_2 . However, Nna Mvondo et al. (2001) detect no N_2O under the same sample conditions subjected to LIDB, despite generating 100 times more NO than with an electric discharge. They attribute this difference to the equilibrated high-temperatures and neutral-radical chemistry generated by LIDB versus the relatively-low-temperature ion chemistry occurring in the discharge. However, in a coronal discharge through flowing air, Hill et al. (1988) find a substantial optimal yield of $(1.0 \pm 0.5) \times 10^{17} \text{ molec J}^{-1}$ and a strong flow-rate dependence, attributing its dominant formation to electronically-excited N_2 .

Our N_2O TC-LIDB yield of $2 \times 10^{16} \text{ molec J}^{-1}$ is well above the apparent detection limit of the table-top LIDB experiment of Nna Mvondo et al. (2001), and in between the range of electric-discharge yields listed in Table 2. We do not attempt to constrain the dominant N_2O formation mechanism in our experiment in the absence of a more systematic set of measurements but the reaction $O(^3P) + N_2 + M \longrightarrow N_2O + M$ was proposed by Donohoe et al. (1977), and Hill et al. (1984) identify its generation as arising from electronically-excited N_2 in the $A^3\Sigma_u^+$ state. A schematic network of high-temperature and pressure chemistry leading N_xO_y species drawn from a recent review of NO_x combustion chemistry (Glarborg et al., 2018) is shown in Fig. 1.

In the following application of extraterrestrial impacts, we prefer to use our mean N_2O yield over other values in Table 2 because the high peak temperature and low electron density generated by the PALS TC-LIDB bears greater similarity to the conditions in an impactor ablation plasma than do the lightning-analogue laboratory electric discharges of Levine et al. (1979) and Hill et al. (1988), and the large shocked volume constitutes a better simulation than does the tabletop LIDB experiment of Nna Mvondo et al. (2001).

3 Nitrogen oxides in the Hadean atmosphere

3.1 Production rate

Laboratory measured and theoretically calculated N_xO_y chemical production efficiencies have been previously adapted to models of their impact production (e.g., Park (1978); Fegley et al. (1986); Prinn and Fegley (1987); Kasting (1990); Silber et al. (2018); Curci et al. (2004); Parkos et al. (2015); Navarro-González et al. (2019)). Theoretical and laboratory-informed computations of the primary NO yield aim to match the physical extremes and time scales occurring in the ablative or explosive shock wave generated by a descending impactor or its post-impact plume for a range of masses, compositions, velocities, and incidence angle. Photochemical and dynamical atmospheric models including surface deposition are needed to estimate the time-dependent abundance of NO_2 following an impact (e.g., Curci et al. (2004)), while the impact-formation of N_2O is not comprehensively studied.

Here, global impact-generated surface fluxes, Φ , of NO_2 , NO, and N_2O are computed directly from the mean yields, S , in Table 1 and assuming a steady impact-energy deposition rate, $\dot{E}_T$, and its efficient conversion into shock products. The surface flux of N_xO_y products is then

$$\Phi = \frac{S\dot{E}_T}{4\pi R^2} \quad (1)$$

where R is the Earth radius. We adopt properties of the late-heavy bombardment as summarised by Abramov et al. (2013). We assume impactors with a single velocity of 20 km s^{-1} deposit a total mass of $2 \times 10^{20} \text{ kg}$ over a period of 100 Myr. The average impact-energy deposition rate is then $1.3 \times 10^{13} \text{ J s}^{-1}$ and leads to NO, N_2O , and NO_2 surface fluxes of $\Phi = 1.5 \times 10^{11}$, 5×10^{10} , $5 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$, respectively, under the assumption of complete conversion of impactor kinetic energy into an atmospheric shock. This latter assumption overestimates the calculated fluxes, with estimated conversion efficiencies (Chyba & Sagan, 1992) falling between 1 and $1/60$, depending on the impactor mass and with the lowest efficiencies occurring for the largest impactors that also deliver most of the impactor energy.

