

Note

Heavy metal frost on Venus

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Abstract

Chemical equilibrium calculations of volatile metal geochemistry on Venus show that high dielectric constant compounds of lead and bismuth such as PbS (galena), Bi₂S₃ (bismuthite) or Pb–Bi sulfosalts condense in the venusian highlands and may be responsible for the low radar emissivities observed by Magellan and Pioneer Venus. Our calculations also show that elemental tellurium is unstable on Venus' surface and will not condense below 46.6 km. This is over 30 km higher than Maxwell Montes, the highest point on Venus' surface. Elemental analyses of Venus' highlands surface by laser induced breakdown spectroscopy (LIBS) and/or X-ray fluorescence (XRF) can verify the identity of the heavy metal frost on Venus. The Pb–Pb age of Venus could be determined by mass spectrometric measurements of the Pb²⁰⁷/Pb²⁰⁴ and Pb²⁰⁶/Pb²⁰⁴ isotopic ratios in Pb-bearing frosts. All of these measurements are technologically feasible now.

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1. Introduction

Pioneer Venus and Magellan radar observations of Venus' surface reveal a puzzling shift in radar properties at a planetary radius of ~ 6054 km (Pettengill et al., 1982, 1996, 1997; Ford and Pettengill, 1983). Below this altitude and over most of Venus, the radar properties are typical for anhydrous rocks, such as dry basalt. In contrast, higher elevation regions have lower radar emissivity indicating the presence of semiconducting minerals with high dielectric constants (Pettengill et al., 1996). A number of models have been proposed to explain the unusual radar properties of the venusian highlands. Among these are: volumetric scattering from decimeter sized voids in surface rock (Pettengill and Ford, 1993), the presence of a low-loss soil layer (Tryka and Muhleman, 1992), the loading of surface rock with small conductors or dielectrics such as pyrite (Pettengill et al., 1982; Ford and Pettengill, 1983) or perovskite (Fegley et al., 1992), the presence of ferroelectric minerals (Shepard et al., 1994), and the vapor phase deposition of high dielectric constant metallic compounds (Brackett et al., 1995). However, Magellan bistatic radar observations of the Maxwell Montes highlands (Pettengill et al., 1996) are best explained by the metallic frost model (Pettengill et al., 1996; Brackett et al., 1995).

Brackett et al. (1995) proposed that the low emissivity minerals in the venusian highlands are metal halides or chalcogenides produced by volcanic outgassing. Halides and/or chalcogenides of several volatile metals (e.g., Cu, As, Pb, Sb, Bi) occur around terrestrial volcanic vents and fumaroles or are present in volcanic gases (Brackett et al., 1995). Although volcanic outgassing may occur anywhere on Venus' surface, the volatile metals and their compounds only condense in the cooler venusian highlands, which are cold traps for the heavy metal frost.

Pettengill et al. (1996) suggested that the metallic frost is elemental tellurium. Assuming an Earth-like Venus, they calculated that only 0.01% of all Te in Venus' crust and mantle needs to be out-gassed to explain their radar observations. Their mass balance calculation implicitly assumes that tellurium does not react with other volcanic gases or with Venus' atmosphere. However, this assumption is unlikely because Te is not inert, but forms compounds with sulfur, which is observed in Venus' atmosphere as SO₂, OCS, S vapor, and H₂S.

Here we use chemical equilibrium calculations to explore volatile metal chemistry on Venus. It is plausible that volatile metals and their compounds are chemically equilibrated at the high temperatures and pressures of Venus' lower atmosphere. First, chemical equilibrium calculations explain the chemistry of terrestrial volcanic gases and the mineralogy of condensates around volcanic vents and fumaroles down to at least 500 °C (Symonds et al., 1994). Second, the observed abundances of HCl and HF in Venus' atmosphere are the same, within error, as the partial pressures of these gases in equilibrium with Cl- and F-bearing mineral assemblages plausibly present on Venus' surface (Fegley et al., 1997). Preliminary results were presented by Schaefer and Fegley (2003).

