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Phosphine on Venus Cannot Be Explained by Conventional Processes

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Abstract

The recent candidate detection of ~ 1 ppb of phosphine in the middle atmosphere of Venus is so unexpected that it requires an exhaustive search for explanations of its origin. Phosphorus-containing species have not been modeled for Venus' atmosphere before, and our work represents the first attempt to model phosphorus species in the venusian atmosphere. We thoroughly explore the potential pathways of formation of phosphine in a venusian environment, including in the planet's atmosphere, cloud and haze layers, surface, and subsurface. We investigate gas reactions, geochemical reactions, photochemistry, and other nonequilibrium processes. None of these potential phosphine production pathways is sufficient to explain the presence of ppb phosphine levels on Venus. If PH_3's presence in Venus' atmosphere is confirmed, it therefore is highly likely to be the result of a process not previously considered plausible for venusian conditions. The process could be unknown geochemistry, photochemistry, or even aerial microbial life, given that on Earth phosphine is exclusively associated with anthropogenic and biological sources. The detection of phosphine adds to the complexity of chemical processes in the venusian environment and motivates *in situ* follow-up sampling missions to Venus. Our analysis provides a template for investigation of phosphine as a biosignature on other worlds. Key Words: Phosphine—Venus—Thermodynamics—Photochemistry—Biosignature gas—Life. Astrobiology 21, xxx–xxx.

1. Introduction

A BIOSIGNATURE is a feature of a planet that provides evidence for the presence of life on that planet (Catling *et al.*, 2018; Schwieterman *et al.*, 2018). Few, if any, remotely detectable features of a planet are unambiguous evidence for life, and so any feature must be interpreted in the context of other knowledge about the planet. Atmospheric trace gases are favored biosignatures both for solar system bodies and for exoplanets, and a wide range has been suggested (Seager *et al.*, 2012; Seager and Bains, 2015). However, a detailed analysis of how a biosignature gas could be generated abiotically has only been carried out for molecular oxygen (Meadows, 2017; Meadows *et al.*, 2018), Other work in general does not discuss potential abiological routes to candidate biosignature gases, noting that on Earth, the only (or major) source of the gas is biology. However, as the case of oxygen illustrates, a solely biological source on Earth does not preclude abiological sources on other planets.

In this article, we provide a detailed analysis of abiological routes to phosphine, specifically in the context of Venus' atmospheric and geological chemistry. The analysis

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is motivated, in part, by recent claims that phosphine is present in Venus' atmosphere, but also more generally to provide a template for the analysis of this gas as a biosignature in any planetary context.

Venus is about the same size and mass as Earth and is sometimes called Earth's sister planet. Venus' atmospheric chemistry and surface conditions, however, are quite different from Earth's. The interior chemical composition of Venus is poorly known. It is assumed to be similar in chemical composition to Earth's crust and mantle, mainly because of the similarity between Earth's and Venus' size and overall bulk density (Smrekar *et al.*, 2014).

Unlike the bulk planet composition, the atmospheres of Earth and Venus are very different. Our understanding of the chemistry of the venusian atmosphere and clouds is incomplete, especially when it comes to the experimentally derived concentrations of chemical species, such as phosphoric acid, that are central to the calculations presented in this article. Nevertheless, the venusian clouds and hazes are known to have a complex vertical atmospheric profile with several distinct layers. The main cloud layer (~48 to ~70 km) is composed of droplets, which are believed to be made primarily of photochemically produced sulfuric acid (Oschlisniok *et al.*, 2012). Haze extends from below the clouds through the cloud layer to at least 100 km and may be composed of elemental sulfur as well as sulfuric acid (Taylor *et al.*, 2018; Titov *et al.*, 2018) (Fig. 1). The main sulfuric acid cloud decks also contain an unidentified UV-absorbing species. The UV absorber is very dynamic, with variable distribution in space and time within clouds (Haus *et al.*, 2016; Lee *et al.*, 2019, 2021) [reviewed in Marcq *et al.* (2018); Taylor *et al.* (2018); Titov *et al.* (2018)]. The complexity of the venusian environment could, *a priori*, provide unexpected chemistry that could lead to the formation of phosphine.

The recent candidate phosphine detection in the Venus' cloud decks adds further questions to the already complex picture of the chemical composition of the atmosphere of Venus (Greaves *et al.*, 2020c). The detection was based on a single-millimeter wavelength absorption line and requires confirmation by the detection of additional phosphine spectral features. The detection has been contested (as discussed in detail below), but reanalysis of the data by several methods and the tentative detection of a phosphine signal in the Pioneer MS data support the detection. This article does not address the presence of phosphine in the atmosphere of Venus. For our purposes of using Venus as a test case for phosphine as a biosignature on a rocky planet, we will assume that the detection is valid.

If the detection of phosphine in Venus' clouds at 55–60 km altitude is correct, the presence of phosphine in Venus' atmosphere is highly unexpected, and requires explanation, as would the detection of phosphine on any other solar system body, or on any exoplanet. For some solar system planets such as Jupiter, Saturn, and Earth, the explanation of phosphine production is well known, as we discuss in Section 1.1 below. This article is the first step in providing such an explanation for the case of Venus. We start the introduction with a short summary of the recent detection of phosphine in the atmosphere of Venus and put it in the context of similar detections on other solar system planets. Next, we review the chemistry and biology of phosphine gas, focusing on its unique production by life here on Earth (Section 1.1). We conclude the introduction with the motivation for the work presented in this article (Section 1.2), the overall approach (Section 1.3), and the outline of the used methods and the obtained results (Section 1.4).

1.1. Phosphine in solar system bodies

1.1.1. Detection of phosphine on Venus and other planets. The recent candidate detection of ppb amounts of phosphine in the atmosphere of Venus is a highly

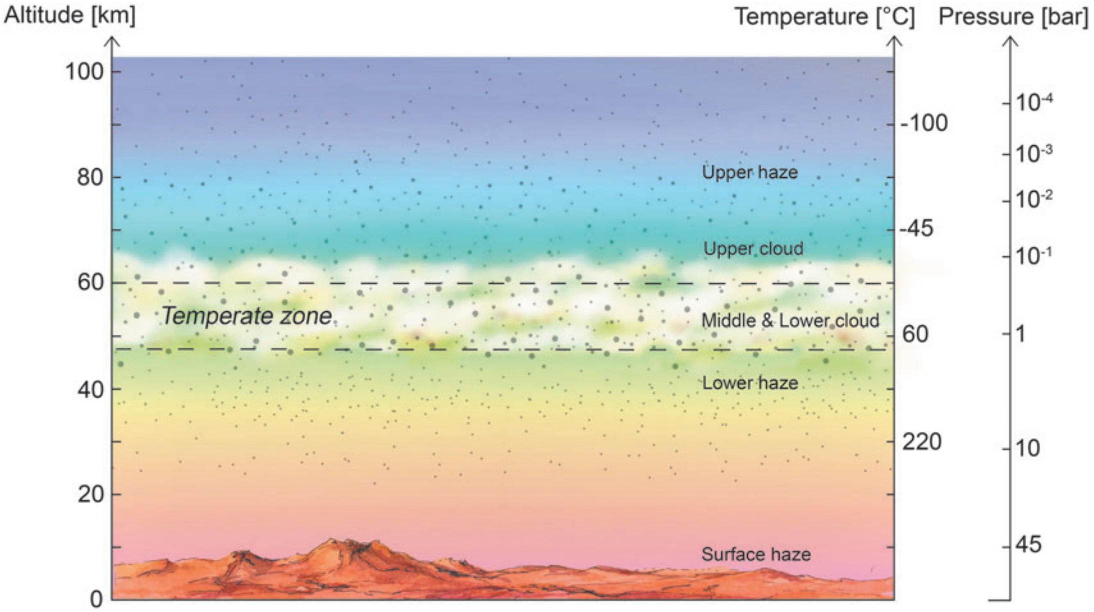

FIG. 1. A simplified schematic representation of the vertical structure of the main atmospheric layers on Venus [figure modified from Seager *et al.* (2021)].

unexpected discovery. Millimeter-waveband spectra of Venus from both Atacama Large Millimeter/submillimeter Array (ALMA) and the James Clerk Maxwell Telescope (JCMT) telescopes at 266.9445 GHz show a PH_3 absorption-line profile against the thermal background from deeper, hotter layers of the atmosphere. The initial detection using the JCMT telescope in 2017 suggested an abundance of $\sim$20 ppb, and the initial follow-up detection using ALMA in 2019 suggested an abundance of $\sim$7 ppb (Greaves *et al.*, 2020c). Both detections have been disputed; we discuss this debate in more detail below (Section 2.2.1). Mogul *et al.* (2020a, 2020b) have also claimed detection of phosphine in historical Pioneer spacecraft Pioneer Venus Large Probe Neutral Mass Spectrometer (LNMS) mass spectrometry data. If the Greaves *et al.* (2020a, 2020b, 2020c) and Pioneer LNMS (Mogul *et al.*, 2020a, 2020b) detections are valid, then there is at least 1 ppb phosphine present in the atmosphere of Venus, and there may periodically be substantially more. Throughout this article, we describe the predicted abundance as 1 ppb unless otherwise stated, as a conservative minimum. The thermal emission has a peak emission at 56 km with the full-width at half-minimum (FWHM) spanning $\sim$53–61 km (Greaves *et al.*, 2020c). Phosphine is therefore presumed to be present above $\sim$55 km: whether it is present below this altitude, and if present, what its abundance is, is not determined by these observations. The upper limit on phosphine occurrence is not defined by the observations but is set by the half-life of phosphine at <80 km, as discussed below.

Phosphine has previously been detected in the atmospheres of three solar system planets: Jupiter, Saturn, and Earth. Phosphine is present in the giant planet atmospheres of Jupiter and Saturn, as identified by ground-based telescope observations at submillimeter and infrared wavelengths (Bregman *et al.*, 1975; Larson *et al.*, 1977; Tarrago *et al.*, 1992; Weisstein and Serabyn, 1996). In giant planets, PH_3 is expected to contain the entirety of the atmospheres' phosphorus in the deep atmosphere layers (Visscher *et al.*, 2006), where the pressure, temperature, and the concentration of H_2 are sufficiently high for PH_3 formation to be thermodynamically favored. In the upper atmosphere, phosphine is present at concentrations several orders of magnitude higher than predicted by thermodynamic equilibrium (Fletcher *et al.*, 2009). Phosphine in the upper layers is dredged up by convection after its formation deeper in the atmosphere, at depths greater than 600 km (Noll and Marley, 1997).

An analogous process of forming phosphine under high H_2 pressure and high temperature followed by dredge-up to the observable atmosphere cannot happen on worlds such as Venus or Earth for two reasons. First, molecular hydrogen is a trace species in the atmospheres of rocky planets such as Earth or Venus, and so the formation of phosphine is not favored as it is in the deep atmospheres of the H_2-dominated giant planets. On Earth, H_2 reaches 0.55 ppm levels (Novelli *et al.*, 1999), and on Venus, it is much lower at $\sim$4 ppb (Krasnopolsky, 2010; Gruchola *et al.*, 2019). Second, rocky planet atmospheres do not extend to a depth where, even if the atmospheres were composed primarily of hydrogen, phosphine formation would be favored (the possibility that phosphine could be formed below the surface and then being erupted out of volcanoes is addressed separately in Section 3.2.3 and Section 3.2.4, but is also unlikely).

Despite such unfavorable conditions for phosphine production, Earth is known to have PH_3 in its atmosphere at ppq to ppt levels [see *e.g.*, Gassmann *et al.* (1996); Glindemann *et al.* (2003); Pasek *et al.* (2014) and reviewed in Sousa-Silva *et al.*, (2020)]. PH_3's persistence in the Earth atmosphere is a result of the presence of microbial life on Earth's surface (as discussed in Section 1.1.2 below), and of human industrial activity.

Neither the deep formation of phosphine and subsequent dredging to the surface nor its biological synthesis has hitherto been considered a plausible process to occur on Venus.

1.1.2. Phosphine is exclusively associated with life on Earth.

On Earth, phosphine is a gas exclusively associated with life and is not made by any other natural atmospheric or geological chemical process [see *e.g.*, Gassmann and Glindemann (1993); Glindemann *et al.* (1996, 2003, 2005a) and reviewed in Bains *et al.* (2019a, 2019b); Sousa-Silva *et al.* (2020)]. Terrestrial phosphine fulfills the criteria for being a biosignature gas, a gas whose detection indicates the presence of life (Seager and Bains, 2015; Seager *et al.*, 2016; Catling *et al.*, 2018; Walker *et al.*, 2018; Sousa-Silva *et al.*, 2020). Previous work predicted that, if detected on a temperate rocky planet, phosphine would be a robust biosignature gas due to spectroscopic potential and limited false positives in such environments, although detection with a near-future telescope will only be possible for a few planetary scenarios (Sousa-Silva *et al.*, 2020). Since phosphine is mostly studied in the context of industrial chemistry, agriculture, and laboratory chemical synthesis, its biology is not widely known. This warrants a brief introduction on the chemistry and biology of phosphine in the context of its biosignature potential on rocky planets.

On Earth, biological PH_3 production is associated with microbial activity in environments that are strictly anoxic (lacking oxygen) and highly reduced. Most reports of biological PH_3 production come from the studies of environments with anaerobic niches such as wetlands, sewage, and animal intestinal tracts, flatus, and feces [reviewed in Sousa-Silva *et al.* (2020)]. Several studies have also reported the production of PH_3 from mixed bacterial cultures in the laboratory (Rutishauser and Bachofen, 1999; Jenkins *et al.*, 2000). Even though the exact metabolic pathway leading to PH_3 production in anaerobic bacteria is still unknown, it is clear that phosphine is a biosignature gas on Earth, although strictly associated with the anaerobic biosphere. On Earth, phosphine could be made directly by microbial reduction of more oxidized phosphorus species or indirectly by microbial production of reduced phosphorus compounds, such as hypophosphite, and their subsequent disproportionation to PH_3 (Gassmann and Glindemann, 1993; Glindemann *et al.*, 1996, 1999, 2005a). In either case, however, the presence of phosphine is an indicator of the presence of life. For more information on phosphine in the context of terrestrial biology, see recent studies by Bains *et al.* (2019a, 2019b); Sousa-Silva *et al.* (2020).

1.2. Motivation

As discussed, we wish to extend the analysis of phosphine as a candidate biosignature gas by analyzing possible abiotic sources of phosphine. As a case study, and a base for future research, we model the production of phosphine in the venusian environment. The presence of phosphine in the atmosphere of Venus would be unexpected, and so its detection, if confirmed, requires explanation. If the detection is confirmed by further observations, the presence of phosphine in Venus' atmosphere suggests that our understanding of venusian atmospheric chemistry is at least incomplete, and that the source of that phosphine needs to be identified. Considering the exclusively biological production of phosphine on Earth, the only rocky planet hitherto known to have phosphine in its atmosphere, the question arises whether the detection of phosphine on Venus could indicate the presence of life. For such a claim to even be entertained, all other possible sources of phosphine should be identified and eliminated. Regardless of whether phosphine is present on Venus, this investigation serves as a starting point for future detections of phosphine features in observational data of temperate exoplanets. We emphasize that, even if the detection of phosphine is confirmed in the atmosphere of Venus, this can only be considered evidence of the presence of life if *all* other sources of phosphine can be ruled out (Catling *et al.*, 2018). This article is a first step in that undertaking, considering possible nonbiological mechanisms for making phosphine in the atmosphere, surface, or subsurface of Venus.

1.3. Approach: photochemistry, kinetics, and thermodynamics

The ideal approach to identify the possible source of any gas in a planet's atmosphere would be to exhaustively model the rate of all possible reactions that could create and destroy that gas. Presently this is impossible. Exhaustive modeling requires knowledge of all the components of the atmosphere, surface, and subsurface of the planet. While some components of Venus' atmosphere are well known, many, including gases relevant to phosphine reactivity, remain unknown. In addition, exhaustive modeling requires accurate knowledge of the rates of all possible reactions between component molecules under all relevant conditions. Many reaction rates for known species in the venusian environment have not been measured.

We therefore break the modeling problem into two parts. (1) We construct a photochemical model accounting for the formation and destruction of phosphine based on previous photochemical models of Venus' atmosphere. (2) We separately and complementarily use a thermodynamic approach to model formation pathways for phosphine. While the thermodynamic modeling is not intended to substitute for the full kinetic modeling of chemical reactions, it plays a useful and necessary role to *rule out* chemical reactions that could spontaneously produce phosphine.

Together, the two modeling units provide upper bounds on venusian phosphine production.

1.4. Article outline

In this article, we apply chemical modeling to attempt to explain the production of the highly unexpected discovery of the trace gas phosphine in the atmosphere of Venus (Greaves *et al.*, 2020c).

The main body of the article is divided into two sections, modeling the photochemistry and kinetics of phosphine in the atmosphere (Section 2) and thermodynamics in the atmosphere, surface, and subsurface (Section 3). Detailed methods for these sections are provided in Supplementary Data S1 (Supplementary Sections 1.1, 1.2, and 1.3).

In Section 4, we summarize other processes, including lightning and exotic physical and chemical phenomena that could in principle lead to the formation of phosphine on Venus.

In the Discussion section (Section 5), we explore several unconventional explanations for the phosphine on Venus, including exotic geochemistry, photochemistry, and biologically driven formation of phosphine. A range of chemical reactions can produce phosphine under Venus conditions, but all of these require reactants that are themselves extremely unlikely to form on Venus, a problem we term ''displaced improbability.'' We conclude the article by arguing that the source of phosphine on Venus, if the presence of PH_3 is confirmed, cannot be explained by our current knowledge of the planet. All potential sources fall short by many orders of magnitude. We argue that further aggressive observations of Venus and its atmosphere, as well as the development of astrobiology-focused space missions, should get the highest priority and would be crucial for an unambiguous explanation for the source of phosphine in the venusian atmosphere.

2. Photochemistry and Kinetics of Phosphine in the Atmosphere of Venus

The overall goal of our photochemical calculations is to determine if photochemically driven mechanisms can maintain the detected 1 ppb of PH_3 at any altitude. This is not yet possible within a self-consistent model because synthesis rates of PH_3 from oxidized species are largely unknown. To account for the limitations caused by missing PH_3 kinetics, we make the complex chemistry of phosphine in the venusian atmosphere tractable by modeling phosphine photochemical destruction and synthesis networks separately.

We proceed by first calculating the destruction rates for PH_3, for which the reaction kinetics is relatively well known. We do so by (1) using a photochemical model to estimate the vertical radical concentration profiles in the venusian atmosphere, and (2) using the radical profiles to estimate PH_3 lifetimes (and hence destruction rates) throughout the atmosphere. Separating the photochemical model calculations and lifetime estimates enables us to repeat our lifetime calculations with radical profiles derived from a different model (Bierson and Zhang, 2020), permitting us to test the sensitivity of our conclusions to the choice of a photochemical model (Ranjan *et al.*, 2020). Second, we explore the photochemical pathways for the synthesis of PH_3 and determine whether the PH_3 synthesis network can compensate for the known PH_3 destruction mechanisms and sustain an ~ 1 ppb concentration of phosphine at any altitude in the venusian atmosphere.

We show that the photochemical synthesis of PH_3 is unable to explain the observed PH_3 concentration. Although the major source of uncertainty in this calculation is the extremely poor knowledge of the PH_3 synthesis pathways, our approach is conservative such that these uncertainties do not affect our main conclusions.

2.1. Introduction to photochemistry and kinetic analysis

In Section 2.2, we summarize the photochemical models used in this work (Section 2.2.1, Section 2.2.2, and Section

2.2.3), including the addition of PH_3 to the photochemical network, and estimate the lifetime of phosphine in the venusian atmosphere (see Supplementary Section 1.1 and its subsections). We discuss in detail all the known processes that affect the lifetime of phosphine, including the destruction of phosphine by atmospheric radicals, direct UV photolysis, and vertical transport in the atmosphere of Venus. We also discuss significant limitations and uncertainties of phosphine lifetime calculations.

The estimation of the lifetime of phosphine on Venus is key for determining production rates that are required to maintain the detected ~1 ppb concentration in the venusian atmosphere. We compare the photochemical destruction rates from our photochemical model with the predicted maximum possible photochemical production rate of phosphine, to assess the possibility of its photochemically driven formation (Section 2.2.2 and 2.2.3). We explain why our predicted phosphine photochemical production is many orders of magnitude lower than that needed to explain the observed abundance of phosphine.

