



OPEN ACCESS

EDITED BY

Alberto Fairén,
CSIC-INTA, Spain

REVIEWED BY

Sanjay Limaye,
University of Wisconsin-Madison,
United States
Kevin Baines,
California Institute of Technology,
United States

*CORRESPONDENCE

William Bains,
✉ bains@mit.edu

RECEIVED 17 January 2024

ACCEPTED 18 March 2024

PUBLISHED 10 April 2024

CITATION

Bains W, Seager S, Clements DL, Greaves JS, Rimmer PB and Petkowski JJ (2024), Source of phosphine on Venus—An unsolved problem. *Front. Astron. Space Sci.* 11:1372057. doi: 10.3389/fspas.2024.1372057

COPYRIGHT

© 2024 Bains, Seager, Clements, Greaves, Rimmer and Petkowski. This is an open-access article distributed under the terms of the [Creative Commons Attribution License \(CC BY\)](https://creativecommons.org/licenses/by/4.0/). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

Source of phosphine on Venus—An unsolved problem

William Bains^{1,2*}, Sara Seager^{1,3,4}, David L. Clements⁵,
Jane S. Greaves², Paul B. Rimmer⁶ and Janusz J. Petkowski^{1,7,8}

¹Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, United States, ²School of Physics and Astronomy, Cardiff University, Cardiff, United Kingdom, ³Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, United States, ⁴Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, MA, United States, ⁵Department of Physics, Backett Laboratory, Imperial College London, London, United Kingdom, ⁶Astrophysics Group, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom, ⁷Faculty of Environmental Engineering, Wrocław University of Science and Technology, Wrocław, Poland, ⁸JJ Scientific, Mazowieckie, Warsaw, Poland

The tentative detection of ppb levels of phosphine (PH₃) in the clouds of Venus was extremely surprising, as this reduced gas was not expected to be a component of Venus' oxidized atmosphere. Despite potential confirmation in legacy Pioneer Venus mass spectrometry data, the detection remains controversial. Here we review the potential production of phosphine by gas reactions, surface and sub-surface geochemistry, photochemistry, and other nonequilibrium processes. None of these potential phosphine production pathways is sufficient to explain the presence of phosphine in Venus atmosphere at near the observed abundance. The source of atmospheric PH₃ could be unknown geo- or photochemistry, which would imply that the consensus on Venus' chemistry is significantly incomplete. An even more extreme possibility is that a strictly aerial microbial biosphere produces PH₃. The detection of phosphine adds to the complexity of chemical processes in the Venusian environment and motivates better quantitation of the gas phase chemistry of phosphorus species and *in situ* follow-up sampling missions to Venus.

KEYWORDS

Venus, clouds, atmospheric chemistry, phosphine, PH₃, volcanoes, photochemistry

1 Introduction

The tentative discovery of phosphine (PH₃) in the cloud decks of Venus in 2020 (Greaves et al., 2021b) has sparked substantial debate, both in the literature and elsewhere. The debate is around three aspects of the discovery: whether there is phosphine in the atmosphere of Venus, whether that phosphine has an abiological origin, and whether *a priori* there could be life in Venus' clouds to be a source of phosphine. This paper will focus on the second aspect of the PH₃ debate, what sources of phosphine are plausible, so we will review the first of these points of contention only briefly.

The initial detection of phosphine was strongly contested on the grounds that the apparent signal was the result of processing or statistical errors (Snellen et al., 2020; Thompson, 2020; Akins et al., 2021; Villanueva et al., 2021) that the signal was from sulfur dioxide and not phosphine (Lincowski et al., 2021; Villanueva et al., 2021), and that other measurements ruled out detectable phosphine (Encrenaz et al., 2020p; Trompet et al., 2021; Cordiner et al., 2022). The original group have responded to these criticisms (Greaves et al., 2021a; Greaves et al., 2021c). A major subsequent observation campaign (the JCMT-Venus campaign, number M22AL006: see JCMT (2023) Clements (2022) has found new mm

absorption evidence for phosphine in the clouds with high significance, using different data reduction approaches from those that were disputed in the original reports (Greaves, 2023). Further work on far infrared spectroscopy (Greaves et al., 2023) has supported the presence of phosphine in Venus' clouds, although (Cordiner et al., 2023) dispute the far infrared spectroscopy interpretation. Analysis of legacy spacecraft mass spectrometry data (Mogul et al., 2021) has shown the presence of phosphorus atoms in gas phase, which are hard to explain other than as fragmentation products of phosphine; Brinckerhoff et al. (2021) suggest phosphorus could be a fragmentation products of phosphoric acid or phosphorus oxides, but this seems unlikely on the chemical level. However three analyses have found that at least some of the 1.1 mm absorption signal originates in the mesosphere above the clouds (Lincowski et al., 2021; Villanueva et al., 2021; Greaves et al., 2022), where the photochemical lifetime of phosphine is predicted to be less than 1 s (Bains et al., 2021b). As all candidate sources of PH_3 are in or below the clouds its mesospheric detection therefore implies an enormous (and implausible) source of phosphine in the clouds that is inefficiently mixed up into the mesosphere. The observation of mesospheric PH_3 therefore remains problematic, and implies either that the mesospheric absorption is not from phosphine or that the photochemical models of phosphine chemistry are significantly incomplete (or both). Both explanations appear implausible, the former requiring a new component of Venus' atmosphere that happens to absorb exactly at the PH_3 1–0 transition, the latter requiring rewriting several decades of Venusian atmospheric modelling, and specifically require levels of SO_2 that are substantially higher than any observed (Greaves et al., 2022). This debate is reviewed in (Bains et al., 2021c; Cleland and Rimmer, 2022; Clements, 2022), and is efficiently summarized in the "Phosphine back and forth" web site (Petkowski and Seager, 2023). Questions remain, such as how phosphine can exist in a fog of concentrated sulfuric acid droplets. Concentrated sulfuric acid (>80% weight/weight) is well known to efficiently remove phosphine from the gas phase by oxidation at temperatures between 0°C and 20°C (Leeds and Butterfield, 1910; Perraudin, 1962; Air Liquide, 1963; Lorenz et al., 1963; Hyman and Arp, 1987; Dorfman et al., 1991). The presence of phosphine in the cloud decks of Venus is therefore still debated, and is the subject of research, despite claims to the contrary (Kasting and Harman, 2021). For the purpose of this paper, we assume that there is phosphine in Venus' clouds, and seek to explain its source.

