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Article:

Egan, J.E., Feng, W., James, A.D. et al. (Accepted: 2026) Ferric chloride: the Venusian unknown UV absorber? *Journal of Geophysical Research: Planets*. ISSN: 2169-9097 (In Press)

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Ferric chloride: the Venusian unknown UV absorber?

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Key points

- ~1 wt% FeCl₃ in the Venusian clouds can reproduce the observed near-UV absorption, consistent with descent probe measurements.
- FeCl₃ can be produced from Fe ablated from cosmic dust above 100 km, and atmospheric HCl and Cl.
- The best fit to observations occurs when FeCl₃ is mostly present in mode 1 cloud droplets.

Abstract

Near-ultraviolet imaging of the planet Venus reveals inhomogeneous absorption features in the otherwise bright clouds. This absorption has been studied for nearly 100 years, but identification of the near-UV absorber remains one of the largest open questions in Venusian research. Based on a multiple scattering radiative transfer model, the observed absorption between 300 and 600 nm can be produced by 1.0 – 1.2 wt% ferric chloride (FeCl_3) in the mode 1 ($\sim 0.2 \mu\text{m}$ radius) sulfuric acid cloud droplets – less than the in-cloud iron mass loading measured during the Venera-12 mission. We present a novel chemical network within a global chemistry-climate model, which provides the required source of FeCl_3 in the upper cloud region from the reaction of Fe-containing molecules, produced by the ablation of cosmic dust particles, with atmospheric HCl. A residence lifetime of ~ 3000 years is required to provide sufficient optical absorption from a purely meteoric source of FeCl_3 .

Plain language summary

Iron chloride has been proposed to cause the strong absorption seen in Venus's clouds. Using computer modeling of light in the atmosphere, we test the effect of iron chloride in the droplets that make up the Venusian clouds. We find that a modest concentration of 1.0 – 1.2 % (by mass) in the smallest cloud droplets can reproduce the shape and strength of the absorption recorded by the MESSENGER spacecraft. We present chemical reactions that produce iron chloride from the reaction of atmospheric hydrochloric acid gas and iron atoms produced from vapourised cosmic dust, and estimate that the iron chloride would take approximately 3000 years to concentrate enough to match observations of the clouds.

Index terms and keywords

6295 Venus; 5405 Atmospheres; 3337 Global Climate Models; 3359 Radiative Processes; 0317

Chemical Kinetics and photochemical properties

Venus; unknown UV absorber; FeCl_3 ; meteoric material, atmospheric modelling

1. Introduction

The Venusian cloud deck is known to consist of a persistent multimodal system of cloud droplets, composed predominantly of concentrated sulfuric acid (Esposito et al., 1983; Knollenberg & Hunten, 1980; Titov et al., 2018). Sulfuric acid is bright when viewed at near-ultraviolet (NUV) wavelengths; however, spectra and images of the cloud tops show strongly-absorbing regions, spanning wavelengths between 300 – 600 nm, at most latitudes (e.g. Crisp, 1986; Lee et al., 2022; Pérez-Hoyos et al., 2018; Ross, 1928; Rossow et al., 1980; Wright, 1927). Many sulfur-containing candidates have been proposed to account for the NUV absorption, including polysulfur (Francés-Monerris et al., 2022; Hapke &

Graham, 1989; Pinto et al., 2021), polysulfur oxide (Hapke & Graham, 1989; Pinto et al., 2021), and iron-sulfur minerals (Jiang et al., 2024), but none have been conclusively identified as the cause of the absorption. The identification of the “unknown UV absorber” remains one of the largest open questions in Venusian atmospheric research (Crisp, 1986; Titov et al., 2018).

