



Volcanically extruded phosphides as an abiotic source of Venusian phosphine

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We hypothesize that trace amounts of phosphides formed in the mantle are a plausible abiotic source of the Venusian phosphine observed by Greaves et al. [*Nat. Astron.*, <https://doi.org/10.1038/s41550-020-1174-4> (2020)]. In this hypothesis, small amounts of phosphides (P^{3-} bound in metals such as iron), sourced from a deep mantle, are brought to the surface by volcanism. They are then ejected into the atmosphere in the form of volcanic dust by explosive volcanic eruptions, which were invoked by others to explain the episodic changes of sulfur dioxide seen in the atmosphere [Esposito, *Science* 223, 1072–1074 (1984)]. There they react with sulfuric acid in the aerosol layer to form phosphine ($2 P^{3-} + 3H_2SO_4 = 2PH_3 + 3SO_4^{2-}$). We take issue with the conclusion of Bains et al. [arXiv:2009.06499 (2020)] that the volcanic rates for such a mechanism would have to be implausibly high. We consider a mantle with the redox state similar to the Earth, magma originating deep in the mantle—a likely scenario for the origin of plume volcanism on Venus—and episodically high but plausible rates of volcanism on a Venus bereft of plate tectonics. We conclude that volcanism could supply an adequate amount of phosphide to produce phosphine. Our conclusion is supported by remote sensing observations of the Venusian atmosphere and surface that have been interpreted as indicative of currently active volcanism.

Venus | phosphine | volcanism

Greaves et al. (1) reported detecting phosphine in the Venus atmosphere at ~ 20 ppb abundance, with an approximate error bar inferred from their paper of ± 10 ppb, using the James Clerk Maxwell Telescope (JCMT) and Atacama Large Millimeter/submillimeter Array (ALMA) radio telescopes. Subsequent to the publication of their paper, a recalibration of ALMA data and other challenges to their analysis approach (2–4) led the authors to decrease both the abundance of phosphine and its level of significance, to somewhere between 1 and 5 ppb at 5-sigma (5). While this is consistent with an upper limit from infrared observations (6), it is significantly less than what Greaves et al. (1) derive from the JCMT. However, that observation by itself has very large error bars, and we are skeptical that one can ascribe the difference to time variability in contrast to Greaves et al. (5). Another infrared observation made by the SOIR (Solar Occultation in the InfraRed) instrument on Venus Express gives a much lower upper limit abundance of 0.5 ppb at 60 km (7). After a rebuttal (5, 8), other groups again challenged the phosphine detection, suggesting that the reprocessing spectral feature, which is now significantly reduced in significance from the original discovery paper, is consistent with SO_2 in the mesosphere (9, 10). While the latter two papers do not rule out the possibility of phosphine in the stratospheric clouds, they argue that it is challenging for ALMA to detect ~ 1 ppb abundance at that altitude. A reanalysis of Pioneer Venus low-resolution mass spectrometry data does support the presence of phosphorus-bearing compounds in the atmosphere, which might be attributed to phosphine (11). However, it is also important to note that the analysis is based on an observation from four decades ago, not the present day, and time variability on that scale is plausible.

It is of value to ask why phosphine is in the Venus atmosphere, if it is there. Phosphine had been considered and proposed as a potential biosignature in oxidizing terrestrial exoplanets' atmospheres (12); however, the specific pathway of biological production of PH_3 still remains uncertain with no known direct metabolic pathway (13, 14). In the original paper, Greaves et al. (1) investigated potential pathways of the formation of phosphine and conclude that the presence of PH_3 at their originally derived abundance is difficult to explain by geologic or atmospheric chemistry, invoking the possibility of biology. A more extensive examination of abiotic sources by the same group (15) dismissed all such abiotic hypotheses, including the generation of phosphine from volcanically extruded phosphides. On the other hand, Cockell et al. (14) have argued that invoking biological sources is problematic, saying “one cannot use evidence consistent with a single, isolated biochemical pathway as a plausible basis invoking for biological processes in an environment where many more fundamental biochemical pathways are blocked by unfavorable conditions.”

In this paper, we argue for the plausibility of volcanically extruded phosphide as an abiotic source of Venusian phosphine. In oxidizing terrestrial environments, elemental phosphorous would be in other oxidized forms such as phosphate on the surface. For an abiotic source to be plausible, the presence of small amounts of phosphides (P^{3-} bound in metals such as iron, magnesium, etc.) in volcanic dust would be energetically essential, leading to the facile production of hydrogen phosphide, that is, phosphine. Another possibility that may lead to the production of phosphine but not quantified here is the unknown chemistry of phosphorus in the clouds. Here, we are limited by our lack of knowledge of Venusian clouds as well as the kinetics of phosphine-related reactions given that phosphine has not yet been extensively studied experimentally.