One of the most contentious aspects of the initial announcement was the suggestion that phosphine could be the product of life. Previous work has established phosphine as a 'biosignature' gas, a gas whose presence in an atmosphere of a rocky planet suggests that life may be present on that planet (Sousa-Silva et al., 2020; Bains et al., 2019a; b). This is because on Earth phosphine is almost exclusively made by life (Gassmann and Glindemann, 1993), and is thermodynamically unlikely to be generated by geochemistry. The suggestion that the same logic could be applied to Venus has generated much heated argument, with several authors stating that Venus is uninhabitable because of the extreme aridity and acidity of its atmosphere, and hence that life could be ruled out *a priori* as a candidate source for phosphine (Cockell et al., 2021; Hallsworth et al., 2021). However, the potential habitability of the clouds is still debated (Bains et al., 2021a; Limaye et al., 2021a;

Limaye et al., 2021b; Cleland and Rimmer, 2022; Bains et al., 2024), so we must take the habitability of Venus' cloud decks as unresolved. Here we assume that we cannot prove that Venus is uninhabitable, and so we retain life as a candidate explanation for the presence of phosphine. We discuss the plausibility of phosphine as a biological product in section 2.6 below.

This paper focuses on what we know, model, or speculate about the source of phosphine on Venus. Bains et al. (2021b) explored a range of potential geochemical and atmospheric chemical sources. Subsequent work has explored these and other potential sources of phosphine in Venus' clouds. In this paper we summarize this work on the proposed sources of PH_3 on Venus.

2 Potential sources of venusian phosphine

2.1 Geochemical sources cannot be a source of phosphine

The most commonly discussed 'false positive' source for biosignature gases is geochemical, primarily volcanism. It is quite difficult to determine whether a small amount of a gas could be produced by geochemistry. Earth's bulk crustal geochemistry suggests that volcanism should outgas carbon exclusively as carbon dioxide; nevertheless hydrothermal systems can produce significant methane (Schwieterman et al., 2018) (although geochemical methane production is much less than biological production of methane on Earth). Therefore, we should be careful about dismissing potential sources based on planetary average properties. However, phosphine is a strongly reducing gas, and it takes quite unusual chemical circumstances to generate it from the phosphorus species expected to dominate in surface crustal rocks of rocky planets, which are P (+5) species (phosphate, phosphorus pentoxide or equivalents). The crust of Venus is known from the Soviet Venera and Vega lander missions to have an elemental abundance broadly similar to basalt (Koehler, 1982; Surkov et al., 1986; Garvin and Bryan, 1987). For this material to be able to reduce phosphate to phosphine, it would have to be 8–15 orders of magnitude more reduced than typical terrestrial crustal rocks (Bains et al., 2021b). Even the most reduced plausible surface rocks at the Iron/Wustite redox state (an equilibrium between metallic iron and FeO) would not favour phosphine production (Bains et al., 2021b). The volcanic production of phosphine would also require the rocks to have a high water content, which is unlikely given Venus' desiccated surface and atmosphere. Bains et al. (2021b) concluded that volcanism derived from crustal rocks was extremely unlikely as a source for phosphine.

Truong and Lunine (2021) suggested that, contrary to Bains et al.'s estimates, volcanic sources of PH_3 are plausible on Venus. Volcanic mechanisms focus on the delivery of P (+3) as phosphide in volcanic ejecta. Phosphides are known to react efficiently with dilute acids to form phosphine (Geng et al., 2010), although their reaction with concentrated sulfuric acid has not been studied; the precedent of the reaction of mineral sulfides with sulfuric acid suggests that concentrated sulfuric acid may oxidize phosphides rather than hydrolyse them, depending on the concentration of acid and other conditions (Prater et al., 1970; Bains et al., 2021b). Only rare, trace minerals contain phosphides on Earth, which argues against such