2. Methods

We calculated equilibrium chemistry of the volatile metals listed in Table 1 in Venus' atmosphere from –2.6 km (Diana Chasma) to 50.6 km in the vicinity of the global sulfuric acid clouds. Computations were done using a Gibbs free energy minimization code and the Venus International Reference Atmosphere (VIRA) pressure and temperature profile (Seiff et al., 1986). The calculations shown in Fig. 1 included the elements O, C, N, S, H, Cu, Cl, As, Pb, Tl, Se, Br, F, In, Ag, Sb, I, Bi, and Te. We also considered Zn, Ge, Sn, Cd, Hg, and Au. Approximately 660 compounds of the trace metals were considered. Thermodynamic data for the compounds are

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Table 1
Elemental abundances, major gases and condensates of the trace metals

Element	Oceanic crust abundances (ppm) ^a	Major gases	Condensates	Altitude (km) ^b
Cu	86	CuCl, CuBr, CuI	Cu ₂ S CuS	−2.6 to 18.8 > 18.8
Cl	–	HCl, PbCl ₂ , InCl	PbCl ₂ InCl ₃	> 42.6 > 48.6
As	1.0	As ₄ O ₆ , As ₄ S ₄	As ₂ S ₃	> 26.6
Pb	0.8	PbCl ₂ , PbBr ₂	PbS PbBr ₂ PbCl ₂	−2.6 to 42.6 > 42.6 > 42.6
Se	0.16	Se ₂ , SeS, TeSe	Se	> 46.6
Br	0.15	HBr, InBr, PbBr ₂	PbBr ₂ TlBr	> 42.6 > 42.6
F	–	HF, InF, TlF	InF ₃	> 24.6
In	0.072	InBr, InCl, InBr ₂ , InCl ₂	In ₂ O ₃ InF ₃ InCl ₃	−2.6 to 48.6 > 24.6 > 48.6
Ag	0.026	Ag, Ag ₂	Ag ₂ S	> −2.6
Sb	0.017	Sb ₄ O ₆ , SbS, SbSe	Sb ₂ S ₃	> 16.6
I	0.008	HI, I, PbI ₂	–	–
Tl	0.012	TlCl, TlBr, TlI	TlBr	> 42.6
Bi	0.007	BiSe, BiS, Bi	Bi ₂ S ₃	> 1.6
Te	0.003	TeS, TeSe, BiTe, Te ₂	Te	> 46.6

^a ppm = parts per million by mass.

^b Relative to modal radius, 6051.4 km.

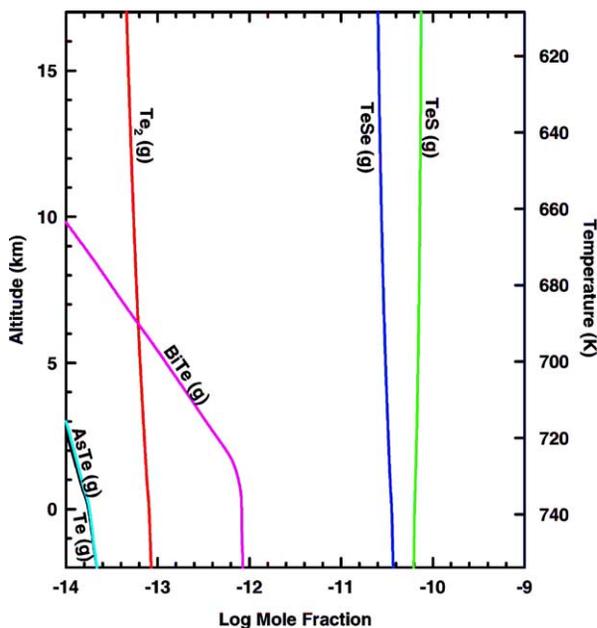


Fig. 1. Tellurium chemistry near the venusian surface as a function of altitude. Elemental tellurium condenses near ~ 46.6 km altitude, which is not shown here.

from the IVTANTHERMO database (Belov et al., 2000, 1999). All altitudes are relative to the modal radius 6051.4 km (0 km level).

We focus here on chemistry below 17 km, which is several km higher than Maxwell Montes. Major element abundances (O, C, N, S, H, Cl, and F) are taken from analyses of Venus' atmosphere (Lodders and Fegley, 1998). Terrestrial basaltic oceanic crustal abundances (Lodders and Fegley, 1998) of the trace metals, Br and I are taken as analogs to Venus' crustal abundances because the crust of Venus is apparently basaltic. We take the same element/sulfur ratio as in the terrestrial oceanic crust normalized to the total

abundance of sulfur in Venus' atmosphere:

$$A_i = n_i \times \frac{A_S}{n_S}, \quad (1)$$

where n_i is the molar abundance of element i in the terrestrial oceanic crust, and A_i is the atomic abundance of element i in ppmv in the venusian atmosphere. We use $A_S = 157.4$ ppmv, and take the terrestrial oceanic crust S abundance as 960 ppm (Alt, 1995). We assume the ideal case of equal degassing efficiencies for all elements.