In the phosphide hypothesis we advocate here, small amounts of phosphides (P^{3-} bound in metals such as iron) sourced from a

Significance

Published observations suggest small amounts of phosphine in the atmosphere of Venus, and various abiotic mechanisms for its generation have been rejected in the literature, including active volcanism. We reexamine a volcanic source and find it to be sufficient to supply the observed amount of phosphine given that Venus might be subject to episodes of active volcanism and magmas originating deep in the mantle and brought up by plume volcanism.

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deep mantle are brought to the surface by volcanism. They are then subsequently ejected into the atmosphere in the form of volcanic dust by explosive volcanic eruptions: Sufficiently large explosive eruptions similar to the scale of Krakatau could inject material directly into the sulfuric acid cloud layer, explosions invoked by Esposito (16) to explain the episodic changes of sulfur dioxide seen in the atmosphere at 70 km by the Pioneer Venus UV spectrometer. There, the phosphides react with sulfuric acid in the aerosol layer to form phosphine ($2\text{P}^{3-} + 3\text{H}_2\text{SO}_4 = 2\text{PH}_3 + 3\text{SO}_4^{2-}$). While one might argue that sulfur trioxide SO_3 could oxidize PH_3 in this reaction to H_3PO_3 and H_3PO_4 (which depends on the temperature/pressure, the thermodynamics and kinetics of reactants), we note that the H_3PO_4 is created by hydrolysis of SO_3PH_3 and therefore would be limited by the lack of water; on the other hand, H_3PO_3 will spontaneously decompose under 200 °C to form PH_3 .

Below, we use published laboratory data that demonstrate an extremely efficient conversion of phosphides to phosphine via sulfuric acid, larger than that in water. Second, we consider a mantle with a redox state similar to the Earth, and invoke magmas originating deep in Venus's mantle—a likely scenario for the origin of plume volcanism on Venus (17). Magmas originating deep in the mantle allow a higher amount of phosphides in volcanically extruded mantle material. In section 1, we calculate how much phosphide is required and the volume of lofted dust required. We find that major explosive volcanism—similar to the scale of Krakatau—is required to loft material as high as 70 km. That this might be possible is argued in section 2.

On Earth, it is well known that phosphine gas is produced by strong acid from phosphorous-containing impurities in iron (18, 19). In the Tanaka et al. experiment (18), iron phosphide is converted to phosphine with a conversion yield of 75–80% in three out of four samples when dissolved in hydrochloric acid. In the Geng et al. experiment (19), aqueous corrosion produced a significant amount of phosphine gas comparable to the amount detected in natural terrestrial environments. However, they also find that sulfuric acid corrosion produces an amount of phosphine gas three orders of magnitude higher than when water is the corrosive agent.

Those two experiments demonstrate a high efficiency of phosphine production from the small amounts of phosphides potentially available in volcanic dust in the strongly acidic environment relevant to the Venusian middle atmosphere. In contrast, the aqueous corrosion pathway invoked by Bains et al. (15) from ref. 20 did not actually demonstrate the production of phosphine from phosphide, and Pasek et al. (21) could only generate phosphine with the involvement of microbial activity.

The experiments we cite here are relevant in geological circumstances when sufficient phosphides are available in the volcanic flows. In section 1b, we argue that Venus could well produce more phosphide-rich lava than Earth. First, we must calculate how much is required to supply the observed amount of phosphine.

1. Constraints on the Amount of Phosphide Needed to Account for the Phosphine

1a. The Mass Loss and Resupply Rates of Phosphine in the Atmosphere.

We start by calculating the mass loss rate of phosphine in the atmosphere. As a significant fraction (~1–5 ppb) of the tentatively detected phosphine in the atmosphere is at the height of 53–61 km above the surface (1, 5), we calculate the volume of the atmosphere in the 8-km layer shell between 53 and 61 km (Fig. 1) and then scale this value by a fraction of ~1–5 ppb to get a volumetric abundance of phosphine in the atmosphere. The mass loss rate of phosphine in the atmosphere is given by the following equation:

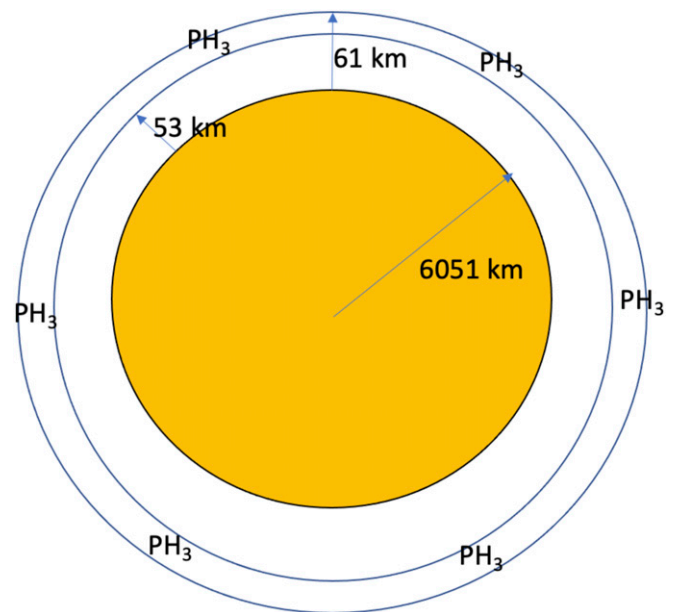


Fig. 1. Schematic of Venus's atmosphere considered in this calculation.

$$L = \frac{4\pi R^2 H f(\text{PH}_3) \rho_{\text{air}} \mu_{\text{PH}_3}}{\tau_{\text{PH}_3} \mu_{\text{CO}_2}} \quad [1]$$

Here, ρ_{air} is the atmospheric density in this layer, for an average atmospheric pressure of about 0.5 bar, and an average temperature of about 60 °C (22), $\rho_{\text{air}} \sim 0.5 \text{ kg}\cdot\text{m}^{-3}$; R is the Venus's radius (6,051 km); H is the thickness of the considered atmospheric layer (8 km); $f(\text{PH}_3)$ is the volume mixing ratio of phosphine in the atmosphere (1–5 ppb); $\mu_{\text{PH}_3} = 34 \text{ g/mol}$; $\mu_{\text{CO}_2} = 44 \text{ g/mol}$; τ_{PH_3} is the destruction lifetime of PH_3 in the atmosphere. In the high atmosphere, PH_3 could be destroyed quickly by UV and $-\text{OH}$, $-\text{Cl}$ radicals (as well as other radicals); close to the surface, thermal decay could rapidly destroy PH_3 . One way to estimate the lifetime of PH_3 is by using the eddy diffusion timescale, which controls the transport of PH_3 to the destructive regions. Values of the eddy diffusion coefficient vary in the literature, with K becoming smaller for a more humid atmosphere at heights of the middle and lower cloud layers (23). At the cloud layers, K ranges from $\sim 10^3$ to $10^4 \text{ cm}^2\cdot\text{s}^{-1}$ as measured by radio scintillations experiments and estimates from the size distribution and production rate of cloud particles (23–26). In order to enable the dramatic changes in the vertical profiles of most minor species, the presence of statically stable layers within the clouds may act as a barrier to limit the dynamical exchanges between the lower and upper atmosphere (26, 27). Using the eddy diffusion coefficient within the cloud layers, $K = 10^3 \text{ cm}^2\cdot\text{s}^{-1}$, the transport timescale is estimated as $\tau_{\text{PH}_3} \sim (z^2/K) = 10^9 \text{ s}$. Since this timescale depends sensitively on the eddy diffusion value, in the next section, we will also discuss the results for $\tau_{\text{PH}_3} \sim 10^8 \text{ s}$; corresponding to $K = 10^4 \text{ cm}^2\cdot\text{s}^{-1}$.

The resupply rate of phosphine by phosphides from volcanoes is given by the following equation:

$$P = E \rho_{\text{mag}} X_P f_{\text{P}(3-)}, \quad [2]$$

where E is the volume of lofted volcanic dust, ρ_{mag} is the density of magma ($2,900 \text{ kg}\cdot\text{m}^{-3}$) given the value for basalt as the nominal composition of magma, X_P is the total phosphorous content in magma, and $f_{\text{P}(3-)}$ is the mass fraction of phosphide over the total phosphorous content in magma. In section 1b, we will discuss the possible value for the total phosphorous content in magma X_P and

the mass fraction of phosphide over the total phosphorous content in magmas $f_{P(3-)}$.

1b. The Total Phosphorous Content in Magma X_P and Mass Fraction of Phosphides over the Total Phosphorous Content in Magma $f_{P(3-)}$. We consider a mantle with a redox state similar to the Earth's, and magma originating deep in the mantle of Venus—a likely scenario for the origin of plume volcanism on Venus (17). Here, magmas originating deeper in the mantle allow a higher amount of phosphides in volcanically extruded mantle material on Venus. The present-day redox state of the Earth's mantle decreases with depth such that it could reach 4–5 log units below the FMQ (fayalite–magnetite–quartz) buffer (28). Under such conditions, volatile species in the mantle would be dominated by CH_4 and H_2 rather than by H_2O and CO_2 (28). Even though not widespread on Earth, more recent evidence has shown that lavas can be sourced from the deep mantle (29, 30); the presence of SiC in some basaltic rocks, which requires a redox state of at least –6 log units below IW (iron–wüstite), suggests that reduced fluids containing $\text{CH}_4 + \text{H}_2$ could move upward from the deep Earth's mantle where the oxidation state is low (31–33). Heating experiments and calculations suggest that a high temperature, reducing environment (containing C, CH_4 , H_2 , etc.) with a redox state similar to IW (iron–wüstite) is favorable to the production of at least some amount of phosphide from phosphates (34–38). For a slightly reducing deep mantle slightly below or close to IW (iron–wüstite), we adopted a fraction of phosphides over the total phosphorous content of 5% as calculated by Pasek (38) only as a way to estimate the phosphide content in our calculation.