a mechanism unless the geology of Venus is substantially different from Earth. However [Truong and Lunine \(2021\)](#) suggested that mantle plume volcanism could bring phosphorus from the deep mantle, where it is predominantly present as phosphide, to the surface. It is well known that small fragments of material a few millimeters in diameter can be dredged from the lower mantle by volcanism and appear as xenoliths in surface rocks on Earth ([Sasse et al., 2020](#)). However this potential possibility for phosphide delivery confuses two mechanisms ([Bains et al., 2022b](#)). [Bains et al. \(2022a\)](#) argued that the amount of phosphide surviving in the fluid magma as it makes the long, slow transit from lower mantle to crust would be trivially small. [Truong and Lunine \(2022\)](#) responded with the observation that reduced minerals are seen on Earth, but as noted these are all extremely rare materials, mostly present as xenoliths. Xenoliths are small fragments of minerals usually derived from the continental keel, the rigid cores of continental cratons that can reach depths of 350 km. Such xenoliths have survived as solid particles while being transported in upper mantle melts that have lower melting point than the xenolith mineral. Consequently, these highly refractory materials are very rare. The fact that *xenoliths* often contain high abundances of FeC or SiC does not mean that the *melt* contains high abundances of these minerals. For example, [Truong and Lunine \(2022\)](#) specifically mentioned the reduced minerals SiC and FeC found in the Luobusa ophiolite. However these are rare (and hence remarkable and publishable) xenoliths, recovered from over 1.5 tonnes of mineral that was processed to yield some 10s of kg of high density chromite, from which numerous mm sized inclusions of FeC, SiC, diamond and other highly reduced, highly refractile minerals were obtained ([Huang et al., 2020](#)). Such rarity is typical of xenoliths. This suggests an abundance of reduced species (which might contain phosphides, although no such species were reported) of <0.1%, which is in line with the calculations of [Bains et al. \(2022a\)](#).

We also note that no phosphide mineral has been reported in xenoliths to our knowledge. This may be because xenoliths have to be highly refractory mineral inclusions to survive in mantle melts; for example, iron phosphide (Fe₃P), with a melting temperature of ~1200°C ([American Elements, 2023](#)), would not survive as a distinct mineral at the temperature of basaltic melts.

In conclusion, phosphides are extremely rare in crustal rocks, regardless of whether we calculate the abundance of phosphides in bulk rock from thermodynamics or estimate the presence of phosphide xenoliths. To produce sufficient phosphide to explain Venus' phosphine, huge amounts of volcanism would be required, covering an area in the order of 2,100 km² per year with new magma ([Bains et al., 2022a](#)), which is greatly in excess of the ~2.2 km² seen in an 8 month period by the Magellan spacecraft ([Herrick and Hensley, 2023](#)), and would resurface the whole planet in a few tens of thousands of years. In conclusion, we rule out volcanism as a source of phosphine on Venus.

2.2 Atmospheric chemistry cannot generate phosphine

The atmosphere of Venus is chemically complex, and not well understood ([Petkowski et al., 2023](#)). In principle, chemistry in the atmosphere could generate phosphine by reactions within the atmosphere, through photochemistry of atmospheric components,

or through reaction of the atmosphere with solid materials on the surface or as dust. Surface reactions were deemed highly implausible as a source of phosphine by [Bains et al. \(2021b\)](#), a conclusion that has not been disputed. The most plausible reaction in the atmosphere would be disproportionation of P (+3) species, canonically represented as “phosphorus trioxide” (P₄O₆). [Bains et al. \(2021b\)](#) argued that the disproportionation of P₄O₆ was not a thermodynamically favourable mechanism to synthesize phosphine under Venus conditions. [Omran et al. \(2021\)](#) said that it was, and suggested that the P₄O₆ could be synthesised by reduction of P (+5) species by carbon monoxide. The two groups subsequently found that the difference in their conclusions came from differences in the ‘reference’ thermodynamic data on which their respective calculations were based, which were wildly different ([Bains et al., 2023](#)). However, the choice of reference data does not affect whether phosphine is predicted to be present on Venus. The data used by [Bains et al. \(2021b\)](#) predicted that P₄O₆ would be present in Venus' lower atmosphere, but would not disproportionate to phosphine, the data used by [Omran et al. \(2021\)](#) suggested that P₄O₆ would disproportionate if it were present, but that P₄O₆ would not be present in Venus' atmosphere. [Bains et al. \(2023\)](#) explored the effect of assuming different gas abundances, temperatures and thermodynamic ‘reference’ values, and found that there is no combination of conditions that allows phosphine to accumulate to >1 ppb in Venus' atmosphere. The overall conclusion therefore is that a thermodynamically-driven gas phase reactions producing phosphine is implausible.

2.3 Cloud droplet chemistry cannot generate phosphine

The routes for potential formation of phosphine on Venus discussed so far all assume gas phase chemistry in which the atmosphere is homogenous over a scale of meters. However, in the clouds there are at least two phases (gas/vapour and liquid droplets), and possibly solid material as well, and the abundance of minor species (such as SO₂ and H₂O) and trace species (such as the enigmatic “unknown absorber”) in the atmosphere vary substantially with altitude over distances of 100s of meters or more.

The composition of the cloud droplets or particles is not well defined. They are usually assumed to be concentrated sulfuric acid, but the VeGa 2 descent probe found high levels of a phosphorus species in some particles in the lower clouds (reviewed in [Titov et al. \(2016\)](#)). Moreover, measurements performed by Pioneer Venus probe suggest the larger cloud particles are not spherical ([Knollenberg and Hunten, 1980](#)), which if confirmed means they cannot be liquid. Therefore, there is substantial latitude for models that explain the production of phosphine from phosphorus species either in cloud particles or at the interface of those particles and the atmosphere.

