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## Phosphine Generation Pathways on Rocky Planets

Arthur Omran  
*University of South Florida*

Christopher Oze  
*Occidental College*

Brian Jackson  
*Boise State University*

Chris Mehta  
*University of South Florida*

Laura M. Barge  
*California Institute of Technology*

*See next page for additional authors*

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**Authors**

Arthur Omran, Christopher Oze, Brian Jackson, Chris Mehta, Laura M. Barge, Jeffrey Bada, and Matthew A. Pasek

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**Arthur Omran**

Department of Geosciences  
University of South Florida  
Tampa, FL, USA

**Brian Jackson**

Department of Physics  
Boise State University  
Boise, ID

**Laura M. Barge**

NASA Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA

**Christopher Oze**

Geology Department  
Occidental College  
Los Angeles, CA

**Chris Mehta**

Department of Geosciences  
University of South Florida  
Tampa, FL, USA

**Jeffrey Bada**

Scripps Institution of Oceanography Department  
University of California at San Diego  
La Jolla, CA

**Matthew A. Pasek\***

Department of Geosciences  
University of South Florida  
Tampa, FL, USA  
[mpasek@usf.edu](mailto:mpasek@usf.edu)

## Abstract

The possibility of life in the Venusian clouds was proposed in the 1960s, and recently this hypothesis has been revived with the potential detection of phosphine in Venus' atmosphere. These observations may have detected ~5-20 ppb phosphine (PH<sub>3</sub>) Venus (Greaves et al., 2020), which raises questions about Venusian atmospheric/geochemical processes, and puts forth a suggestion that this phosphine could possibly be generated by biological processes. In such a claim, it is essential to understand the abiotic phosphorus chemistry that may occur under Venus-relevant conditions, particularly those processes that may result in phosphine generation. Here we discuss two related abiotic routes for phosphine generation within the atmosphere of Venus. Based on our assessment, corrosion of large impactors as they ablate near Venus' cloud layer and the presence of reduced phosphorus compounds in the sub-cloud layer could result in production of phosphine and may explain the phosphine detected in Venus' atmosphere or on other rocky planets. We end on a cautionary note: although there may be life in the clouds of Venus, the detection of a simple, single gas, phosphine, is likely not a decisive indicator.

**Keywords:** Venus, biosignatures, disproportionation, impact, phosphorus, phosphine, astrobiology

## 1. Introduction

### 1.1. Venus and Life

When considering the prospect of life on Venus, the astronomer Sir Harold Spencer Jones in his 1952 book "*Life on Other Worlds*" ardently wrote: "The whole planet is a desert. The surface is sequently steeped in a Stygian gloom. The heat is intense. Venus, then, is a world where life as we know it cannot exist". Jones' (1952) gloomy assessment was one of many on the habitability of Venus (e.g., Sagan 1961), with Sagan (1961) stating that Venus mission scientists would be "exceedingly perplexed over whether to send along a paleobotanist, a mineralogist, a petroleum geologist, or a deep-sea diver" due to the many disparate estimations of the environment of Venus. Although data eventually pointed in the direction of a hot desert climate for Venus, this did not prevent scientists from thinking about life on our 'sister' planet, as scientists focused their attention away from the hellish surface to the possibility of life in the clouds of Venus. Harold Morowitz and Carl Sagan (1967) speculated that life might have originated on the surface of Venus during an early, more hospitable era prior to its evolution to a 90 bar, 96% CO<sub>2</sub>-dominated atmosphere. This

high pressure, CO<sub>2</sub> atmosphere is the cause and result of a runaway greenhouse effect (Hoffman et al., 1980; Schubert et al., 1980; Donahue and Pollack, 1983), with scorching surface temperatures (>400 °C). During the hospitable period, this putative life migrated to the Venusian clouds (Morowitz and Sagan, 1967).

The idea of life in the clouds of Venus has continued to be a hypothesis with circumstantial evidence but little proof. Central to the idea of life in the clouds of Venus is the presence of near-UV absorbers in the atmosphere (Morowitz and Sagan, 1967) that could be due to life (Sagan 1963; Limaye et al., 2018; Morowitz and Sagan, 1967). In the case of Venus, the extremely low water activity of the clouds of Venus (Hallsworth et al. 2021) presents an issue, as life as we know it requires water well in excess of the activity that has been inferred assuming pure sulfuric acid composition of Venus cloud particles. Other issues surround this problematic claim in H<sub>2</sub>SO<sub>4</sub> clouds, as outlined by Cockell et al. (2021) for more discussion. Effectively, for life to be present in Venus, it would require life “as we don’t know it”, a form of life suitably different from terrestrial life that uses different metabolic pathways and generates biosignatures that may vary from terrestrial life (e.g., Morowitz and Sagan 1967, Cokell et al. 2021, Hallsworth et al. 2021). For perspectives of life as we “don’t know it”, see the article on “Lyfe” by Bartlett and Wong (2020), which focuses on specific metrics for identifying biochemically dissimilar life elsewhere. Life “as we don’t know it” has received attention recently, as recognizing life—in its various forms defined better by action rather than material content—has been discussed for instance by Schulze-Makuch and Irwin (2018) and by Lingam and Loeb (2021).

Abiotic explanations for the UV absorption phenomenon goes back decades as well (Toon et al. 1982, Na and Esposito 1997, see review in Limaye et al. 2021a) with proposed sources mostly consisting of a plethora of sulfur compounds (Toon et al. 1982, Na and Esposito 1997, Krasnopolsky 2006, Wu et al. 2018) but also organics (Morowitz and Sagan 1967) and iron compounds (Kuiper 1969). Recent work suggests the UV absorber are various sulfur oxide species (Pinto et al. 2021). Venus’ atmosphere contains many sulfur compounds such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), sulfur dioxide (SO<sub>2</sub>), disulfur monoxide (S<sub>2</sub>O), and sulfur monoxide (SO) as well (Barker, 1979; Na et al. 1990; Sandor et al. 2010; Hapke and Nelson, 1975, Wu et al. 2018). Sulfur oxides in Venus’ atmosphere may form as a product of atmospheric reactions, such as the photolysis of sulfuric acid (Zhang et al. 2010; Zhang et al. 2012). Some sulfur compounds such as sulfur dioxide exist in amounts as high as ~150 ppm, much higher than Earth’s 0.2 ppb of sulfur dioxide (Taylor et al., 2018). Thus, the UV-absorbers may then have a completely abiotic explanation as sulfur-based compounds (Perez-Hoyos et al., 2018; Titov et al., 2018; Wu et al., 2018), such as the polysulfur and polysulfur oxides species (Pinto et al. 2021). However, a complete match to the UV absorbers has not been demonstrated (Krasnopolsky 2018, Perez-Hoyos et al. 2018) and the question of the identity(s) of the UV absorber is still open and biological absorbers are still plausible (Limaye et al. 2018).