On Earth, the total phosphorous content X_P may range between 0.1 and 0.3% for typical continental crust and ~0.2% for midocean ridge basalt (39) to a value as high as 1% and up to 3% in magmatic rocks originating from deep-seated lithospheric and asthenospheric mantle sources (29, 30, 40). More recent evidence has shown that lavas can be sourced from the deep mantle, where the magma composition is more enriched in total phosphorous than mid-ocean ridge basalt (29, 30). In the case we consider, namely magmas originating from deep within the mantle, we use the total phosphorous content for magmatic rocks X_P of 1%. This is more relevant for deep plume volcanism than the value for midocean ridge basalt, which corresponds to volcanism from the upper mantle.

In steady state, balancing the mass loss rate of phosphine in the atmosphere in Eq. 1 and the resupplying rate of phosphine by phosphides from volcanoes in Eq. 2 gives us the required volcanic rate of delivery of dust to the stratosphere:

$$E = \frac{4\pi R^2 \text{Hf}(PH_3) \rho_{\text{air}} \mu_{PH_3}}{\tau_{PH_3} \mu_{CO_2} \rho_{\text{mag}} f_{P(3-)} X_P} \quad [3]$$

With all parameters as discussed above, Eq. 3 gives us the volume of lofted volcanic dust needed per year to produce the observed PH_3 . Given the error bar inferred from the new analysis (5) of between 1 and 5 ppb in the tentatively detected abundance of phosphine, this value could range from 0.03 to 0.15 km^3/y for $\tau_{PH_3} = 10^9$ s; and 0.3 to 1.5 km^3/y or 0.03 to 0.15 km^3/mo for $\tau_{PH_3} = 10^8$ s.

2. Is There Sufficient Volcanism on Venus to Produce Enough Phosphide?

The episodic spikes of sulfur dioxide at the cloud tops of Venus and the variation in the amount of submicron haze above the clouds seen by Pioneer Venus data imply the episodic injection of sulfur dioxide, hypothesized to have a volcanic source (16). A rough rule of thumb is that volcanic plumes on Venus rise to 60% of the height that they would in the Earth's atmosphere (16). Eruptions like Krakatau, which may have lofted material as

high as 80 km [although another estimate is 40 km (41)] are a possible analog to Venusian eruptions that might produce a variation of sulfur dioxide at 70 km (16). Our model requires that the phosphides in volcanic dust be lofted to the aerosol layer in order to be converted to phosphine by sulfuric acid. Rampino and Self (41) argue that the amount of very fine dust (<2 μm) lofted by Krakatau was between 0.002 and 0.16 km^3 overlapping what is needed in our calculation (0.03–0.15 km^3) per year for $\tau_{PH_3} = 10^9$ s. Alternatively, for $\tau_{PH_3} = 10^8$ s, that same amount of dust could also supply ~1–5 ppb, but only in a shorter time-scale (approximately months instead of approximately years), so any detected phosphine would be a transient phenomenon. Therefore, explosive volcanism like Krakatau, with eruption volumes of ~10 km^3 , would provide enough buoyancy to supply a sufficient amount of phosphide to generate phosphine in the atmosphere. While other mechanisms to explain the spikes have subsequently been published (42, 43), if the spikes are produced by volcanism, that volcanism would be sufficiently energetic to inject enough phosphide into the sulfuric acid layer to produce 1–5 ppb phosphine.

Putative evidence for explosive volcanism on Venus has also been suggested from morphology and radar backscattering analysis, with some features consistent with pyroclastic flow deposits (44, 45). In the analysis by Ghail and Wilson (44), the total eruption volume was estimated at about 225–875 km^3 , exceeding the volume of the Taupo, Yellowstone, and Toba caldera-forming events; but they also noted that it may have been emplaced in more than one event. The volatile concentrations were estimated to be at least 1.8 wt% H_2O , 4.3% CO_2 , or 6.1 wt% SO_2 , suggesting magma sourced directly from the mantle and a kimberlite-type explosive eruption (44). Since crustal or subducted water is unlikely under Venusian conditions, the volatile source is most likely primordial water in the mantle, concentrated through fractionation (44). Campbell et al. (45) went further and identified several putative pyroclastic flow units in a total area up to 40,000 km^2 with depths of tens of centimeters to a few meters from Magellan and Earth-based radar data. If those are confirmed, it would imply that a portion of the interior of Venus may be relatively volatile-rich. While it is not a unique constraint, Kaula (46) proposed that Venus may have outgassed ^{40}Ar to a lesser extent than on Earth, suggesting an appreciable amount of water has remained in the lower mantle.