However, as explored in detail by [Bains et al. \(2021b\)](#) production of phosphine within cloud particles in the absence of an external energy source to drive the reaction seems unlikely. The rapid reaction of phosphine with concentrated sulfuric acid has been known since the 19th Century, when it was used as a means of removing phosphine from acetylene used in gas lighting ([Retgers, 1894](#); [Leeds and Butterfield, 1910](#)). This occurs rapidly at European

ambient temperatures, i.e., $<20^{\circ}\text{C}$, and would be expected to happen faster at the elevated temperatures of the lower clouds of Venus. The end product of the reaction is not known, but it is not volatile and hence is presumably phosphorus oxides or oxyacids. Therefore, the idea that reactions occurring in the presence of concentrated sulfuric acid would be net producers of phosphine seem implausible.

2.4 Photochemistry as a potential source of phosphine

Thermodynamic constraints on the formation of phosphine can be overcome if an external energy source drives a reaction. The most abundant energy source in Venus' clouds is light (as there is little energy available in the redox disequilibria in the clouds (Jordan et al., 2022)). Potential photochemical routes to phosphine synthesis were not exhaustively explored in Bains et al. (2021b), except for an approximate gas phase kinetic model. One group has modelled potential photochemistry occurring on the acid surface of dust in the clouds as a potential source of phosphine on Venus (Kaiserová, 2021; Ferus et al., 2022). Other reduced gases, like methane and ammonia can potentially be produced photochemically under such conditions. Ferus et al. (2022) and Kaiserová (2021) argue on the basis of quantum mechanics modelling of the relevant reaction intermediates that phosphine could be made as well, *via* reduction of PO (generated by photochemical breakdown of H_3PO_4) by HCO radicals (generated by reduction of CO_2 on the acidic dust surface). This intriguing hypothesis would explain the detection of phosphine in the clouds, and is eminently testable with Earth-based experiments. However the mechanism by which dust can be lofted from the surface to the cloud layer remains to be explored.

A second route is the photochemical reduction of P_4O_6 in the clouds, which has been modelled by Wunderlich et al. (2023). This route is only valid if P_4O_6 actually exists in the atmosphere at the altitude of the clouds, which Bains et al. (2021b) and Omran et al. (2021) concluded that it did not. The mechanism analysed by Wunderlich et al. (2023) assume an efficient net production of PO from P_4O_6 at rates comparable to the production of methane on modern Earth. They do not suggest a mechanism for this unprecedented chemistry, and indeed thermodynamic calculation suggests that it is extremely unlikely (Bains et al., 2021b). Wunderlich et al. (2023) also assume that the kinetics of reaction that break the phosphorus-oxygen double bond could be modelled with reference to the kinetics of analogous chemistry of the nitrogen-oxygen double bond, a parallel that Bains et al. (2021b) has shown is very inaccurate. However Wunderlich et al. (2023)'s overall conclusion, that the quantitation of the phosphorus photochemistry in Venus' atmosphere is uncertain by many orders of magnitude, and that more experiments and observations are essential for resolving whether PH_3 can be explained abiotically, is consonant with the conclusions of Bains et al. (2021b, 2023) and Omran et al. (2021).

Given these uncertainties, a photochemical source therefore remains an open option as a source of Venusian phosphine. We note that McTaggart (2022) explores whether cosmic rays could power the production of PH_3 in Venus' upper clouds, and conclude that they could not.

2.5 Other sources of phosphine

Other considered sources of Venusian PH_3 have included lightning (Bains et al., 2021b) and meteoritic infall (Bains et al., 2021b; Omran et al., 2021). The mineral schreibersite ((Fe,Ni) $_3$ P) reacts efficiently with aqueous sulfuric acid to form phosphine (Geng et al., 2010); its reaction with concentrated sulfuric acid has not been explored to our knowledge. Schreibersite is found in meteorites, and so meteoritic infall could be a source of phosphine through this reaction. Bains et al. (2021b) estimated that the rate of infall was insufficient to explain phosphine, and Omran et al. (2021) estimate the infall rate of small particles and dust falls short of the required rate by at least 10-fold. However, Omran et al. (2021) also suggested that a single, large impactor could deliver phosphide: a 10^{12} kg object would ablate primarily 30–60 km above the surface, and would not form any significant crater. Such an object would be a one in a million year event, and so it is unlikely that Greaves et al. were observing soon after such an impact (the half-life of phosphine is 100s of years in the deeper clouds, reducing to minutes or seconds above the clouds.) It is also improbable that the Akatsuki spacecraft, which has been studying Venus' atmosphere since 2015, would not have seen such an event. Meteoritic infall, either constant or a single large event, is therefore unlikely as a realistic scenario for phosphine production on Venus.

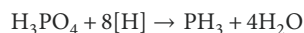
The lower clouds of Venus may contain substantial phosphorus (Titov et al., 2018), unlike the clouds of Earth, and so lightning passing through those clouds could be a source of phosphine. Bains et al. (2021b) argued on semi-quantitative grounds against lightning as a source. We can also note that lightning on Earth produces no detectable ammonia (the nitrogen analogue of phosphine) despite clouds on Earth being made of water vapour and the atmosphere being 80% nitrogen. Lightning chemistry strongly favours oxidized species rather than the more labile hydrides as products; essentially all the nitrogen compounds made by lightning on Earth are nitrogen oxides (Schumann and Huntrieser, 2007).