## **1.2. A Recent Discovery in the Clouds of Venus**

Recent telescopic observations may have detected the gas phosphine (PH<sub>3</sub>, structure as Figure 1) in the atmosphere of Venus (Greaves et al., 2020). This potential detection was accompanied by a body of work that suggest phosphine gas may be a biosignature (Bains et al., 2019a, b, 2021; Sousa-Silva et al., 2020). Accompanied by geochemical models and operating in the paradigm that the Venusian clouds may be a habitable environment—specifically the hyper-acidic cloud decks (47–60 km high, ~1 bar, ~60 °C)—this hypothesis connects phosphine detection with life to the idea phosphine is biologically produced on Venus. This claim is contingent on an unequivocal detection of phosphine and the production of it by microbes (Greaves et al., 2020). This claim of life was cautious as the manuscript recognized that alternatives sources of phosphine are feasible, which we explore below.

[FIGURE 1]

Here we consider possible abiotic sources of phosphine. We also consider the evidence for the biotic production of this gas, and whether or not other routes may be sources of this gas even on Earth.

## **1.3. Is Phosphine Present on Venus?**

The responses in the literature to the possible Venusian phosphine detection were swift (Villanueva et al., 2020; Encrenaz et al., 2020; Lincowski et al. 2021; Akins et al., 2021). In particular, Villanueva et al. (2020) and Lincowski et al. (2021) suggest that the phosphine detected was erroneously identified, and could be accounted for by the gas SO<sub>2</sub>, whose spectra may not have been removed during the data processing methods. Revisiting the data set resulted in a downward revision of the upper limit of phosphine detection of ~ 5 ppbv (Encrenaz et al. 2020), compared to 20 ppb in Greaves et al. (2020). There are a multitude of sulfur compounds in the atmosphere of Venus, and these

compounds absorb light in the same spectral regions as phosphine. This results in a certain degree of cross contamination in the detection of compounds such as phosphine. While the study that may have detected phosphine tried to account for this cross-contamination (Greaves et al., 2020) they may not have done so sufficiently (Villanueva et al., 2020).

If it turns out that phosphine is not present in the atmosphere of Venus, no further work would obviously be necessary for elucidating abiotic sources of phosphine for this planet. Infrared data have not yet supported the results of the initial study on phosphine, and, thus, there are calls for additional measurements to validate if phosphine was detected successfully (Encrenaz et al., 2020). Additionally, the data from the ALMA telescope has been called into question (Villanueva et al., 2020), the group that used it has cited a calibration error, and subsequently downgraded the strength of their assertion (Voosen, 2020). Also, reanalysis of the JCMT data was unable to recover a statistically significant detection of phosphine (Thompson 2021). With no significant evidence for phosphine absorption in the JCMT spectrum or the ALMA spectrum the original detection may have been in error. While phosphine may not have been detected, sulfur species have been conclusively detected for decades (Na et al. 1990; Sandor et al. 2010; Hapke and Nelson, 1975; Barker, 1979). Those sulfur compounds, especially sulfur dioxide, could be responsible for a false positive detection of phosphine (Villanueva et al., 2020).

Finally, there exists a possibility that even if phosphine is produced on Venus, it may not be present in gaseous form. Hyman and Arp (1987) demonstrate that concentrated sulfuric acid efficiently removes contaminant phosphine from acetylene, reducing its concentration to below detection limits. Although such an experiment has not been performed under conditions applicable to Venus, this process is suggestive that  $\text{H}_2\text{SO}_4$  is an effective phosphine trap (removing it either through protonation and dissolution or through oxidation). Given the prevalence of  $\text{H}_2\text{SO}_4$  on Venus, this removal pathway merits further study if the Venusian phosphine is verified. In one of the most recent studies, a reexamination of Pioneer Venus LNMS data concluded that  $\text{PH}_3$  was detected (Mogul et al. 2021). Regardless, the certainty of  $\text{PH}_3$  and its concentration in the atmosphere of Venus is ongoing.

## 2. Discussion

The possibility of life on Venus based on a detection of phosphine in its upper atmosphere is contingent on several assumptions. The first is that phosphine has been conclusively identified. As stated in the introduction above, such an identification has been called into question by recent work as sulfur compounds may overlap with the spectra of phosphine, and thus the identification of this gas may be in error. The second assumption is that there exist no major or sufficient abiotic pathways leading to the production of phosphine. Greaves et al. (2020) analyze several phosphine production routes and conclude none could produce abundant phosphine, though the possibility that unidentified production pathways may be present was acknowledged by the authors. The third assumption is that life is a producer of phosphine in its metabolic pathways. With this latter point, it is worth reviewing what is known about phosphine's production in the environment.

### 2.1. Phosphine as an Indicator of Life

Phosphine is a small molecule, akin to  $\text{CH}_4$ ,  $\text{NO}_x$ ,  $\text{O}_2$ , and other molecules that have been employed as potential indicators of life (Krissansen-Totton et al., 2018; Schwieterman et al., 2018). Small molecules are generally ambiguous life detection tools, as abiotic production pathways complicate the search for life (e.g., Krasnopolsky et al., 2004; Oze and Sharma, 2005). The lack of complexity of phosphine makes its use as a biomarker ambiguous, as argued by Marshall et al. (2021), a case echoed by the detection of Martian methane and arguments over its origin (Formisano et al. 2004).

Phosphine was first noted in nature in a pig slurry processing facility (Devai et al. 1988; Glindemann and Bergmann, 1995). It has since been identified as a ubiquitous trace gas throughout the earth's atmosphere (Morton and Edwards 2005; Zhu et al., 2007), present at about  $1 \text{ ng/m}^3$  with variations of about 4-5 orders of magnitude from this typical concentration (Pasek et al., 2014). Phosphine is most closely associated with anaerobic environments such as swamps and landfills (Devai and Delaune, 1995; Eismann et al., 1997; Glindemann et al., 2005).

The association of phosphine with anaerobic biological environments implicates it as a potential biogas, at least in a terrestrial context. However, a biochemical pathway leading to the production of phosphine has not actually been observed or metabolically demonstrated. Indeed, phosphine stands out as an endergonic outcast in the metabolic reactions of anaerobic respiration (Glindemann et al., 2005). Phosphine has not so far been demonstrated to be a

phosphorus source for biological processes, unlike other reduced phosphorus compounds that are incorporated into metabolic processes such as phosphite and hypophosphite (Inglett et al., 2005). Phosphides may also be used as sources of P for organisms (Iverson 1968) though little is known of this reaction pathway. As a result, if this gas is produced biotically, then its production results in a loss of phosphorus, as no enzymes have been shown to recapture phosphine and incorporate it as a biological feedstock molecule. For an element that has been referred to as “the staff of life” (Karl 2000) such a loss is problematic.