Other modeling work also concluded that sufficiently large eruptions on Venus may be capable of producing plumes that rise buoyantly to 70 km, for a sufficiently large amount of volatiles (4–5% H_2O or 3% H_2O with 3% CO_2) (47, 48) crudely consistent with the estimates in the previous paragraph. There exists the possibility that a portion of the mantle may still contain appreciable amounts of volatiles that support an extreme explosive eruption—melts that solidify at depth would retain water on the order of ~1% (48). Volatiles might recycle back into the deep mantle; if Venus formed with a significant volatile reservoir, then no amount of partial melting could entirely deplete the volatiles (49). Finally, by constraining the viscosity of pancake domes from the morphology and the altimetric profiles, magmas consistent with such features may be created by wet melting at depth (50).

Additional observations also support the presence of widespread active volcanism today on Venus (51–53), and others have argued that plume volcanism is very likely to originate from deep in the mantle (17). A high near-infrared emissivity observed by the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) instruments on Venus Express has been interpreted as due to lava flows with young ages, which expose unweathered Fe^{2+} -bearing silicates to view (less than 250,000 y to 2.5 million years depending on the resurfacing model), with the volume of these flow features estimated to range from about 2,350 to

23,500 km³ (52). Rescaling the steady resurfacing model with a rate of 1 km³/y would lead to an age of 25,000 y, the more likely ages for those young flow features (52). Experiments measuring the weathering rate at Venus surface conditions (54–56) support even younger ages of the lava flows identified by Smrekar et al. (52), possibly decades to hundreds of years. VIRTIS emissivity data also show evidence of recent volcanism at Quetzelpetlatl Corona, in which volcanism is on the scale of the Deccan Traps (51, 53). Even with limited coverage, VIRTIS data suggest that regions of recent volcanism on Venus may have produced peak volcanic rates within the past 100 y similar to the peak rate at the Deccan Traps (10 km³/y) (57). If they represent a fortuitous spike in volcanism, this would be consistent with episodic spikes on annual-to-decadal timescales of sulfur dioxide seen in the atmosphere (16, 42), if produced by the same eruptive events that formed the young lava flows.

All observed sites of high emissivity in the VIRTIS data occur in regions that have been identified as locations of mantle plumes (52, 53). Smrekar and Sotin (17) argued that if volcanism is indeed confined to occurring above mantle plumes, it may be because materials must be brought from the deep mantle to enable melting. They also proposed that water from the deep mantle might be required to enable melting, although other factors or volatiles could enable melting. However, regardless of whether or not these are the only locations of present-day volcanism (VIRTIS data cover <50% of the surface) or if water is needed to enable melting, plume volcanism is very likely to originate from deep in the mantle.

Bains et al. (15) point out that even recent catastrophic volcanic events on Earth, such as those associated with the Siberian and Deccan traps only correspond to a peak volcanic rate of 1 km³/y and conclude that it would be highly implausible to sustain phosphide eruption. However, the 1 km³/y value invoked (15) actually corresponds to an average volcanic rate over ~1 My rather than the peak rate. A more recent estimate of the Deccan eruption rate with uranium–lead (U–Pb) geochronology suggests there were four high-volume eruptive periods with a maximum eruption rate of 10 km³/y, occurring right before the Cretaceous–Paleogene extinction (57). For comparison, on average over the last 180 My, the total global extrusive volcanic productivity is 3–4 km³/y (58). We thus conclude that there is evidence supporting recent large volcanic events consistent with very high maximum eruption rates on Venus, and analogous explosive eruptions of the scale needed to inject phosphides have been observed on Earth.

Finally, a better analogy for Venusian volcanism might be Yellowstone rather than Krakatau, since most explosive eruptions like Krakatau occur at a subduction zone; and notwithstanding the limited evidence for subduction on Venus, there is no evidence for water-logged tectonic plates introducing melt to the overriding continental lithosphere. However, we also note that even the analogy to Yellowstone is also not perfect as Yellowstone is a supervolcano formed by a mantle upwelling impinging and fractionally crystallizing within continental crust. A partial analogy for Venus is magmatism caused by sinking of compositionally dense lithospheric material into the mantle (49); the sinking material may carry a range of incompatible elements and may refertilize the mantle with volatiles and eclogite. Melting these new eclogite

sources may allow distinctive subduction-related magmas in the absence of a subduction zone; and in long term, this process of melting and refertilization could produce materials similar to the tonalite–trondjemite–granodiorite provinces, the earliest continental crust on Earth.