The N_2O impact-generated surface flux is significantly larger than the $8.3 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$ attributable to modern-day lightning (Schumann & Huntrieser, 2007). Chyba and Sagan (1992) estimate a $4.8 \times 10^{10} \text{ J s}^{-1}$ lightning and coronal-discharge energy dissipation rate at 4 Gya that corresponds to 300 times less N_2O produced than for the impact rate estimated here when assuming the same chemical formation efficiency.

3.2 Steady-state abundance

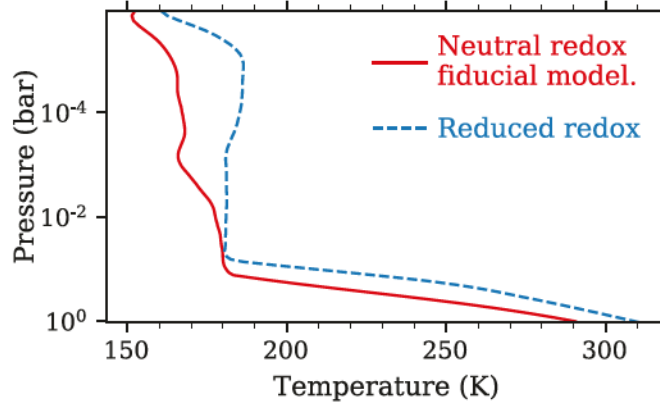
We estimate the lifetime of impact-generated nitrogen oxides in a model Hadean atmosphere with the ARGO one-dimensional Lagrangian photochemistry and diffusion program. This code and the accompanying STAND photochemical reaction network are designed for general planetary-atmosphere applications, have been described in detail elsewhere (Rimmer & Helling, 2016; Rimmer & Rugheimer, 2019), and previously applied to studies of lightning- and impact-induced chemistry of the early and modern Earth (Ardaseva et al., 2017; Ranjan et al., 2019; Rimmer et al., 2020). The ARGO model propagates a parcel of atmosphere from the surface to a maximum height and back again while time-integrating its photochemistry and partially mixing it with an initially-approximate ambient atmospheric composition at each vertical grid point traversed. The differential equation solved at each step is

$$\frac{dn_i}{dt} = P_i - L_i - \frac{\partial \Phi_i}{\partial x} \quad (2)$$

where n_i (cm^{-3}) is the height-dependent concentration of species i , P_i and L_i ($\text{cm}^{-3} \text{ s}^{-1}$) are its chemical production and loss rates, and Φ_i ($\text{cm}^{-2} \text{ s}^{-1}$) is the combined flux due

Table 3. Surface mixing ratio and modelled N₂O lifetimes.

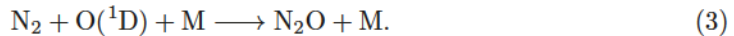
Model	Surface mixing ratio						N ₂ O lifetime (y)
	N ₂	CO ₂	NH ₃	H ₂ O	H ₂	CO	
Neutral redox – fiducial model	0.8	0.2	0	0.01	10 ^{−3}	10 ^{−5}	2.2
Neutral redox – enhanced CO ₂	0.6	0.4	0	0.01	10 ^{−3}	10 ^{−5}	2.9
Neutral redox – reduced CO ₂	0.95	0.05	0	0.01	10 ^{−3}	10 ^{−5}	1.5
Reduced redox – NH ₃ /CO dominated	0	0	0.5	0.01	10 ^{−3}	0.5	2.7

**Figure 2.** Temperature profile of the neutral redox and reduced atmosphere models.

to eddy and molecular diffusion. A height-independent eddy diffusion coefficient of $K = 10^5 \text{ cm}^2 \text{ s}^{-1}$ is adopted in all models presented here. By means of Eq. (2), diffusion is modelled in an efficient Lagrangian manner (Rimmer & Helling, 2016) and a steady state is reached between the propagated parcel and the atmospheric column after repeated traversals.