Environmental phosphine is usually determined from two reservoirs: air and solid matrix. The atmospheric detection of phosphine is generally unambiguous and follows a diurnal cycle. In hours of peak sunlight, phosphine is photolyzed and decreases to concentrations below detection limits. At night, phosphine is regenerated from a yet-unidentified source (Han et al., 2000; 2002). The most likely source of phosphine for this regeneration is termed “matrix-bound phosphine” and is the solid material that generates phosphine upon treatment with acid (e.g., Yu and Song 2003). Matrix-bound phosphine correlates with organic phosphorus concentration within sediment (Yu and Song 2003), and, like atmospheric phosphine, varies significantly in its total phosphine content.

Phosphine sourced from “matrix-bound phosphine” may be present in a few reservoirs. Notably these include several that are not phosphine initially but generate phosphine upon acid treatment (Fu and Zhang 2020). It may be present as phosphine dissolved in water or organic polymers. It may also be generated by nanoscale metal phosphides that may be formed by microbes (Iverson 1968), though Sousa-Silva et al. (2020) argue that since metal phosphides are not found in several biological environments associated with phosphine, this pathway is, therefore, not a requisite for phosphine production. It may be sourced from organic phosphorus compounds, which include already reduced molecules such as the phosphonates (Horiguchi and Kandatsu 1959; Horsman and Zechel 2017). Or, related to these molecules, it may be sourced from reduced phosphorus oxyacids such as phosphorous and hypophosphorous acids with phosphite and hypophosphite, respectively, for the conjugate bases.

This variety of sources that may potentially provide gaseous phosphine from a matrix-bound precursor highlights an issue with assuming phosphine is generated by life. An alternative pathway for the generation of phosphine, even in settings that contain life, is that phosphine is an abiotic product of a biologically produced molecule or compound (White and Metcalf, 2007). As such, phosphine cannot serve as an unambiguous biosignature if the biologically produced molecule/compound that leads to phosphine can be synthesized abiotically. We explore here two such alternative molecules that can lead to phosphine generation: the reduced oxidation state phosphorus oxides or oxyacids, and the metallic phosphides (Shechkov et al., 2003).

As a reduced oxidation state phosphorus compound, terrestrial phosphine (with  $P^{3-}$ ) ultimately is sourced from phosphate that bears the most stable P oxidation state ( $P^{5+}$ ). Intermediates between this addition of 8 electrons to phosphate are hypophosphite ( $P^+$ ) and phosphite ( $P^{3+}$ ). Both hypophosphite and phosphite have been observed in natural environmental samples (Pech et al., 2009; Pech et al., 2011; Han et al., 2013; Qiu et al., 2016) and have been shown to participate in metabolic pathways (Feingersch et al., 2012; Polygiou et al., 2015; Figueroa et al., 2017, 2018; Figueroa and Coates, 2017), including as an electron shuffle (Schink et al., 2002). This is in contrast to phosphine, whose generation and utilization by biologic processes has yet to be demonstrated. Indeed, the production of phosphine in association with anaerobic environments could happen external to cells, implying that the life-phosphine connection may be at most an environmental one: that microbes make the environment conducive to phosphine generation. For example, as reduced P compounds may produce phosphine, if these compounds can be demonstrated to arise abiotically, then that precludes phosphine itself as being a direct biosignature, though it can still be associated with biological settings.

## **2.2. Abiotic Phosphorus Chemistry**

If phosphine is present in the atmosphere of Venus and is not a biosignature, then there must be an abiotic explanation for its presence other than a life-based metabolic processes. Elsewhere in the solar system the temperatures and pressures of gas giants allow phosphine to be formed abiotically; this is due to their reducing atmospheres containing ubiquitous  $H_2$  (Prinn and Lewis, 1975; Kaye and Strobel, 1983; Irwin et al., 2004; Fletcher et al., 2009).

Venus is not a gas giant with a reducing atmosphere, but either some unknown geochemistry or atmospheric chemistry may be responsible for the production of phosphine (if present) rather than life. What abiotic reactions might support the production of phosphine? Previous literature has shown that there are several chemical reactions that can account

for the formation of phosphine in a planetary context. Specifically, the corrosion of schreibersite in iron-based meteors by acidic conditions (an exogenic source, Herschy 2013) and reduced phosphorus oxyacid disproportionation (an endogenic source, Pasek et al., 2014).

The exogenic source, which may be very common in our solar system, is iron-bearing asteroids that contain schreibersite, (Fe,Ni)<sub>3</sub>P. The corrosion of schreibersite by acidic media produces phosphine gas (Hersch 2013), and such acidic media include the sulfuric acid clouds on Venus.

In addition to phosphides, products of the disproportionation reactions (reactions defined as a molecule reacting with itself to produce dissimilar products) of phosphorous acid (H<sub>3</sub>PO<sub>3</sub>) or hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) include phosphine and phosphate. Bains et al. (2019) demonstrated that higher temperature (>40°C) and low pH (>4) environments are most conducive to phosphine production from phosphite disproportionation, and Pasek et al. (2014) argue that terrestrial phosphine is in local equilibrium with low concentrations of these acids.

With simple chemistry leading to phosphine and with occurrences of precursors being plausible in a planetary context, and in the absence of other biosignature gases, we analyze abiotic production pathways of phosphine to determine the most likely sources of phosphine on rocky planets such as Venus.

### 2.2.1 Abiotic Phosphide Chemistry

Iron phosphides such as schreibersite generate phosphine through biological corrosive processes (Glindemann et al., 1998), or through reactions associated with an acidic medium (Glindemann et al., 1998; Herschy 2013). This latter case is pertinent to an abiotic origin of phosphine on Venus. Herschy (2013) demonstrated that the schreibersite analog Fe<sub>3</sub>P reacts with H<sub>2</sub>SO<sub>4</sub> in aqueous solution to generate phosphine in the absence of any biological process. In this reaction, phosphorus as phosphide reacts with acid (as H<sub>2</sub>SO<sub>4</sub>) to generate phosphine:



This reaction is highly favorable from the range of 273 to 1773 K, with a log K that ranges from 10<sup>18</sup> at the lower temperatures to 10<sup>5</sup> at 1773 K (see Table 1 for calculation details). At even lower temperatures (e.g., 250 K) the log K is even larger (10<sup>20</sup>). With such an exergonic reaction, it would be expected that all phosphide should transform into phosphine, and hence phosphide would be the limiting reagent for the production of phosphine in an atmosphere. Note that the rate of such a reaction is unclear at present (Hersch 2013) used experiment timescales on the order of days to observe phosphine from ~10 μm-sized Fe<sub>3</sub>P particles), and the presence of compounds reduced compounds is time-dependent (e.g., Holm et al. 2015). An investigation of PH<sub>3</sub> generation rate from schreibersite would be meritorious if the detection of PH<sub>3</sub> on Venus is validated.