Ferric chloride (FeCl_3) has also been proposed as a candidate for the unknown absorber (Krasnopolsky, 2017; Kuiper, 1969; Zasova et al., 1981). Zasova et al. (1981) suggested that 1 wt% FeCl_3 in the mode 2 ($\sim 1 \mu\text{m}$ radius) sulfuric acid cloud droplets would satisfactorily match the observed planetary albedo, but did not provide their reference spectrum of FeCl_3 . Comparisons of the relative agreement of different absorber candidates with measured spectra therefore used an absorption spectrum of FeCl_3 which was not measured under Venusian conditions (Aoshima et al., 2013; Pérez-Hoyos et al., 2018), and gave poor agreement with the Venusian spectrum, leading to the rejection of FeCl_3 as a candidate compared to other species. While some proposed candidates for the absorber have similar spectral shapes, none have yet been able to reproduce the precise spectrum of the NUV absorption at reasonably achievable atmospheric concentrations (e.g. Egan et al., 2025a; Jiang et al., 2024; Lefèvre et al., 2026; Pérez-Hoyos et al., 2018; Pinto et al., 2021; Skog et al., 2024). A recent measurement of the absorption spectrum of FeCl_3 in sulfuric acid (Egan et al., 2025b) showed much improved agreement of the FeCl_3 spectrum to that of the unknown absorber, compared with previous FeCl_3 spectra available in the literature. Furthermore, re-analysis of data from the Pioneer Venus Large Probe Gas Chromatograph (Mogul et al., 2025) revealed high concentrations of iron in the clouds, similar to reported X-ray fluorescence measurements of iron from Venera 12 (Petryanov et al., 1981). In light of the combination of observed high iron concentrations and the availability of a more applicable FeCl_3 spectrum, the suitability of FeCl_3 to provide significant NUV absorption should be reconsidered.

Here we investigate whether there is a feasible source of Fe from meteoric ablation, and chemical pathways to produce enough FeCl_3 in the upper clouds, to reproduce the observed NUV features in the reflectance spectrum of Venus. The possibility of a meteoric component to the NUV absorber has been suggested in the past (Knollenberg & Hunten, 1979; Pollack et al., 1979), though small fragments of meteoric material were considered, rather than the products of ablated (i.e. vaporized) elements. In addition, the role of meteoric material was recently investigated by Karyu et al. (2026), who found that ablated cosmic dust particles drive the formation of the lower haze, and can act as condensation nuclei for the main cloud deck. Studies of the atmospheres of Earth and Mars (Carrillo-Sánchez et al., 2020; Crismani et al., 2017; Gómez Martín et al., 2017; Grebowsky et al., 2017; Plane, 2003a; Plane et al., 2018a; Plane et al., 2015) have shown that the ablation of cosmic dust particles from comets and asteroids injects a variety of metals (Fe, Mg, Na, etc.) into the atmospheres of the terrestrial planets. The Fe meteoric input function for Venus has been estimated using an astronomical dust model

coupled to a chemical ablation model (Carrillo-Sánchez et al., 2020). Here we then model the production of FeCl_3 from the reaction of meteoric Fe-containing molecules (primarily carbonates) and chlorine-containing species (HCl , Cl) of presumably volcanic origin, using a new chemical network implemented in the Venus Planetary Climate Model (V-PCM) (Gilli et al., 2021; Martinez et al., 2024; Martinez et al., 2023; Stolzenbach et al., 2023). The required concentration of FeCl_3 to reproduce the observed top-of-atmosphere (TOA) reflectance is estimated using the multiple scattering radiative transfer model SOCRATES (Egan et al., 2025a; Manners et al., 2022a, 2022b), from which the residence lifetime of FeCl_3 in the upper clouds can be estimated.

2. Modelling

Two modelling approaches are used in this study: the chemical network for the formation of gas phase FeCl_3 from meteoric Fe was studied using a 3D global climate model (Section 2.1). A separate 1D radiative transfer model (Section 2.2) was run to predict the required FeCl_3 concentration in the clouds to reproduce observations.

2.1 Photochemical modelling

3D photochemical modelling was performed using the V-PCM (e.g., Garate-Lopez & Lebonnois, 2018; Martinez et al., 2024; Martinez et al., 2023; Stolzenbach et al., 2023), version r3188. A horizontal grid size of $1.875^\circ \times 3.75^\circ$ was used, with 90 pressure levels from the surface to 8×10^{-9} Pa, ~ 250 km, resulting in model layers of 2 – 3 km thickness through the clouds. The model was initialised with steady-state conditions from the Venus Climate Database v2.3 (Martinez et al., 2024), available at <http://www-venus.lmd.jussieu.fr/>). For illustrative purposes, the equatorial mean of the initial temperature, vertical diffusion coefficient, and mixing ratios of relevant species are shown in Figure S1 (Supplemental Information, SI). The model was run for 3.0 Venus solar days (Vd).