It is also worth noting that while extensive studies of Hawaii have formed the basis for models of nonexplosive basaltic volcanism, explosive basaltic eruptions also occur (i.e., Cerro Negro's 1992 eruption) (59). Some basaltic eruptions are now recognized as extremely violent, i.e., generating widespread phreatomagmatic, sub-Plinian and Plinian fall deposits (i.e., the eruption of Tarawera 1886) (60). In those cases, the explosive behavior depends on many other factors other than high viscosity, i.e., the decompression history, the contribution of other volatiles such as CO₂, SO₂ besides water (61), and conduit processes such as the development of largely stagnant and outgassed melt restricting the effective radius of the conduit (60).

On Earth, however, volcanoes are known to be an insignificant source of phosphine. There are two main reasons for the differences between Earth and Venus independent of the volcanism rate or the oxidation state of the mantle: 1) Due to the much less corrosive nature of water on Earth compared to sulfuric acid on Venus, the conversion efficiency of phosphine from phosphide sources is three orders of magnitude lower on Earth than on Venus (19). 2) Because of the much higher concentration of OH radicals in the Earth's troposphere, the lifetime of phosphine in the most stable layer in Earth's atmosphere could be much shorter than that on Venus (62), that is, a few days compared to a few years or decades depending on the value of the eddy diffusion coefficient. Together, those two effects suggest that the same volcanic rate to produce 1–5 ppb in Venusian atmosphere could only generate about 0.6–30 ppq of phosphine on Earth. For comparison, the lowest concentration of phosphine typically detected on the Earth's atmosphere is ~10 ppq (12).

3. Conclusion

Given the ongoing debate about the robustness of the phosphine detection itself, our results only suggest a roadmap to assessing the level of Venusian volcanic activity today. That roadmap begins with additional observations and reassessment of existing claims of detection of phosphine. Beyond ground-based observations, future missions such as those to deploy an aerostat equipped with a mass spectrometer and/or tunable laser spectrometer should also say definitively whether phosphine is present in the Venusian clouds. Should the phosphine be there, it might point to Venus experiencing a modestly elevated epoch of active plume volcanism with magma originating deep in the mantle. That, in turn, would strengthen the case for additional missions to understand the geologic state and history of the planet closest to us in space and bulk physical properties.

Data Availability. All study data are included in the article and/or supporting information.

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1. J. S. Greaves et al., Phosphine gas in the cloud decks of Venus. *Nat. Astron.*, 10.1038/s41550-020-1174-4 (2020).
2. I. A. G. Snellen et al., Reanalysis of the 267-GHz ALMA observations of Venus: No statistically significant detection of phosphine. *A&A* **644**, L2 (2020).
3. M. A. Thompson, The statistical reliability of 267 GHz JCMT observations of Venus: No significant evidence of phosphine absorption. *Mon. Not. R. Astron. Soc.* **501**, L18–L22 (2021).
4. G. Villanueva et al., No phosphine in the atmosphere of Venus. arXiv [Preprint] (2020). <https://arxiv.org/abs/2010.14305> (Accessed 28 October 2020).

5. J. S. Greaves et al., Reanalysis of phosphine in Venus' clouds. arXiv [Preprint] (2020). <https://arxiv.org/abs/2011.08176> (Accessed 16 November 2020).
6. T. Encrenaz et al., A stringent upper limit of the PH₃ abundance at the cloud top of Venus. *Astron. Astrophys.* **643**, L5 (2020).
7. L. Trompet et al., Phosphine in Venus' atmosphere: Detection attempts and upper limits above the cloud top assessed from the SOIR/VEx spectra. *A&A* **645**, L4 (2021).
8. J. S. Greaves et al., On the robustness of phosphine signatures in Venus's clouds. arXiv [Preprint] (2020). <https://arxiv.org/abs/2012.05844> (Accessed 12 October 2020).