### 2.2.2 Abiotic Disproportionation Reactions

The production of phosphine from reduced oxidation state phosphorus oxyacids occurs through disproportionation reactions, which under acidic conditions originates from two sources:



Disproportionation has been experimentally demonstrated for both these acids and salts of these reduced phosphorus compounds. Hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) begins disproportionating at temperatures of ~30°C, whereas phosphorous acid disproportionates at higher temperatures (>190 °C, Shechkov et al., 2003). The hypophosphite salts have higher temperatures of disproportionation (occurring at >310 °C), whereas the phosphite salts tend to be less reactive. This disproportionation is supported by thermodynamic calculations (Table 1) that show phosphine production for hypophosphorous acid is exergonic (log K ~10<sup>10</sup> at 298 K), but for phosphorous acid (H<sub>3</sub>PO<sub>3</sub>) is much less exergonic (log K ~ 1-10). However, both indicate that if these acids are produced then the production of phosphine should follow, and are more exergonic at lower temperature. Routes to production of these phosphorus compounds are discussed below.

[TABLE 1]

In addition to the reactions of reduced oxidation state phosphorus oxyacids, the compound  $P_4O_6$  also readily disproportionates to phosphine:



This likely proceeds through hypophosphorous acid as an intermediate:



With a reaction K at 298K of  $\sim 10^{100}$ , such a reaction (iv) is extremely favorable even under dry conditions.

### **2.3 Relevance as Sources of Phosphine in the Atmosphere of Venus**

Greaves et al. (2020) discussed some potential geological/abiotic phosphine sources in the Venus atmosphere. These sources included lightning, surface phosphate reduction, and meteorites, all of which were dismissed as being many orders of magnitude too low to provide the phosphine at the level needed to sustain 20 ppb on Venus (Greaves et al., 2020). Following this argument, we assess whether phosphides or reduced phosphorus compound disproportionation could sustain the detected phosphine concentrations, at least at a level approaching the same order of magnitude.

The total mass of phosphine on Venus according to the 5 ppb revised estimate would be between  $\sim 6 \times 10^9$  and  $2 \times 10^{12}$  kg. This is calculated from the area of the planet observed in Greaves et al. (2020):

$$A = 2 \times 2\pi R_{Venus}^2 \int_{\theta=15^\circ}^{60^\circ} \sin\theta d\theta \quad (1)$$

where the first factor of 2 comes from the fact that Greaves et al. (2020) report the strongest detection between  $15^\circ$  and  $60^\circ$  north and south latitude, with modification by the downward total phosphine abundance of 5 ppb (Encrenaz et al., 2020). Then the atmospheric column abundance for phosphine (in  $cm^{-2}$ ),  $\sigma_{PH_3}$  is:

$$\sigma_{PH_3} = \int_{z=52km}^{\infty} f_{PH_3} n(z) dz, \quad (2)$$

where  $n(z)$  is the number density in Venus's atmosphere, taken from Supplemental Figure 8 in Greaves et al. (2020), and  $f_{PH_3}$  is the reported number fraction, 5 ppb. Greaves et al. (2020) state that their calculation is insensitive to phosphine present below the cloud deck.

The mass of phosphine is hence

$$\sigma_{PH_3} \times \frac{A}{N_A} \times m_{PH_3} = 6 \times 10^9 kg \quad (3)$$

where  $N_A$  is Avogadro's number and  $m_{PH_3}$  is the molar mass of phosphine.

The maximum amount of phosphine is in contrast 5 ppb of the total atmospheric mass ( $4.8 \times 10^{20}$  kg), or  $2 \times 10^{12}$  kg. Greaves et al. (2020) state that thermal degradation of phosphine is rapid at the higher temperatures beneath the clouds, however, suggesting that its presence there is less likely (extended data, figure 8 of Greaves et al., 2020).

Greaves et al. (2020) suggest that the phosphine degradation rate below the cloud layer is sufficiently fast such that phosphine may not be present; hence we use the lower value as a minimum requirement for providing an explanation for alternative sources of the detected phosphine. Alternatively, if this phosphine is persistent and not just observed as a comparatively rare stochastic event, then a steady state flux of  $10^{11}$ - $10^{12}$  kg of phosphine per million years (calculated by taking the flux of  $10^6$  molecules/ $cm^2$ s of Greaves et al. (2020) and converting to kg/Ma for the whole of Venus).

In conclusion, two possibilities are capable of maintaining this steady state flux of phosphine in the Venusian clouds: 1) the injection of reduced phosphorus from large impactors as a stochastic event (Reaction (i)), and 2) the persistent production of phosphine from the disproportionation of phosphorus compounds in the upper atmosphere of Venus (Reactions (ii)-(iv)).



## 2.4 Exogenous Phosphine Quantification

The surface of Venus is ~500 Ma (Schaber et al., 1992; Nimmo and McKenzie, 1998) as calculated from the size frequency statistics of ~800 craters across the surface. Most to all of the smaller craters we might expect to find are absent as the atmosphere is too thick to allow smaller impactors to penetrate and maintain hypervelocity. Thus, many craters that are about 32 km and less in diameter, and nearly all craters 8 km and less in size are absent.

The mass of material that has impacted Venus' surface can be determined from the cratering record transformed into impactor mass through a relationship between impactor diameter  $D_{imp}$ , and crater diameter  $D_{fin}$  (Collins et al., 2005; Johnson et al. 2016, see equations 4 & 5):

$$D_{fin} = 1.66 \left( \frac{\rho_{imp}}{\rho_{targ}} \right)^{0.38} D_{imp}^{0.94} v_{imp}^{0.38} D_{SC}^{-0.13} g^{-0.19} (\sin \theta)^{0.38} \quad (4)$$

where  $\rho_{imp}$  and  $\rho_{targ}$  are the impact and target densities, respectively and assumed to be roughly equal;  $v_{imp}$  is the impact velocity (20 km/s);  $D_{SC}$  is the crater diameter where simple craters transition to complex and assumed to be 4 km;  $g$  is the acceleration due to gravity on Venus (8.9 m/s<sup>2</sup>); and  $\theta$  is the angle of impact (45° on average). The average mass delivered by large impactors since Venus's resurfacing (~500 Mya) is about 10<sup>13</sup>-10<sup>14</sup> kg per million years (Figure 2). Outside of the largest impactors (impact frequency < 1 per million years, mass > approximately 10<sup>12</sup> kg), an average mass of 10<sup>11</sup> to 10<sup>12</sup> kg is delivered every million years. This flux ignores the larger, stochastic impacts that deliver more mass in a single event. In addition, on Earth, ~10<sup>7</sup> kg/yr (Love and Brownlee, 1993) of fine dust particles are delivered; this rate presumably does not vary significantly for Venus (Greaves et al., 2020), but also does not include the largest impactors (e.g., Chicxulub). This dust would bear a P content roughly similar to meteoritic sources, or about 1000 ppm (Pasek and Lauretta, 2008). Notably, this flux of large impactors does not appreciably change the total mass delivered to Venus, nor does it significantly alter the crustal platinum group inventory (e.g., Esser and Turekian 1988), as 10<sup>11</sup>-10<sup>12</sup> kg/million years is less than the 10<sup>7</sup> kg/yr observed on the earth by a factor of 10-100.