The ablation of meteoric material in the atmosphere provides a flux of many metals, including iron, into the upper atmosphere. The ablated Fe injection rate of 4.09 t d^{-1} from Carrillo-Sánchez et al. (2020) was adopted, with 72% injected as Fe and the remainder as Fe^+ . Note that the evaporating Fe atoms initially have essentially the same velocity as the parent meteoroid from which they ablate. The first (hyperthermal) collision with the main atmospheric constituent (CO_2) can then lead to ionization with a probability that increases with increasing velocity (Janches et al., 2017), and also reaction to produce $\text{FeO} + \text{CO}$ (as investigated previously for the ablation of Mg (Plane et al., 2018b)). FeO will be quickly reduced to Fe by reaction with O or CO (Table 1). Further collisions with CO_2 of any surviving translationally hot Fe atoms will rapidly quench them (within typically 10 collisions) to the temperature of the background atmosphere, so that further chemistry will involve thermal reactions.

The Fe chemistry network added to the V-PCM is shown in Table 1 and Figure 1. Novel reactions, which have not been included previously in models of Fe in the upper atmospheres of Earth (Feng et al., 2013) or Mars (Whalley & Plane, 2010), are identified by footnote 5 in Table 1. The rate coefficients for these reactions were calculated using electronic structure (ab initio quantum) theory combined with statistical rate theories (Frisch et al., 2016; Georgievskii & Klippenstein, 2005; Gilbert & Smith, 1990; Glowacki et al., 2012; Montgomery et al., 2000; Scalmani et al., 2006; Smith, 1980; Tobiska et al., 2000), described in detail in the SI. For ease of reproduction, both the full polynomial forms of the reaction coefficients for reactions 5 and 9 and a simplified Kooij form that may be more readily implemented in other photochemical models are provided. The calculation of the photolytic rate coefficients and the photodissociation threshold wavelengths for each photochemically active species are also described in the SI.

We have extensively used these theoretical methods of rate coefficient calculation to fit measured rate coefficients for reactions of both neutral and ionized metal atoms, oxides and hydroxides with atmospheric species, reactions which often occur over multi-well potential energy surfaces (e.g. Bones et al., 2020; Gómez-Martín et al., 2017; Mangan et al., 2020; Plane, 2003b). While this experience means that we expect a rate coefficient estimated purely theoretically to be uncertain perhaps within a factor of 2, the important first step is to establish whether the reaction is likely to be important at low temperatures (< 300 K in the case of Venus's upper atmosphere). This means that the overall reaction should be exothermic and that any barriers between local minima are submerged with respect to the entrance channel. Global mean mixing ratios of key iron species after three Venus solar days are shown in Figure 2. Profiles of all iron species are shown in Figure S2 (SI). Cross-sections of photolytically active species are shown in Figure S5 (SI).

140 **Table 1.** Fe chemistry network in the V-PCM.