3. Results

Table 1 summarizes our results. Tellurium is found entirely in the gaseous state and over 99% is TeS (g) and TeSe (g), as shown in Fig. 1. Contrary to the prediction of Pettengill et al. (1996), solid tellurium does not condense until an altitude of ~ 46.6 km for our nominal abundance model. To produce tellurium frost at 2.6 km, we required a very large tellurium abundance of ~ 182 parts per million (ppm), which is $\sim 60,000$ times larger than the Te abundance in Earth's basaltic oceanic crust and is geochemically implausible. This abundance is similar to the oceanic crustal abundances of Cl and Ni, and is larger than the Te abundance in the undifferentiated CI chondrites or in any terrestrial, lunar, or meteoritic basalt (Lodders and Fegley, 1998; Lodders, 1998; Kitts and Lodders, 1998). Considering the actual degassing efficiencies for tellurium makes matters worse. A survey of the volcanic gas literature shows that Te is less efficiently out-gassed than S (Greenland and Aruscavage, 1986; Taran et al., 1995). Thus, the actual Te abundance required for elemental Te condensation at 2.6 km on Venus is substantially larger than ~ 182 ppm. We therefore conclude tellurium frost cannot be the high dielectric material found in the highlands because of its low abundance and thermodynamic instability.

We next considered condensates of the other trace metals studied, shown in Fig. 2. Copper condenses over Venus' entire surface as Cu₂S (chalcocite) and converts to CuS (covellite) at an altitude of ~ 19 km. Other condensates that are stable at all elevations (i.e., above -2.6 km) include Ag₂S (acanthite), In₂O₃ and PbS (galena). Bismuthite (Bi₂S₃) condenses at an altitude of ~ 1.6 km and stibnite (Sb₂S₃) condenses at ~ 16.6 km. Of these

Table 2
Dielectric constants

Materials	Dielectric constant (ϵ') ^a	T/K	Frequency	Reference
Venus' highlands	~ 100	650–720	~ 2.3 GHz	Pettengill et al. (1996)
PbS	190	77	IR	Young and Frederikse (1973)
Bi ₂ S ₃	~ 108	~ 720	30 GHz	Lukaszczwicz et al. (1999)

^a The dielectric constant is the real part of the complex emissivity ϵ , where $\epsilon = \epsilon' + i\epsilon''$.

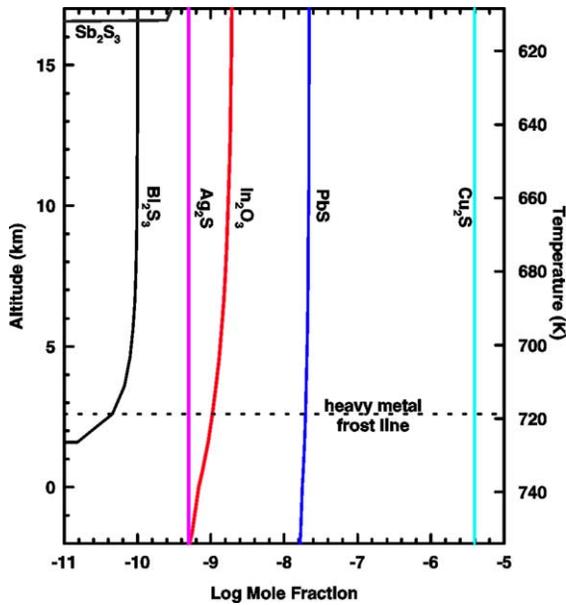


Fig. 2. Trace metal condensates for conditions near the venusian surface as a function of altitude. The x axis represents the molar fractional abundance of the trace metal condensates relative to the total venusian atmosphere (i.e., relative to CO₂ + N₂). For our nominal abundance model, PbS (galena) condenses at the surface and Bi₂S₃ (bismuthite) condenses at 1.6 km. Decreasing the abundances of Bi and Pb causes galena and bismuthite to condense at 2.6 km.

compounds, only galena and bismuthite have both dielectric constants high enough to be interesting (see Table 2) and reasonable abundances.

Figures 3 and 4 show the lead and bismuth chemistry for our nominal abundances as a function of altitude near the venusian surface. The major lead species for our nominal abundance model are galena and PbCl₂ (g), and the major bismuth species are BiSe (g) and BiS (g) until bismuthite condenses at ~ 1.6 km. Galena and bismuthite will condense at 2.6 km if the Pb and Bi elemental abundances are decreased. The Bi abundance must be decreased from 7 parts per billion (ppb) to 4 ppb and the Pb abundance must be reduced by a factor of ~ 9 to ~ 86 ppb. These values are less than those for Bi and Pb in the terrestrial oceanic crust, but they are within the range of Bi and Pb abundances for eucrites, basaltic meteorites that may also serve as an analog to the venusian crust (Kitts and Lodders, 1998).