[FIGURE 2]

However, the cratering record speaks to one route to the formation of phosphine: a single, large impactor, enriched in phosphorus, that supplies the entirety of Venus's phosphine inventory in one event. Such a case would provide abundant phosphorus for phosphine, but the phosphine would be lost over a relatively short period, estimated by Greaves et al. (2020) as 10<sup>3</sup> years. However, a transient event could supply abundant phosphine to a planet with an acidic environment

A 10<sup>12</sup> kg impactor strikes Venus roughly once every million years. This frequency is based on the crater distribution of Schaber et al. (1992) and is extended to include smaller objects (whose craters are not completely visible due to the ablation of the impactor within the atmosphere of Venus, which include the 10<sup>12</sup> kg objects that make craters ~2-3 km in diameter). Amongst meteorites, the IIG iron meteorites bear 2% phosphorus by mass. If a 10<sup>12</sup> kg IIG iron impactor were to have struck Venus, the mass of phosphorus delivered (2×10<sup>10</sup> kg at 2% P) could entirely account for the 5 ppb phosphine. Greaves et al. (2020) suggest a phosphine lifetime of around 1000 years, implying that such an impact would have had to have happened within 1000 years before present (a probability of about 0.1%). Moreover, as noted, impactors of this size are missing from the crater record of Venus, due to the filtering of large objects by the thick Venusian atmosphere.

We modeled the ablation of meteoroid material in the Venusian atmosphere to address this issue. This model is based on formulae presented in (Bland and Artemieva, 2006) and modified for Venus in the equations:

$$\frac{dV}{dt} = -C_D \frac{\rho_g A V^2}{m} + g \sin(\theta) \quad (5)$$

$$\frac{dm}{dt} = -A \frac{C_H \rho_g V^3}{2Q} \quad (6)$$

where a spherical meteoroid of mass  $m$  changes both its velocity  $V$  and mass  $m$  with respect to time through ablation of material. In these equations,  $\rho_g$  is the density of Venus's atmosphere at a given height (defined by the scale height, ~15.9 km, and surface density of 67 kg/m<sup>3</sup>),  $A$  is the cross-sectional area of the meteoroid,  $g$  is gravity on Venus (8.9

$m/s^2$ ),  $\theta$  is the angle the meteoroid enters Venus's atmosphere, an average of  $45^\circ$ , and  $c_h$  is the heat transfer coefficient and  $Q$  is the heat of ablation. Together the term  $C_h/2C_DQ$  has a value of 0.07 for an iron impactor (Bland and Artemieva, 2006). For these calculations, we assume that Venus's atmosphere is isothermal. We justify this because most of the ablation of the largest meteorites happens at the denser parts of the atmosphere, which does not vary significantly from isothermal over this range (e.g., the density of Venus's atmosphere is about 60% of what is predicted from an isothermal atmosphere at 50 km, and matches well below that height). Notably, other models of ablation (Register et al. 2017) yield different results with respect to material vs. height that has ablated, but Register et al. (2017) argue that the extent of variation is not generally high.

As Venus' atmosphere is thick and has a large scale height in contrast to Earth, large meteoroids undergo significant ablation and slow to terminal velocity prior to reaching Venus' surface. For Earth, the slowdown of meteoroids by ablation has a velocity-dependent cutoff of about  $10^4$  kg (Mehta et al., 2018), with larger objects not slowing sufficiently, and reaching the surface at supersonic speeds. Due to the thick atmosphere of Venus, objects  $\sim 10^{12}$  to  $10^{13}$  kg and smaller decelerate to velocities of  $<1000$  m/s. For most of these objects, their mass is lost primarily 30-60 km above the surface of Venus (Figure 3).

[FIGURE 3]

This ablation occurs in the cloud region of Venus, and occurs even for larger objects ( $\sim 10^{13}$  kg), including many other iron meteorite classes that tend to be about a factor of 10 less rich in P than the IIG meteorites. This is a significant amount of mass lost specifically in the region dominated by acidic  $H_2SO_4$  droplets. Given schreibersite's reactivity towards acid, an impactor containing abundant schreibersite would have its phosphorus readily transformed into phosphine (reaction (i)). Hence, the ablation of large impactors in the cloud region is sufficient to temporarily provide enough phosphorus to generate 5-20 ppb of phosphine. Such an impact would also not leave a crater, as the ablation decelerates the impactor to terminal velocity, allowing the remaining mass to strike the Venusian surface without excavating significant surrounding material.

## **2.5 Endogenous Phosphine Sources**

If phosphine on a rocky planet is not transient, then impactors would be insufficient to drive a steady production of phosphine through a phosphide source. Instead, for the case of a steady phosphine source, we posit that intrinsically reduced phosphorus compounds such as  $P_4O_6$ , phosphorous acid and/or hypophosphorous acid could serve as a source of phosphine through disproportionation.

As evidence of this pathway, phosphoric acid ( $H_3PO_4$ ) comprises a portion of the acidic clouds on Venus and of the haze below the cloud layer; and this phosphoric acid likely originates from the surface (possibly as  $P_4O_6$  and/or  $P_4O_{10}$ ). Note that these steps likely occur as transfers of electrons or electron pairs, but that the net reaction is described through a reduction process.

The presence of phosphoric acid on Venus is inferred from measurements of the composition of Venusian aerosols within the lower cloud layers, which found both chlorine and phosphorus associated with the sulfuric acid droplets (Andreichikov, 1987). This detection by x-ray fluorescence by the Vega 1 & 2 probes suggests that phosphorus is a substantive constituent of aerosols within the cloud layer (Titov et al., 2018), and suggests that phosphorus, likely as phosphoric acid, is a significant component of the haze in the regions below the cloud layer (Krasnopolsky, 1989), and may possibly be the dominant component where  $H_2SO_4$  liquid is unstable. In addition to phosphorus, iron was also detected within the aerosols by the Venera-13 and -14 probes (Petryanov-Sokolov, 1981). Iron is likely present as  $FeCl_3$  (Krasnopolsky, 2017).

The presence of  $P_4O_6$  as a gas on Venus was suggested by Krasnopolsky (1989), and may be the major P-bearing gas phase above the surface of Venus (Visscher et al., 2006; Bains et al., 2021).  $P_4O_6$  is possibly formed from  $P_4O_{10}$  (e.g., phosphate) at the  $CO/CO_2$  conditions of the lower Venusian atmosphere:



though these reactions are all contingent on the stability of  $P_4O_6$ , which is based on data from Barin et al. (Barin et al., 1977). Some datasets have suggested  $P_4O_6$ 's stability may be erroneous (c.f., Iorish and Belov, 1997; Belov et al., 1997). If correct, however, then  $P_4O_6$  is a ready source of reduced P in Venus's atmosphere, with P bearing a +3 oxidation state.