No.	Reaction	Rate Coefficient ^a	Note
Neutral reactions			
1	$\text{Fe} + \text{O}_3 \rightarrow \text{FeO} + \text{O}_2$	$3.4 \times 10^{-10} \exp(-146/T)$	1
2	$\text{FeO} + \text{O} \rightarrow \text{Fe} + \text{O}_2$	$4.6 \times 10^{-10} \exp(-350/T)$	2
3	$\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$	$1.2 \times 10^{-13} (T/300)^{2.307} \exp(-820/T)$	3
4	$\text{FeO} + \text{O}_3 \rightarrow \text{FeO}_2 + \text{O}_2$	$3.0 \times 10^{-10} \exp(-177/T)$	4
5	$\text{FeO} + \text{CO}_2 (+\text{M}) \rightarrow \text{FeCO}_3$	$\log_{10}(k_{\text{rec},0}) = \log_{10}(2)$ $- 37.87 + 7.074 \log_{10} T - 1.649 (\log_{10} T)^2$ or $2.67 \times 10^{-30} (T/300)^{-2.53} \exp(-410/T)$	4
6	$\text{FeO}_2 + \text{O} \rightarrow \text{FeO} + \text{O}_2$	$1.4 \times 10^{-10} \exp(-580/T)$	2
7	$\text{FeO}_2 + \text{CO}_2 (+\text{M}) \rightarrow \text{OFeCO}_3$	$1.3 \times 10^{-30} (T/300)^{-4.06}$	5
8	$\text{OFeCO}_3 + \text{O} \rightarrow \text{FeCO}_3 + \text{O}_2$	$2.0 \times 10^{-10} (T/300)^{0.167}$	5
9	$\text{FeCO}_3 + \text{CO}_2 (+\text{M}) \rightarrow \text{FeCO}_3 \cdot \text{CO}_2$	$\log_{10}(k_{\text{rec},0}) = \log_{10}(2) - 51.8343$ $+ 26.43 \log_{10} T - 6.335 (\log_{10} T)^2$ or $5.78 \times 10^{-24} (T/300)^{-8.67} \exp(-1173/T)$	5
10	$\text{FeCO}_3 \cdot \text{CO}_2 + \text{O} \rightarrow \text{OFeCO}_3 + \text{CO}_2$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
11	$\text{FeCO}_3 \cdot \text{CO}_2 (+\text{M}) \rightarrow \text{FeCO}_3 + \text{CO}_2$	$k_9 / (6.78 \times 10^{-25} \exp(13387/T))$	5
12	$\text{FeCO}_3 + \text{HCl} \rightarrow \text{HOFeCl} + \text{CO}_2$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
13	$\text{FeCO}_3 \cdot \text{CO}_2 + \text{HCl} \rightarrow \text{HOFeCl} + 2\text{CO}_2$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
14	$\text{HOFeCl} + \text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{O}$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
15	$\text{FeCO}_3 + \text{Cl} \rightarrow \text{OFeCl} + \text{CO}_2$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
16	$\text{FeCO}_3 \cdot \text{CO}_2 + \text{Cl} \rightarrow \text{OFeCl} + 2\text{CO}_2$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
17	$\text{OFeCl} + \text{Cl} \rightarrow \text{FeCl}_2 + \text{O}$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
18	$\text{FeCl} + \text{O}_3 \rightarrow \text{OFeCl} + \text{O}_2$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
19	$\text{FeCl}_2 \cdot \text{H}_2\text{O} + \text{Cl} \rightarrow \text{FeCl}_3 + \text{H}_2\text{O}$	$2.0 \times 10^{-10} (T/200)^{0.167}$	5
20	$\text{FeCl}_2 + \text{H}_2\text{O} (+\text{M}) \rightarrow \text{FeCl}_2 \cdot \text{H}_2\text{O}$	$8.6 \times 10^{-26} (T/200)^{-5.06}$	5
21	$\text{FeCl}_3 + \text{CO}_2 (+\text{M}) \rightarrow \text{FeCl}_3 \cdot \text{CO}_2$	$1.2 \times 10^{-28} (T/200)^{-6.53}$	5
22	$\text{FeCl}_3 \cdot \text{CO}_2 (+\text{M}) \rightarrow \text{FeCl}_3 + \text{CO}_2$	$5.1 \times 10^{-8} \exp(-3012/T)$	5
Ion-molecule reactions			
23	$\text{Fe}^+ + \text{O}_3 \rightarrow \text{FeO}^+ + \text{O}_2$	$7.1 \times 10^{-10} \exp(-129/T)$	6
24	$\text{FeO}^+ + \text{O} \rightarrow \text{Fe}^+ + \text{O}_2$	3.2×10^{-11}	7
25	$\text{FeO}^+ + \text{CO} \rightarrow \text{Fe}^+ + \text{CO}_2$	1.6×10^{-10}	7
26	$\text{FeO}^+ + \text{CO}_2 (+\text{M}) \rightarrow \text{FeO}^+ \cdot \text{CO}_2$	$3.2 \times 10^{-27} (T/300)^{-3.11}$	5
27	$\text{Fe}^+ + \text{CO}_2 (+\text{M}) \rightarrow \text{Fe}^+ \cdot \text{CO}_2$	$8.1 \times 10^{-29} (T/300)^{-2.31}$	8
28	$\text{Fe}^+ \cdot \text{CO}_2 + \text{CO}_2 (+\text{M}) \rightarrow \text{Fe}^+ \cdot (\text{CO}_2)_2$	$4.6 \times 10^{-28} (T/300)^{-5.38}$	5
29	$\text{Fe}^+ \cdot \text{CO}_2 + \text{O} \rightarrow \text{FeO}^+ + \text{CO}_2$	4.6×10^{-10}	5
30	$\text{Fe}^+ \cdot (\text{CO}_2)_2 + \text{O} \rightarrow \text{FeO}^+ \cdot \text{CO}_2 + \text{CO}_2$	5.0×10^{-10}	5
31	$\text{FeO}^+ \cdot \text{CO}_2 + \text{CO}_2 (+\text{M}) \rightarrow \text{FeO}^+ \cdot (\text{CO}_2)_2$	$2.3 \times 10^{-26} (T/300)^{-5.52}$	5