All models computed here have a 1 bar surface pressure and the major constituents of the fiducial case are N₂ and CO₂ in a 80:20 ratio. Fixed surface densities of the dominant species in this case, and for some comparative models, are listed in Table 3. The Hadean-eon solar photon flux at the top of the atmosphere is taken from the 3.8 Ga case computed by Claire et al. (2012) and as used by Rimmer et al. (2019). Fluxes longwards of 200 nm are reduced on average by 23% from the modern day, while shorter-wavelength radiation is progressively enhanced, reaching a factor of 5 by 100 nm. The pressure and temperature profiles are computed from a one-dimensional climate model as in Rimmer et al. (2019) and plotted in Fig. 2. The version of the STAND reaction network used here to compute kinetic and photolytic rates is described in Rimmer et al. (2021).

The computed densities of some species in the fiducial model are shown in Fig. 3 neglecting the N_xO_y impact production. The N₂O density plotted in Fig. 3 is driven by its production from the reaction



NO in the impact-free model is, broadly speaking, the product of N₂O photodissociation and is itself the precursor of NO₂, primarily through the reaction $\text{NO} + \text{HO}_2 \longrightarrow \text{NO}_2 + \text{OH}$.

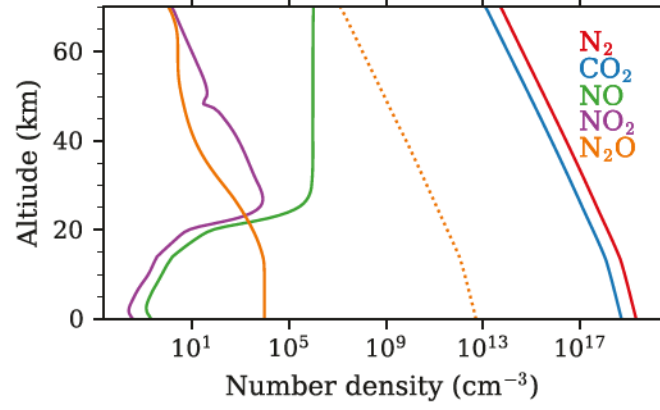


Figure 3. *Solid lines:* Densities computed by the fiducial atmospheric model with $\text{N}_2:\text{CO}_2=80:20$ and without impact formation. *Broken line:* An N_2O density of 200 ppb after consideration of its impact formation.

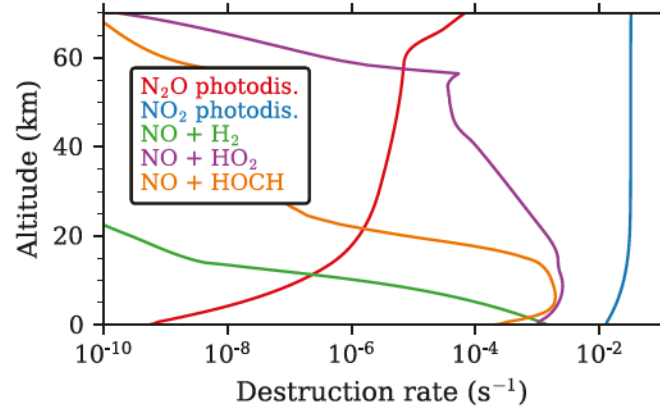


Figure 4. Dominant destruction mechanisms of NO , NO_2 , and N_2O in the neutral redox atmosphere.

If the photochemical destruction of continuously impact-generated N_xO_y species is irreversible, their steady-state column density sustained in the atmosphere is given by

$$N = \tau \times \Phi \quad (4)$$

where τ is a photochemical lifetime. The rates for the dominant processes destroying N_xO_y species computed with ARGO are plotted in Fig. 4, with N_2O being nominally more stable than NO or NO_2 . However, products of the leading NO and NO_2 destruction processes shown in Fig. 4 are, respectively, NO_2 and NO, forming a closed cycle that invalidates the use of Eq. (4). Instead, we assume that the rapid conversion of NO and NO_2 into HNO_2 and HNO_3 , followed by their dissolution and wet deposition is sufficient to eliminate these gases from the atmosphere such that no significant steady-state abundance is maintained, as is the case in the modern Earth atmosphere.