Greaves *et al.* (2020c) provided a preliminary description of a photochemistry model for the venusian atmosphere that includes phosphorus species. Here we provide a more complete description of that model and apply it to phosphine chemistry on Venus. The model uses the ARGO 1D photochemistry-diffusion code (Rimmer and Helling, 2016) to solve the atmospheric transport equation for the steady-state vertical composition profile. ARGO is a Lagrangian photochemistry/diffusion code. The code follows a single parcel of gas as it moves from the bottom to the top of the atmosphere, as determined by a prescribed temperature profile. The code updates temperature, pressure, and actinic ultraviolet flux at each height in the atmosphere. In this reference frame, bulk diffusion terms are accounted for by time-dependence of the chemical production, P_i ($cm^3\ s^{-1}$), and loss, L_i (s^{-1}), and so, below the homopause, the chemical equation being solved is effectively as follows:

$$\frac{\partial n_i}{\partial t} = P_i[t(z, v_v)] - L_i[t(z, v_z)]n_i, \quad (1)$$

where n_i (cm^{-3}) is the number density of species i, t (s) is time, z (cm) is atmospheric height, and $v_z = K_{zz}/H_0$ (cm/s) is the effective vertical velocity due to Eddy diffusion, from the Eddy diffusion coefficient K_{zz}($cm^2\ s^{-1}$). The model is run until the abundance of every major and significant minor species (any with $n_i > 10^5\ cm^{-3}$) does not change by more than 1% between two global iterations.

The handful of known reactions of PH_3 with the major reactive venusian species O, Cl, OH, and H were combined with previously published Venus atmospheric networks of Krasnopolsky (2012, 2013) and Zhang *et al.* (2012), and the network of STAND2019 (Rimmer and Rugheimer, 2019), which includes H/C/N/O species. This model and its results are the same as those presented in Greaves *et al.* (2020c). Details of the reaction networks, initial conditions, and modeling are provided in Supplementary Section 1.1 and its subsections. See also Supplementary Figs. S1, S2 and Supplementary Tables S1, S2.

This whole-atmosphere model allows us to assess the lifetime of PH_3 throughout the atmosphere self-consistently. The model accounts for photochemistry, thermochemistry, and chemical diffusion. UV transport calculation was modified in two ways. First, we ignore the UV absorption of SO_2 for the first three global iterations and include it afterward. This seems to help the model to converge. After the first three global iterations, we include UV absorption by SO_2 and absorption by the ''mysterious absorber'' with properties described by Krasnopolsky (2007) (see Supplementary Section 1.1.1).

With these conditions, using the photochemical network described below, convergence required 33 global iterations of the model.

The counterbalance of photochemical destruction of phosphine is the possibility that phosphine is photochemically generated in gas or droplet phases. The possibility of gas-phase production was considered as follows. A network of reactions that could generate PH_3 from H_3PO_4 was constructed; H_3PO_4 was selected as the starting molecule because H_3PO_4 is predicted to be the most abundant phosphorus species in Venus' atmosphere at cloud level and above; and because H_3PO_4 is the only phosphorus species for which gas-phase kinetic data are available. The maximum possible rate of phosphine production was calculated as the flux through this network, assuming no back reactions. More details on the network, its construction and estimation of the reaction rates, are provided in Supplementary Section 1.2, Supplementary Figs. S4–S7. The possibility of photochemical production of phosphine in cloud droplets is discussed briefly in Section 5.2.

2.2. Results of the photochemistry and kinetic analysis

2.2.1. Abundance of phosphine. We chose to model processes that can maintain a stable abundance of 1 ppb phosphine in the atmosphere of the planet, for the following reason.

The initial detection by Greaves *et al.* using the JCMT telescope (Greaves *et al.*, 2020c) in 2017 was interpreted as an abundance of ~20 ppb, derived from three different analytical methods (Greaves *et al.*, 2020a). The reprocessed follow-up detection using ALMA in 2019 (Greaves *et al.*, 2020b) was interpreted as an abundance of 1–4 ppb, when planet averaged, variable across the planet, an interpretation that is robust to a variety of analytical methods (Greaves *et al.*, 2020a, 2020b). The original detections have both been challenged, both on statistical grounds (Snellen *et al.*, 2020; Thompson, 2021) and interpretation of data, suggesting that the detection is SO_2 instead of PH_3 (Villanueva *et al.*, 2020; Akins *et al.*, 2021; Lincowski *et al.*, 2021). The TEXES/NASA-IRTF NIR spectrometry data have been interpreted as showing an upper phosphine abundance limit of 5 ppb in March 2015 (Encrenaz *et al.*, 2020). The upper limits for phosphine above the cloud top assessed from the SOIR/VEx spectra from a localized region of the Venus terminator collected between August 2006 and January 2010 suggest PH_3 abundances of less than 1 ppb (Trompet *et al.*, 2020). The Pioneer LNMS data have not been used directly to infer an abundance, but suggest a similar order of magnitude to H_2S in 1978, which is modeled to be present at ~1 ppb at the cloud level (see Supplementary Fig. S3) (Krasnopolsky, 2008). The differences in the estimates of the abundance of PH_3 in Venus' atmosphere could therefore be due to variability of phosphine abundance in space and time, due to differences in detection methods or analyses, or both. If phosphine is present, however, the detections are all consistent with an abundance of at least 1 ppb in the cloud decks. As the purpose of this article is to explore potential abiotic routes to this biosignature gas, the presence of the gas is taken as a starting point. To be conservative, we assume an abundance of 1 ppb. If a process cannot produce enough phosphine to explain 1 ppb, then it also cannot produce enough phosphine to explain 20 ppb. If any process (biotic or abiotic) *can* explain the presence of phosphine at 1 ppb, this does not mean that it can produce enough to maintain the 20 ppb that was potentially seen in 2017 by using the JCMT telescope. So as a criterion to rule out potential sources of phosphine, assuming a lower abundance is a conservative assumption.

2.2.2. Lifetime and necessary production rate of PH_3 in the venusian atmosphere. The abundance of phosphine on Venus is a result of a balance between its production and destruction. Estimating venusian PH_3 destruction rate (and hence its lifetime) as a function of altitude is key for understanding the PH_3 production rates required to maintain an ∼1 ppb atmospheric concentration. Figure 2 presents our estimates of PH_3 destruction rate and lifetime as a function of altitude, broken down by specific destruction mechanisms.

We begin by commenting broadly on PH_3 photochemical destruction rates in the venusian atmosphere. Attack by O is the main loss mechanism in the high atmosphere (>60–80 km), attack by Cl the main loss mechanism in the middle atmosphere, and thermolysis the main loss mechanism at the planet surface; this is consistent with calculations performed with radical profiles derived from other models of Venus, although ones that do not consider PH_3 (Bierson and Zhang, 2020). Direct photolysis is included but is found not to be the dominant loss mechanism at any height in the atmosphere for any of the models considered. The presence of PH_3 suppresses radical concentrations in the lower atmosphere. The concentrations of radicals are low in the lower atmosphere, and so even in small abundances, PH_3 becomes a significant scavenger; consequently, models that exclude PH_3 [*e.g.*, Bierson and Zhang (2020)] may overestimate photochemical destruction rates in the deep atmosphere.

We next discuss the chemistry of atomic chlorine, which determines the profile of PH_3 in the middle atmosphere. Atomic Cl is predicted to occur well below the limit of detection, with mixing ratios of $<10^{-17}$ beneath the clouds according to all the atmospheric models we consider. Even at these mixing ratios, Cl significantly affects the lifetime of PH_3 below the clouds of Venus. In our model, the vertical profile of Cl atoms is complex. In brief, ClS_2 is produced by thermal reactions between sulfur species, CO and HCl below 5 km, and is efficiently broken down to Cl atoms by 327–485 nm photons that penetrate below 35 km. Above 30 km, Cl is removed by reaction with chemical products of SO_3, which itself is produced by thermal dissociation of H_2SO_4. Cl abundance is predicted to be $<1\,cm^{-3}$ near the surface (the Cl is produced thermochemically near the surface, and then locked into ClS_2), $>100\,cm^{-3}$ at 25–35 km (from ClS_2 photolysis), and above 50 km, $<1\,cm^{-3}$ between 42 and 54 km (due to reactions with chemical products of SO_3), and then increases from 1 to $10^8\,cm^{-3}$ between 58 and 100 km due to HCl photolysis (see Supplementary Section 1.1.5.3 for further details on Cl chemistry in our model).

However, other models that use different networks show different Cl atom abundances. The atomic and radical profiles from Bierson and Zhang (2020) and Krasnopolsky (2007) and our profiles disagree with each other by approximately five orders of magnitude, which means that the predicted chemical lifetimes for PH_3 due to destruction by these atoms and radicals differ by several orders of magnitude.

If destruction by atoms and radicals was the only way to remove PH_3, then the lifetime of PH_3 would be very poorly constrained. It would depend on abundances of species that cannot be measured, and which can vary over almost five orders of magnitude between models. However, the thermal decomposition, diffusion timescale, and photochemical destruction of PH_3 are robust to differences in chemical networks and provide us with a confident upper limit to the lifetime of PH_3 in the atmosphere of Venus. We therefore move on to the role of transport.

PH_3 has a lifetime of <1 s in the high atmosphere (>78–98 km) due to high levels of UV radiation and its concomitant radicals. In the deep atmosphere (<50 km), which is UV-shielded, PH_3 lifetime to photochemical destruction may be much longer (up to 10^{11} s). Vertical transport of PH_3 to high altitudes ultimately limits the PH_3 lifetime in much of the lower atmosphere. However, transport in the lower atmosphere of Venus is slow: consequently, PH_3 lifetimes may be as high as ∼400 years in parts of the lower atmosphere. If we instead estimate the lifetime by using the radical concentration profiles of Bierson and Zhang (2020), we predict lifetimes of ≤700 years in the deep atmosphere, because the PH_3 must diffuse to a higher z_0[‡] (up to 98 km), compared with our model (78 km).

The comparatively long lifetime of PH_3 predicted for parts of the deep atmosphere (∼100s of years) motivates us to consider the possibility that low photochemical or abiotic production of PH_3 could result in accumulation of phosphine over time and diffuse upward to explain 1 ppb PH_3 abundance at the level probed by Greaves *et al.* (2020c). This scenario requires an efficient unknown phosphine formation mechanism deep in the atmosphere, and/or efficient transport to the detection altitudes of 53–61 km, but not to the destruction altitude (>78–98 km). Our calculations suggest that there is no such transport pattern for the venusian atmosphere.

The rate of destruction of PH_3 (at the cloud level or below) is much slower than on Earth, because of the much lower concentration of OH radicals in the venusian atmosphere. A much smaller production rate is therefore needed to generate a 1 ppb concentration in the atmosphere than would be true on Earth. We calculated the total, planet-wide outgassing flux necessary to maintain an atmospheric concentration of 1 ppb in the atmosphere of Venus at the detection altitudes of 53–61 km. We find that a flux of $\sim 10^8$ phosphine molecules $cm^{-2}\,s^{-1}$ (averaged across the whole planet) is needed to reproduce the observed phosphine mixing ratio of 1 ppb above 55 km (Greaves *et al.*, 2020c). This is equivalent to ∼26 kg/second or $\sim 8\times10^5$ tons

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[‡] Altitude at which the photochemical lifetime of PH_3 becomes short ($\leq 10^4$ s), that is, where the radical population becomes high; see Supplementary Section 1.1.1.

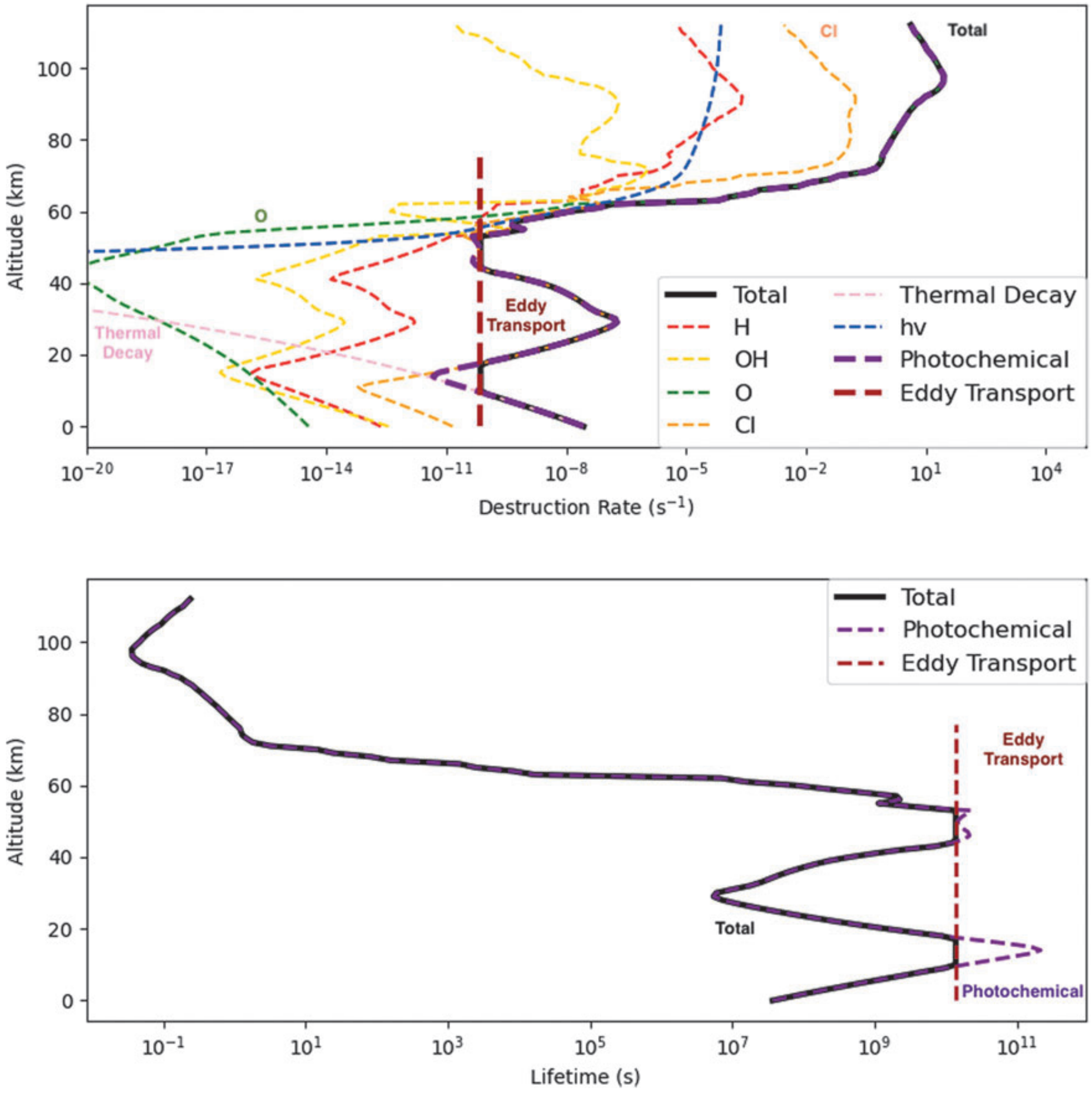


FIG. 2. The lifetime of phosphine in the venusian atmosphere. Top panel: Removal rates for PH_3 in the venusian atmosphere, as a function of altitude. x axis: Destruction rate (s^{-1}), y axis: Altitude (km). Individual photochemical loss processes are shown in thin dashed lines. Also shown is the loss rate due to diffusion to the upper atmosphere, calculated by inverting the diffusion timescale. Thick black line presents overall loss rate, which is the minimum of the photochemical and diffusion loss rates. Bottom panel: Photochemical, diffusion, and overall lifetimes of PH_3 in the venusian atmosphere, calculated by inverting the corresponding loss rates. x axis: Lifetime (s), y axis: Altitude (km). Overall, the photochemical lifetime of PH_3 is long in the lower atmosphere but short in the upper atmosphere, meaning that transport to the upper atmosphere ultimately limits PH_3 lifetime in much of the lower atmosphere. Even so, PH_3 lifetimes of order centuries are possible in the lower atmosphere.

year^{-1}. For comparison, methane is produced at a rate of $\sim 340 \times 10^6$ tons year^{-1} from nonanthropogenic sources on Earth, $\sim 14 \times 10^6$ tons of which are geological (*i.e.*, not dependent on life) (Saunois *et al.*, 2016).

In the remainder of this article, we explore the possibility of an efficient abiotic phosphine formation mechanism in the venusian atmosphere.

2.2.3. Photochemical synthesis of phosphine cannot explain the observed PH_3 abundance in the atmosphere of Venus. Photochemical synthesis of phosphine, by reduction of oxidized phosphorus species by atmospheric radicals, could in principle lead to the formation of phosphine. We argue, however, that photochemically driven reactions in Venus' atmosphere cannot produce PH_3 in sufficient amounts to explain the detection of ~ 1 ppb. We find that the reactions involving atmospheric radicals capable of reducing oxidized phosphorus species (*e.g.*, hydrogen radicals) are too slow, and the required forward reaction rates are too low, by factors of 10^5 or more (Fig. 3). We present our reasoning in detail below.

Figure 3 shows that there is no altitude at which the maximum possible forward reaction rate is sufficient to counter the destruction rate: the minimum ratio of

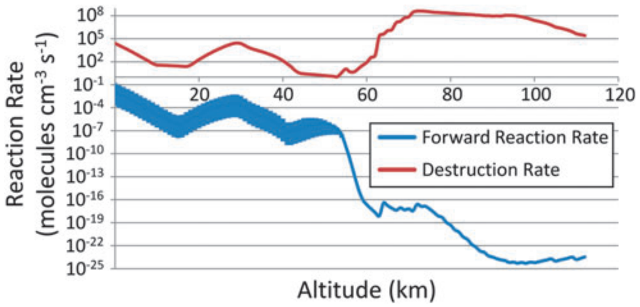


FIG. 3. The photochemical production and destruction rates of phosphine. x axis: Altitude (km), y axis: Reaction rate (molecules cm^{-3} s^{-1}). Maximum rate of forward reaction through the kinetic network as a function of altitude (blue line) compared with the photochemical destruction rate (red line). The base of the clouds is assumed to be at any altitude between 45 and 55 km, which gives a range of forward rates reflecting a range of phosphorus species concentrations, themselves depending on the lower boundary of the cloud layer as described in Supplementary Section 1.3.2.2. Under no conditions the rate of the photochemical formation of phosphine is sufficient to balance the photochemical destruction rate, therefore making the photochemical production of phosphine unlikely.

destruction/synthesis rates is 8.46×10^{-6}. Figure 4 analyzes which reactions in the network are responsible for the slow production of phosphine. The main ''blockage'' in the network (Fig. 4) for PH_3 synthesis is the series of reactions that can lead from P=O to PH or PH_2. The conversion of phosphoric acid (H_3PO_4) to the $P^{(+3)}$ radical H_2PO_3 is also a rate-limiting process, supporting the idea that the spontaneous production of phosphite or phosphorous acid is not favored (discussed further below in Section 3.2.1.2); note that phosphorous acid itself — H_3PO_3 — is not stable in gas phase. We discuss the potential chemistry of H_3PO_3 in the droplet phase, as well as its potential role as a transient intermediate, in Section 3.2.1.2 and Section 3.2.1.3 below.

We note in summary that that our analysis is very conservative because it is purposely highly biased toward predicting the production of phosphine, for the following two reasons:

1. We assume that *all* of the atmospheric phosphorus is concentrated into one species, the species that is reacting in each reaction. Such a scenario is highly improbable. In reality, the phosphorus species would predominantly be present as H_3PO_4 or P_4O_{10} (see Section 3.2.1.1), and all other species would be trace gases.
2. We assume that only forward (reducing) reactions occur. If back (oxidizing) reactions were also considered, they would reduce the calculated net rate of reduction, and lower the overall production rate of phosphine.