32	$\text{FeO}^+.\text{CO}_2 + \text{O} \rightarrow \text{FeO}_2^+ + \text{CO}_2$	$7.0 \times 10^{-11} (T/300)^{-0.33}$	5
33	$\text{FeO}^+.\text{CO}_2 + \text{O} \rightarrow \text{Fe}^+.\text{CO}_2 + \text{O}_2$	$3.1 \times 10^{-10} (T/300)^{0.03}$	5
34	$\text{FeO}_2^+ + \text{O} \rightarrow \text{FeO}^+ + \text{O}_2$	6.3×10^{-11}	7
35	$\text{FeO}^+ + \text{e}^- \rightarrow \text{Fe} + \text{O}$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	9
36	$\text{FeO}_2^+ + \text{e}^- \rightarrow \text{Fe} + \text{O}_2$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	10
37	$\text{Fe}^+.\text{CO}_2 + \text{e}^- \rightarrow \text{Fe} + \text{CO}_2$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	10
38	$\text{Fe}^+.(\text{CO}_2)_2 + \text{e}^- \rightarrow \text{Fe} + \text{CO}_2 + \text{CO}_2$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	10
39	$\text{FeO}^+.\text{CO}_2 + \text{e}^- \rightarrow \text{FeO} + \text{CO}_2$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	10
40	$\text{FeO}^+.(\text{CO}_2)_2 + \text{e}^- \rightarrow \text{FeCO}_3 + \text{CO}_2$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	10
41	$\text{FeO}_2^+.\text{CO}_2 + \text{e}^- \rightarrow \text{FeO}_2 + \text{CO}_2$	$5.5 \times 10^{-7} (T/300)^{-0.5}$	10
42	$\text{FeO}^+.(\text{CO}_2)_2 + \text{O} \rightarrow \text{FeO}_2^+.\text{CO}_2 + \text{CO}_2$	$3.1 \times 10^{-10} (T/300)^{0.03}$	5
43	$\text{Fe} + \text{O}_2^+ \rightarrow \text{Fe}^+ + \text{O}_2$	1.1×10^{-9}	11
44	$\text{Fe} + \text{NO}^+ \rightarrow \text{Fe}^+ + \text{NO}$	9.2×10^{-10}	11
45	$\text{FeCO}_3 + \text{O}_2^+ \rightarrow \text{FeO}^+.\text{CO}_2 + \text{O}_2$	1.0×10^{-9}	12
46	$\text{FeCO}_3 + \text{NO}^+ \rightarrow \text{FeO}^+.\text{CO}_2 + \text{NO}$	1.0×10^{-9}	12
47	$\text{FeCO}_3.\text{CO}_2 + \text{O}_2^+ \rightarrow \text{FeO}^+.(\text{CO}_2)_2 + \text{O}_2$	1.0×10^{-9}	12
48	$\text{FeCO}_3.\text{CO}_2 + \text{NO}^+ \rightarrow \text{FeO}^+.(\text{CO}_2)_2 + \text{NO}$	1.0×10^{-9}	12
49	$\text{Fe}^+ + \text{e}^- \rightarrow \text{Fe} + h\nu$	$6.5 \times 10^{-12} (T/300)^{-0.51}$	13
Photochemical reactions			
50	$\text{Fe} + h\nu \rightarrow \text{Fe}^+ + \text{e}^-$	3.2×10^{-6}	14
51	$\text{FeCl} + h\nu \rightarrow \text{Fe} + \text{Cl}$	0.15	5
52	$\text{FeCl}_2 + h\nu \rightarrow \text{FeCl} + \text{Cl}$	2.0×10^{-3}	5
53	$\text{FeCl}_3 + h\nu \rightarrow \text{FeCl}_2 + \text{Cl}$	2.3×10^{-2}	5
54	$\text{FeCO}_3 + h\nu \rightarrow \text{FeO} + \text{CO}_2$	0.17	5
55	$\text{FeCl}_3.\text{CO}_2 + h\nu \rightarrow \text{FeCl}_3 + \text{CO}_2$	0.41	5
56	$\text{FeCO}_3.\text{CO}_2 + h\nu \rightarrow \text{FeO} + 2\text{CO}_2$	0.20	5
57	$\text{OFeCO}_3 + h\nu \rightarrow \text{FeO}_2 + \text{CO}_2$	0.34	5