Reactions (ii) and (iii) provide the disproportionation reaction of both hypophosphorous and phosphorous acids. Phosphorous acid is readily generated from  $P_4O_6$  hydrolysis. Reaction (iv) ( $K \sim 10^{100}$ ) provides the disproportionation reaction of  $P_4O_6$ . Of these, both  $P_4O_6$  and hypophosphorous acid would be expected to stoichiometrically convert to phosphine, at a 1:1 or 2:1 ratio, respectively. The conversion of phosphorous acid to phosphine is less clear from thermodynamic calculations, though experiments have shown such a reaction occurs readily at  $>190^\circ\text{C}$  (Shechkov, 2003).

A source of reductant is needed to promote the formation of these reduced phosphorus compounds.  $P_4O_6$  may be formed through reduction by CO in the lower atmosphere (reaction (v), Krasnopolsky, 1989; Visscher et al., 2017). In contrast, in the absence of this source of phosphine, phosphoric acid must serve as a source. If so, iron as either metal or  $\text{Fe}^{2+}$  would also be sufficient to drive this reductive chemistry (see table 1), or UV light under the redox conditions of the upper Venusian atmosphere (which potentially phosphoric acid to phosphorous acid at  $\lambda < 336 \text{ nm}$  (Pasek 2008) in solution, or  $< 124 \text{ nm}$  as solids (Turner et al. 2018)). Whether UV light reaches the region where phosphoric acid is present is unclear and hence vertical transport between the cloud region to the mesosphere could invoke a wide variety of photochemical reactions, including this reduction. The thermodynamic data of these reactions demonstrate that iron—including ferrous iron in silicates—is capable of reducing phosphoric acid to phosphine. The concentration of  $\text{FeCl}_3$  on Venus appears to be consistent with this pathway being active (as the stoichiometric ratio of  $\text{FeCl}_3/\text{PH}_3$  required is 8:1), and, based on a concentration of  $0.2 \text{ mg/m}^3$  (Krasnopolsky 1989, 2017), the  $\text{FeCl}_3$  present is sufficient to balance 5-20 ppb of phosphine. Much of this  $\text{FeCl}_3$  is located within aerosols in the clouds, and with  $\sim 5 \text{ mg/m}^3$  of aerosols over the cloud layer (52-62 km), a corresponding mass of  $10^{14} \text{ kg}$  of  $\text{FeCl}_3$  is reasonable (Krasnopolsky 2006). With between  $10^{10}$  and  $10^{12} \text{ kg}$  of  $\text{PH}_3$  (section 2.3) this  $\text{FeCl}_3$  is between 20 and 10000 times as abundant, with its precursor compounds having been more than enough to have been the source of electrons for reduction to generate  $\text{PH}_3$ . The source of iron for  $\text{FeCl}_3$  may have been provided by exogenous material (as Fe/P is  $\sim 100$  in extraterrestrial material (Anders and Grevesse 1989)), or could be endogenous in origin as  $\text{FeO}$  is common to volcanic dust, though the mass balance of this iron source is unclear at present.

Thus, we propose a potential source of phosphine on Venus (and potentially other rocky planets with runaway greenhouse effects and acidic clouds) to be the reduction of  $\text{P}^{5+}$  to  $\text{P}^{3+}/\text{P}^+$  followed by disproportionation. Whether this begins as near-surface geochemical processes (as per  $P_4O_6$ ), or occurs as phosphoric acid reacts with iron metal or ferrous silicates in the cloud-layer, this reduction ultimately results in phosphine production.

### 3. Conclusions

The detection of phosphine on Venus has so far defied expectations and highlights many unknowns about phosphorus chemistry in the solar system. Even if this detection ends up being erroneous, understanding phosphorus chemistry on rocky planets as a whole assists in constraining both planetary science processes and the potential for these compounds to be used to identify potential extant biology. We propose here two possible abiotic sources of phosphine on Venus: a large impactor that ablates completely within the sulfuric acid cloud layer of the atmosphere of Venus as a transient event; or the disproportionation of reduced P species as a phosphine source (Figure 4).

[FIGURE 4]

The presence of oxidized iron and HCl may be consistent with iron involvement in this reduction if phosphoric acid is the source, with iron coming from both exogenous and endogenous sources. The likely presence of phosphoric acid at and below the cloud layers lends further credence that phosphorus is involved in the atmospheric chemistry of Venus. Notably the disproportionation of  $P_4O_6$ —a gas predicted to be a major P phase on Venus (Krasnopolsky, 1989; Visscher et al., 2006; Bains et al., 2021)—could generate this phosphine.

Extending these potential sources to other rocky planets, the production of  $\text{PH}_3$  through schreibersite corrosion is especially relevant to extrasolar planets. With much higher bombardment rates on younger planets with larger debris disks, phosphine may be an abundant small molecule formed as schreibersite reacts in planetary atmospheres, and would obviously not be biological in origin.

These routes to  $\text{PH}_3$  production can be contrasted to Truong and Lunine (2021), wherein a reduced, deep mantle source of phosphides within volcanic material is explosively erupted into the atmosphere, which then reacts with  $\text{H}_2\text{SO}_4$  to generate  $\text{PH}_3$ . The exogenous source mechanism proposed here is similar to that proposed in Truong and Lunine (2021), except that Truong and Lunine (2021) suggest Venus's mantle petrology includes some amount of phosphides

that are the source of PH<sub>3</sub> instead of extraterrestrial phosphides. Both mechanisms would result in PH<sub>3</sub> generation from phosphides by reaction with acid. Differentiating between these two hypothesized phosphine sources is the source of the phosphides. Phosphides are well-known to occur as a component of meteoritic material and especially of core material from asteroids (Pasek and Lauretta 2005). However, phosphides are comparatively uncommon in mantle and crustal lithologies, and are absent from most achondritic mantle material, from HEDs, to Martian meteorites, to angrites (e.g., Gooley and Moore 1976, Rubin 1997). However, if Venus's mantle lithology is akin to either lunar lithology (e.g., Pasek 2015) or to aubrites (Ritson et al. 2020), then a mantle phosphide source is feasible for Venus, affirming the plausibility of the Truong and Lunine (2021) source. Independent of the source of phosphorus, multiple sources have highlighted a role for P in the atmosphere of Venus (Krasnopolsky 1989, Titov et al. 2018), which should then participate in some amount of reductive chemistry, depending on the presence of other reductants. However, the mantle plume source requires ejection of mantle phosphides to the upper atmosphere of Venus where the phosphides can react with acid to generate PH<sub>3</sub>, and Glaze (1999) and Airey et al. (2015) both note that explosive plumes may not reach very high to provide PH<sub>3</sub>. That said, the presence of P above the surface of Venus seems almost certain (Andreichikov, 1987), though its origin and speciation are not wholly clear.