2.6 Life as a source of phosphine

By far the most contentious candidate source for the phosphine is the idea that the cloud droplets are inhabited by microorganisms that are making it (Benner, 2021). Bains et al. (2021b,c) showed that biochemical production of phosphine was not thermodynamically impossible, based on a model where an organism maintained a neutral aqueous interior while living in a sulfuric acid droplet, but did not speculate where the energy to do this might come from. Jordan et al. (2022) show that some limited sulfur-based metabolic strategies either cannot provide enough energy, or would produce chemical signatures that contradict what is currently observed in Venus's atmosphere, but Bains et al. (2024) show that more than enough solar energy is available for a biosphere in the clouds, and alternative photosynthetic metabolisms may not create the same anomalies in Venus's atmosphere as the metabolisms explored by Jordan et al. Such an organism is therefore not ruled out by what we know of life, but nevertheless seems intuitively implausible.

The principle argument against life being a source of phosphine is evolutionary, not chemical. To make phosphine from the P (+5) compounds that are likely to be the dominant phosphorus

chemical species in the clouds, the putative organism has to capture substantial energy, source hydrogen atoms from the cloud droplet, and perform the highly endothermic overall transformation



Hydrogen-bearing species are rare in the atmosphere of Venus, so finding eight hydrogen atoms per phosphine molecule produced would require investment in energy. The reaction is highly endergonic, requiring energy to reduce P (+5) to P (-3). Having invested substantial energy in making PH_3 , life then allows it to diffuse away into the clouds. There seems to be no evolutionary rationale for doing such a wasteful process (Benner, 2021), unlike on Earth where PH_3 production is of thermodynamic benefit in a highly reducing environment (Bains et al., 2019a). This may be a failure of our imaginations, but absent any rationale for spending so much resource of making a product, an evolutionary biologist would be highly skeptical that life is the source of phosphine.

3 Conclusion

We have discussed a range of candidate sources of phosphine in the atmosphere of Venus. No known process satisfactorily explains the presence of phosphine. Cloud particle or droplet surface photochemistry remain the most plausible abiotic source in our view, but remain to be explored in the lab to confirm if they can actually happen under Venus-like conditions. Uncertainties about phosphorus species kinetics and thermodynamics are a major barrier to accurate modelling of Venus atmosphere, surface and sub-surface chemistry, and would benefit from new measurements. However, such measurements are often difficult to perform, hence the narrow experimental base for current knowledge. A biological source for phosphine is not ruled out *a priori*, but is at best highly speculative. The biological explanation for Venusian PH_3 seems to suffer from a lack of an apparent plausible evolutionary reason why life should expend substantial energy to produce a gas that it then appears to throw away.

These conclusions assume that there actually is phosphine in the atmosphere of Venus. If there is no phosphine on Venus, then the need to explain it goes away. The most pressing need is therefore to confirm the presence of phosphine. The results from the current JCMT-Venus campaign (Clements, 2022; JCMT, 2023) are a major step towards confirming the presence of phosphine (Greaves, 2023). Realistic models of the cloud chemistry and photochemistry in terrestrial laboratories will answer some questions about non-homogenous chemistry in the clouds, and will be of value in resolving the uncertainties and anomalies in Venus' atmosphere

References

- Air Liquide, (1963). "Improvements in or relating to the purification of acetylene." UK patent application GB929645 (Paris, France: AIR LIQUIDE).
- Akins, A. B., Lincowski, A. P., Meadows, V. S., and Steffes, P. G. (2021). Complications in the ALMA detection of phosphine at Venus. *Astrophysical J.* 907, 27. doi:10.3847/2041-8213/abd56a
- American Elements, 2023. Iron phosphide, Fe_3P (<https://www.americanelements.com/iron-phosphide-fe3p-12023-53-9>) [Online]. American Elements Inc.

whether phosphine is there or not. However it is likely that we will only know if phosphine is there, and if it is there what process is making it, when new missions to visit Venus bring back data, and ultimately samples, to reveal what is happening in those clouds.

Author contributions

WB: Conceptualization, Writing—original draft, Writing—review and editing. SS: Conceptualization, Writing—review and editing. DLC: Writing—review and editing. JSG: Writing—review and editing. PBR: Writing—review and editing. JJP: Conceptualization, Writing—original draft, Writing—review and editing.

Funding

The author(s) declare that no financial support was received for the research, authorship, and/or publication of this article.

Acknowledgments

We are very grateful to Sukrit Ranjan (University of Arizona) for constructive criticism, to Matt Pasek (University of South Florida) for discussions and comment on phosphorus chemistry, and to two reviewers for constructive comments.