^a Units: photolysis reactions, s⁻¹; bimolecular reactions, cm³ molecule⁻¹ s⁻¹; termolecular, cm⁶ molecule⁻² s⁻¹.

1. Helmer and Plane (1994). 2. Self and Plane (2003). 3. A best fit using Transition State Theory to the literature rate coefficients for the reverse reaction, $\text{Fe} + \text{CO}_2 \rightarrow \text{FeO} + \text{CO}$ (Giesen et al., 2002; Smirnov, 2008). 4. Rollason and Plane (2000). 5. This work (see text and SI). 6. Rollason and Plane (1998). 7. Woodcock et al. (2006). 8. Vondrak et al. (2006). 9. Bones et al. (2016). 10. Set to the measured rate coefficient for $\text{FeO}^+ + \text{e}^-$ (Bones et al., 2016). 11. Rutherford and Vroom (1972). 12. Set to a typical charge transfer rate coefficient cf. reactions 43 and 44. 13. Nahar et al. (1997). 14. Whalley and Plane (2010), rescaled for Venus.

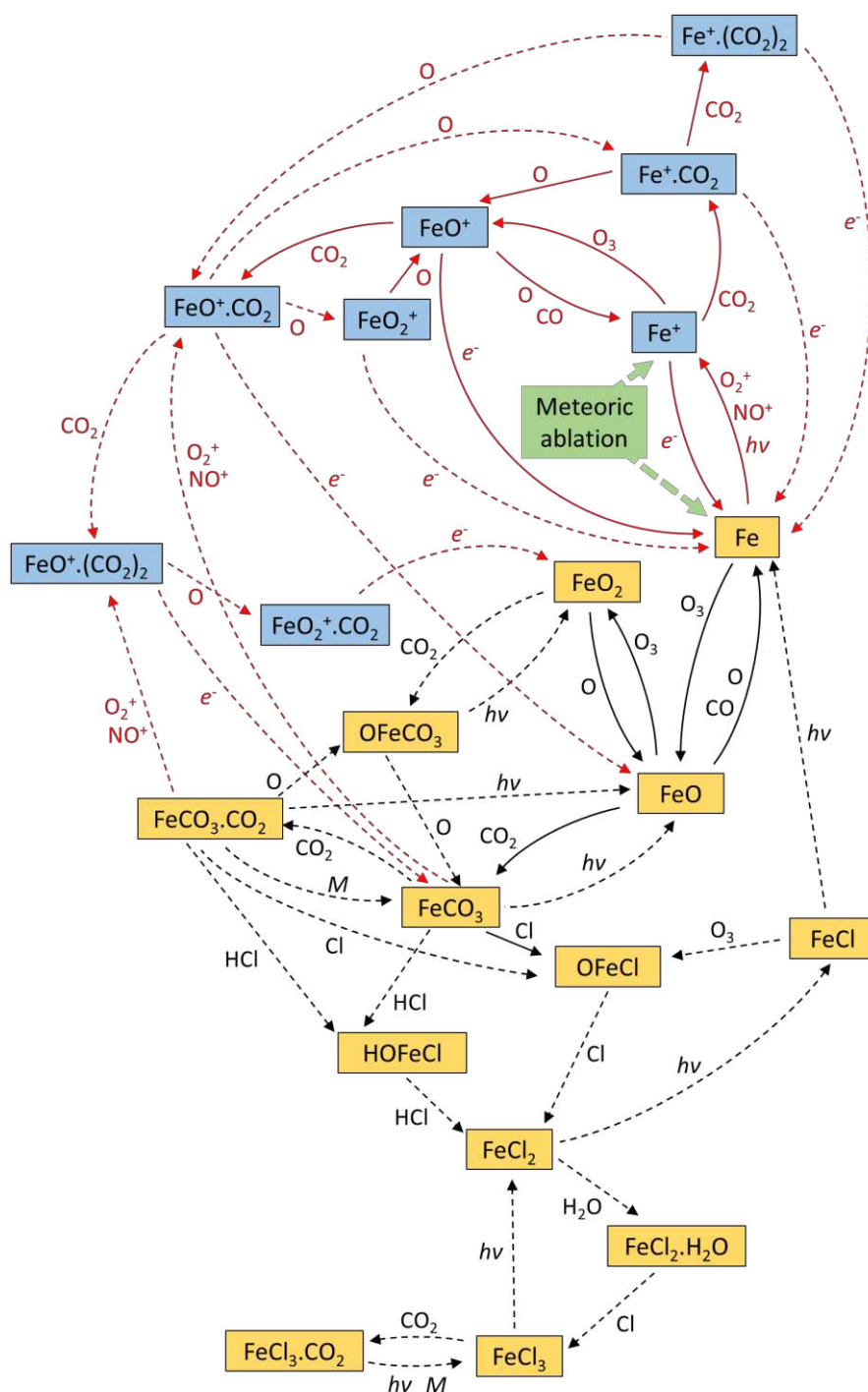


Figure 1. Chemical network of 57 Fe-species reactions implemented in the V-PCM (see Table 1 for reaction rate coefficients). Neutral and ionized species are shown in gold and blue boxes, respectively. Ion-molecule reactions (red) and neutral reactions (black) that have been measured experimentally are indicated with solid arrows, predicted rates are shown with dashed arrows. $h\nu$ indicates photolysis or photoionisation, e^- are electrons, and M is a third body (usually CO_2).

The V-PCM cloud treatment, described in Stolzenbach et al. (2023) distributes the calculated liquid phase from the microphysical cloud model to the cloud modes according to the mass loading of the Venus standard cloud model (Knollenberg & Hunten, 1980), derived from the