The photolysis of N_2O branches to produce both $N_2 + O(^1S)$ and $N_2 + O(^1D)$ but most metastable $O(^1D)$ is irreversibly collisionally de-excited before it can reform N_2O by Eq. (3), and we adopt Eq. (4) to estimate the equilibrium N_2O abundance. We make a simplifying assumption that the mixing ratio of impact-generated N_2O is independent of altitude. Then, the column-averaged N_2O destruction rate, J_{av} , computed from the photodissociation rate, $J(z)$, shown in Fig. 4 is

$$J_{av} = \frac{\int_0^{\text{top}} J(z)n(z) dz}{\int_0^{\text{top}} n(z) dz} \quad (5)$$

and corresponds to an average N_2O lifetime of 2.2 years in the fiducial model. This is significantly reduced from the 130 year lifetime of N_2O in the present-day atmosphere (Prather et al., 2012) which is greatly extended by ultraviolet shielding from O_2 and O_3 (Roberson et al., 2011). The equilibrium column density of impact-sourced N_2O according to Eq. (4) is then $4.0 \times 10^{19} \text{ cm}^{-2}$, corresponding to an average mixing ratio of 200 ppb. This is similar to the present-day mixing ratio of 300 ppb (Prather et al., 2012), despite the shortened lifetime, because of the sheer magnitude of the impact source term. The density of impact-generated N_2O thus computed is compared in Fig. 3 with its purely photochemical production.

A greater mixing ratio of N_2O could occur if its impact production predominantly occurs where it is effectively shielded from ultraviolet radiation, that is, below 20 km. In this case the $10^5 \text{ cm}^2 \text{ s}^{-1}$ eddy-diffusion coefficient adopted in our model implies a mixing timescale from the surface up to 20 km of about a year, such that the steady-state N_2O column density may increase by a factor of a few.

Further models with the CO_2 mixing ratio increased to 40% and decreased to 5% were used to compute further N_2O lifetimes, listed in Table 3. These lifetimes are affected by the presence of more or less ultraviolet shielding by CO_2 and vary within 40%. We also compute the N_2O destruction rate under the assumption of a reducing atmosphere with dominant components NH_3 and CO, as listed in Table 3, and find a 20% increased N_2O lifetime when assuming its mixing ratio to be height independent. This small change following a complete chemical substitution of the atmosphere arises from a balance between modelled N_2O photodissociation rates below 45 km and above, combined with its chemical destruction below 8 km by



as shown in Fig. 5. In the lower atmosphere, a multiple-orders-of-magnitude reduced photodissociation rate is the result of more effective shielding of N_2O photodissociation by NH_3 than by CO_2 in the primary model. At higher altitudes, the greater solar photolysis rate of NH_3 relative to CO_2 reduces its abundance dramatically and leaves N_2O unshielded. The location of N_2O impact production will then have a greater impact on its residence time in an NH_3 -rich atmosphere than for the $N_2 + CO_2$ case.

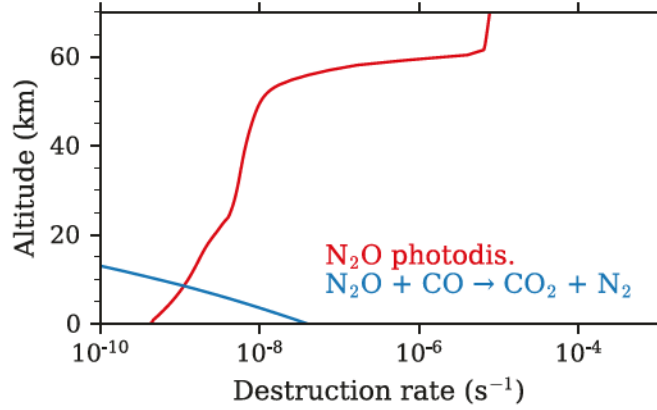


Figure 5. Dominant destruction mechanisms of N_2O in the reduced redox atmosphere.