9. A. B. Akins *et al.*, Complications in the ALMA detection of phosphine at Venus. *ApJL* **907**, L27 (2021).
10. A. P. Lincowski *et al.*, Claimed detection of PH₃ in the clouds of Venus is consistent with mesospheric SO₂. *ApJL* **908**, L44 (2021).
11. R. Mogul, S. S. Limaye, J. Way, J. A. Cordova Jr, Venus' mass spectra show signs of disequilibrium in the middle clouds. *Geophys. Res. Lett.* **48**, e2020GL091327 (2021).
12. C. Sousa-Silva *et al.*, Phosphine as a biosignature gas in exoplanet atmospheres. *Astrobiology* **20**, 235–268 (2020).
13. J. Roels, W. Verstraete, Biological formation of volatile phosphorus compounds. *Bioreour. Technol.* **79**, 243–250 (2001).
14. C. S. Cockell, S. McMahon, J. F. Biddle, When is life a viable hypothesis? The case of Venusian phosphine. *Astrobiology* **21**, 261–264 (2021).
15. W. Bains *et al.*, Phosphine on Venus cannot be explained by conventional processes. arXiv [Preprint] (2020). <https://arxiv.org/abs/2009.06499> (Accessed 14 September 2020).
16. L. W. Esposito, Sulfur dioxide: Episodic injection shows evidence for active venus volcanism. *Science* **223**, 1072–1074 (1984).
17. S. E. Smrekar, C. Sotin, Constraints on mantle plumes on Venus: Implications for volatile history. *Icarus* **2**, 510–523 (2012).
18. T. Tanaka, Y. Nakamura, A. Mizuike, A. Ono, Simultaneous determination of phosphorus, sulfur and arsenic in steel by hybri generation and gas chromatography. *Anal. Sci.* **12**, 77–80 (1996).
19. J. Geng, R. Zhang, X. Wang, "Chemical origin of phosphine in nature" in *Fourth International Conference on Bioinformatics and Biomedical Engineering (IEEE, 2010)*, pp. 1–12.
20. M. A. Pasek, D. S. Lauretta, 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 (2005).
21. M. A. Pasek, J. M. Sampson, Z. Atlas, Redox chemistry in the phosphorus biogeochemical cycle. *Proc. Natl. Acad. Sci. U.S.A.* **111**, 15468–15473 (2014).
22. L. W. Dartnell *et al.*, Constraints on a potential aerial biosphere on Venus: I. Cosmic rays. *Icarus* **257**, 396–405 (2015).
23. V. A. Krasnopolsky, Chemical composition of Venus clouds. *Planet. Space Sci.* **33**, 109–117 (1985).
24. R. Woo, A. Ishimaru, Eddy diffusion coefficient for the atmosphere of Venus from radio scintillation measurements. *Nature* **289**, 383–384 (1981).
25. R. Woo, J. W. Armstrong, A. J. Kliore, Small-scale turbulence in the atmosphere of Venus. *Icarus* **52**, 335–345 (1982).
26. C. J. Bierson, X. Zhang, Chemical cycling in the Venusian atmosphere: A full photochemical model from the surface to 110 km. *J. Geophys. Res.* **125**, e2019JE006159 (2020).
27. E. Marcq, F. P. Mills, C. D. Parkinson, A. C. Vandaele, Composition and chemistry of the neutral atmosphere of Venus. *Space Sci. Rev.* **214**, 10 (2018).
28. D. J. Frost, C. A. McCammon, The redox state of Earth's mantle. *Annu. Rev. Earth Planet. Sci.* **36**, 389–420 (2008).
29. S. E. Mazza *et al.*, Sampling the volatile-rich transition zone beneath Bermuda. *Nature* **569**, 398–403 (2019).
30. S. E. Mazza *et al.*, Major and Trace Element Data and Sr-Nd-Pb-Hf Isotope Ratios for Bermuda Volcanic Rocks, Version 1.0 (IEDA, 2019).
31. W. L. Griffin *et al.*, Super-reducing conditions in ancient and modern volcanic systems: Sources and behaviour of carbon-rich fluids in the lithospheric mantle. *Mineral. Petrol.* **112**, 101–114 (2018).
32. W. L. Griffin *et al.*, Extreme reduction: Mantle-derived oxide xenoliths from a hydrogen-rich environment. *Lithos* **358–359**, 105404 (2020).
33. J.-X. Huang *et al.*, Immiscible metallic melts in the deep Earth: Clues from moissanite (SiC) in volcanic rocks. *Sci. Bull. (Beijing)* **65**, 1479–1488 (2020).
34. L. A. Taylor, K. C. Misra, B. M. Walker, "Subsolidus reequilibration, grain growth, and compositional changes of native FeNi metal in lunar rocks" in *Proceedings of the Seventh Lunar Science Conference* (Elsevier, 1976), pp. 837–856.
35. J. J. Friel, J. I. Goldstein, A. D. Romig Jr, "The effect of carbon on phosphate reduction" in *Proceedings of the Eighth Lunar Science Conference* (Pergamon Press, 1977), pp. 3941–3954.