Pioneer Venus Large Probe Cloud Particle Size Spectrometer (LCPS) measurements. All modes are described with log-normal distributions. The values used for these cloud modes are listed in Table S4 (SI). The condensed mass of H₂O and H₂SO₄ calculated by the V-PCM and adopted for use in SOCRATES is shown in Figure S6 (SI).

2.2 Radiative transfer modelling

1D multiple scattering radiative transfer modelling was performed using SOCRATES (Manners et al., 2022a, 2022b). A two-stream approximation is used to resolve the upward and downward direct and diffuse fluxes through the atmosphere (Edwards & Slingo, 1996). Before the two-stream equations can be formed and solved, the gas absorption coefficients are determined, and a spectral file produced. The correlated-k method (Goody et al., 1989) is used to treat the absorption. SOCRATES was developed to model the Earth's atmosphere, but has been adapted for Venus (Egan et al., 2025a). The atmosphere is modeled with 5 nm bands from 175 – 700 nm. Temperature, pressure, cloud modes, and gas abundances (except SO₂) from the V-PCM are adopted wherever possible, or taken from Eymet et al. (2009) for species that are not included in the V-PCM (HF, H₂S, and the HDO:H₂O ratio). The V-PCM is unable to reproduce the observed decrease in SO₂ through the clouds (a significant unsolved issue in all Venus models (Vandaele et al., 2017)), so a constructed SO₂ profile, in line with observations, was adopted instead (see figure S7, SI). Gas absorption coefficients from Gordon et al. (2022) and the refractive indices for sulfuric acid from Palmer and Williams (1975) were used.