Therefore, our network provides the maximum possible phosphine production rate from known photochemical processes. The maximum rate predicted is more than four orders of magnitude too low to account for the presence of ~1 ppb PH_3 in Venus' atmosphere. In reality, back reactions would significantly lower the efficiency of the formation of PH_3. Several such back reactions could occur; the net result of forward and back reactions occurring at the same time is the phosphorus-catalyzed recombination of H, O, and OH into H_2O instead of the production of reduced

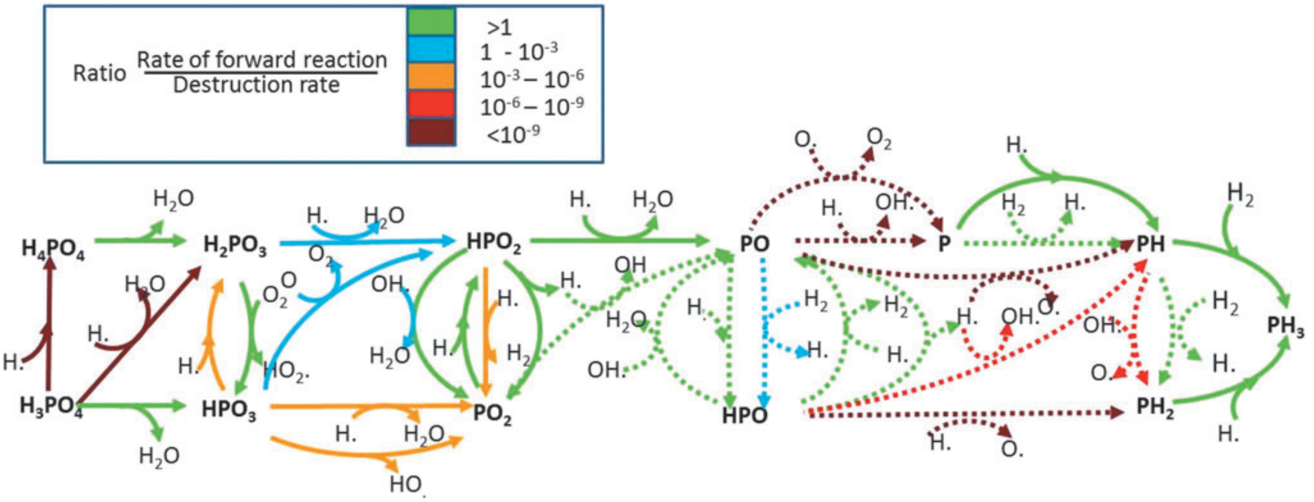


FIG. 4. Exploration of the potential photochemical pathways for the synthesis of PH_3. The reaction network was constructed as described in Supplementary Section 1.2. The destruction rate of phosphine was calculated from the photochemical model (Supplementary Section 1.1.1). Maximum possible forward reaction rates were calculated as described in Supplementary Section 1.2. For each altitude, the ratio R = reaction rate/destruction rate was calculated for each reaction. The reactions are colored by the *maximum R* for any altitude for that reaction. There is no path to PH_3 synthesis through the network that does not cross at least one reaction that has an $R<10^{-6}$, that is, at least nine orders of magnitude too slow to account for the observed levels of phosphine. Therefore, there is no reaction path that can efficiently produce phosphine photochemically. The transformation of P=O to PH or PH_2 is the main bottleneck of the network. The forward kinetic network is constructed as a function of altitude. Reactions are colored for the assumption that the cloud base occurs at 48 km. Figure modified from Greaves *et al.* (2020c).

phosphorus species. The precedent for such phosphorus-catalyzed recombination chemistry is known in terrestrial flame chemistry (Twarowski, 1993, 1995, 1996). We note, however, that this hypothesis needs more detailed modeling and experimental studies to be confirmed.

Our forward PH_3 production reaction network contains no provision for reactions of oxidized phosphorus species with sulfur or oxidized chlorine species such as ClO, which play a substantial role in venusian atmospheric chemistry (Taylor and Hunten, 2014; Marcq *et al.*, 2018; Sandor and Clancy, 2018). No reaction kinetics is reported for reaction of oxidized phosphorus species with reactive, oxidizing S or Cl species. It is unknown if such hypothetical photochemical processes involving sulfur or chlorine species can lead to the reduction of oxidized phosphorus species and, as a result, to the production of phosphine. We discuss such unknown chemical processes as a potential source of phosphine on Venus in Section 5.2.

Our approach suggests that phosphorus monoxide (PO) could be a significant component of the reaction chemistry of phosphorus in Venus' atmosphere. PO has not been observed or modeled as an atmospheric species on Venus to date. PO's presence could be confirmed by directed observation, as it was done in the past for PO (Tenenbaum *et al.*, 2007) and phosphorus oxoacids (Turner *et al.*, 2018) in the interstellar medium. We emphasize, however, that we are postulating the existence of PO as a transient intermediate species, not a major component of the venusian atmosphere.

2.3. Summary and conclusion of the photochemistry and kinetic analysis

We have carried out a detailed analysis of photochemical and other endergonic chemistry that could produce phosphine under Venus conditions. Our models provide the destruction rate and lifetime for phosphine in Venus' atmosphere, and hence, a flux rate necessary to maintain ∼1 ppb phosphine stably in the atmosphere. Our analysis confirms that none of the modeled kinetic pathways can explain the levels of phosphine observed, falling short by many orders of magnitude, even when using the most conservative assessments available.

We note that these are all calculations of gas-phase photochemistry. Solid-phase photochemistry is not relevant, as no significant UV penetrates to the ground on Venus. We address the question of UV photochemistry of cloud droplets in Section 5.2.

3. Thermodynamic Analysis of Potential Phosphine-Producing Reactions

3.1. Introduction to thermodynamics of phosphine production

In the absence of the kinetic data for chemical reactions that could lead to phosphine formation, we use a thermodynamic approach to investigate the plausibility of phosphine production on Venus.

Thermodynamics predicts the free energy to be gained from allowing a system to relax to equilibrium. For example, a gas mixture of hydrogen and oxygen will be predicted to be of higher energy than the same gas mixture in which some hydrogen has been reacted with some oxygen to produce water, and so, we predict that if the system reacts then water will be produced. The *amount* of each of the reagents is an important component of this analysis (see Supplementary Section 1.3 for more detailed exposition and Supplementary Section 2.1 for an example of thermodynamic calculation). We can ask whether the reaction

$$P_4O_{10} + H_2 \rightarrow PH_3 + H_2O$$

will have a net positive or a net negative free energy of reaction *only if* we know the concentrations of all four reactants. If the energy of reaction is positive given the concentration of these species under venusian conditions, then thermodynamics predicts that the forward reaction will require energy, the back reaction will release energy, and so, the reaction will proceed *from* PH_3 and H_2O *to* P_4O_{10} and H_2. Thus, if this reaction is predicted to have a positive free energy, given the abundance of atmospheric gases and assuming 1 ppb PH_3, then we can say robustly that the production of 1 ppb PH_3 by this reaction is not consistent with our knowledge of Venus. This is not to say that *no* PH_3 could be produced. For example, if the abundance of phosphine was 4.3×10^{-34} ppb, and all the other reagents were at the temperature, pressure, and concentration expected at 60 km on Venus, then the reaction above would be at equilibrium. What thermodynamic analysis shows is that, at 60 km, 1 ppb PH_3 cannot be explained by the formation from this reaction. For every 10 kJ/mol free energy of reaction calculated under the assumption of Venus conditions at the base of the clouds, the abundance of phosphine has to be reduced 23-fold from 1 ppb to bring the reaction to equilibrium.

If no combination of conditions (different temperatures, pressures, reducing agents, and concentrations), from any observation or model, yields a negative free energy for this reaction assuming 1 ppb of phosphine, then this reaction can be confidently *ruled out* as a source of 1 ppb phosphine on Venus. A thermodynamic analysis cannot substitute for the full kinetic modeling of chemical reactions. A rapidly reacting system will approach thermodynamic equilibrium. If the reaction is slow compared with the timescale of the system (*e.g.*, transport or observational timescales), then the reaction will not reach equilibrium and phosphine will not be produced regardless of the thermodynamics (as is illustrated by the case of the reduction of calcium phosphate in the high atmosphere of Venus, discussed in Section 4.2). If a reaction is fast but it is thermodynamically disfavored, 1 ppb of phosphine cannot be produced by this reaction under Venus conditions. This is true of catalyzed and uncatalyzed reactions; the reason that the reaction is fast does not matter. Thus, thermodynamics does not predict when a reaction can occur, but predicts when one cannot explain the presence of 1 ppb phosphine. It is therefore a useful tool to rule out possible chemical pathways for phosphine production if the kinetic data are not available.

We approach the calculation of the thermodynamics of chemical reactions in the venusian environment by calculating the free energy (ΔG) of any reaction involving stable chemical species detected or modeled in Venus' atmosphere that could generate phosphine, both in the atmosphere and on the surface. We tested hundreds of partial pressure and cloud altitude combinations, for a total of thousands of conditions for each of the dozens of reactions.

We also explore the thermodynamics of the subsurface formation of phosphine by using the concept of oxygen fugacity of crustal and mantle rocks.

Calculation of the free energy of reaction was performed by using standard methods (see Supplementary Section 1.3.1), See also Supplementary Tables S3, S4. Nonideality of gases was calculated with Berthelot's equation (Rock, 1969). Solids were assumed to be in their ideal state, that is, as pure materials. Reactions were chosen as follows. To produce phosphine, a reaction must have (1) a source of phosphorus, (2) a source of hydrogen, and (3) a reducing agent. The relative abundance of the sources of phosphorus in the atmosphere was calculated as described below (see Supplementary Section 1.3.2). All reducing gases, potential reducing solids, and gaseous sources of hydrogen that have been measured or modeled were used to construct all possible hypothetical reducing reactions with all sources of phosphorus. The vertical concentration profiles of gases were taken from the photochemical model described above in Section 2 and in Supplementary Section 1.1. The thermodynamics of the production of phosphine and of phosphorous acid (which could disproportionate to form phosphine) was also modeled (see Supplementary Section 1.3.2 for further details). Detailed modeling of the venusian subsurface chemistry is not practical, as the rock compositions are not known, and a very large number of different minerals could be present. We therefore modeled the oxygen fugacity (fO_2), for a range of temperatures (700–1600 K), of subsurface rocks needed to generate phosphine in the subsurface venusian environment, as described in more detail below in Section 3.2.3 and in Supplementary Section 1.3.3. See also Supplementary Tables S7, S8.

3.2. Results of the thermodynamic analysis of potential phosphine-producing reactions

3.2.1. Surface and atmospheric thermodynamics of phosphine production. *3.2.1.1. Identification of dominant atmospheric phosphorus species.* Phosphine, a reduced form of phosphorus, is not a dominant species in the oxidized venusian environment. The oxidized venusian conditions favor the formation of oxidized phosphorus compounds. To identify the dominant atmospheric phosphorus species, we have modeled the relative abundance of oxidized phosphorus species under Venus' atmosphere conditions.

Both P(+3) and P(+5) oxidized phosphorus species can be present as oxyacids or as acid anhydrides. The thermodynamic model shows that P_4O_6 is thermodynamically preferred over P_4O_{10} in Venus' lower atmosphere (<35 km) (Fig. 5). In the lower atmosphere, dehydrated forms of phosphorus dominate over hydrated forms, due to the combination of high temperature and low water concentration.

P_4O_6 as a dominant phosphorus species on Venus may be surprising, but it agrees with previous theoretical studies on brown dwarfs and gas giants done by Visscher *et al.* (2006). At temperature and pressure regimes of higher altitudes, we find that H_3PO_4 dominates. Visscher *et al.* find that the most stable form of phosphorus in analogous regimes in brown dwarfs is $NH_4H_2PO_4$ (*i.e.*, ammonium dihydrogenphosphate). This species would not form on Venus, where the gas-phase concentration of ammonia is essentially zero. Its free acid analogue, which would be formed by incubating $NH_4H_2PO_4$ in acid, is H_3PO_4.

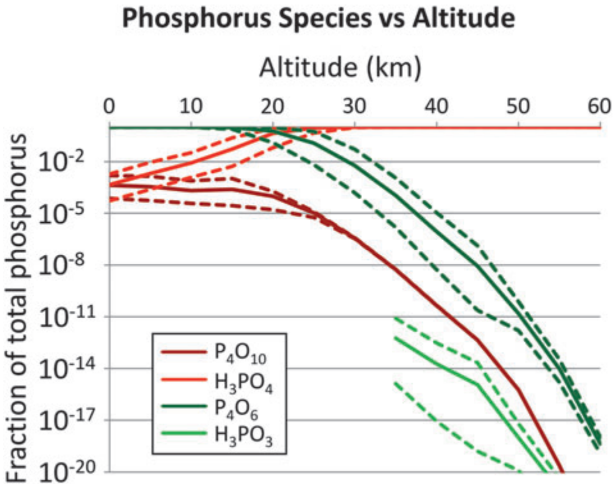


FIG. 5. Model of the relative abundance of phosphorus oxyacid species under Venus atmosphere conditions, as a function of altitude. x axis: Altitude (km), y axis: Fraction of total phosphorus. Solid lines show the dominant phosphorus species. Dashed lines show upper and lower limits for the relative fractions of each species, as modeled in different chemical environments (Supplementary Section 1.3.2.2). P_4O_6 and H_3PO_4 are the thermodynamically dominant phosphorus species in the lower (<35 km) and the upper (>35 km) atmosphere of Venus, respectively. Note that phosphorous acid (H_3PO_3) cannot exist in gas phase, and so only exists in the cloud droplets.

The model predicts that by far the dominant species in the cloud layer is phosphoric acid (H_3PO_4). The principal uncertainties in the model are the abundance of water in the atmosphere (which influences the ratio of oxide to oxyacid) and the abundance of reducing agents. We discuss the abundance of reducing agents in the next section.

We note that our model is incomplete. In reality, highly concentrated H_3PO_4 consists of a mixture of ''pure'' H_3PO_4, $H_3PO_4 \cdot H_2O$ complexes, and many dehydration products (*e.g.*, $H_4P_2O_7$ and $H_5P_3O_{10}$). However, detailed thermodynamic data for such minor phosphorus species under Venus conditions are not available, and therefore, our model serves as a best possible approximation.

3.2.1.2. Formation of phosphine by reduction of P species in the venusian atmosphere-surface environment cannot proceed spontaneously. Our calculations show that formation of phosphine in the venusian atmosphere and on the surface is very unlikely to proceed spontaneously. None of the tested reactions in the thousands of considered conditions that make phosphine or phosphorous acid is thermodynamically favorable. All chemical reactions that can produce phosphine in the venusian environment are on average 100 kJ/mol too energetically costly (10–400 kJ/mol) to proceed spontaneously (Fig. 6 and Supplementary Figs. S9–S11).

We divide our analysis into separate analyses of reduction reactions and of disproportionation reactions. In principle, P(V) or P(III) species present in Venus' atmosphere could be reduced by gases in the atmosphere to form phosphine. P(III) species could also disproportionate to P(V) species and phosphine; specifically, the disproportionation of phosphorous acid (H_3PO_3) to phosphine is a well-known laboratory preparation method for phosphine, and it could be that analogous reactions are forming phosphine in Venus' atmosphere. In this section, we consider reduction reactions, and in the next section (Section 3.2.1.3) we consider disproportionation reactions.

Reduction of P(V) or P(III) species by atmospheric gases is highly unlikely to be a net producer of phosphine. Reduced gases known or modeled to be present in Venus' atmosphere include H_2, OCS, CO, H_2S, and elemental sulfur (as gas or haze). In the case of OCS, CO and elemental sulfur a third component is needed to convert P_4O_{10} or P_4O_6 to PH_3 to provide hydrogen atoms. None of the reactions has a negative free energy of reaction under Venus atmospheric conditions.

The reduction of oxidized phosphorus species by surface minerals is ruled out. The only common reduced surface minerals are likely to be iron minerals. Iron(II) sulfide and iron(II) chloride are not stable under Venus surface conditions (Fegley, 1997) (Supplementary Fig. S8) and reduced iron oxides cannot reduce P_4O_6 to PH_3 (Supplementary Fig. S11).

As noted above, surface mineral phosphorus (if present) is likely to be present as phosphate (Zolotov and Garvin, 2020). The reduction of mineral phosphate by reduced atmospheric species to produce PH_3 is also highly unlikely thermodynamically (Supplementary Fig. S10). We considered four model minerals, calcium phosphate (whitlockite) $Ca_3(PO_4)_2$, calcium fluorophosphate (fluorapatite) $Ca_5(PO_4)_3F$, magnesium phosphate $Mg_3(PO_4)_2$, potassium phosphate K_3PO_4, and their reduction by the reducing atmosphere species: H_2, OCS, H_2S, CO, and elemental sulfur (S_8 or S_2). We note that, although chemical reactions occurring below 30 km are unlikely to be the source of the observed phosphine, there remains the possibility that surface minerals could be transported above 30 km as dust, and so, we considered mineral reduction as a source of phosphorus at all altitudes up to 60 km.

We summarize the thermodynamics of reduction of atmospheric and surface phosphorus species in Fig. 6, where we show the distribution of a number of reduction reactions that make phosphine as a function of their free energy and as a function of altitude (Fig. 6).

The minimum free energy of reduction reactions under any Venus conditions was found to be 47 kJ/mol, which implies that the maximum phosphine abundance that these reactions can explain is $\sim 2.8 \times 10^{-6}$ ppb.

We note here that reduced phosphorus species are reported to be formed from phosphate under hydrothermal environments on Earth (Herschy *et al.*, 2018). However, formation of reduced phosphorus species (*e.g.*, phosphite) under the hydrothermal conditions on Earth is not a model for the formation of reduced phosphorus species formation on Venus. The mechanism of formation of reduced phosphorous species in hydrothermal systems relies on the abundant presence of liquid water. Such conditions cannot occur on the surface of Venus, where water is a trace species and is present as a supercritical gas.

We could argue that the complex atmosphere of Venus is not fully characterized, and specifically that the clouds may be more reduced than we think, and that the more reduced character of the venusian atmosphere might explain the presence of phosphine. While such a statement is formally true, it is not supported by the current observational evidence of the atmosphere of Venus and therefore it is unlikely.

3.2.1.3. Formation of phosphine from disproportionation of P(III) species in the venusian atmosphere-surface environment cannot proceed spontaneously. The disproportionation of the P(III) compound phosphorous acid (H_3PO_3) to form phosphine via the following reaction:

$$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4$$

is a well-known laboratory preparative route for phosphine. We therefore ask whether similar chemistry could be a source of phosphine on Venus. H_3PO_3 cannot exist in gas phase, where P(III) oxides are present solely as P_4O_6; however, H_3PO_3 can exist in solution in water and in concentrated sulfuric acid (Sheldrick, 1966). Thus, H_3PO_3 could be formed in the cloud decks by the reduction of H_3PO_4 or by the solution of P_4O_6 in the liquid phase of the clouds. It could also be formed as a transient intermediate in a reaction of P_4O_6 with an H-bearing species at any altitude, and then rapidly disproportionate to phosphine and H_3PO_4 or P_4O_{10}.

There are therefore two classes of reactions that could lead from P(III) species to phosphine; the conversion of P_4O_6 to a notional intermediate H_3PO_3 in gas phase, where it can be considered an intermediate that immediately disproportionates to PH_3 and H_3PO_4, and the formation of H_3PO_3 in liquid phase in cloud droplets that subsequently rain out to the lower regions of the atmosphere where H_3PO_3 disproportionates to PH_3. Below we show that both are highly unlikely as sources of phosphine.