Conflict of interest

Author JJP is an owner of JJ Scientific.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

- Bains, W., Pasek, M. A., Ranjan, S., Petkowski, J. J., Omran, A., and Seager, S. (2023). Large uncertainties in the thermodynamics of phosphorus (III) oxide (P_4O_6) have significant implications for phosphorus species in planetary atmospheres. *ACS Earth Space Chem.* 7, 1219–1226. doi:10.1021/acsearthspacechem.3c00016

- Bains, W., Petkowski, J. J., Rimmer, P. B., and Seager, S. (2021a). Production of ammonia makes venusian clouds habitable and explains observed cloud-level chemical anomalies. *Proc. Natl. Acad. Sci.* 118, e2110889118. doi:10.1073/pnas.2110889118

- Bains, W., Petkowski, J. J., and Seager, S. (2024). Venus' atmospheric chemistry and cloud characteristics are compatible with venusian life. *Astrobiology* 12. doi:10.1089/ast.2022.0113
- Bains, W., Petkowski, J. J., Seager, S., Ranjan, S., Sousa-Silva, C., Rimmer, P. B., et al. (2021b). Phosphine on Venus cannot be explained by conventional processes. *Astrobiology* 21, 1277–1304. doi:10.1089/ast.2020.2352
- Bains, W., Petkowski, J. J., Seager, S., Ranjan, S., Sousa-Silva, C., Rimmer, P. B., et al. (2021c). Venusian phosphine: a 'wow!' signal in chemistry? *Phosphorus, Sulfur, Silicon Relat. Elem.* 197, 438–443. doi:10.1080/10426507.2021.1998051
- Bains, W., Petkowski, J. J., Sousa-Silva, C., and Seager, S. (2019a). New environmental model for thermodynamic ecology of biological phosphine production. *Sci. Total Environ.* 658, 521–536. doi:10.1016/j.scitotenv.2018.12.086
- Bains, W., Petkowski, J. J., Sousa-Silva, C., and Seager, S. (2019b). Trivalent phosphorus and phosphines as components of biochemistry in anoxic environments. *Astrobiology* 19, 885–902. doi:10.1089/ast.2018.1958
- Bains, W., Shorttle, O., Ranjan, S., Rimmer, P. B., Petkowski, J. J., Greaves, J. S., et al. (2022a). Constraints on the production of phosphine by Venusian volcanoes. *Universe* 8, 54. doi:10.3390/universe8010054
- Bains, W., Shorttle, O., Ranjan, S., Rimmer, P. B., Petkowski, J. J., Greaves, J. S., et al. (2022b). Only extraordinary volcanism can explain the presence of parts per billion phosphine on Venus. *Proc. Natl. Acad. Sci.* 119, e2121702119. doi:10.1073/pnas.2121702119
- Benner, S. (2021). Aristotle and the search for life on Venus. *Primordial scoop*.
- Brinckerhoff, W., Li, X., Mahaffy, P., and Atreya, S. (2021). Re-analysis of phosphorus and related trace species in the lower Venus atmosphere from pioneer Venus neutral mass spectrometer data. *52nd Lunar Planet. Sci. Conf.* 1382.
- Cleland, C. E., and Rimmer, P. B. (2022). Ammonia and phosphine in the clouds of Venus as potentially biological anomalies. *Aerospace* 9, 752. doi:10.3390/aerospace9120752
- Clements, D. L. (2022). Venus, phosphine and the possibility of life. *Contemp. Phys.* 63, 180–199. doi:10.1080/00107514.2023.2184932
- Cockell, C. S., McMahon, S., and Biddle, J. F. (2021). When is life a viable hypothesis? The case of Venusian phosphine. *Astrobiology* 21, 261–264. doi:10.1089/ast.2020.2390
- Cordiner, M. A., Villanueva, G. L., Wiesemeyer, H., Milam, S. N., De Pater, I., Moullet, A., et al. (2022). Phosphine in the venusian atmosphere: a strict upper limit from sofia great observations. *Geophys. Res. Lett.* 49, e2022GL101055. doi:10.1029/2022GL101055
- Cordiner, M., Wiesemeyer, H., Villanueva, G., De Pater, I., Stutzki, J., Luzzi, G., et al. (2023). Author's Reply to Comment by Greaves et al. on "Phosphine in the Venusian Atmosphere: a Strict Upper Limit From SOFIA GREAT Observations". *Geophys. Res. Lett.* 50, e2023GL106136. doi:10.1029/2023GL106136
- Dorfman, Y., Yukht, I., Levina, L., Polimbetova, G., Petrova, T., and Emelyanova, V. (1991). Oxidation of Ph₃ and Ash₃ through metal-complexes, free and connected oxygen. *USPEKHI KHIMII* 60, 1190–1228. doi:10.1070/RC1991v06n06ABEH001097
- Encrenaz, T., Greathouse, T. K., Marcq, E., Widemann, T., Bézard, B., Fouchet, T., et al. (2020). A stringent upper limit of the PH₃ abundance at the cloud top of Venus. *Astronomy Astrophysics* 643, L5. doi:10.1051/0004-6361/202039559
- Ferus, M., Cassone, G., Rimmer, P., Saija, F., Mrázíková, K., Knížek, A., et al. (2022). Abiotic chemical routes towards the phosphine synthesis in the atmosphere of Venus. *Eur. Planet. Sci. Congr.* 198. doi:10.5194/eps2022-198
- Garvin, J., and Bryan, W. (1987). Comparison of the compositions of Venusian surface rocks with those of the terrestrial ocean floor. *Astron. Vestn.* 21.
- Gassmann, G., and Glindemann, D. (1993). Phosphane (PH₃) in the biosphere. *Angewandte Chemie Int. Ed. Engl.* 32, 761–763. doi:10.1002/anie.199307611
- Geng, J., Zhang, R., and Wang, X. (2010). "Chemical origin of phosphine in nature," in 2010 4th International Conference on Bioinformatics and Biomedical Engineering, Chengdu, China, 18–20 June 2010 (IEEE), 1–12.
- Greaves, J. S., Petkowski, J. J., Richards, A. M. S., Sousa-Silva, C., Seager, S., and Clements, D. L. (2023). Comment on "Phosphine in the Venusian Atmosphere: a Strict Upper Limit From SOFIA GREAT Observations" by Cordiner et al. *Geophys. Res. Lett.* 50, e2023GL103539. doi:10.1029/2023GL103539
- Greaves, J. S., Richards, A. M., Bains, W., Rimmer, P. B., Clements, D. L., Seager, S., et al. (2021a). Reply to: No evidence of phosphine in the atmosphere of Venus from independent analyses. *Nat. Astron.* 5, 636–639. doi:10.1038/s41550-021-01424-x
- Greaves, J. S., Richards, A. M., Bains, W., Rimmer, P. B., Sagawa, H., Clements, D. L., et al. (2021b). Phosphine gas in the cloud decks of Venus. *Nat. Astron.* 5, 655–664. doi:10.1038/s41550-020-1174-4