4. Discussion

4.1. Lead and bismuth

4.1.1. Abundances

It is easy to rationalize why Bi and Pb may be depleted on Venus relative to Earth. If Venus formed in a higher temperature region of the solar nebula it accreted fewer volatiles than the Earth (Lewis and Prinn, 1984). This possibility is supported by comparisons of the Hg budgets of Venus and Earth, with Venus having less than ~ 0.6% of the terrestrial Hg abun-

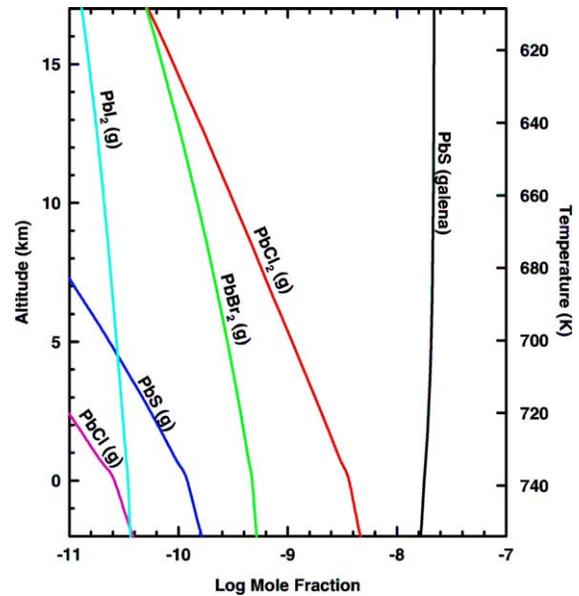


Fig. 3. Lead chemistry near the venusian surface as a function of altitude. Galena is stable at all surface conditions.

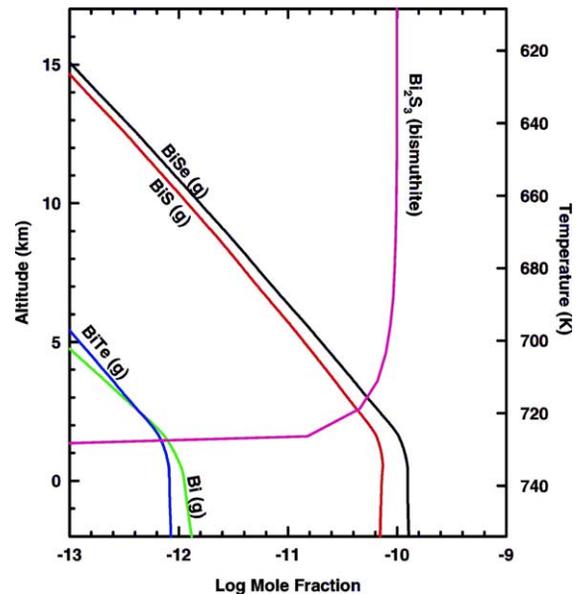


Fig. 4. Bismuth chemistry near the venusian surface as a function of altitude. Bismuthite condenses at ~ 1.6 km, which is close to the heavy metal frost line.

dance. We used the upper limit of Hg in Venus' atmosphere from Venera 11/12 given by Barsukov et al. (1981) for the Hg budget of Venus because Hg is so volatile that it should be entirely in the atmosphere. The terrestrial

Hg budget was determined from values for the oceanic crust by Taylor and McLennan (1985) and for the continental crust from Wedepohl (1995).

Another possible explanation is that out-gassing on Venus is less efficient than on the Earth. Measurements of ^{40}Ar in Venus' atmosphere and of K in Venus' surface support this argument. Modeling using these geochemical data suggest that only $\sim 24\%$ of ^{40}Ar has been out-gassed from Venus' mantle compared with $\sim 52\%$ on Earth (Kaula, 1999). It is also possible that Venus is both depleted in volatiles relative to Earth and has less efficient out-gassing. These arguments suggest that the terrestrial trace metal abundances we chose for our model are likely overestimates, so reducing the abundances of Bi and Pb to form heavy metal frost at 2.6 km is reasonable. The dielectric constants and abundances of bismuthite and galena therefore make these two compounds good candidates for the high dielectric surface material.