For P_4O_6 to be converted to H_3PO_4 and PH_3 (via the notional formation of H_3PO_3 as a reaction intermediate, as recently discussed by Schulze-Makuch (2021)), a source of hydrogen atoms is required. H_2O, HCl, and H_2S could potentially be such a source. The reaction with water is well known on Earth, where P_4O_6 dissolves in clean, cold liquid water to form phosphorous acid. Notional reactions of P_4O_6 with HCl yield PCl_3 as a coproduct, and with H_2S yield a phosphorus sulfide. The free energy of PCl_3 is known. P_4S_3 is the only phosphorus sulfide, of many, for which gas-phase free energy of formation is known. We therefore use the following reactions as models for reaction of P_4O_6 with H_2O, HCl, and H_2S (where the species in square brackets are transient intermediates) (see also Supplementary Fig. S12):

1. $P_4O_6 + 6H_2O \rightarrow [4H_3PO_3] \rightarrow 3H_3PO_4 + PH_3$
2. $P_4O_6 + 1\,{}^1/{}_2\,H_2O \rightarrow [4H_3PO_3] \rightarrow {}^3/{}_4\,P_4O_{10} + PH_3$
3. $P_4O_6 + 3HCl + 3H_2O \rightarrow [3H_3PO_3 + PCl_3] \rightarrow 2\,{}^1/{}_4\,H_3PO_4 + {}^3/{}_4\,PH_3 + PCl_3$
4. $P_4O_6 + 6HCl \rightarrow [2H_3PO_3 + 2PCl_3] \rightarrow 1\,{}^1/{}_2\,H_3PO_4 + {}^1/{}_2\,PH_3 + 2PCl_3$
5. $P_4O_6 + 9HCl \rightarrow [H_3PO_3 + 3PCl_3 + 3H_2O] \rightarrow {}^3/{}_4\,H_3PO_4 + {}^1/{}_4\,PH_3 + 3PCl_3$
6. $P_4O_6 + 3H_2S \rightarrow [2H_3PO_3 + {}^1/{}_2\,P_4S_3 + 1\,{}^1/{}_2\,S] \rightarrow {}^1/{}_2\,P_4S_3 + 1\,{}^1/{}_2\,S + {}^1/{}_2\,PH_3 + 1\,{}^1/{}_2\,H_3PO_4$

There is no realistic way to estimate the concentration of P_4S_3, PCl_3, or $POCl_3$, so this was assumed for the sake of exposition to be 10^{-13} ppt (*i.e.*, 1 part in 10^{22}). This corresponds to around 1 molecule per liter at 1 bar and seems a plausible lower limit (lower concentrations favor the forward reaction producing phosphine, and so, this is a conservative assumption).

The free energy of reaction of the reactions above, as well as the disproportionation of H_3PO_3 in the clouds, was calculated for all combinations of plausible Venus conditions. The result is summarized in Fig. 7. No set of conditions favors the production of phosphine.

The minimum free energy of disproportionation reactions under any Venus conditions was found to be 22 kJ/mol, which implies that the maximum phosphine abundance that these reactions can explain is $\sim 1.1 \times 10^{-3}$ ppb.

Why does reaction $P_4O_6 + 6H_2O \rightarrow [4H_3PO_3] \rightarrow 3H_3PO_4 + PH_3$ presented above not produce phosphine on Venus when analogous chemistry does in the laboratory on Earth? There are three reasons. First, the terrestrial laboratory reaction is done in liquid water. The activity of water in liquid water is much higher than the activity of gaseous water in Venus' very dry atmosphere; low water activity disfavors the reaction. Second, the reaction is strongly disfavored at high temperatures (where P_4O_6 is abundant on Venus); at low temperatures (such as at cloud level), P_4O_6 is a rare, trace species, disfavoring the forward reaction. Lastly, reaction $P_4O_6 + 6H_2O \rightarrow [4H_3PO_3] \rightarrow 3H_3PO_4 + PH_3$ is *not* thermodynamically favored under terrestrial laboratory conditions. The reaction that is favored is the reaction of P_4O_6 with liquid water to form H_3PO_3 solution. If that solution is then dried (which requires input of energy) to yield pure H_3PO_3, and if that H_3PO_3 is then heated (which requires input of energy), then the state of the system is changed such that the reaction to form PH_3 is favored. Adding P_4O_6 to cold water on its own does not produce PH_3, even on Earth, because solutions of H_3PO_3 do not spontaneously disproportionate under cold water temperature conditions.

Finally, H_3PO_3 could be formed either by solution of P_4O_6 or by reduction of H_3PO_4 in the cloud droplets, where H_3PO_3 is stable. If droplets then fall to lower, hotter regions of the atmosphere, H_3PO_3 could disproportionate to form PH_3. We evaluate the amount of phosphine that this process could produce below.

Figure 5 shows the equilibrium amounts of phosphorus species as a function of altitude in the atmosphere, which illustrates that H_3PO_3 is a small fraction of phosphorus species at cloud level on Venus. This calculation takes into account the equilibrium between P_4O_6 in gas and droplet phase and H_3PO_3 in droplet phase, and so accounts for the equilibrium

$$P_4O_6 + 6H_2O \leftrightarrow 4H_3PO_3$$

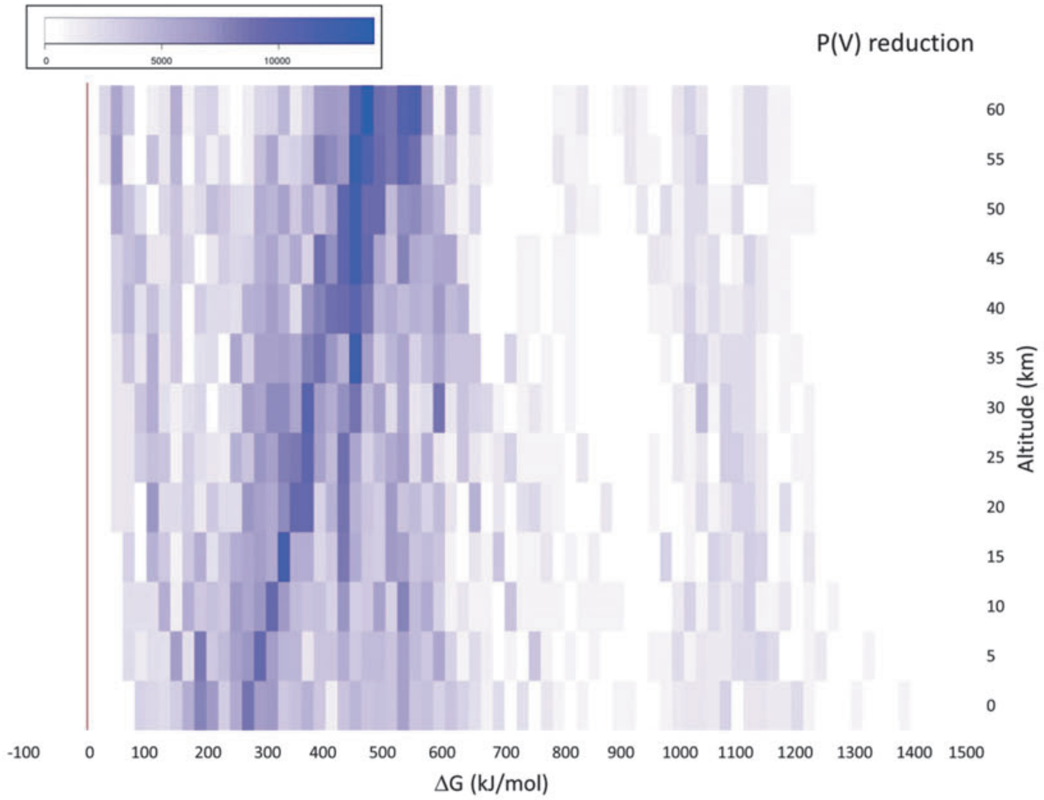
We calculate the amount of H_3PO_3 in the clouds as follows. We can calculate from the volume of cloud particles (Esposito *et al.*, 1983), the fraction of P that is present as H_3PO_3, and assuming that P is present in all cloud particles at an average of 1 molar, that there would be 0.25 mmol, or 20 mg in the *entire* cloud deck of Venus (see Supplementary Section 2.5.2 and Supplementary Table S12). This assumes that the cloud layer extends down to 40 km, which is probably below its actual extent.

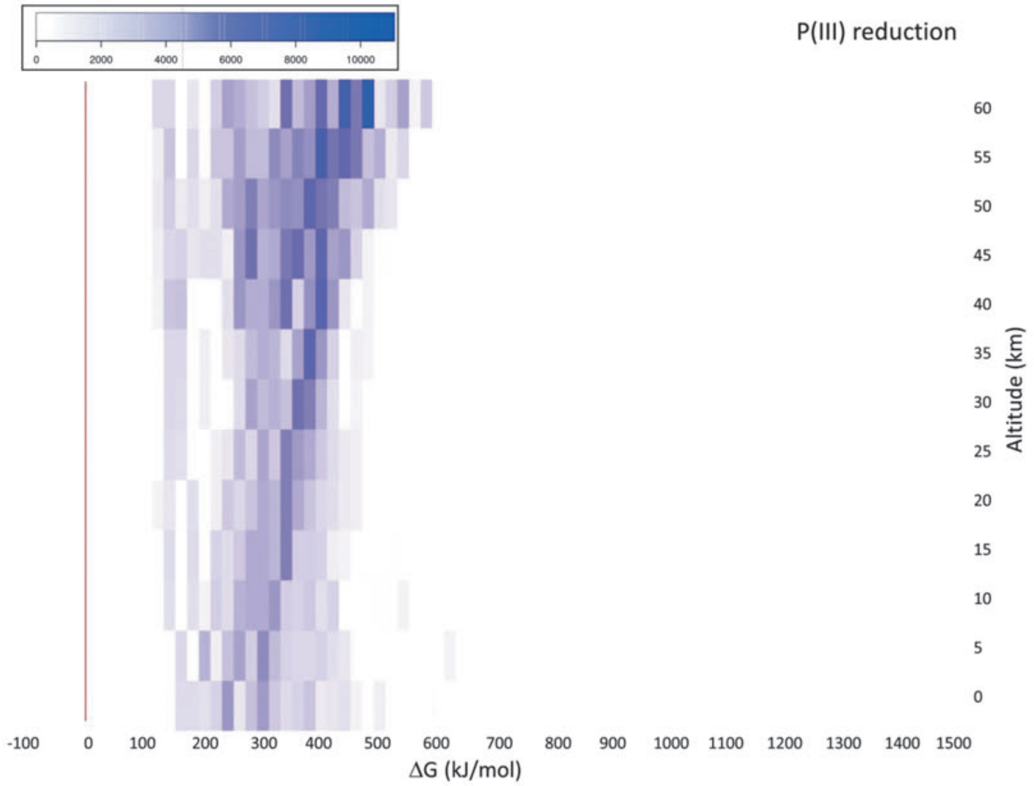
H_3PO_3 would not disproportionate appreciably in the temperature regime of the clouds. The kinetics of the disproportionation of phosphorous acid has not been studied. We can, however, use the disproportionation of hypophosphorous acid (H_3PO_2) as a proxy:

$$3H_3PO_2 \rightarrow 2H_3PO_3 + PH_3$$

As H_3PO_3 accumulates as a product of this reaction, H_3PO_3 cannot disproportionate substantially faster than H_3PO_2 under the same conditions. The kinetics of H_3PO_2 disproportionation has been studied (Shechkov *et al.*, 2003). The first-order rate of disproportionation at 420 K (approximately the cloud base temperature) is $\sim 2 \times 10^{-4}$ s^{-1}. If this rate applies to H_3PO_3 disproportionation, then a constant concentration of 22 mg/planet of H_3PO_3 disproportionating at this rate would produce a flux of phosphine of ~ 130 g/year/planet (assuming that the solution of P_4O_6 into droplets and its subsequent conversion to H_3PO_3 were not rate limiting). The disproportionation of the H_3PO_3 would be faster if droplets containing H_3PO_3 fell below the cloud layer and evaporated (Seager *et al.*, 2021), and the H_3PO_3 disproportionated in the higher temperature regions of the lower atmosphere. However, to generate 800,000 tons/year of PH_3 necessary to maintain a constant 1 ppb PH_3 through this mechanism, the entire cloud deck would have to ''rain out'' every microsecond, which is ridiculous. These calculations discount the fact that P_4O_6 is oxidized in sulfuric acid to H_3PO_4 (Krasnopolsky, 1989), which will further reduce the concentration of *all* P(III) species in the droplets.

FIG. 6. The infeasibility of phosphine production in the venusian atmosphere and surface by reduction. The y axis shows altitude above the surface and each column (x axis) is a bin of data in a range of Gibbs free energy (ΔG). Red vertical line shows $\Delta G = 0$. The darker the color of a cell the more reactions/conditions fall within a given ΔG range. The Gibbs free energies are from reactions of surface and atmospheric phosphorus species with gaseous or solid reducing agents. Reactions with gases were calculated with a high or a low gas concentration, derived from published data (Supplementary Table S5), in all combinations, assuming a concentration of 1 ppb PH_3. Reduction reactions of P_4O_6, P_4O_{10}, H_3PO_4, and H_3PO_3 were considered (the last of these only in solution phase in the clouds), as well as the surface reduction of phosphate minerals (see also Supplementary Table S6). None of the conditions give a negative free energy, which would indicate a reaction that spontaneously produced phosphine. Thermodynamics was only followed to the altitude of the cloud tops, after which phosphorus species and water are expected to freeze out making reactions of stable phosphorus compounds kinetically implausible. Phosphine production by reduction is not thermodynamically favored under the conditions of the venusian atmosphere, and surface and subsurface conditions. Heatmaps were generated by using Heatmapper (Babicki *et al.*, 2016).


0
5000
10000
P(V) reduction
60
55
50
45
40
35
30
25
20
15
10
5
0
Altitude (km)
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
ΔG (kJ/mol)


0
2000
4000
6000
8000
10000
P(III) reduction
60
55
50
45
40
35
30
25
20
15
10
5
0
Altitude (km)
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
ΔG (kJ/mol)

3.2.2. Sensitivities in thermodynamic analysis. We note that the sensitivity analysis to the concentrations of gases in the venusian atmosphere shows that only very substantial systematic errors (at least 10^4-fold difference) in gas abundance measurements or modeling could account for the production of phosphine. Such dramatic differences from current expectation are therefore highly unlikely (see Supplementary Section 2.3 and Supplementary Fig. S13).

If an unknown, nonvolatile material that was a less powerful reducing agent than hydrogen was present in the clouds, could it reduce phosphoric acid to phosphorus acid? (If it were more powerful than hydrogen, then it would split water and generate hydrogen, as discussed below.) This cannot be definitively ruled out in the absence of specifics, but if hydrogen cannot reduce phosphoric acid to phosphorous acid under Venus conditions, then a less powerful reducing agent is unlikely to be able to do so.

3.2.3. Subsurface thermodynamics of phosphine production. *3.2.3.1. Phosphorus abundance in venusian rocks.* The abundance of phosphorus in venusian rocks is not known. The only direct measurement of the composition of Venus is X-ray fluorescence data from the Vega landers. These did not detect phosphorus, although it detected abundant silicon (Smrekar *et al.*, 2014). As phosphorus and silicon X-ray fluorescence signals are very close (Leake *et al.*, 1969), all that the Vega result can tell us is that at the site of the Vega landers, phosphorus was not an abundant element compared with silicon. Models of the bulk composition of Venus suggest one similar to that of Earth (Smrekar *et al.*, 2014). We therefore take Earth as our model.

A survey of igneous terrestrial rock shows a wide range of phosphorus content, but an average of ∼0.2% P by weight. Notably, isotopic markers of lower mantle rocks (Hart *et al.*, 1992) are not associated with increased phosphorus content. This suggests that both surface volcanism and mantle plume volcanism will produce rocks with similar phosphorus content (see Supplementary Section 2.4.4 for details).

3.2.3.2. Formation of phosphine in the venusian subsurface environment cannot proceed spontaneously. Volcanism could contribute phosphine to the atmosphere through two mechanisms. The first is if the equilibrium thermodynamics

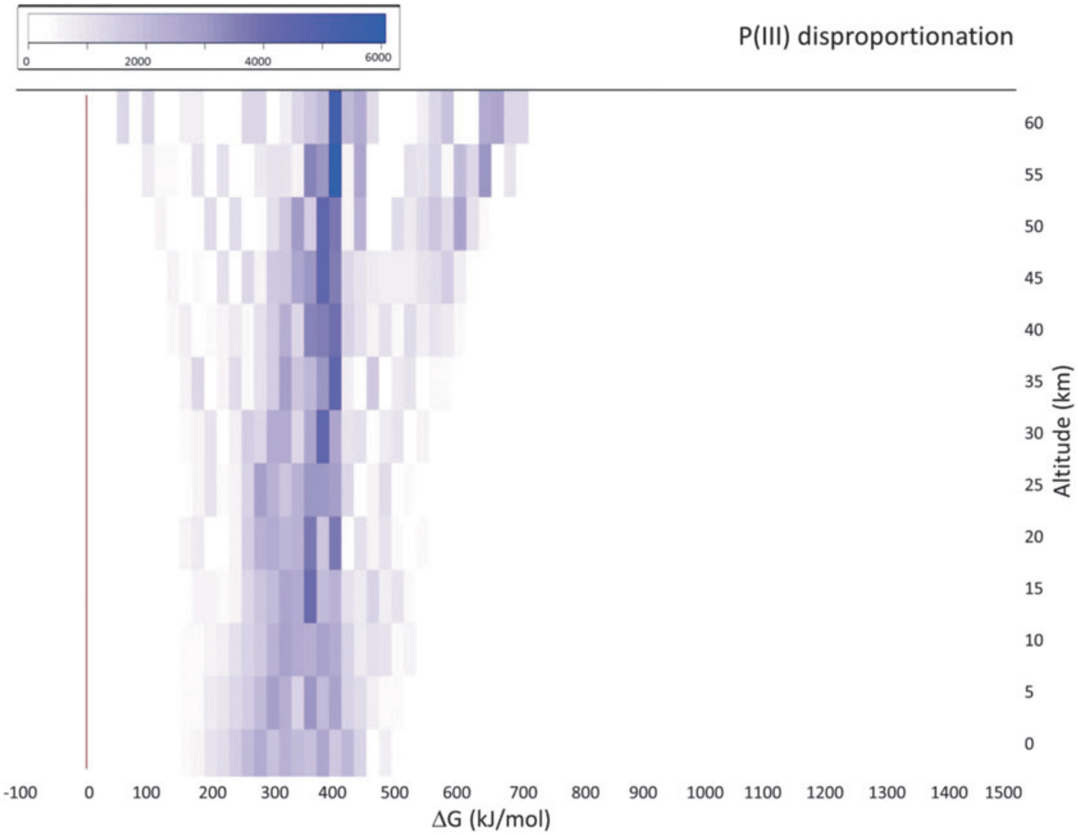


FIG. 7. The infeasibility of phosphine production in the venusian atmosphere and surface by disproportionation. The y axis shows altitude above the surface and each column (x axis) is a bin of data in a range of Gibbs free energy (ΔG). Red vertical line shows ΔG = 0. The darker the color of a cell the more reactions/conditions fall within a given ΔG range. The Gibbs free energies are from disproportionation reactions of P(III) species, either P_4O_6 via H_3PO_3 as an intermediate or from H_3PO_3 in the cloud deck (see also Table S6). None of the conditions gives a negative free energy, which would indicate a reaction that spontaneously produced phosphine. Thermodynamics was only followed to the altitude of the cloud tops, after which phosphorus species and water are expected to freeze out making reactions of stable phosphorus compounds kinetically implausible. Phosphine production by disproportionation is not thermodynamically favored under the conditions of the venusian atmosphere, and surface and subsurface conditions. Heatmaps were generated by using Heatmapper (Babicki *et al.*, 2016).

of rocks near the surface (*i.e.*, in the upper mantle or crust) favored phosphine production. The second is if rocks from the lower mantle, under different conditions of temperature and pressure, could be brought to the surface through plume volcanism and react to generate phosphine. In this section, we address the first, surface chemistry source. In Section 3.2.4 below, we address mantle plume volcanism.

We note that the rate of volcanism on Venus is not known. Studies of surface topology and cratering suggest that Venus is volcanically active. Volcanism is believed to be primarily through hotspot volcanism driven by mantle plumes, and not plate tectonics. Smrekar *et al.* identify nine volcanic hotspots (Smrekar *et al.*, 2010) analogous to the Hawaii Island chain on Earth (for comparison, Earth has 6–8 such currently active plume volcanic regions, depending on definition and scale). Gülcher *et al.* (2020) identify 37 potentially currently active volcanic areas [compared with an average of 32 terrestrial volcanoes that have erupted in any one of the past 50 years (Siebert, 2013)]. The volume of flood volcanism on Venus is more than five times the combined area of flood volcanic basalts on Earth (Ivanov and Head, 2013), Byrne (Byrne, 2020) reviewed evidence of volcanism on Venus, and concluded that the planet was probably 2–3 times as volcanically active as Earth. However, Mikhail and Heap (2017) postulated that the overall volcanic flux is much lower than that on Earth. We must conclude therefore that the rate of volcanism on Venus is unknown, but is unlikely to be more than five times that on Earth.