36. L. A. Taylor, R. H. Hunter, "The significance of Cl/P₂O₅ ratios from lunar samples" in *Proceedings of the 12th Lunar Science Conference* (Pergamon Press, 1982), pp. 323–331.
37. M. A. Pasek, Phosphorous as a lunar volatile. *Icarus* **255**, 18–23 (2015).
38. M. A. Pasek, Schreibersite on the early earth: Scenarios for prebiotic phosphorylation. *Geoscience Frontiers* **8**, 329–335 (2017).
39. A. Gale *et al.*, The mean composition of ocean ridge basalts. *Geochem. Geophys.* **14**, 489–518 (2013).
40. J. Konzett, D. J. Frost, The high p-T stability of hydroxyl-apatite in natural and simplified MORB—an experimental study to 15 GPa with implications for transport and storage of phosphorous and halogen in subduction zones. *J. Petrol.* **50**, 2043–2062 (2009).
41. M. R. Rampino, S. Self, Historic eruptions of Tambora (1815), Krakatau (1883) and Agung (1963), their stratospheric aerosols, and climatic impact. *Quat. Res.* **18**, 127–143 (1982).
42. E. Marcq, J. L. Bertaux, F. Montmessin, D. Belyaev, Variations of sulphur dioxide at the cloud top of Venus's dynamic atmosphere. *Nat. Geosci.* **6**, 25–28 (2013).
43. P. Kopparla, A. Seshadri, T. Imamura, Y. J. Lee, A recharge oscillator model for interannual variability in Venus' clouds. *J. Geophys. Res. Planets* **125**, e2020JE006568 (2021).
44. R. C. Ghail, L. Wilson, A pyroclastic flow deposit on Venus. *Geo. Soc. London* **401**, 97–106, 10.1144/SP401.1 (2015).
45. B. A. Campbell *et al.*, Pyroclastic flow deposits on Venus as indicators of renewed magmatic activity. *J. Geophys. Res. Planets* **122**, 1580–1596 (2017).
46. W. M. Kaula, Constraints on Venus evolution from radiogenic argon. *Icarus* **139**, 32–39 (1999).
47. L. Glaze, Transport of SO₂ by explosive volcanism on Venus. *J. Geophys. Res. Planets* **104**, 18899–18906 (1999).
48. M. W. Airey *et al.*, Explosive volcanic activity on Venus: The roles of volatile contribution, degassing, and external environment. *Planet. Space Sci.* **113–114**, 33–48 (2015).
49. L. T. Elkins-Tanton *et al.*, Volcanism and volatile recycling on a one-plate planet: Application to Venus. *J. Geophys. Res.* **112**, E04506 (2007).
50. D. McKenzie *et al.*, Pancake-like domes on Venus. *J. Geophys. Res.* **97**, 15967–15976 (1992).
51. M. Ivanov, J. W. Head, Lada Terra rise and Quetzalpetlatl Corona: A region of long-lived mantle upwelling and recent volcanic activity on Venus. *Planet. Space Sci.* **58**, 1880–1894 (2010).
52. S. E. Smrekar *et al.*, Recent hotspot volcanism on Venus from VIRTIS emissivity data. *Science* **328**, 605–608 (2010).
53. A. Davaille, S. E. Smrekar, S. Tomlinson, Experimental and observational evidence for plume-induced subduction on Venus. *Nat. Geosci.* **10**, 349–355 (2017).
54. J. Filiberto, D. Trang, A. H. Treiman, M. S. Gilmore, Present-day volcanism on Venus as evidenced from weathering rates of olivine. *Sci. Adv.* **6**, eaax7445 (2020).
55. K. S. Cutler, J. Filiberto, A. H. Treiman, D. Trang, Experimental investigation of oxidation of pyroxene and basalt: Implications for spectroscopic analyses of the surface of Venus and the ages of lava flows. *Planet. Sci. J.* **1**, 21 (2020).
56. M. D. Dyar *et al.*, Surface weathering on Venus: Constraints from kinetic, spectroscopic, and geochemical data. *Icarus* **358**, 114139 (2021).
57. B. Schoene *et al.*, U-Pb constraints on pulsed eruption of the Deccan Traps across the end-Cretaceous mass extinction. *Science* **363**, 862–866 (2019).
58. J. A. Crisp, Rates of magma emplacement and volcanic output. *J. Volcanol. Geotherm. Res.* **20**, 172–211 (1984).
59. K. Roggensack *et al.*, Explosive basaltic volcanism from Cerro Negro volcano: Influence of volatiles on eruptive style. *Science* **277**, 1639–1641 (1997).
60. B. F. Houghton *et al.*, The influence of conduit processes on changes in style of basaltic Plinian eruptions: Tarawera 1886 and Etna 122 BC. *J. Volcanol. Geotherm. Res.* **137**, 1–14 (2004).
61. C. M. Allison, K. Roggensack, A. B. Clarke, Highly explosive basaltic eruptions driven by CO₂ exsolution. *Nat. Commun.* **12**, 217 (2021).
62. D. Gliedemann, M. Edwards, P. Kusch, Phosphine gas in the upper troposphere. *Atmos. Environ.* **37**, 2429–2433 (2003).