Without further in-situ measurements of phosphine and other associated gases in Venus' atmosphere, it is not possible at present to distinguish between these, or other possible abiotic formation mechanisms of phosphine, if the gas is even present. Future missions may be able to determine whether the phosphine in Venus' atmosphere is transient or not, and this could help distinguish between different formation pathways (e.g., Hein et al. 2020, Baines et al. 2021, Frank et al. 2021). It is more likely that if phosphine is present, then it is formed by an ongoing geochemical process than a biological process, though a transient process cannot be excluded. This is especially the case in any considerations of possibility that the phosphine could be indicative of a biological process (Hoffman et al., 1980; Sousa-Silva et al. 2020).

At present there is no information about whether life exists elsewhere in the solar system, and so technically a biotic phosphine source elsewhere cannot theoretically be ruled out. However, life should always remain the "hypothesis of last resort" (Sagan et al., 1993) for explaining planetary geochemical phenomena. The possibility of life being the source for Venus atmospheric phosphine must also entail the origin of life at some point in its the geologic past (Way et al., 2016, Limaye et al. 2021b). Scenarios for the origin of life still have many uncertainties, and we do not fully understand how likely it is to occur on rocky planets, or how likely "abiotic dead ends" may result instead (Scharf et al., 2015). Moreover, it would also require that the evolution of Venusian life over geologic time would yield a metabolic pathway needed to generate a specific chemical signature such as phosphine. Of course, there is also the remote possibility that any putative life on Venus is related to terrestrial life via panspermia, but this would open a host of many additional questions.

The possibility that phosphine may be transient and we are witnessing the effects of a rare geological event such as a large impactor every few million years also cannot be ruled out. This requires fewer extraordinary assertions than a life hypothesis. There still may be Venusian geochemical phosphine synthesis processes that remain unknown, or poorly understood in a Venus context.

Carl Sagan, one of the original postulators of life in the clouds of Venus, stated "extraordinary claims require extraordinary evidence" (Sagan, 1980). There seems to be insurmountable issues with the idea that detecting a single, simple gas in the clouds of Venus equates to life having produced it. That said, there could in fact be life in the clouds of Venus, but evidence based on a this single putative potential biosignature does not offer much support for this possibility. Multiple lines of evidence are needed including detecting other biologically-derived gases and eventually directly sampling the Venus clouds.

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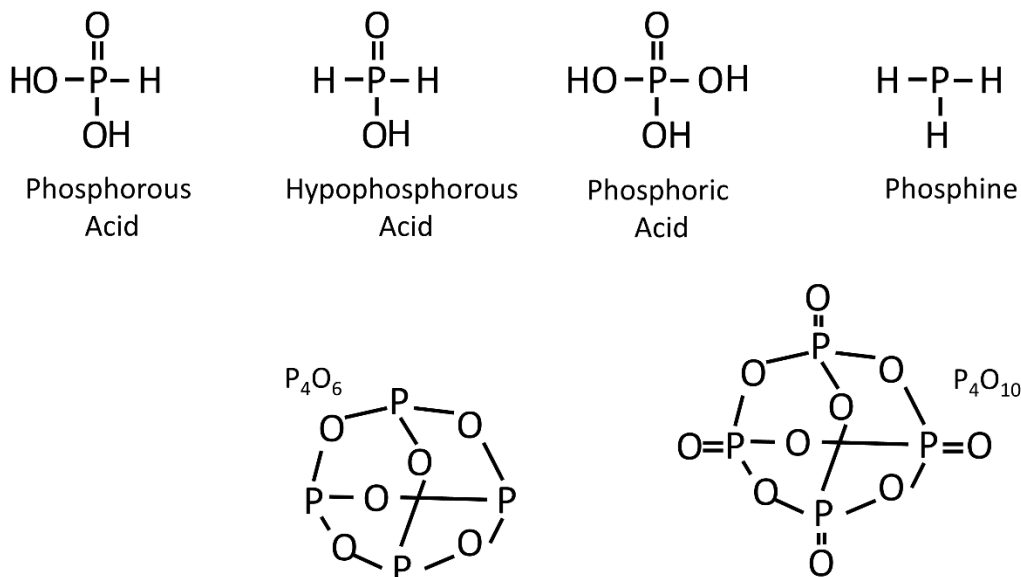
Table 1.

Reactions*	log K @ 298
$2\text{Fe}_3\text{P} + 3\text{H}_2\text{SO}_4(\text{l}) = 2\text{PH}_3(\text{g}) + 3\text{FeSO}_4 + 3\text{Fe}$	18.4
$4\text{H}_3\text{PO}_3(\text{a}) = \text{PH}_3(\text{g}) + 3\text{H}_3\text{PO}_4$	1.3
$2\text{H}_3\text{PO}_2 = \text{PH}_3(\text{g}) + \text{H}_3\text{PO}_4$	15.6
$\text{P}_4\text{O}_6(\text{g}) + 6\text{H}_2\text{O} = \text{PH}_3(\text{g}) + 3\text{H}_3\text{PO}_4$	102
$8\text{FeO} + \text{H}_3\text{PO}_4 + 24\text{HCl}(\text{g}) = 8\text{FeCl}_3 + \text{PH}_3(\text{g}) + 12\text{H}_2\text{O}(\text{g})$	16.4
$4\text{Fe}_2\text{SiO}_4 + \text{H}_3\text{PO}_4 + 24\text{HCl}(\text{g}) = 8\text{FeCl}_3 + \text{PH}_3(\text{g}) + 12\text{H}_2\text{O}(\text{g}) + 4\text{SiO}_2$	2.8