We use thermodynamics to estimate the potential production of phosphine by crustal volcanism. It is impractical to perform calculations of the thermodynamics of specific reactions in the subsurface of Venus, because the composition of the rocks is not known and the thermodynamics of individual reactions is not known. We therefore simplify the problem of calculating whether subsurface chemistry could generate phosphine by using the concept of oxygen fugacity (fO_2). Oxygen fugacity is the notional concentration of free oxygen in a mineral at thermodynamic equilibrium; the higher the concentration, the more oxidizing the rock is [see Frost (1991) and Supplementary Section 1.3.3 for more details on fO_2 and its calculation]. See also Supplementary Tables S7, S8. A higher oxygen fugacity (concentration of free oxygen in the crustal rocks) means a more oxidized rock and a lower probability of reduction of phosphates. We find that the oxygen fugacity of plausible crust and mantle rocks is 8–15 orders of magnitude too high to support reduction of phosphate. It is therefore extremely unlikely that subsurface activity on Venus, including volcanism, would produce substantial amounts of phosphine.

We present our reasoning as follows. We compared the fugacity of the phosphate/phosphine equilibrium to the fugacity of standard mineral buffers representative of terrestrial rocks. The results are shown in Fig. 8.

To interpret any fO_2 curve, any point above a fugacity line will mean that the oxidized member of a reaction will be favored, anything below a fugacity line means that the reduced member is favored.

The phosphate/phosphine fO_2 curves lie substantially below the quartz-iron-fayalite (QIF) buffer line, which itself falls well below the typical fO_2 of mantle or crustal rocks. Rare cases of very reduced rocks are found in some locations, for example, Ulff-Møller (1985) with an fO_2 of ∼QIF-1. However, such rocks are unlikely to contain any water, because it would react with the metallic iron in the rock. The fO_2 of lunar and asteroidal olivines and plagioclase is usually around IW −2 to IW +2 (Karner *et al.*, 2004). All of them are too oxidized to produce PH_3 from phosphate. This means that in crustal and mantle rocks, phosphorus will overwhelmingly be present as phosphate.

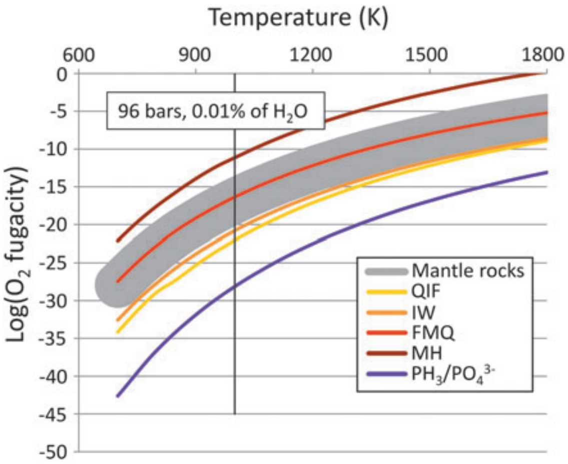


FIG. 8. Comparison of the fugacity of the phosphate/phosphine equilibrium with the fugacity of the standard mineral buffers of terrestrial rocks. x axis: Log O_2 fugacity, y axis: Temperature (K). Fugacity of the production of phosphine from phosphate minerals is calculated for 96 bars and 0.01% water in the rocks. The fugacity of the phosphate/phosphine equilibrium is shown as a purple line. The other curves are O_2 fugacities of standard rock buffers. The phosphate/phosphine fO_2 curve lies below the QIF buffer line (the most reduced rock of the buffers shown), which falls below the typical fO_2 of terrestrial mantle or crustal rocks (gray band region). Therefore, typical terrestrial rocks are too oxidized to produce PH_3 from phosphates and the formation of phosphine is highly unlikely under venusian subsurface conditions. FMQ, fayalite-magnetite-quartz; IW, iron/wüstite; MH, magnetite/hematite; QIF, quartz-iron-fayalite.

The results of our fugacity calculations are also supported by observations that PH_3 is not known to be made by volcanoes on Earth, although in principle, reduced phosphorus species could be produced in ocean-floor hydrothermal systems through serpentinization reactions (Pasek *et al.*, 2020) (an environment with no analogue on Venus). Estimation of the production of PH_3 through volcanism on a simulated anoxic early Earth concluded that only trace amounts of volcanic phosphine can be produced through this process. The predicted maximum production rate of phosphine on the early Earth is only ∼100 tons per year (Holland, 1984), even assuming a highly reduced planet with abundant water. The volcanic production of phosphine in more oxidized, dehydrated planetary scenarios is even more unlikely.

The redox state of the crustal rocks on Venus is unknown. The relatively reduced QIF buffer is an Fe(II)/Fe(0) buffer: to have a substantially more reducing rock, a more electropositive metal than iron would need to be present in significant amounts as elemental metal, which itself would imply that all the iron (and nickel) in the rock would have to be reduced to elemental metal as well. This is a possible but implausible scenario.

We validate our approach by calculation of the fugacity of the terrestrial H_2S/SO_2 equilibrium. The results from the computed SO_2/H_2S line (Supplementary Fig. S14) are qualitatively consistent with field observations on Earth and modeling on Mars (see Supplementary Section 2.4.1). Another way to demonstrate that subsurface chemistry cannot generate atmospheric phosphine is to consider the amount of volcanism that would be necessary to generate the observed amount of phosphine in the atmosphere. We find that to maintain ~1 ppb of PH_3 on Venus, a volcanic flux many orders of magnitude greater than that on Earth is required. We modeled volcanic outgassing as follows.

The thermodynamics inherent in Fig. 8 does not state that phosphine cannot be made by geochemistry, just that the ratio of phosphine to phosphate would be extremely small. We estimate the amount of volcanism that would be needed to maintain an atmospheric abundance of ~1 ppb as follows. We calculated the ratio of phosphate to phosphine (formally of P(+5):P(−3)) that would be produced by volcanic rocks using the $f(O_2)$ approach described above, based on the $f(O_2)$ values of six redox buffers with redox states between iron/wüstite (IW: Fe/FeO) and magnetite/hematite (MH: Fe_3O_4/Fe_2O_3) buffers, including the IW and MH buffers themselves, and for a range of temperatures, pressures, and rock water content that reflect the extreme ranges plausible for Venus' crust. From this, the amount of phosphorus that would have to be erupted to provide the flux of 25.96 kg/sec (needed to maintain an abundance of ~1 ppb in the atmosphere) can be calculated. These fluxes are shown in Fig. 9 (see Supplementary Section 2.4.3 [Supplementary Fig. S16] and Supplementary Section 2.4.4 [Supplementary Fig. S17] for details of the data sources and calculations).

Few conditions require a total flux of less than 10^9 g of phosphorus per second. For comparison, the flux of phosphorus from modern-day Earth volcanism (of all sorts) is ~143 kg/second (shown as a vertical red line of Fig. 9—see Supplementary Section 2.4.3 for details). This is 1390 times lower than the most extreme rate predicted for Venus, representing outgassing at 90 bar and 1600 K, with a fugacity of the IW buffer (at the bottom range of plausibility for mantle rocks), and from rocks containing 1.5% water. Water, 1.5%, is a high value even for terrestrial midocean ridge and mantle plume melts (Moore, 1970; Saal *et al.*, 2002; Weis *et al.*, 2015). Arc volcano magmas can have up to 5% water (Anderson, 1973), but as these are directly derived from the subducted crustal ocean floor, their high water levels cannot be replicated on a planet without oceans. More realistic values of $f(O_2)$, water content, temperature, and pressure require tens of thousands of times more volcanism on Venus than on Earth to produce the amount of phosphine required. We note that the venusian crust (and by inference the upper mantle, due to the resurfacing event) may be more oxidized than Earth (Wordsworth, 2016), making the lower outgassing rates even less probable. We consider it highly unlikely that Venus has >1000 times the volcanic activity of Earth needed to explain the presence of phosphine in its atmosphere.

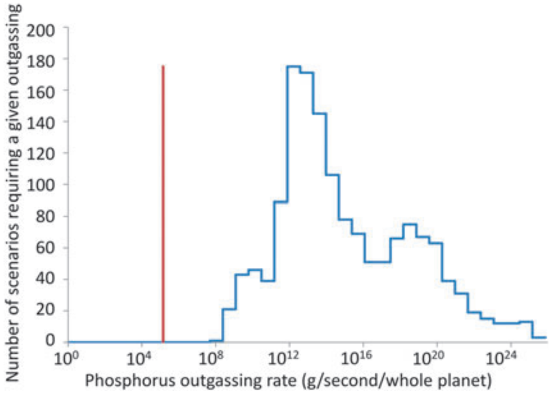


FIG. 9. The assessment of the volcanic production of phosphine. x axis: Total phosphorus outgassing rate in grams of phosphorus per second across the whole planet, binned in log(5) bins. y axis: Number of combinations of $f(O_2)$ buffer, temperature, pressure, and water content for which that outgassing rate provided 25.96 kg/sec phosphine flux. Blue line—model output. Red line—estimated terrestrial phosphorus outgassing flux (see Supplementary Section 2.2.3 for details). To explain the observed abundance of phosphine, at least many hundred times more volcanism on Venus than on Earth is required.

Fugacity is dependent on pressure, temperature, and water concentration. We probed the sensitivity of our conclusions to variation in all three parameters (see Supplementary Section 2.4.2 and Supplementary Fig. S15). No realistic values of pressure (up to 10,000 bar), water content (up to 5%), or temperature (up to 1800 K) can support phosphine production (Supplementary Fig. S15). We note that phosphorous acid and phosphites cannot be produced by volcanoes, as they break down at temperatures >~450 K. We discuss other reduced phosphorus species in Section 3.2.1.2 and Section 3.2.1.3.

3.2.4. Mantle phosphides as a source of phosphine.

Our argument above suggests that crustal and upper mantle phosphorus is overwhelmingly present as oxidized P(V), and that these are unlikely sources of PH_3. By contrast, Earth's lower mantle contains at least some regions that are highly reduced (Smith *et al.*, 2016) and in which phosphorus is likely to be present as phosphides rather than phosphate. Phosphides are stable to extremely high temperatures and pressures (Japel *et al.*, 2002), and so could be formed deep in the mantle and brought to the surface through plume volcanism, if such volcanism occurs on Venus. Mineral phosphides are hydrolyzed by acid solutions in water to form phosphine (Bumbrah *et al.*, 2012), or phosphite or hypophosphite, which could subsequently disproportionate to phosphine (Pasek and Lauretta, 2005). Therefore, if phosphide were erupted from the lower mantle to the surface, it could be converted to phosphine. We note that Truong and Lunine have recently suggested that plume volcanism could be a source of 1 ppb phosphine (Truong and Lunine 2021). We find this scenario unlikely for four independent reasons.

First, it is not clear that lower mantle phosphides are commonly erupted to the surface unchanged. On Earth, mantle plume magma is estimated to rise on a timescale of 10^6–10^7 years at temperatures in excess of 3000 K (Condie, 2001), during which time phosphorus species would reach thermodynamic equilibrium relevant to the temperature and pressure of the upper mantle and then the base of the crust, that is, P(V) phosphate or P(III) P_4O_6-related anions. Thus, although mantle plume volcanism *originates* in the lower mantle, its chemistry will not be *lower mantle chemistry* by the time it erupts.

Second, it is not clear that solvolysis of mineral phosphides in concentrated sulfuric acid will generate phosphine. While hydrolysis of industrial-grade iron in dilute (0.5 M) sulfuric acid efficiently generates phosphine (Geng *et al.*, 2010), and hydrolysis of phosphide chemicals (Bumbrah *et al.*, 2012) and minerals by water or dilute acid generates reduced phosphorus species (Pasek *et al.*, 2014), there have been no studies on the reaction of phosphides with *concentrated* sulfuric acid. The attack of concentrated sulfuric acid on materials follows different chemistry than the attack on those same materials by solutions of sulfuric acid in water. Concentrated sulfuric acid is an oxidizing agent, and is known to rapidly oxidize phosphine at low temperatures (see Supplementary Section 2.5.3.1); hot concentrated sulfuric acid will also oxidize metals such as iron and copper, producing SO_2 as a gaseous product (rather than reacting with iron to produce hydrogen, as is the case with dilute acid). A likely outcome of reacting phosphides with *concentrated* sulfuric acid would be an oxidation reaction, such as the following:

$$\mathrm{Fe_2P + 7H_2SO_4 \rightarrow FePO_4 + {}^{1}/{}_{2}\,Fe_2(SO_4)_3 + 5\,{}^{1}/{}_{2}\,SO_2 + 7H_2O}$$

In the lower atmosphere where H_2SO_4 is likely to be dissociated into SO_3 and H_2O, direct oxidation of phosphides by SO_3 is likely. This is speculative but more in line with the known chemistry of sulfuric acid (Liler, 1971) than the generation of a highly reducing gas (PH_3) using a strong oxidizing agent (H_2SO_4). This chemistry could be experimentally tested.

Third, even if we assume both rapid and efficient delivery of phosphides to the surface and rapid and efficient conversion of phosphides to phosphine, the amount of phosphides released into the atmosphere, and the scale and frequency of such volcanic eruptions needed for this scenario of phosphine production to be possible, makes it seem unlikely. We argue as follows. If mineral phosphides were efficiently converted to phosphine, then 800,000 tons of phosphorus would need to be erupted from the lower mantle every year, as noted above, to explain the presence of $\sim$1 ppb phosphine in the atmosphere. An average abundance of $\sim$0.2% of P in terrestrial rocks (by weight) implies a mass of $\sim 4 \times 10^8$ tons of lower mantle rock would have to be erupted per year to account for the observed phosphine level, or $\sim$0.2 km^3 of lower mantle basalt. This would be quite a substantial eruption, and it would be unlikely for it to be happening just when Greaves *et al.* (Greaves *et al.*, 2020c) were making their observations. For context, the Siberian and Deccan traps, vast volcanic flood plains that represent the most extensive volcanism in the Phanerozoic on Earth, were probably created by massive plume eruptions that at their peak produced 1.3 km^3 of basalt/year, which would deliver $\sim 10^{12}$ g of phosphorus to the surface, per year, the large majority as phosphate (Renne and Basu, 1991; Sen, 2001). As discussed above, no evidence for such recent catastrophic volcanism exists on Venus, although more observations would be needed to rule out such active flood volcanism on modern Venus.

Lastly, we note that if solvolysis of phosphide minerals in rocks is generating phosphine, then it would also be expected to generate other reduced gases. Any rock sufficiently reduced to contain phosphorus as phosphide would contain carbon as carbide and sulfur as sulfide, and possibly nitrogen as nitride. Hydrolysis of that rock would produce hydrogen sulfide quantitatively, and possibly methane, acetylene, or ammonia as well. The precedent of terrestrial rock abundance suggests an S:P ratio of $\sim$2:1 as noted in Supplementary Section 2.4.3. There is no evidence for anomalous hydrogen sulfide levels in the venusian atmosphere.

We conclude that four lines of argument suggest that lower mantle volcanism is not a source of phosphine on Venus. However, if lower mantle plume volcanism is generating significant atmospheric gases, there should be other evidence such as extensive highly reduced flood basalts on the surface. This prediction can be tested by *in situ* sampling.

3.2.4.1. Possible scenarios for a volcanic origin of venusian phosphine. What set of assumptions could allow volcanism to explain the presence of 1 ppb phosphine in the atmosphere? Photochemical models are complex, and the estimates of phosphine production rates derived thereof are not easy to derive from first principles. Here we outline a simple analytical calculation to place an extreme lower bound on phosphine production rate required to explain the reported signal. The advantage of this approach is that it is easy to understand and validate. In this way, it complements the full photochemical calculation also presented in this article.

Photochemical models agree that phosphine will be efficiently destroyed at high altitudes by photolysis and reactions with photolytically generated radicals; phosphine that diffuses to this altitude must be destroyed, and its destruction must be counterbalanced by production in steady state. We can calculate an extreme lower bound on the minimum production flux of phosphine required to compensate solely for destruction by transport to the upper atmosphere and explain the reported 1 ppb phosphine detected at 61 km altitude as follows:

For reasons discussed above, we assume a phosphine column equivalent to 1 ppb phosphine at altitudes ≥61 km. One ppb of phosphine at 61 km corresponds to a phosphine column density (N_{PH3}; cm^{-2}) at $z \geq 61$ km only if

$$N_{PH_3} = r_{PH_3} * p(61\ \mathrm{km})/(g_{Venus} * u_{Venus})$$

where $r_{PH_3} = 10^{-9}$ is the phosphine mixing ratio, $p(61\ \mathrm{km}) = 1.94 \times 10^5$ Barye is the atmospheric pressure at 61 km, $g_{Venus} = 887\ \mathrm{cm\ s^{-2}}$ is the acceleration due to gravity on Venus, and $u_{Venus} = 43.45$ amu is the mean molecular mass of the venusian atmosphere.[§] Then, $N_{PH_3} = 3 \times 10^{15}\ \mathrm{cm^{-2}}$. In reality, due to diffusion, there must also be substantial phosphine below 61 km, but, in the interest of conservatism, let us ignore that: at least this much PH_3 must be present to explain the reported signal (if PH_3 is present at all).

[§] https://nssdc.gsfc.nasa.gov/planetary/factsheet/venusfact.html, accessed 2/1/2021.

Now, let us calculate the timescale for this PH_3 to circulate to the upper atmosphere, where it is destroyed. We consider this altitude to be $z_1 = 98$ km, corresponding to the altitude by which PH_3 lifetime is <1 s in all three of the models of the venusian atmosphere we consider here. This vertical mixing timescale is (Jacob, 1999, equation 4.23) as follows:

$$T = \frac{(\delta z)^2}{2 \cdot K_z}$$

where δz is the height difference and K_z is the eddy diffusion coefficient. The longer the timescale, then the slower the transport of PH_3 to the destruction altitude, and hence, the lower the flux needed to explain a given abundance. In the interest of conservatism, we choose extremal δz and K_z to maximize the timescale and minimize the required PH_3 production flux. $\delta z = z_1 – z_0$, where z_0 is the altitude where PH_3 is transported from. A reasonable choice for z_0 would be 61 km, the PH_3 detection altitude; we instead adopt $z_0 = 0$, that is, assume it takes as long for phosphine to diffuse to 98 km from the surface as it does from 61 km. We make this unphysical choice in the name of conservatism. So, $\delta z =$ 98 km. Finally, we adopt $K_z = 2200\,\text{cm}^2\ \text{s}^{-1}$, that is, the minimum eddy diffusion coefficient in the atmosphere (realized near the surface). Then:

$$\text{T} = (98\ \text{km})^2 / \left(2 * 2200\ \text{cm}^2\text{s}^{-1}\right) = 2.2 \times 10^{10}\ \text{s}$$

Inverting, that is, assuming that destruction is solely by transport from surface to 98 km, the corresponding ''destruction rate'' is: $4.5 \times 10^{-11}\ \text{s}^{-1}$.

By multiplying these two numbers, we arrive at our very conservative lower bound on the required production flux:

$$1.3 \times 10^5\ \text{cm}^{-2}\text{s}^{-1}$$

Which is $\sim 10^{-3}$ times the rate estimated from a full photochemical model. This is the flux that could be produced by surface volcanoes under the most extreme of the scenarios modeled above, and is within what might be expected from mantle plume delivery of phosphides to the surface assuming that those phosphides were efficiently converted to phosphine.

To summarize, we can explain the phosphine on Venus as being the result of volcanism only if we assume that *both* [1] *and* [2] below are true

[1]: volcanism can produce phosphine at 800 tons/year or more:

EITHER plume mantle volcanism delivers phosphine efficiently to the surface (which requires:-

- Deep mantle phosphides traverse the mantle over a period of >1 million years essentially unchanged, AND
- phosphides are efficiently converted to a highly reducing gas in an oxidizing atmosphere, AND
- other reduced volatile elements, notably sulfur, are not converted to reduced gases at the same time.

OR upper mantle/crust volcanism delivers phosphine to the surface, which requires:-

- The mantle of Venus is substantially more reduced than that of Earth, AND
- the upper mantle contains as much water as MORBs with the highest water content on Earth, AND
- eruptions occur at 1500 K or above.

[2]: phosphine's lifetime is 10^3 times longer than the photochemical model suggests

- There is a mechanism that efficiently transfers PH_3 from the surface to 61 km, so efficiently that no PH_3 remains at low altitudes and PH_3 experiences no photochemical loss, OR equivalently the majority of erupted phosphide is transported to 61 km without loss, AND
- PH_3 transport from 61 km to its destruction altitude of ≤98 km is slow, occurring on timescales comparable with the whole-atmosphere circulation timescale. PH_3 is not destroyed during this slow transport.

