Hypothesis Perspectives: Might active volcanisms today contribute to the presence of phosphine in Venus’s atmosphere?

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**Abstract:** We propose an abiotic geological mechanism that accounts for the abundance of phosphine detected by Greaves et al., 2020. We hypothesize that trace amounts of phosphides formed in the mantle would be brought to the surface by volcanism, and then subsequently ejected into the atmosphere, where they could react with water or sulfuric acid to form phosphine. To investigate the plausibility of this hypothesis, we carry out an order of magnitude calculation. We suggest that active volcanism today could produce a rate comparable to that required to produce the phosphide-source of the phosphine. Our hypothesis requires that Venus be currently experiencing a high rate of basaltic volcanism, one that is consistent with spacecraft observations and laboratory experiments.

1. **Hypothesis**

Greaves et al., 2020 claim a radio detection of phosphine at about ~ 20 ppb abundance in the atmosphere of Venus. These authors investigated potential pathways of formation of phosphine
and conclude that the presence of PH$_3$ at that abundance is difficult to explain by geologic or atmospheric chemistry, invoking the possibility of biology. Given the high oxidation state of the environment, elemental phosphorous in the atmosphere would be highly oxidized (i.e. in the form of phosphate) and the reduction of phosphate would be extremely unfavorable energetically and hence unlikely. Here we propose a geological mechanism for the production of PH$_3$ not considered by Greaves et al. (2020).

We consider production of PH$_3$ from less energetically unfavorable precursors such as P or P$^{3-}$ (phosphide). On Earth, one of the known processes is the production of phosphine gas by aqueous or acid corrosion from phosphorous-containing impurities in iron (Pasek & Lauretta, 2005, Geng et al., 2010). In the Geng et al. (2010) experiment, aqueous corrosion produced a significant amount of phosphine gas comparable to the amount detected in natural terrestrial environments, while sulfuric acid corrosion could produce an amount of phosphine gas three orders of magnitude higher than aqueous corrosion.

Here, we hypothesize that trace amounts of phosphides formed in the mantle would be brought to the surface by volcanism, and then subsequently ejected into the atmosphere, where these species could react with water or sulfuric acid to form phosphine. To investigate the plausibility of this hypothesis, we carry out an order of magnitude calculation.

2. **Constraints on the amount of phosphide needed**
We will first start by calculating the volume of phosphine present in the atmosphere. As a significant fraction (~20 ppb) of the detected phosphine in the atmosphere is at the height of 53-61 km above the surface (Greaves et al., 2020), we calculate the volume of atmosphere in the 8 km layer shell between 53-61 km (Figure 1) as $4\pi R_{\text{Venus}} d_{8\text{km}} = 3.7 \times 10^{18}$ m$^3$ and then scale this value by a fraction of ~20 ppb to get a volumetric abundance of $V_{\text{phosphine}} = (20 \times 10^{-9}) \times V_{53-61 \text{ km}} = 7.3 \times 10^{10}$ m$^3$.

Figure 1. Schematic diagram of Venus’s atmosphere considered in this calculation.

The density of gas in this layer, which has an average atmospheric pressure of about 0.5 bar, and an average temperature of about 60°C (Fig. 1 in Dartnell et al., 2015), is ~0.5 kgm$^{-3}$, so that the total mass of 20 ppb by number of phosphine is ~0.5 x $3.7 \times 10^{18}$ x 20 x $10^{-9}$ x 33/44 = $2.7 \times 10^{10}$ kg.

The destruction rate of phosphine in the atmosphere has been extensively discussed in Greaves et al., 2020, with values ranging from $10^3$ s to $10^8$ s. We shall assume here that, in the layer 53-61 km, phosphine could be stable for their uppermost value-- about a year. Based on this assumption, volcanoes would need to produce ~$2.7 \times 10^{10}$ kg of new phosphide every year to continuously pump into the middle atmosphere, which then react with the sulfuric acid droplets to produce the observed phosphine.

Assuming 0.01% of phosphide in lavas and given the density of basalt of 2900 kgm$^{-3}$, the volume amount of lava needed per year to produce the observed PH$_3$ is ~93 km$^3$. Note that the
total phosphorous content in terrestrial basalt is estimated to be about 0.3-0.5% with a large fraction in more oxidized forms such as phosphate, so our estimate of the fraction of phosphides fraction relative to the total phosphorous content is very conservative, equivalent to ~ 2-3% of the total phosphorous content.

3. Could volcanisms produce enough phosphide (P³⁻ ions)?

A high NIR-emissivity observed by the VIRTIS instruments on Venus Express has been interpreted as due to lava flows with young ages, which expose unweathered Fe²⁺- bearing silicates to view (Smrekar et al., 2010). Age estimates range from younger than 2.5 million years to as little as a tenth that. The volume of these flow features was also estimated to range from about 2350 to 23,500 km³ (Smrekar et al., 2010). The upper age was calculated based on catastrophic resurfacing in the past with little volcanism today (0.01 km³/year) and the highest volume of flow features, while the lower bound corresponds to a steady outgassing rate of 10 km³/year and the smallest volume. Another estimate based on an equilibrium resurfacing model with a rate of 1 km³/year results in ages of 2500 to 25,000 years. However, Smrekar et al. (2010) also note that the upper estimate of 2.5 million years is very conservative, and that the limited laboratory data on weathering rates under Venusian conditions could permit even younger ages.

More recent experiments measuring the weathering rate at Venus surface conditions (Filiberto et al., 2020; Cutler et al., 2020) support even younger ages of the lava flows identified by Smrekar et al., 2010. Under simulated conditions at Venus’s surface, olivines become quickly
coated with alteration products (i.e. hematite) on timescales of weeks to months (Filiberto et al., 2020); pyroxenes would take a longer amount of time, but still only decades to hundreds of years (Cutler et al., 2020). If the unweathered Fe$^{2+}$-bearing silicates are responsible for the high NIR-emissivity of lava flows, these flows might have been formed within years or less. If they represent a fortuitous spike in volcanism, this would be consistent with episodic spikes of sulfur dioxide seen in the atmosphere (Esposito, 1984, Marcq et al., 2013), if produced by the same eruptive events that formed the young lava flow.

The flow rate per year estimated based on the flow volumes calculated by Smrekar et al., 2010 and an upper estimate of a hundred years from the weathering rate experiments ranges from 23 km$^3$/year up to 235 km$^3$/year. As noted by Cutler et al., 2020, it is unlikely that those lavas are fully crystalline and contains no olivine or glass; therefore, it might be possible that the lavas have been on the surface for a shorter timescale than the upper bound estimate. If that is the case, then the volume production rate might be a factor of 10 higher. All these estimates are comparable to the 93 km$^3$/year we calculate as required to produce the phosphide-source of the phosphine.

The Greaves et al., 2020 hypothesis that life is producing PH$_3$ in the clouds of Venus requires both the extraordinary claim that life exists in the clouds, and a mechanism to maintain its viability as droplets in the aerosol layer grown and sink (Seager et al., 2020). Our hypothesis, instead, requires that Venus be currently experiencing a high rate of basaltic volcanism, but one that is consistent with spacecraft observations and laboratory experiments. Rather than pointing to the existence of life in the clouds, we argue that phosphine is pointing to a Venus
that is geologically active today—a conclusion perhaps disappointing to biologists but surely intriguing to planetary scientists.

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Figure 1. Schematic diagram of Venus’s atmosphere considered in this calculation.