Airapetian et al. (2016) compute the N_2O formation due to charged particles injected by flaring of the highly-active young Sun into an early-Earth atmosphere similar to the one modelled here (80% N_2 and 20% CO_2). They find the potential for an enhanced N_2O abundance well above our impact-estimate at altitudes above 30 km, but significant less below this and when integrated over the full atmospheric column.

3.3 N_2O greenhouse warming

Greenhouse warming in the modern atmosphere is sensitive to the N_2O abundance (Myhre et al., 2013) and Roberson et al. (2011) use a one-dimensional climate model to evaluate the warming potential of elevated levels of this molecule during the Proterozoic, finding approximately 8 K climate warming following the addition of 30 ppm N_2O and 1 K of warming for 2 ppm. Byrne and Goldblatt (2014) computed radiative forcing for a range of greenhouse gases in an Archean atmosphere, and find good agreement with the climate model of Roberson et al. (2011) for an assumed climate sensitivity to N_2O consistent with the modern Earth. They also compute the reduction of N_2O radiative forcing due to its spectral overlap with CO_2 and CH_4 , finding approximately 33% reductions for abundances of 10 000 and 100 ppm, respectively. The radiative forcing due to N_2O will be reduced further in our model Hadean atmosphere composed of 20% CO_2 , but, in partial compensation, the N_2O lifetime is simultaneously increased from the ultraviolet shielding of enhanced CO_2 and CH_4 .

A decrease of the 100 Myr duration of the LHB assumed in Sec. 3.1 will increase the production rate of N_2O and its warming potential. However, to achieve 1 K warming, according to the Proterozoic climate model Roberson et al. (2011), an LHB spanning only 10 Myr is needed, and would then have only a transient influence on the Hadean eon. Furthermore, an LHB extended in time is also possible, or a non-cataclysmic steadily-decreasing late accretion that deposits its energy (on average) more gradually. Our assumption in Sec. 3.1 of continuous energy deposition further overestimates the steady-state abundance N_2O , with most energy actually delivered episodically by large impacts (Abramov et al., 2013). A larger transient column density of N_2O than computed may then occur following a large impact, but its climatological influence would be likely overshadowed by direct impact effects. In view of the above discussion it is clear that the excess of impact-generated N_2O computed here is insufficient to meaningfully warm the Hadean climate.

4 Conclusion

TC-LIDB chemistry initiated by a 150 J-per-pulse laser system is used as an analogue to the high-energy chemistry accompanying a meteor impact, and provides a better model of this process than small-scale LIDB experiments or high-temperature chemistry initiated by pulsed electric discharges. By post-analysing the products of shock chemistry we determine the final abundances of NO, N₂O, and NO₂ when probing two possible compositions of a Hadean-eon O₂-free atmosphere, 80% N₂ with 20% CO₂ and 50% CO with 50% NH₃. The NO and NO₂ yields in these anoxic mixtures are consistent with existing experimental data for the modern and early Earth. The measured N₂O yield falls between 4×10^{14} and 4×10^{16} molec J⁻¹ and is higher than implied by its non-detection in a tabletop LIDB experiment (Nna Mvondo et al., 2001), while previous electric-discharge yields are divergent (Levine et al., 1979; Hill et al., 1988).

We compute the steady-state abundance of N₂O in a photochemical model of an N₂ and CO₂ dominated Hadean atmosphere to be 200 ppb, when assuming an impact-generated N₂O flux consistent with a late-heavy bombardment of 100 Myr duration. The computed N₂O impact production rate far exceeds its generation by photochemical means or modern-day lightning production. The greenhouse warming attributable to the computed N₂O abundance is insufficient to raise the climatic temperature by a significant amount. Nonetheless, given the large N₂O yield found relative to other sources, the transient impact-generation of N₂O on the Hadean Earth or exoplanets undergoing heavy bombardment should be considered in comprehensive models of their chemistry and as a source of nitrogen fixation that may be significant for early-Earth and astrobiological prebiotic chemistry.

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