The assumptions made in the atmospheric chemistry are not physically plausible, or even self-consistent. Nevertheless, it is necessary to make them to arrive at a PH_3 production flux that can match volcanic production in even the most extreme scenario. More physical assumptions regarding photochemistry and transport are represented by the full photochemical model, which produces a required flux three orders of magnitude higher.

The combination of unlikely volcanic chemistry fluxes, unlikely volcanic chemistry, and physically unrealistic atmospheric chemistry assumptions appears to us to be unlikely to be applicable to Venus.

3.2.4.2. Other sources of phosphide-containing materials as a source of phosphine.

We also exclude other phosphide sources as likely sources of phosphine on Venus.

Mineral phosphides are known on Earth, where they are rare but widely distributed. A mineral fulgurite—a glass resulting from lightning strikes, was proposed as a potential source that could in principle contain reduced phosphorus species (Pasek and Block, 2009). It is estimated that fulgurites probably contain <0.5% phosphorus (Gailliot, 1980), and are widely stated as being ''rare'' (*e.g.*, Petty, 1936; Glover, 1979; Pye, 1982). Phosphides can also originate in pyrometamorphic rocks. Pyrometamorphic rocks form as a result of fossil fuel fires, a process that is probably not relevant to Venus (Britvin *et al.*, 2019; Kruszewski *et al.*, 2020).

We also consider that meteoritic delivery of phosphides to Venus is unlikely as a potential source of observed amounts of phosphine.

Iron/nickel meteorites are known to contain reduced species of phosphorus, mostly as phosphides (Geist *et al.*, 2005). Such metal-rich meteorites could also be a source of phosphide and hence, upon its hydrolysis, of phosphine. For example, reduced phosphorus species can be found in the meteoritic mineral schreibersite $(Fe,Ni)_3P$, the most common mineral containing reduced phosphorus (Pech *et al.*, 2011), and in other minerals (Buseck, 1969; Pratesi *et al.*, 2006; Zolensky *et al.*, 2008; Ma *et al.*, 2014). It has been suggested that schreibersite was a source of reduced phosphorus species on early Earth (Baross *et al.*, 2007), and could in principle continue to be a trace source of reduced phosphorus species today.

The accretion rate of meteoritic material to Earth today is of the order of 20–70 kilotons/year (Peucker-Ehrenbrink, 1996), ~6% of this material is iron/nickel meteorites (Emiliani, 1992), which contain phosphides at a level of an average of 0.25% phosphorus by weight (Geist *et al.*, 2005). If we rely on the extremely conservative assumption that hydrolysis of $(Fe,Ni)_3P$ phosphides to phosphine is 100% efficient, that would deliver a maximum of ~10 tons of phosphine to the Earth every year, or about 110 mg/s, which is a negligible amount globally (Greaves *et al.*, 2020c; Sousa-Silva *et al.*, 2020). This estimated maximal yearly meteoritic delivery of phosphine on Venus is approximately five orders of magnitude too low to explain detected amounts.

Our calculations are also in agreement with previous estimates of the phosphine production through meteoritic delivery, which were also found to be negligible (Holland, 1984), and with the very recent work by Carrillo-Sánchez who show that the great majority of meteoritic phosphorus species is oxidized (even though the severe conditions of atmospheric entry do create trace amounts of elemental P, this elemental P gets readily oxidized as well) (Carrillo-Sánchez *et al.*, 2020).

3.3. *Conclusions of the thermodynamic analysis of potential phosphine-producing reactions*

We show with our thermodynamic analyses that none of the known possible routes for production of PH_3 on Venus can explain the presence of ~1 ppb phosphine. All fall short, often by many orders of magnitude.

The thermodynamics of known reactions between chemical species in the atmosphere and on the surface of Venus is too energetically costly and cannot be responsible for the spontaneous formation of phosphine.

Similarly, the formation of phosphine in the subsurface is not favored. Oxygen fugacity of the crustal and mantle rocks is many orders of magnitude too high to reduce mineral phosphates to phosphine.

Finally, we show that the hydrolysis of phosphide minerals, both from crustal and mantle rocks, as well as delivered by meteorites, cannot provide sufficient amounts of phosphine.

4. Other Potential Processes of Phosphine Formation

4.1. *Potential endergonic processes of phosphine formation*

Several potential sources of energy that could drive the formation of PH_3 should be mentioned briefly for completeness, although we argue that none of them could be responsible for the observed abundance of phosphine on Venus.

Lightning strikes cannot create sufficient amounts of phosphine to explain the observed ~1 ppb amounts of phosphine in the atmosphere of Venus. Lightning may be capable of producing a plethora of molecules that are thermodynamically disfavored. However, our calculations suggest that lightning's production of PH_3 is at most approximately five orders of magnitude too low to explain detected amounts (Sousa-Silva *et al.*, 2020). We estimate that the maximum amount of phosphine produced by lightning in one venusian year under some very optimistic assumptions is 3.5 tons, which is five orders of magnitude lower than that necessary to explain ~1 ppb in the atmosphere (see Supplementary Section 2.5.1 [Supplementary Fig. S18; Supplementary Tables S9–S11]) for details on the estimation of phosphine production by lightning).

We note that our predicted value of phosphine production through lightning is an upper bound and, in reality, the lightning-induced production of reduced phosphorus species in venusian atmosphere is likely to be much less efficient. The well-studied formation of analogous N species by lightning strikes on Earth favors formation of nitrates and nitrites, and not the thermally less stable reduced forms of N such as ammonia (Mancinelli and McKay, 1988; Rakov and Uman, 2003; Ardaseva *et al.*, 2017).

Moreover, the above calculations agree with several studies on the formation of reduced phosphorus species, including PH_3, by laboratory-simulated lightning. Such experiments can produce traces of phosphine from discharges onto phosphate salt solutions, but at very low efficiency (Glindemann *et al.*, 1999, 2004).

Mechanochemically driven reduction of phosphate to phosphine in rocks, by tribochemical weathering at quartz and calcite or marble inclusions, was postulated as a potential abiotic source of phosphine (Glindemann *et al.*, 2005b). However, scaling the results presented in Glindemann *et al.* (2005b) to plausible global earthquake activity (even under very optimistic assumptions that all the rock moved during an Earthquake-induced landslide can be the substrate for this chemistry) suggests that the flux of phosphine produced would be at least two orders of magnitude too small to account for the observed abundance of phosphine in Venus' atmosphere. In addition, tribochemical production of phosphine in crustal rocks requires a local fluid to provide hydrogen atoms, which is very unlikely to be present in Venus' crust. The crustal rocks are above the critical temperature of water and under an atmosphere with $\sim 3 \times 10^{-5}$ partial pressure of water; they are therefore expected to be extremely desiccated with no local hydrogen source (see Supplementary Section 2.5.5 for more details on tribochemical production of phosphine).

A very large comet or asteroid impact could theoretically generate a highly reduced atmosphere for millions of years that could lead to the formation of conditions that are more favorable for phosphine production (Kasting, 1990). We note, however, that a scale of such impact has to be comparable with the hypothetical impact that is postulated to have created a transient H_2-rich atmosphere on early Earth ~4.48 billion years ago (Service, 2019; Benner *et al.*, 2020). Even the Chicxulub impactor, which resulted in a crater 150 km wide and contributed to the extinction of the dinosaurs, did not manage to significantly change the redox state of Earth's atmosphere [although it had dramatic effects on radiative balance, and hence climate (Toon *et al.*, 2016; Brugger *et al.*, 2017)]. An impact as large as Chicxulub occurs every 50–100 million years. It is statistically highly unlikely that an even larger cataclysm of this sort happened in recent venusian history. The radar mapping of the surface of Venus does not show sufficiently large recent craters on the surface of Venus and therefore does not support the recent large impact scenario (Ivanov and Head, 2011; Kreslavsky *et al.*, 2015). Smaller impacts could only generate phosphine through delivery of meteoritic phosphide, which is insufficient to account for phosphine production as discussed above in Section 3.2.4.2 and in Greaves *et al.* (2020c).

Lastly, solar X-rays and solar wind protons carry substantial energy, but are absorbed at high altitudes, and so could not penetrate to the clouds where phosphorus species might be found and where phosphine is detected, and hence cannot drive the formation of phosphine.

4.2. Other potential exergonic processes as sources of phosphine

In principle, some exotic chemistry on Venus, not considered before, could be responsible for the formation of phosphine. In this section, we address a few potential examples, including formation of phosphine from elemental phosphorus or production of phosphine with reducing agents more powerful than molecular hydrogen. We argue that all such scenarios just replace the implausibility of making phosphine with another equally implausible set of conditions, which could then produce phosphine (*i.e.*, a ''displaced improbability'').

For example, if elemental phosphorus could be erupted from venusian volcanoes, it could be reduced by atmospheric gases to phosphine. However, the production of elemental phosphorus from phosphate rock chemistry under Venus' conditions is itself extremely improbable on thermodynamic grounds (see Supplementary Section 2.5.3.2 [Supplementary Fig. S19] and Supplementary Section 2.5.3.3 [Supplementary Fig. S21] for details on the possibility of formation of elemental phosphorus on Venus). In principle, elemental phosphorus could be generated from phosphoric acid by reaction with elemental carbon. Graphite has been suggested as the ''unknown UV absorber'' (Shimizu, 1977). However, the thermodynamics of this reaction do not favor phosphorus production under cloud conditions (see Supplementary Section 2.5.3.2 [Supplementary Fig. S20]). Thus, invoking elemental phosphorus as a source of phosphine by any route replaces the implausibility of making phosphine with the implausibility of making elemental phosphorus.

Other minerals could be suggested as being present on the surface, such as highly reduced lower mantle minerals as suggested above. As another example, we consider berlinite (aluminum phosphate $AlPO_4$). If berlinite were present, then there is a possibility that berlinite be reduced by atmospheric gases at the surface to produce phosphine in a reaction with a negative free energy under Venus conditions. Specifically, the reaction

$$4H_2S + AlPO_4 \rightarrow PH_3 + {}^1/_2\ Al_2O_3 + 2\ {}^1/_2\ H_2O + 4S$$

has a negative free energy at below 5 km altitude if PH_3 is present at 1 ppb, H_2S is at its highest modeled level, and H_2O is simultaneously at its lowest predicted level. This is an improbable but not impossible series of assumptions. However, berlinite itself is thermodynamically unlikely to be present on Venus' surface (see Supplementary Section 2.5.4 [Supplementary Fig. S23 and Supplementary Table S13]). Similarly, the thermodynamics of calcium phosphate reduction by carbon monoxide to phosphine is favorable at 120 km altitude: however, this requires the reaction to occur at 170 K (where any reaction will be extremely slow), and that the mineral to be lofted to this altitude, both of which are extremely unlikely (see Supplementary Section 2.5.3.4 [Supplementary Fig. S22]). The presence of unexpected minerals, or expected minerals at unexpected locations, on Venus is a testable hypothesis that could be the subject of remote or *in situ* observation.

Other reducing agents could exist on the surface of Venus and be more powerful reducing agents than hydrogen. Previous suggestions for rare venusian surface minerals include lead or bismuth sulfide, elemental metals, or other materials (Schaefer and Fegley Jr., 2004; Treiman *et al.*, 2016). Some venusian mountaintops show ''snowcaps'' of a highly radar-reflective material. The chemical composition of these deposits is unknown (Taylor *et al.*, 2018), and could conceivably be a source of exotic chemistry. However, we know that water is present (as gas) in Venus' atmosphere. If a more powerful reducing agent than hydrogen is present on the surface, then the following reaction:

$$X + H_2O \rightarrow H_2 + XO$$

would happen spontaneously, oxidizing that reducing agent and reducing water to hydrogen. To invoke a more powerful reducing agent than hydrogen, one therefore has to explain both what it is *and* why it does not react with water present in the atmosphere. However, again their presence could be testable by observation.

5. Summary and Discussion

5.1. Summary

Phosphorus-containing species have not been modeled for Venus' atmosphere before Greaves *et al.* (2020), other than the overall thermodynamic calculation of the dominant phosphorus oxidation and hydration states (Krasnopolsky, 1989). This work represents the first full description of a model of phosphorus species on Venus.

We have modeled processes that might produce phosphine under Venus conditions. This does not address whether phosphine is present, which is still a matter of controversy as noted above. While we do not wish to distance ourselves from the controversy, the purpose of this article is to explore where phosphine might come from a rocky planet, using Venus as a specific example, if it is present. We have assumed here that it is present, at ~1 ppb, and that presence requires an explanation.

We have explored every plausible chemical and physical process (and a number of implausible but possible ones) that could lead to the formation of phosphine on Venus, making conservative estimates where exact values were not known. We have shown that all conventional explanations of phosphine production that can explain the recent tentative detection ~1 ppb of phosphine in the venusian atmosphere (Greaves *et al.*, 2020c) are highly unlikely. Specifically, we have explored photochemical production (at least five orders of magnitude below the rate required to explain the observed ~1 ppb levels), atmospheric equilibrium thermodynamics (on average ~100 kJ/mol too energetically costly), surface and subsurface chemistry (8–15 orders of magnitude too low), and a range of other processes. We conclude that phosphine on Venus is produced by a physical or chemical process that is not expected to occur on terrestrial rocky planets.

5.2. Unknown chemistry as an explanation for the presence of PH_3

If no conventional chemical processes can produce phosphine, is there a not-yet considered process or set of processes that could be responsible for its formation?

One of the possibilities is that chemical species exist in the crust, or in the atmosphere of Venus, that we have not considered. Perhaps an unknown atmospheric chemical drives phosphine formation, especially considering that the photochemistry of Venus' atmosphere is not fully understood. Such a mechanism would have to be compatible with what we do know about Venus; for example, a powerful reductant would have to be compatible with the observed presence of water in Venus' atmosphere, as discussed in Section 4.2.

A specific example of such a mechanism would be photochemistry in the cloud droplets. The photochemistry of phosphorus species in sulfuric acid droplets is completely unknown, and so in principle, phosphine could be produced photochemically in the sulfuric acid droplets of the cloud layer. However, we consider this unlikely, not least because it is known that phosphine is rapidly oxidized by sulfuric acid to phosphoric acid. Even if a photochemical process did produce phosphine in sulfuric acid, it seems unlikely that it would escape oxidation back to phosphoric acid. In fact, we expect the sulfuric acid cloud layer to be a sink for phosphine (one that we have not incorporated into the models above for lack of kinetic data). See Supplementary Section 2.5.3.1 for more on cloud droplet chemistry, and the chemistry of phosphine in sulfuric acid.

Other, completely unknown, chemistry could be a source of phosphine, but in the absence of suggestions as to what that chemistry might be, such speculation cannot be considered a hypothesis to be tested.

5.3. Phosphine as a Venus cloud biosignature gas

Could living organisms in the temperate clouds of Venus produce phosphine? For decades many have speculated that the venusian clouds are a suitable habitat for life (Morowitz and Sagan, 1967; Grinspoon, 1997; Cockell, 1999; Schulze-Makuch and Irwin, 2002, 2006; Schulze-Makuch *et al.*, 2004; Grinspoon and Bullock, 2007). The anomalous UV absorber in Venus' atmosphere has been proposed as a biosignature (Limaye *et al.*, 2018; Seager *et al.*, 2021), although chemical processes may be the source (Pérez-Hoyos *et al.*, 2018; Wu *et al.*, 2018; Frandsen *et al.*, 2020). Unknown chemical species in the clouds absorb more than half of the UV flux that the planet receives, an absorption that is not constant across the planet but has unexplained temporal and spatial differences and constraints (Lee *et al.*, 2019; Jessup *et al.*, 2020; Marcq *et al.*, 2020). Recent work has developed the case for phosphine as a biosignature gas in anoxic environments (Bains *et al.*, 2019a, 2019b; Sousa-Silva *et al.*, 2020). We emphasize that a biosignature is a sign that life is present. It may or may not be produced directly by life. While we do not know whether life on Earth produces phosphine itself, or rather if life produces reduced phosphorus species such as phosphite or hypophosphite that subsequently disproportionate to phosphine, the association of phosphine with biology (and in recent centuries with human technology) is clear (Gassmann and Glindemann, 1993; Glindemann *et al.*, 1996, 1999, 2005a; Bains *et al.*, 2019a; Sousa-Silva *et al.*, 2020). Specifically, we previously proposed that PH_3 production on Earth is associated with strictly oxygen-free, highly reduced, hot, moderately acid ecosystems (pH <5, 80°C) or cooler, very acid conditions (pH <2, 20°C) (Bains *et al.*, 2019a, 2019b; Sousa-Silva *et al.*, 2020). The venusian clouds have some apparent parallels to these environments on Earth where life produces PH_3, although obviously the venusian clouds are not reduced. We therefore explored the possibility that the venusian PH_3 is produced by life.

We emphasize that the presence of phosphine in Venus' atmosphere does not prove the presence of life. Any explanation for the unexpected finding of PH_3 in Venus' atmosphere has to be tested, and to be tested it has to be articulated. Here we apply the same thermodynamic methods used above to test the hypothesis that life could explain the presence of phosphine on Venus. The reader should understand that this leaves *unexplored* the many other problems with the concept of life on Venus, such as the extremely low water activity, and the presence of concentrated sulfuric acid, which is a powerful oxidizing agent and rapidly destroys the large majority of terrestrial biochemicals.

Could PH_3 on Venus also be associated with biological activity? We have argued above that producing phosphine in the venusian atmosphere requires energy. A unique feature of life is that it captures chemical energy and uses it to drive chemical reactions that would not happen spontaneously in the environment (such as production of O_2 via photosynthesis on Earth). One widely accepted criterion for a biosignature is a gas completely out of equilibrium with its environment (Lovelock, 1975; Krissansen-Totton *et al.*, 2016), as phosphine is on Venus.

To make phosphine from phosphate, an organism would have to use a reducing agent. Here we ask whether such a reducing agent is within the scope of the reducing power of terrestrial biochemicals. The redox reactions involving phosphorus species that could be of biochemical origin are of the general form of:

$$(1)\ XH + H^+ + H_2PO_4^- \rightarrow H_2PO_3^- + H_2O + X^+$$

$$(2)\ 4XH + 4H^+ + H_2PO_4^- \rightarrow PH_3 + 3H_2O + OH^- + 4X^+$$

$$(3)\ 3XH + 3H^+ + H_2PO_3^- \rightarrow PH_3 + 2H_2O + OH^- + 3X^+$$

where XH and X^+ are the reduced and oxidized form of a biological reducing agent, respectively. Reactions are assumed to occur at pH = 7. We test whether under Venus conditions, an unreasonably strong reducing agent would be required to produce phosphine (*i.e.*, we assess if we can we rule out biological production of phosphine on biochemical thermodynamic grounds). To estimate the thermodynamics of biological phosphine production, we assume that a cell living in a cloud droplet is composed mainly of water that takes in phosphorus and reduces it to phosphine (Fig. 10).