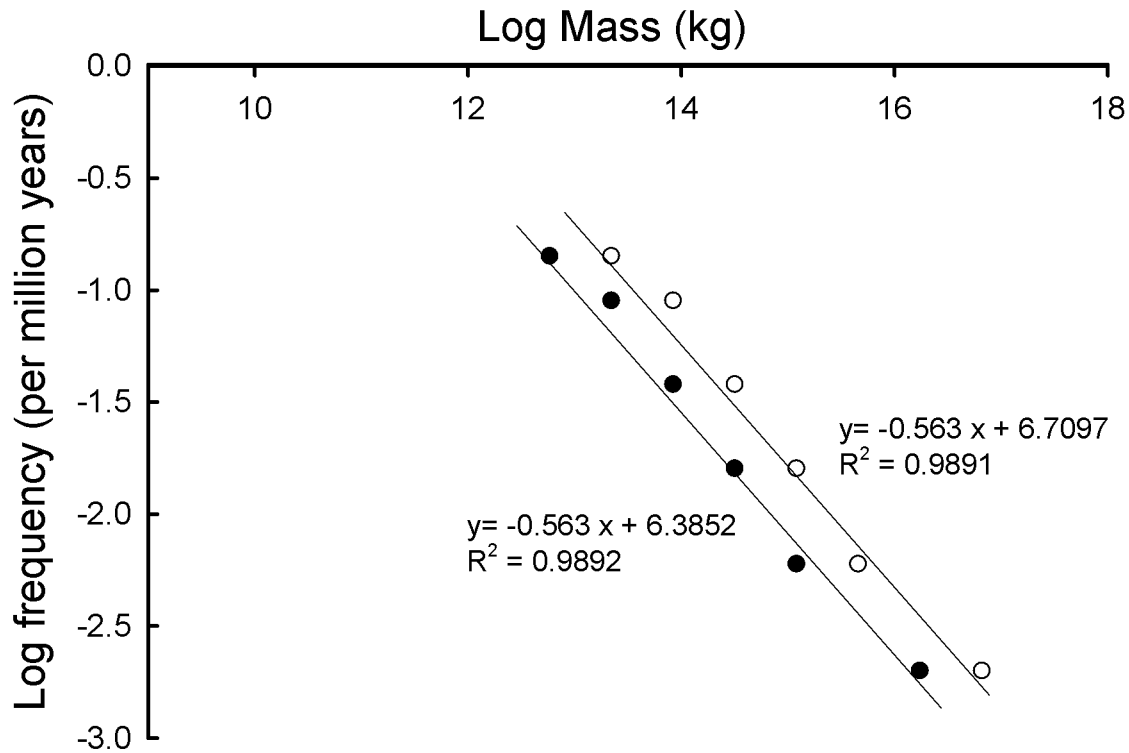
\*We utilized the reaction equations module of HSC Chemistry (version 7.1, Outokompu Research Oy) to determine free energies and log Ks of the reactions shown here. Thermodynamic data for these species are built into the database and are updated regularly (<https://www.outotec.com/products-and-services/technologies/digital-solutions/hsc-chemistry/>)

The following assumptions were made: only data classified as “class 1” was used, which is the most vetted data within the program. FeO was used as wüstite, and phosphoric acid was used as its liquid, anhydrous end-member form. Phosphorous acid and hypophosphorous acid were both used as aqueous species, as data for the solid and liquid forms of both substances is not available. Future work with this system should calculate the reactivity of these acids either as free liquids, or dissolved within  $\text{H}_3\text{PO}_4$ , or dissolved within  $\text{H}_2\text{SO}_4$ . These calculations are thus illustrative, but not fully indicative of the chemical reactions taking place.

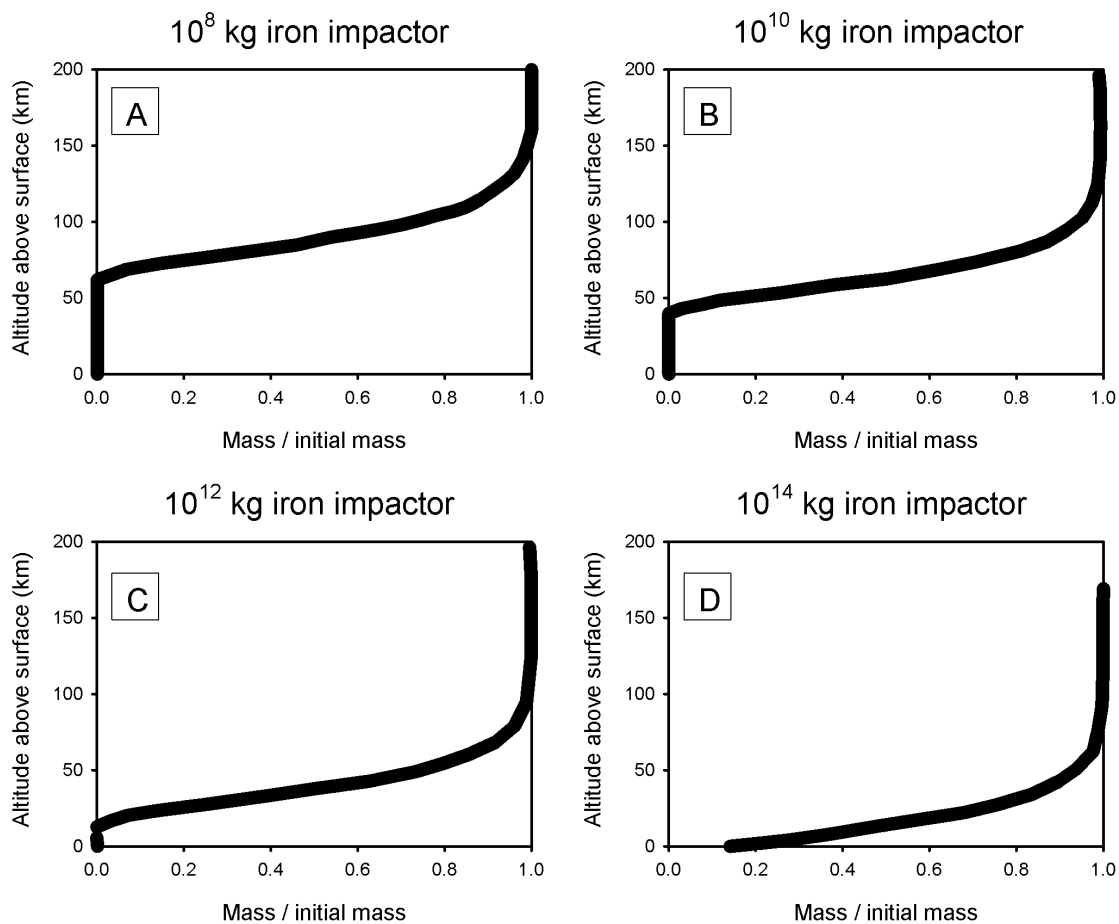
**Figure 1.** Phosphorus compounds discussed in this paper.



**Figure 2.** Frequency of impacts at Venus vs. mass, using impact record of Schaber et al. (1992), coupled with the mass relationship of Johnson et al. (2016). The blue line assumes the larger crater diameter for each bin, whereas the orange line assumes the smaller crater diameter. The cumulative mass can be found by multiplying the frequency by the mass of these impactors, and suggests a mass of  $\sim 10^{13}$ - $10^{14}$  kg per million years over the last 500 million years, much of which was delivered in single, large events. The regression lines provide the relationship between frequency and mass, and show that the frequency of a  $10^{12}$  kg impactor is about one per 1-2 million years.



**Figure 3.** The fate of iron meteoroids as they descend through the Venusian atmosphere. Spherical iron masses initially at  $10^8$ - $10^{14}$  kg with  $45^\circ$  angles of entry and entry velocities of 20 km/s, tend to ablate near the cloud region of Venus (40-60 km). In this region they lose >99% of their initial mass.



**Figure 4.** Schematic summarizing the alternative routes to phosphine production on Venus.