4.1.2. Lead-bismuth sulfosalts

Near terrestrial fumaroles, lead and bismuth often condense together to form lead, bismuth sulfosalts such as galenobismutite (PbBiS_4), lillianite (Pb_3BiS_6), cannizzarite ($\text{Pb}_4\text{Bi}_5\text{S}_{11}$), and cosalite ($\text{Pb}_2\text{Bi}_2\text{S}_5$) (Borodaev et al., 2000, 2001). If present on Venus, these compounds may contain large amounts of Cu, Ag, and Cd, which also form stable condensates at venusian surface conditions. Several other sulfosalts of the elements Pb, Bi, Cu, Ag, As, and Sb also form as volcanic condensates and cannot be ruled out as the heavy metal frost on Venus. A lack of thermodynamic data for these compounds prevents us from including them in our calculations, but it seems plausible that these compounds may also form in the venusian highlands. Experimental determination of the thermodynamic and dielectric properties of lead-bismuth sulfosalts and associated minerals are necessary to determine whether these minerals could produce the observed shift in emissivities.

4.2. Upper critical boundary for the high dielectric material

One of the most puzzling aspects of the highland radar data is that at the highest elevations the dielectric constant drops back to values consistent with bare rock. Some of these summit areas, such as Ovda, Atla, and Beta Regiones, also seem to have a porous surficial deposit with a low dielectric constant (Campbell et al., 1999). The perovskite model for the high dielectric material explains these regions by weathering of perovskite (CaTiO_3) to fluorite (CaF_2) plus rutile (TiO_2) through reaction with HF (g). This reaction produces a significant decrease in volume, leading to an increase in the porosity of the rock (Fegley et al., 1992).

As noted by Fegley et al. (1997), the metallic frost layers can be covered and/or vaporized by fresh volcanic flows, which should display normal radar emissivity. From the work of Brackett et al. (1995), we can estimate a time scale for the deposition of the metallic frost on the order of several thousand to several million years, which limits the possible age of the dark regions at the highest elevations. The longer end of this time range should be sufficient for weathering to occur. It is conceivable that perovskite is present in some of the freshly placed lavas in some regions and is being weathered, or it may be that an entirely different suite of minerals is being weathered. However, it is beyond the scope of this paper to examine such reactions.

4.3. Lead-lead dating

We propose that lead condensed in the venusian highlands is a representative sample of venusian lead, just as Pb in oceanic sediments is apparently a representative sample for terrestrial lead (Patterson, 1956). Therefore, it should be possible to determine the age of Venus by measuring the $\text{Pb}^{207}/\text{Pb}^{204}$ and $\text{Pb}^{206}/\text{Pb}^{204}$ lead isotopic ratios in the heavy metal frost. The basic assumptions for Pb–Pb dating of Venus are that the Holmes–Houtermans model is appropriate (Holmes, 1946; Houtermans, 1953), and that primordial lead for Venus, like the Earth and Moon, is given by the meteoritic value. An updated version of the Viking mass spectrometer should be suitable for performing such a measurement (Nier, 1989). In principle, a Pb–Pb age should be easier to measure (than Rb–Sr or Nd–Sm ages) with

a spacecraft mass spectrometer because the Pb isotopes are relatively free of isobaric interferences from other stable nuclides, and there is no need for chemical separations prior to mass spectrometric measurements.

We have tested our proposal by computing Pb–Pb ages for terrestrial Pb-bearing volcanic condensates analyzed by Houtermans et al. (1964). The average Pb–Pb age is about 4.4 billion years, even though their samples do not fulfill all the requirements of the Holmes–Houtermans model. Nevertheless, our results show that Pb–Pb dating of small samples of volcanic condensates can be done using circa 1963 technology.

5. Summary

In conclusion, our calculations indicate that elemental tellurium does not condense in the venusian highlands and cannot be the low radar emissivity frost. We propose instead that galena, bismuthite or a lead bismuth sulfosalts is responsible for the emissivities observed in the highlands, although sulfosalts of other volatile metals cannot be ruled out. The condensation of Pb and/or Bi sulfides at 2.6 km elevation on Venus is consistent with Venus being volatile-depleted, or less efficiently outgassed, or both, relative to the Earth. High temperature laboratory measurements at radar frequencies of the dielectric properties of galena, bismuthite, and lead bismuth sulfosalts that are vapor deposited on basalt could tell us if these compounds match the radar observations. A lander spacecraft equipped with X-ray fluorescence spectroscopy (XRF) and/or laser induced breakdown spectroscopy (LIBS) could make elemental analyses and determine if heavy metal frost covers the highlands of Venus (Sakurai, 2000; Cremers et al., 2002). Finally, it should be possible to measure the Pb–Pb age of Venus using a spacecraft mass spectrometer, such as an updated version of the Viking mass spectrometer.

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