Phosphorus species were assumed to be present in the extracellular droplet phase as oxyacids at 1 molal

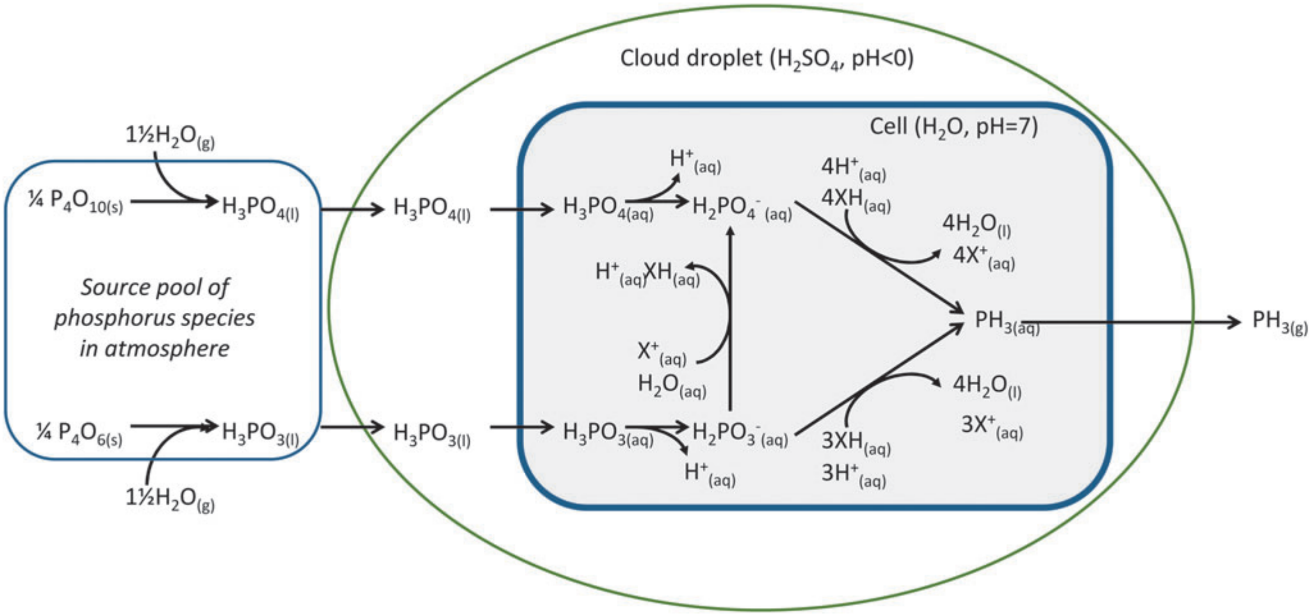


FIG. 10. A model for biological production of phosphine on Venus. The favored path for reduction of atmospheric phosphorus species to phosphine is the reduction of phosphoric acid to phosphine (upper reaction pathway on the schematic above). Correspondingly, the reduction of phosphite to phosphine is disfavored, because of the low concentration of the phosphite reactant (lower reaction pathway on the schematic above). If the concentration of phosphite is allowed to rise in the cell, then the reduction of phosphate to phosphite becomes less energetically favorable, and the reduction of phosphite to phosphine correspondingly more favorable. It is plausible to suggest, although it is speculative, that phosphite would accumulate in cells to a level where its reduction to phosphine was thermodynamically neutral, allowing a multistep reduction pathway for phosphate. HX: Biological reducing agent, such as NADH.

concentration (see Supplementary Section 1.3.2.2). We have assumed that, like terrestrial acidophiles, the putative venusian organisms keep their interior at pH >5, as do Earth organisms, even those living at environments of pH = 0 or pH = 12 (Baker-Austin and Dopson, 2007; Horikoshi, 2016). An internal pH = 7 was assumed here. The energy implicit in converting phosphate from the external pH (pH = 0) to the intracellular pH (pH = 7) was calculated as discussed extensively in Bains *et al.* (2019a), and Supplementary Section 2.6. If the free energy needed to convert extracellular phosphorus to intracellular singly ionized forms at 1 mM was calculated as positive, it was assumed that the cell could not import phosphorus and no phosphine production could occur (*i.e.*, the phosphorus was assumed to enter the cell by passive diffusion). The ratio of $H_2PO_3^-/H_2PO_4^-$ inside the cell immediately after transport was assumed to be the same as the ratio of H_3PO_3/H_3PO_4 outside the cell (see below).

We estimated the thermodynamics of reduction of phosphorus species to phosphine using NADH, $FADH_2$, ubiquinone, and two iron/sulfur proteins as model agents to illustrate the range of reducing power of different biological reducing agents in terrestrial biochemistry (see Supplementary Section 2.6.; Supplementary Fig. S24). We do not expect these specific chemicals to be present in putative venusian life; we use them solely for illustration. Our result shows that NADH or the two iron/sulfur (Fe-S) proteins, but not $FADH_2$ or ubiquinone, can power the production of phosphine (see Supplementary Section 2.6.; Supplementary Fig. S25). Others have also suggested life based on an iron/sulfur-based redox metabolism in the clouds of Venus (Limaye *et al.*, 2018).

We emphasize that the overall process of reducing phosphate in a venusian environment remains energy-consuming. The putative organisms must gain energy to generate the reducing agents that can then make phosphine. However, we note that life on Earth produces many compounds from common chemicals in the environment, sometimes in large amounts, that require substantial energy investment (Seager *et al.*, 2012). In itself the expenditure of energy for the biosynthesis of PH_3 is not a criterion for ruling out a biological source for phosphine.

We conclude that the energy needed to reduce phosphate to phosphine is not beyond that deployed by terrestrial biochemistry in redox reactions. However, there remain major problems with the concept of life in the clouds of Venus. The clouds are often described as being ''habitable'' because of their moderate pressure (~ 1 bar) and temperature (~ 60°C). However, moderate temperature and pressure do not necessarily make the clouds habitable (Seager *et al.*, 2021) [and in any case pressure is irrelevant—terrestrial life can grow at any pressure from >1000 bar (Nunoura *et al.*, 2018) to <1 millibar (Pavlov *et al.*, 2010)]. To survive in the clouds, organisms would have to survive in an extremely chemically aggressive environment, one that is highly acidic and with an extremely low concentration of water (highly dehydrating and very low water activity). Sulfuric acid is a notoriously aggressive reagent toward sugars and aldehydes, reducing dry sucrose to charcoal in seconds. In principle, life could exist in an aqueous droplet inside the sulfuric acid cloud drop (as drawn in Fig. 10), but this poses formidable problems in itself. No known biological membrane could remain intact against such a chemical gradient, and the energy required to counteract leakage of water out of the cell (or sulfuric acid into it) could be orders of magnitude greater than the energy used by terrestrial halophiles to maintain their internal environment.

We conclude that, while we cannot rule out life as a source of phosphine on Venus, the hypothesis that phosphine is produced by life cannot *a priori* be favored over the hypothesis of unknown photochemistry or unknown atmospheric chemistry. All seem unlikely, and hence all call for further investigation. We note, after Catling *et al.* (2018), that the extraordinary claim of life should be the hypothesis of last resort only after all conceivable abiotic alternatives are exhausted.

5.4. Future work on identifying a source for phosphine on Venus

Our analysis argues that no conventional source can explain the presence of ∼1 ppb phosphine on Venus (and hence no source could explain higher abundances either). All the explanations modeled in Sections 2, 3, and 4 above suggest that if phosphine is present on Venus, then it requires a significant change in our understanding of the chemistry of the planet. While one such change could be to postulate the presence of life, geological sources of phosphine are both more accessible to modeling and easier to test by using remote observations or relatively simple *in situ* measurements. The same is true of the other unexplained aspects of chemistry of Venus, such as the ''unknown UV absorber,'' the depletion of SO_2 in the cloud layer, the anomalous destruction of carbonyl sulfide below the clouds, and others [summarized in Bierson and Zhang (2020)]. Such an investigation would likely require a combination of remote observation campaigns combined with orbiter and lander missions, supported by laboratory work on Earth.

Phosphine may be made by an unknown abiotic surface or cloud chemical processes. Knowledge of those processes will rely at least, in part, on more detailed knowledge of the venusian atmosphere and geology. Neither the detailed chemistry nor the photochemistry of any of the potential phosphorus components of Venus' atmosphere is known but could be investigated on Earth as a preliminary step for remote measurements and *in situ* observations. Progress toward identification of the source of phosphine on Venus can be made by laboratory experimentation here on Earth, especially regarding the properties of phosphorus species under Venus atmosphere and cloud conditions, including studies of chemical reactivity and solubility of phosphorus species in concentrated sulfuric acid and high CO_2.

The first priority for observation should be to confirm the presence of phosphine in the atmosphere of Venus with observations of additional spectral features, in the microwave or infrared region of the spectrum where phosphine is a strong absorber (Sousa-Silva *et al.*, 2013, 2014, 2020). Subsequently, observations should focus on constraining the distribution and abundances of phosphine throughout the venusian atmosphere. The photochemical model described above suggests that the lifetime of phosphine in the lower atmosphere could be years to centuries. If this is correct and phosphine diffuses from its source into the lower atmosphere (or originates there), then this would imply substantially higher concentrations in the 20–30 km altitude range than in the cloud decks. If phosphine is made by hydrolysis of mineral phosphides, then we would also expect diphosphine to be generated in the same reaction (Greenwood and Earnshaw, 2012), and to be detectable in the lower atmosphere. Future *in situ* observations might probe this.

The data that are especially lacking relate to reliable chemistry measurements and detailed models of venusian clouds. Such models and measurements should extend their focus beyond sulfur chemistry and focus on phosphorus as well. For example, studies aimed at detection of P-H bonds [strong absorbers around 4.3 and 10 microns (Sousa-Silva *et al.*, 2019)] are currently underway. Such studies would require high-resolution spectroscopy to distinguish PH_3 from overlapping CO_2 absorption; the necessary resolution should be within the capabilities of CRIRES+(VLT). Detection of P = O bonds would also be a valuable goal because our kinetic model suggests that production and reduction of PO are a rate-limiting factor in the pathway to atmospheric, abiotic phosphine production.

Missions focused on planetary geology, including landers, could help with *in situ* assessment of the possibility of geochemical production of phosphine on the surface of Venus and confirm or refute our conclusions that the geochemical processes on rocky planets are incapable of efficient phosphine production. Ultimately, long-term *in situ* observations of the clouds of Venus should also be carried out. Such long-term missions capable of detailed studies of clouds, aerosols, hazes, and their spectral, physical and chemical properties (including mapping any changes over extended time periods) were proposed before [*e.g.*, EnVision mission (Ghail *et al.*, 2016), Aerobot aerial platforms (van den Berg *et al.*, 2006) and the Venus Atmospheric Mobile Platform, developed by Northrop Grumman Aerospace (Lee *et al.*, 2015)]. Simultaneous observation of atmospheric features, such as UV absorber and phosphine distribution, would be more valuable than either alone. Some concepts of the aerial platforms are considered for the upcoming VENERA-D mission by ROSCOSMOS and NASA (Zasova *et al.*, 2017). If such missions provided compelling evidence for biological processes, then a sample return mission would be required for any detailed biochemical characterization of a putative venusian aerial biosphere.

Last but not least, our investigation presented in this article is a useful template for the future investigations of biosignature gases, when these are detected on an exoplanet. Currently, a major focus in exoplanet astronomy is the near-future detection of the presence of life on exoplanets through detection of gases in exoplanet atmospheres that may be attributed to biological activity (Seager and Bains, 2015; Seager *et al.*, 2016; Catling *et al.*, 2018; Schwieterman *et al.*, 2018). A wide range of gases have been suggested, and a smaller number studied, as candidate biosignatures (Seager *et al.*, 2012). However, detection is only the first step. Evaluation of the chemical context of the gas in a given planetary scenario is central to ruling life out or supporting the hypothesis that life is a source for that gas. This requires detailed analysis of possible formation and destruction pathways, local geology, atmospheric composition, all with inadequate knowledge as we will know far less about an exoplanet than we do about Venus (Catling *et al.*, 2018; Schwieterman *et al.*, 2018; Walker *et al.*, 2018). We believe that the tentative discovery of the venusian phosphine and the analysis that is presented in this work can form the basis of a template approach that should be applied to any biosignature gas detection to determine if it is a ''false positive,'' that is, a gas that could be produced by abiotic processes. We note that the step of assessing of false-positive scenarios for any biosignature gas is highly planet specific. The task of replicating our approach here with other, less well-characterized worlds will not be easy, but will be essential for the attribution of any gas to a biological origin.

6. Conclusions

It was previously predicted that any detectable abundance of PH_3 in the atmosphere of a rocky planet would be an indicator of biological activity (Sousa-Silva *et al.*, 2020). In this article, we show in detail that no abiotic mechanism based on our current understanding of Venus can explain the presence of ~1 ppb phosphine in Venus' clouds. If the detection is correct and phosphine is present at 1 ppb or more, then this means that our current understanding of Venus is significantly incomplete.

If phosphine is not a biological product, then it must be produced by planetary geo- or atmospheric chemistry. In either case, our understanding, not only of Venus but of all terrestrial planets and exoplanets, needs a major paradigm shift. Because the source of phosphine is not known, we call for further aggressive observations of Venus and its atmosphere, laboratory studies of phosphorous chemistry in the context of the venusian environment, and the development of Venus space missions to study its atmosphere and search for signs of life.

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Supplementary Material

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References

Akins AB, Lincowski AP, Meadows VS, *et al.* (2021) Complications in the ALMA detection of phosphine at Venus. *Astrophys J Lett* 907:L27.

Anderson AT (1973) The before-eruption water content of some high-alumina magmas. *Bull Volcanol* 37:530–552.

Ardaseva A, Rimmer PB, Waldmann I, *et al.* (2017) Lightning chemistry on Earth-like exoplanets. *Mon Not R Astron Soc* 470:187–196.

Babicki S, Arndt D, Marcu A, *et al.* (2016) Heatmapper: web-enabled heat mapping for all. *Nucleic Acids Res* 44: W147–W153.

Bains W, Petkowski JJ, Sousa-Silva C, *et al.* (2019a) New environmental model for thermodynamic ecology of biological phosphine production. *Sci Total Environ* 658:521–536.

Bains W, Petkowski JJ, Sousa-Silva C, *et al.* (2019b) Trivalent phosphorus and phosphines as components of biochemistry in anoxic environments. *Astrobiology* 19:885–902.

Baker-Austin C and Dopson M (2007) Life in acid: pH homeostasis in acidophiles. *Trends Microbiol* 15:165–171.

Baross J, Benner SA, Cody GD, *et al.* (2007) *The Limits of Organic Life in Planetary Systems*. National Academies Press, Washington, DC.

Benner SA, Bell EA, Biondi E, *et al.* (2020) When did life likely emerge on Earth in an RNA-first process? *ChemSystemsChem* 2:e1900035.

Bierson CJ and Zhang X (2020) Chemical cycling in the Venusian atmosphere: a full photochemical model from the surface to 110 km. *J Geophys Res Planets* 125: e2019JE006159.

Bregman JD, Lester DF, and Rank DM (1975) Observation of the nu-squared band of PH3 in the atmosphere of Saturn. *Astrophys J* 202:L55–L56.

Britvin SN, Murashko MN, Vapnik Y, *et al.* (2019) Zuktamrurite, FeP 2, a new mineral, the phosphide analogue of löllingite, FeAs 2. *Phys Chem Miner* 46:361–369.

Brugger J, Feulner G, and Petri S (2017) Baby, it's cold outside: climate model simulations of the effects of the asteroid impact at the end of the Cretaceous. *Geophys Res Lett* 44:419–427.

Bumbrah GS, Krishan K, Kanchan T, *et al.* (2012) Phosphide poisoning: a review of literature. *Forensic Sci Int* 214:1–6.

Buseck PR (1969) Phosphide from metorites: barringerite, a new iron-nickel mineral. *Science* 165:169–171.

Byrne PK (2020) A comparison of inner solar system volcanism. *Nat Astron* 4:321–327.

Carrillo-Sánchez JD, Bones DL, Douglas KM, *et al.* (2020) Injection of meteoric phosphorus into planetary atmospheres. *Planet Space Sci* 187:104926.

Catling DC, Krissansen-Totton J, Kiang NY, *et al.* (2018) Exoplanet biosignatures: a framework for their assessment. *Astrobiology* 18:709–738.

Cockell CS (1999) Life on Venus. *Planet Space Sci* 47:1487–1501.

Condie KC (2001) *Mantle Plumes and Their Record in Earth history*. Cambridge University Press, Cambridge, United Kingdom.

Emiliani C (1992) *Planet Earth: Cosmology, Geology, and the Evolution of Life and Environment*. Cambridge University Press, Cambridge, United Kingdom.

Encrenaz T, Greathouse TK, Marcq E, *et al.* (2020) A stringent upper limit of the PH3 abundance at the cloud top of Venus. *Astron Astrophys* 643:L5.

Esposito LW, Knollenberg RG, Marov MYA, *et al.* (1983) The clouds and hazes of Venus. *Venus* 484.

Fegley B (1997) Why pyrite is unstable on the surface of Venus. *Icarus* 128:474–479.

Fletcher LN, Orton GS, Teanby NA, *et al.* (2009) Phosphine on Jupiter and Saturn from Cassini/CIRS. *Icarus* 202:543–564.

Frandsen BN, Farahani S, Vogt E, *et al.* (2020) Spectroscopy of OSSO and other sulfur compounds thought to be present in the Venus atmosphere. *J Phys Chem A* 124:7047–7059.

Frost BR (1991) Introduction to oxygen fugacity and its petrologic significance. In: *Reviews in Minerology vol 25. Oxide Minerals: Petrologic and Magnetic Significance,* edited by DH Lindsleys, Mineralogical Society of America, Washington, DC, pp 1–10.

Gailliot MP (1980) ''Petrified lightning'' a discussion of sand fulgurites. *Rocks Miner* 55:13–17.

Gassmann G and Glindemann D (1993) Phosphane (PH3) in the biosphere. *Angew Chem Int Ed Engl* 32:761–763.

Gassmann G, Van Beusekom JEE, and Glindemann D (1996) Offshore atmospheric phosphine. *Naturwissenschaften* 83: 129–131.

Geist V, Wagner G, Nolze G, *et al.* (2005) Investigations of the meteoritic mineral (Fe,Ni)3P. *Cryst Res Technol* 40:52–64.

Geng J, Zhang R, and Wang X (2010) Chemical origin of phosphine in nature. In *4th International Conference on Bioinformatics and Biomedical Engineering*. IEEE, Chengdu, China, pp 1–12.

Ghail R, Wilson CF, and Widemann T (2016) Envision M5 Venus orbiter proposal: opportunities and challenges [abstract 48]. In *AAS/Division for Planetary Sciences Meeting Abstracts*, American Astronomical Society, 47th Lunar and Planetary Science Conference, The Woodlands, Texas, USA.

Glindemann D, Stottmeister U, and Bergmann A (1996) Free phosphine from the anaerobic biosphere. *Environ Sci Pollut Res* 3:17–19.

Glindemann D, de Graaf RM, and Schwartz AW (1999) Chemical reduction of phosphate on the primitive Earth. *Orig Life Evol Biosph* 29:555–561.

Glindemann D, Edwards M, and Kuschk P (2003) Phosphine gas in the upper troposphere. *Atmos Environ* 37:2429–2433.

Glindemann D, Edwards M, and Schrems O (2004) Phosphine and methylphosphine production by simulated lightning—a study for the volatile phosphorus cycle and cloud formation in the earth atmosphere. *Atmos Environ* 38:6867–6874.

Glindemann D, Edwards M, Liu J-a, *et al.* (2005a) Phosphine in soils, sludges, biogases and atmospheric implications—a review. *Ecol Eng* 24:457–463.

Glindemann D, Edwards M, and Morgenstern P (2005b) Phosphine from rocks: mechanically driven phosphate reduction? *Environ Sci Technol* 39:8295–8299.

Glover JE (1979) Formation and distribution of sand fulgurites. *Aust Geogr* 14:172–175.

Greaves JS, Bains W, Petkowski JJ, *et al.* (2020a) On the robustness of phosphine signatures in Venus' clouds. arXiv preprint arXiv:2012.05844.

Greaves JS, Richards A, Bains W, *et al.* (2020b) Re-analysis of phosphine in Venus' clouds. arXiv preprint arXiv: 2011.08176.

Greaves JS, Richards AMS, Bains W, *et al.* (2020c) Phosphine gas in the cloud decks of Venus. *Nat Astron* 1–10. https://doi.org/10.1038/s41550-020-1174-4

Greenwood NN and Earnshaw A (2012) *Chemistry of the Elements*. Elsevier, Amsterdam, Netherlands.

Grinspoon DH (1997) *Venus Revealed: A New Look Below the Clouds of Our Mysterious Twin Planet*. Basic Books: New York, NY, USA.

Grinspoon DH and Bullock MA (2007) Astrobiology and Venus exploration. *Geophys Monogr Am Geophys Union* 176:191.

Gruchola S, Galli A, Vorburger A, *et al.* (2019) The upper atmosphere of Venus: model predictions for mass spectrometry measurements. *Planet Space Sci* 170:29–41.

Gülcher AJP, Gerya TV, Montési LGJ, *et al.* (2020) Corona structures driven by plume–lithosphere interactions and evidence for ongoing plume activity on Venus. *Nat Geosci* 13: 547–554.

Hart SR, Hauri EH, Oschmann LA, *et al.* (1992) Mantle plumes and entrainment: isotopic evidence. *Science* 256:517–520.

Haus R, Kappel D, Tellmann S, *et al.* (2016) Radiative energy balance of Venus based on improved models of the middle and lower atmosphere. *Icarus* 272:178–205.

Herschy B, Chang SJ, Blake R, *et al.* (2018) Archean phosphorus liberation induced by iron redox geochemistry. *Nat Commun* 9:1346.

Holland HD (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, NJ, USA.

Horikoshi K (2016) Alkaliphiles. In: *Extremophiles: Where It All Began*, Springer Japan, Tokyo, pp. 53–78.