- Greaves, J. S., Richards, A. M. S., Bains, W., Rimmer, P. B., Sagawa, H., Clements, D. L., et al. (2021c). Addendum: phosphine gas in the cloud deck of Venus. *Nat. Astron.* 5, 726–728. doi:10.1038/s41550-021-01423-y
- Greaves, J. S., Rimmer, P. B., Richards, A., Petkowski, J. J., Bains, W., Ranjan, S., et al. (2022). Low levels of sulphur dioxide contamination of Venus phosphine spectra. *Mon. Notices R. Astronomical Soc. Lett.* 514, 2994–3001. doi:10.1093/mnras/stac1438
- Greaves, J. (2023). *Phosphine in Venus' clouds: news from far-IR and mm spectra. National Astronomy Meeting*. Cardiff, Wales: Zenodo.
- Hallsworth, J. E., Koop, T., Dallas, T. D., Zorzano, M.-P., Burkhardt, J., Golyshina, O. V., et al. (2021). Water activity in Venus's uninhabitable clouds and other planetary atmospheres. *Nat. Astron.* 5, 665–675. doi:10.1038/s41550-021-01391-3
- Herrick, R. R., and Hensley, S. (2023). Surface changes observed on a Venusian volcano during the Magellan mission. *Science* 379, 1205–1208. doi:10.1126/science.abm773
- Huang, J.-X., Xiong, Q., Gain, S. E. M., Griffin, W. L., Murphy, T. D., Shiryayev, A. A., et al. (2020). Immiscible metallic melts in the deep Earth: clues from moissanite (SiC) in volcanic rocks. *Sci. Bull.* 65, 1479–1488. doi:10.1016/j.scib.2020.05.012
- Hyman, M. R., and Arp, D. J. (1987). Quantification and removal of some contaminating gases from acetylene used to study gas-utilizing enzymes and microorganisms. *Appl. Environ. Microbiol.* 53, 298–303. doi:10.1128/aem.53.2.298-303.1987
- Jcmt, 2023. JCMT-Venus [Online]. Available:.
- Jordan, S., Shorttle, O., and Rimmer, P. B. (2022). Proposed energy-metabolisms cannot explain the atmospheric chemistry of Venus. *Nat. Commun.* 13, 3274. doi:10.1038/s41467-022-30804-8
- Kaiserová, T. (2021). *Phosphine and nitrous oxide as false-positive biosignature gases in planetary spectra*. Přírodovědecká fakulta: Univerzita Karlova.
- Kasting, J. F., and Harman, C. E. (2021). Venus might never have been habitable. *Nature* 259. doi:10.1038/d41586-021-02720-2
- Knollenberg, R., and Hunten, D. (1980). The microphysics of the clouds of Venus: results of the Pioneer Venus particle size spectrometer experiment. *J. Geophys. Res. Space Phys.* 85, 8039–8058. doi:10.1029/JA085iA13p08039
- Koehler, H. (1982). Results of the Venus sondes Venera 13 and 14. *Sterne Weltraum* 21, 282.
- Leeds, F. H., and Butterfield, J. J. A. (1910). *Acetylene, the principles of its generation and use: a practical handbook on the production, purification, and subsequent treatment of acetylene for the development of light, heat and power*. London, UK, C. Griffin.
- Limaye, S. S., Mogul, R., Baines, K. H., Bullock, M. A., Cockell, C., Cutts, J. A., et al. (2021a). Venus, an astrobiology target. *Astrobiology* 21, 1163–1185. doi:10.1089/ast.2020.2268
- Limaye, S. S., Zelenyi, L., and Zasova, L. (2021b). Introducing the Venus collection—papers from the first workshop on habitability of the cloud layer. *Astrobiology* 21, 1157–1162. doi:10.1089/ast.2021.0142
- Lincowski, A. P., Meadows, V. S., Crisp, D., Akins, A. B., Schwieterman, E. W., Arney, G. N., et al. (2021). Claimed detection of PH₃ in the clouds of Venus is consistent with mesospheric SO₂. *Astrophysical J. Lett.* 908, L44. doi:10.3847/2041-8213/abde47
- Lorenz, M. L., Lutzmann, H., and Reichert, M. (1963). "Procédé pour l'épuration d'acétylène obtenu à partir d'hydrocarbures." Belgium patent application (Guimarães, Braga, Portugal: Universalis).
- Mctaggart, R. (2022). The cosmogenic production of phosphorus in the atmosphere of Venus. *Icarus* 374, 114791. doi:10.1016/j.icarus.2021.114791
- Mogul, R., Limaye, S. S., Way, M. J., and Cordova, J. A. (2021). Venus' mass spectra show signs of disequilibria in the middle clouds. *Geophys. Res. Lett.* 48, e2020GL091327. doi:10.1029/2020GL091327
- Omran, A., Oze, C., Jackson, B., Mehta, C., Barge, L. M., Bada, J., et al. (2021). Phosphine generation pathways on rocky planets. *Astrobiology* 21, 1264–1276. doi:10.1089/ast.2021.0034
- Perraudin, R. (1962). "Procédé et dispositif d'épuration de l'acétylène par lavage à l'acide sulfurique." France patent application FR1298938 (Guimarães, Braga, Portugal: Universalis).
- Petkowski, J. J., and Seager, S. (2023). *Phosphine back and forth*. Cambridge, MA, USA: MIT. [Accessed].
- Petkowski, J. J., Seager, S., Grinspoon, D. H., Bains, W., Ranjan, S., Rimmer, P. B., et al. (2023). Astrobiological potential of Venus atmosphere chemical anomalies and other unexplained cloud properties. *Astrobiology*. doi:10.1089/ast.2022.0060
- Prater, J. D., Queneau, P. B., and Hudson, T. J. (1970). The sulfation of copper-iron sulfides with concentrated sulfuric acid. *JOM* 22, 23–27.
- Retgers, J. (1894). Über eine einfache Darstellungsweise des Phosphorwasserstoffes. *Z. für Anorg. Allg. Chem.* 7, 265–266. doi:10.1002/zaac.18940070139
- Sasse, D., Jones, T. J., and Russell, J. K. (2020). Transport, survival and modification of xenoliths and xenocrysts from source to surface. *Earth Planet. Sci. Lett.* 548, 116499. doi:10.1016/j.epsl.2020.116499
- Schumann, U., and Huntrieser, H. (2007). The global lightning-induced nitrogen oxides source. *Atmos. Chem. Phys.* 7, 3823–3907. doi:10.5194/acp-7-3823-2007
- Schiwterman, E. W., Kiang, N. Y., Parenteau, M. N., Harman, C. E., Dassarma, S., Fisher, T. M., et al. (2018). Exoplanet biosignatures: a review of remotely detectable signs of life. *Astrobiology* 18, 663–708. doi:10.1089/ast.2017.1729
- Snellen, I., Guzman-Ramirez, L., Hogerheide, M., Hygate, A., and Van Der Tak, F. (2020). Re-analysis of the 267 GHz ALMA observations of Venus-No statistically significant detection of phosphine. *Astronomy Astrophysics* 644, L2. doi:10.1051/0004-6361/202039717

- Sousa-Silva, C., Seager, S., Petkowski, J. J., Zhan, Z., Hu, R., and Bains, W. (2020). On phosphine as a biosignature gas in exoplanet atmospheres. *Astrobiology* 20, 235–268. doi:10.1089/ast.2018.1954
- Surkov, Y. A., Moskalyova, L. P., Kharyukova, V. P., Dudin, A. D., Smirnov, G. G., and Zaitseva, S. Y. (1986). Venus rock composition at the Vega 2 landing site. *J. Geophys. Res. Solid Earth* 91, E215–E218. doi:10.1029/JB091iB13p0E215
- Thompson, M. A. (2020). The statistical reliability of 267-GHz JCMT observations of Venus: no significant evidence for phosphine absorption. *Mon. Notices R. Astronomical Soc. Lett.* 501, L18–L22. doi:10.1093/mnras/laa187
- Titov, D. V., Ignatiev, N. I., McGouldrick, K., Wilquet, V., and Wilson, C. F. (2018). Clouds and hazes of Venus. *Space Sci. Rec.* 214, 126. doi:10.1007/s11214-018-0552-z
- Trompet, L., Robert, S., Mahieux, A., Schmidt, F., Erwin, J., and Vandaele, A. (2021). Phosphine in Venus' atmosphere: detection attempts and upper limits above the cloud top assessed from the SOIR/VEx spectra. *Astronomy Astrophysics* 645, L4. doi:10.1051/0004-6361/202039932
- Truong, N., and Lunine, J. I. (2022). Reply to Bains et al.: on the plausibility of crustal phosphides as the source of Venusian phosphine. *Proc. Natl. Acad. Sci.* 119, e2122571119. doi:10.1073/pnas.2122571119
- Truong, N., and Lunine, J. (2021). Volcanically extruded phosphides as an abiotic source of Venusian phosphine. *Proc. Natl. Acad. Sci.* 118. doi:10.1073/pnas.2021689118
- Villanueva, G., Cordiner, M., Irwin, P., De Pater, I., Butler, B., Gurwell, M., et al. (2021). No evidence of phosphine in the atmosphere of Venus from independent analyses. *Nat. Astron.* 5, 631–635. doi:10.1038/s41550-021-01422-z
- Wunderlich, F., Grenfell, J. L., and Rauer, H. (2023). Uncertainty in phosphine photochemistry in the Venus atmosphere prevents a firm biosignature attribution. *Astronomy Astrophysics* 676, A135. doi:10.1051/0004-6361/202142548