Ivanov MA and Head JW (2011) Global geological map of Venus. *Planet Space Sci* 59:1559–1600.

Ivanov MA and Head JW (2013) The history of volcanism on Venus. *Planet Space Sci* 84:66–92.

Jacob DJ 1999 Introduction to atmospheric chemistry. (Princeton University Press, 1999), Princeton, NJ.

Japel S, Prewitt C, Boctor N, *et al.* (2002) Iron-nickel phosphides at high pressures and temperatures. In *AGU Fall Meeting Abstracts* MR61A-1025, American Geophysical Union, Fall Meeting 2002, San Francisco, California, USA.

Jenkins RO, Morris TA, Craig PJ, *et al.* (2000) Phosphine generation by mixed-and monoseptic-cultures of anaerobic bacteria. *Sci Total Environ* 250:73–81.

Jessup K-L, Marcq E, Bertaux J-L, *et al.* (2020) On Venus' cloud top chemistry, convective activity and topography: a perspective from HST. *Icarus* 335:113372.

Karner J, Papike J, and Shearer C (2004) Plagioclase from planetary basalts: chemical signatures that reflect planetary volatile budgets, oxygen fugacity, and styles of igneous differentiation. *Am Mineral* 89:1101–1109.

Kasting JF (1990) Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere. *Orig Life Evol Biosph* 20:199–231.

Krasnopolsky VA (1989) Vega mission results and chemical composition of Venusian clouds. *Icarus* 80:202–210.

Krasnopolsky VA (2007) Chemical kinetic model for the lower atmosphere of Venus. *Icarus* 191:25–37.

Krasnopolsky VA (2008) High-resolution spectroscopy of Venus: detection of OCS, upper limit to H2S, and latitudinal variations of CO and HF in the upper cloud layer. *Icarus* 197:377–385.

Krasnopolsky VA (2010) Venus night airglow: ground-based detection of OH, observations of O_2 emissions, and photochemical model. *Icarus* 207:17–27.

Krasnopolsky VA (2012) A photochemical model for the Venus atmosphere at 47–112km. *Icarus* 218:230–246.

Krasnopolsky VA (2013) S3 and S4 abundances and improved chemical kinetic model for the lower atmosphere of Venus. *Icarus* 225:570–580.

Kreslavsky MA, Ivanov MA, and Head JW (2015) The resurfacing history of Venus: constraints from buffered crater densities. *Icarus* 250:438–450.

Krissansen-Totton J, Bergsman DS, and Catling DC (2016) On detecting biospheres from chemical thermodynamic disequilibrium in planetary atmospheres. *Astrobiology* 16: 39–67.

Kruszewski Ł, Fabiańska MJ, Segit T, *et al.* (2020) Carbon-nitrogen compounds, alcohols, mercaptans, monoterpenes, acetates, aldehydes, ketones, SF6, PH3, and other fire gases in coal-mining waste heaps of Upper Silesian Coal Basin (Poland)–a re-investigation by means of in situ FTIR external database approach. *Sci Total Environ* 698:134274.

Larson HP, Treffers RR, and Fink U (1977) Phosphine in Jupiter's atmosphere-The evidence from high-altitude observations at 5 micrometers. *Astrophys J* 211:972–979.

Leake BE, Hendry GL, Kemp A, *et al.* (1969) The chemical analysis of rock powders by automatic X-ray fluorescence. *Chem Geol* 5:7–86.

Lee G, Polidan RS, and Ross F (2015) Venus atmospheric maneuverable platform (VAMP)-a low cost Venus exploration concept. In *AGU Fall Meeting Abstracts*. P23A-2109, American Geophysical Union, Fall Meeting 2015, San Francisco, California, USA.

Lee YJ, Jessup K-L, Perez-Hoyos S, *et al.* (2019) Long-term variations of Venus's 365 nm albedo observed by Venus express, Akatsuki, MESSENGER, and the Hubble Space Telescope. *Astron J* 158:126.

Lee YJ, Muñoz AG, Yamazaki A, *et al.* (2021) Investigation of UV absorbers on Venus using the 283 and 365 nm phase curves obtained from Akatsuki. *Geophys Res Lett* 48: e2020GL090577.

Liler M (1971) *Reaction Mechanisms in Sulphuric Acid and Other Strong Acid Solutions*. Academic Press, London.

Limaye SS, Mogul R, Smith DJ, *et al.* (2018) Venus' spectral signatures and the potential for life in the clouds. *Astrobiology* 18:1181–1198.

Lincowski AP, Meadows VS, Crisp D, *et al.* (2021) Claimed detection of PH_3 in the clouds of Venus is consistent with mesospheric SO_2. *Astrophys J Lett* 908:L44.

Lovelock JE (1975) Thermodynamics and the recognition of alien biospheres. *Proc R Soc Lond B Biol Sci* 189:167–181.

Ma C, Beckett JR, and Rossman GR (2014) Monipite, MoNiP, a new phosphide mineral in a Ca-Al-rich inclusion from the Allende meteorite. *Am Mineral* 99:198–205.

Mancinelli RL and McKay CP (1988) The evolution of nitrogen cycling. *Orig Life Evol Biosph* 18:311–325.

Marcq E, Mills FP, Parkinson CD, *et al.* (2018) Composition and chemistry of the neutral atmosphere of Venus. *Space Sci Rev* 214:10.

Marcq E, Lea Jessup K, Baggio L, *et al.* (2020) Climatology of SO_2 and UV absorber at Venus' cloud top from SPICAV-UV nadir dataset. *Icarus* 335:113368.

Meadows VS (2017) Reflections on O_2 as a biosignature in exoplanetary atmospheres. *Astrobiology* 17:1022–1052.

Meadows VS, Reinhard CT, Arney GN, *et al.* (2018) Exoplanet biosignatures: understanding oxygen as a biosignature in the context of its environment. *Astrobiology* 18:630–662.

Mikhail S and Heap MJ (2017) Hot climate inhibits volcanism on Venus: constraints from rock deformation experiments and argon isotope geochemistry. *Phys Earth Planet Inter* 268:18–34.

Mogul R, Limaye SS, and Way M (2020a) Venus' mass spectra show signs of disequilibria in the middle clouds. *Earth Space Sci Open Arch*. Geophysical Research Letters, 48(7), e2020GL091327.

Mogul R, Limaye SS, Way MJ, *et al.* (2020b) Is phosphine in the mass spectra from Venus' clouds? arXiv preprint arXiv: 2009.12758.

Moore JG (1970) Water content of basalt erupted on the ocean floor. *Contrib Mineral Petrol* 28:272–279.

Morowitz H and Sagan C (1967) Life in the clouds of Venus? *Nature* 215:1259.

Noll KS and Marley MS (1997) Detectability of CO, PH3, AsH3, and GeH4 in the atmosphere of GL 229B. In: David Soderblom *ASP Conference Series*. *Planets Beyond the Solar System and the Next Generation of Space Missions*. Astronomical Society of the Pacific, San Francisco, California, USA, pp 115–118.

Novelli PC, Lang PM, Masarie KA, *et al.* (1999) Molecular hydrogen in the troposphere: global distribution and budget. *J Geophys Res Atmos* 104:30427–30444.

Nunoura T, Nishizawa M, Hirai M, *et al.* (2018) Microbial diversity in sediments from the bottom of the Challenger Deep, the Mariana Trench. *Microbes Environ* 33:186–194.

Oschlisniok J, Häusler B, Pätzold M, *et al.* (2012) Microwave absorptivity by sulfuric acid in the Venus atmosphere: first results from the Venus Express Radio Science experiment VeRa. *Icarus* 221:940–948.

Pasek M and Block K (2009) Lightning-induced reduction of phosphorus oxidation state. *Nat Geosci* 2:553.

Pasek MA and Lauretta DS (2005) Aqueous corrosion of phosphide minerals from iron meteorites: a highly reactive source of prebiotic phosphorus on the surface of the early Earth. *Astrobiology* 5:515–535.

Pasek MA, Sampson JM, and Atlas Z (2014) Redox chemistry in the phosphorus biogeochemical cycle. *Proc Natl Acad Sci U S A* 111:15468–15473.

Pasek M, Omran A, Lang C, *et al.* (2020) Serpentinization as a route to liberating phosphorus on habitable worlds. Preprint. DOI: 10.21203/rs.3.rs-37651/v1

Pavlov AK, Shelegedin VN, Vdovina MA, *et al.* (2010) Growth of microorganisms in martian-like shallow subsurface conditions: laboratory modelling. *Int J Astrobiol* 9:51–58.

Pech H, Vazquez MG, Van Buren J, *et al.* (2011) Elucidating the redox cycle of environmental phosphorus using ion chromatography. *J Chromatogr Sci* 49:573–581.

Pérez-Hoyos S, Sánchez-Lavega A, García-Muñoz A, *et al.* (2018) Venus upper clouds and the UV absorber from MESSENGER/MASCS observations. *J Geophys Res Planets* 123:145–162.

Petty JJ (1936) The origin and occurrence of fulgurites in the Atlantic coastal plain. *Am J Sci* 31:1–18.

Peucker-Ehrenbrink B (1996) Accretion of extraterrestrial matter during the last 80 million years and its effect on the marine osmium isotope record. *Geochim Cosmochim Acta* 60:3187–3196.

Pratesi G, Bindi L, and Moggi-Cecchi V (2006) Icosahedral coordination of phosphorus in the crystal structure of melliniite, a new phosphide mineral from the Northwest Africa 1054 acapulcoite. *Am Mineral* 91:451–454.

Pye K (1982) SEM observations on some sand fulgurites from northern Australia. *J Sediment Res* 52:991–998.

Rakov VA and Uman MA (2003) *Lightning: Physics and Effects*. Cambridge University Press, Cambridge, United Kingdom.

Ranjan S, Schwieterman EW, Harman C, *et al.* (2020) Photochemistry of anoxic abiotic habitable planet atmospheres: impact of new H_2O cross sections. *Astrophys J* 896:148.

Renne PR and Basu AR (1991) Rapid eruption of the Siberian Traps flood basalts at the Permo-Triassic boundary. *Science* 253:176–179.

Rimmer PB and Helling C (2016) A chemical kinetics network for lightning and life in planetary atmospheres. *Astrophy J Suppl Ser* 224:9.

Rimmer PB and Rugheimer S (2019) Hydrogen cyanide in nitrogen-rich atmospheres of rocky exoplanets. *Icarus* 329: 124–131.

Rock PA (1969) *Chemical Thermodynamics: Principles and Applications*. The Macmillan Company, London, United Kingdom.

Rutishauser BV and Bachofen R (1999) Phosphine formation from sewage sludge cultures. *Anaerobe* 5:525–531.

Saal AE, Hauri EH, Langmuir CH, *et al.* (2002) Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature* 419:451–455.

Sandor BJ and Clancy RT (2018) First measurements of ClO in the Venus atmosphere– altitude dependence and temporal variation. *Icarus* 313:15–24.

Saunois M, Bousquet P, Poulter B, *et al.* (2016) The global methane budget 2000– 2012. *Earth Syst Sci Data* 8:697–751.

Schaefer L and Fegley B Jr. (2004) Heavy metal frost on Venus. *Icarus* 168:215–219.

Schulze-Makuch D (2021) The case (or not) for life in the Venusian clouds. *Life* 11:255.

Schulze-Makuch D and Irwin LN (2002) Reassessing the possibility of life on Venus: proposal for an astrobiology mission. *Astrobiology* 2:197–202.

Schulze-Makuch D and Irwin LN (2006) The prospect of alien life in exotic forms on other worlds. *Naturwissenschaften* 93: 155–172.

Schulze-Makuch D, Grinspoon DH, Abbas O, *et al.* (2004) A sulfur-based survival strategy for putative phototrophic life in the Venusian atmosphere. *Astrobiology* 4:11–18.

Schwieterman EW, Kiang NY, Parenteau MN, *et al.* (2018) Exoplanet biosignatures: a review of remotely detectable signs of life. *Astrobiology* 18:663–708.

Seager S and Bains W (2015) The search for signs of life on exoplanets at the interface of chemistry and planetary science. *Sci Adv* 1:e1500047.

Seager S, Schrenk M, and Bains W (2012) An astrophysical view of earth-based metabolic biosignature gases. *Astrobiology* 12:61–82.

Seager S, Bains W, and Petkowski JJ (2016) Toward a list of molecules as potential biosignature gases for the search for life on exoplanets and applications to terrestrial biochemistry. *Astrobiology* 16:465–485.

Seager S, Petkowski JJ, Gao P, *et al.* (2021) The Venusian lower atmosphere haze: a depot for desiccated life particles for the persistence of the hypothetical Venusian aerial biosphere. *Astrobiology* 21 DOI: https://doi.org/10.1089/ast.2020.2244

Sen G (2001) Generation of Deccan trap magmas. *J Earth Syst Sci* 110:409–431.

Service RF (2019) Seeing the dawn. *Science* 363:116.

Shechkov GT, Pevneva IA, and Meshkova OA (2003) Thermal disproportionation of hypophosphorous acid. *Russ J Appl Chem* 76:1354–1355.

Sheldrick GM (1966) *Nuclear Magnetic Resonance Studies of Inorganic Hydrides*. University of Cambridge, Cambridge, United Kingdom.

Shimizu M (1977) Ultraviolet absorbers in the Venus clouds. *Astrophys Space Sci* 51:497–499.

Siebert L (2013) Smithsonian Institution National Museum of Natural History Global Volcanism Program: Volcanoes of the World. University of California Press, Berkeley, CA, USA; https://volcano.si.edu/database/search_eruption_results.cfm

Smith EM, Shirey SB, Nestola F, *et al.* (2016) Large gem diamonds from metallic liquid in Earth's deep mantle. *Science* 354:1403–1405.

Smrekar SE, Stofan ER, Mueller N, *et al.* (2010) Recent hotspot volcanism on Venus from VIRTIS emissivity data. *Science* 328:605–608.

Smrekar SE, Stofan ER, and Mueller N (2014) Venus: surface and interior. In *Encyclopedia of the Solar System*, T Spohn, D Breuer, and TV Johnson. Elsevier, Amsterdam, Netherlands, pp. 323–341.

Snellen IAG, Guzman-Ramirez L, Hogerheijde MR, *et al.* (2020) Re-analysis of the 267GHz ALMA observations of Venus-No statistically significant detection of phosphine. *Astron Astrophys* 644:L2.

Sousa-Silva C, Yurchenko SN, and Tennyson J (2013) A computed room temperature line list for phosphine. *J Mol Spectrosc* 288:28–37.

Sousa-Silva C, Al-Refaie AF, Tennyson J, *et al.* (2014) ExoMol line lists–VII. The rotation–vibration spectrum of phosphine up to 1500K. *Mon Not R Astron Soc* 446:2337–2347.

Sousa-Silva C, Petkowski JJ, and Seager S (2019) Molecular simulations for the spectroscopic detection of atmospheric gases. *Phys Chem Chem Phys* 21:18970–18987.

Sousa-Silva C, Seager S, Ranjan S, *et al.* (2020) Phosphine as a biosignature gas in exoplanet atmospheres. *Astrobiology* 20: 235–268.

Tarrago G, Lacome N, Lévy A, *et al.* (1992) Phosphine spectrum at 4–5 μm: analysis and line-by-line simulation of 2ν2, ν2 + ν4, 2ν4, ν1, and ν3 bands. *J Mol Spectrosc* 154:30–42.

Taylor FW and Hunten DM (2014) Venus: atmosphere. In: *Encyclopedia of the Solar System*, Elsevier, pp. 305–322.

Taylor FW, Svedhem H, and Head JW (2018) Venus: the atmosphere, climate, surface, interior and near-space environment of an Earth-like planet. *Space Sci Rev* 214:35.

Tenenbaum ED, Woolf NJ, and Ziurys LM (2007) Identification of phosphorus monoxide (X 2Πr) in VY Canis Majoris: detection of the First PO Bond in Space. *Astrophys J Lett* 666:L29.

Thompson MA (2021) The statistical reliability of 267-GHz JCMT observations of Venus: no significant evidence for phosphine absorption. *Mon Not R Astron Soc Lett* 501:L18–L22.

Titov DV, Ignatiev NI, McGouldrick K, *et al.* (2018) Clouds and hazes of Venus. *Space Sci Rec* 214:126.

Toon OB, Bardeen C, and Garcia R (2016) Designing global climate and atmospheric chemistry simulations for 1 and 10 km diameter asteroid impacts using the properties of ejecta from the K-Pg impact. *Atmos Chem Phys* 16:13185–13212.

Treiman A, Harrington E, and Sharpton V (2016) Venus' radar-bright highlands: different signatures and materials on Ovda Regio and on Maxwell Montes. *Icarus* 280:172–182.

Trompet L, Robert S, Mahieux A, *et al.* (2020) Phosphine in Venus' atmosphere: detection attempts and upper limits above the cloud top assessed from the SOIR/VEx spectra. *Astron Astrophys* 645:L4.

Truong N and Lunine JI (2021) Volcanically extruded phosphides as an abiotic source of Venusian phosphine. *Proceedings of the National Academy of Sciences*. 118: e2021689118, doi:10.1073/pnas.2021689118.

Turner AM, Bergantini A, Abplanalp MJ, *et al.* (2018) An interstellar synthesis of phosphorus oxoacids. *Nat Commun* 9:3851.

Twarowski A (1993) The influence of phosphorus oxides and acids on the rate of H + OH recombination. *Combust Flame* 94:91–107.

Twarowski A (1995) Reduction of a phosphorus oxide and acid reaction set. *Combust Flame* 102:41–54.

Twarowski A (1996) The temperature dependence of H + OH recombination in phosphorus oxide containing post-combustion gases. *Combust Flame* 105:407–413.

Ulff-Møller F (1985) Solidification history of the Kitdlit Lens: immiscible metal and sulphide liquids from a basaltic dyke on Disko, central West Greenland. *J Petrol* 26:64–91.

van den Berg ML, Falkner P, Atzei AC, *et al.* (2006) Venus microsat explorer programme, an ESA technology reference study. *Acta Astronaut* 59:593–597.

Villanueva G, Cordiner M, Irwin P, *et al.* (2020) No phosphine in the atmosphere of Venus. arXiv preprint arXiv:2010.14305.

Visscher C, Lodders K, and Fegley B (2006) Atmospheric chemistry in giant planets, brown dwarfs, and low-mass dwarf stars. II. Sulfur and phosphorus. *Astrophys J* 648:1181.

Walker SI, Bains W, Cronin L, *et al.* (2018) Exoplanet biosignatures: future directions. *Astrobiology* 18:779–824.

Weis FA, Skogby H, Troll VR, *et al.* (2015) Magmatic water contents determined through clinopyroxene: examples from the Western Canary Islands, Spain. *Geochem Geophys Geosyst* 16:2127–2146.

Weisstein EW and Serabyn E (1996) Submillimeter line search in Jupiter and Saturn. *Icarus* 123:23–36.

Wordsworth RD (2016) Atmospheric nitrogen evolution on Earth and Venus. *Earth Planet Sci Lett* 447:103–111.

Wu Z, Wan H, Xu J, *et al.* (2018) The near-UV absorber OSSO and its isomers. *Chem Commun* 54:4517–4520.

Zasova L, Ignatiev N, Korablev O, *et al.* (2017) Venera-D: expanding our horizon of terrestrial planet climate and geology through the comprehensive exploration of Venus. Venera-D Joint Science Definition Team Final Report, Space Research Institute, Moscow, Russia, pp 1–93.

Zhang X, Liang MC, Mills FP, *et al.* (2012) Sulfur chemistry in the middle atmosphere of Venus. *Icarus* 217:714–739.

Zolensky M, Gounelle M, Mikouchi T, *et al.* (2008) Andreyivanovite: a second new phosphide from the Kaidun meteorite. *Am Mineral* 93:1295–1299.

Zolotov MY and Garvin JB (2020) Phosphorous-bearing compounds and atmosphere-surface chemical interactions on Venus. In: *AGU*, Fall Meeting 2020, Online abstract #P091-0004.

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Abbreviations Used

ALMA = Atacama Large Millimeter/submillimeter Array
FMQ = fayalite-magnetite-quartz
IW = iron/wüstite
JCMT = James Clerk Maxwell Telescope
LNMS = Pioneer Venus Large Probe Neutral Mass Spectrometer
MH = magnetite/hematite
PO = phosphorus monoxide
QIF = quartz-iron-fayalite