The effect of the inclusion of FeCl₃ in each cloud mode was modelled using the FeCl₃ spectra measured by Egan et al. (2025b). Spectra measured for sample x0C (1.72(3) M FeCl₃ in 76.7(5) wt% sulfuric acid, with an initial HCl concentration of $9.2(3) \times 10^{-3}$ M, see that paper for further details) were used in all cases. SOCRATES employs Mie theory to calculate the aerosol extinction for each cloud mode. The measured molar absorptivity, ϵ (units: L mol⁻¹ m⁻¹), was converted to imaginary refractive index, k , using

$$k = \frac{\epsilon c \lambda_0}{4\pi \log_{10}(e)} \quad (1)$$

where c is the concentration of Fe (in mol dm⁻³) in the solution and λ_0 is the vacuum wavelength of light (in m). The real refractive index was held constant for all concentrations of Fe, and the imaginary refractive index was taken to be that of pure sulfuric acid beyond 600 nm. Spectra were compared to MASCS/MESSENGER reflectance spectrum 151 (Pérez-Hoyos et al., 2018).

Figure 3 shows the effect of the progress of the reaction (i.e., the ratio of ferric chloride to ferric sulfate ions) on the shape of the absorption, which was considered by adopting spectra measured on days 1, 4, 9, and 18 in Egan et al. (2025b) (from their Figure S1b). Samples consisting of 70:30% ferric chloride:ferric sulfate ions (measured on day 4 of reaction progress) provided the best spectral fit to observations. Tests of FeCl_3 concentrations in different cloud modes found that FeCl_3 in all modes, or mode 1 only, provided the best fit to observations (Figures 3 and 4), so further consideration was limited to mode 1 only.

2.3 Residence lifetime calculation

The meteoric flux of iron into the Venusian atmosphere is $31 \pm 18 \text{ t d}^{-1}$, of which approximately 13% (4.1 t d^{-1}) ablates (vaporizes) (Carrillo-Sánchez et al., 2020), becoming available for conversion to FeCl_3 .

The required FeCl_3 atmospheric dynamical residence time (i.e. ignoring chemical removal of FeCl_3), τ_{FeCl_3} , for a purely meteoric source of iron in the upper clouds is estimated by

$$\tau_{\text{FeCl}_3} = \frac{\zeta_{\text{FeCl}_3}}{\Phi_{m,\text{FeCl}_3}} \quad (2)$$

where ζ_{FeCl_3} is the required FeCl_3 column mass density, and Φ_{m,FeCl_3} is the meteoric mass flux of FeCl_3 . The radiative transfer model was found to be sensitive only to the FeCl_3 concentration in the upper clouds (see Section 3.3), so only the required column mass density above 60 km is considered in this calculation. In this region, sedimentation of mode 1 particles is slow compared to the upwelling timescale (Stolzenbach et al., 2023). We therefore assume that sedimentation can be neglected in this calculation.

The FeCl_3 column mass density is calculated from the column mass density of mode 1, ζ_1 , found from the V-PCM cloud model (Figure S6, SI) to be $231 \mu\text{g cm}^{-2}$ above 60 km, and the best fit FeCl_3 wt% in the mode 1 droplets, denoted w_{FeCl_3} :

$$\zeta_{\text{FeCl}_3} = w_{\text{FeCl}_3} \zeta_1 \quad (3)$$

The molar iron flux, $\Phi_{n,\text{Fe}}$, at the height of injection of iron h in the atmosphere is given by

$$\Phi_{n,\text{Fe}} = \frac{\dot{m}_{\text{Fe}}}{4\pi (R + h)^2 M_{\text{Fe}}} \quad (4)$$

where $\dot{m}_{\text{Fe}}$ is the meteoric mass injection rate of ablated Fe, R is the radius of Venus and M_{Fe} is the molar mass of iron. Assuming the upper limit of complete conversion of meteoric iron to FeCl_3 , which remains in mode 1, $\Phi_{n,\text{Fe}} = \Phi_{n,\text{FeCl}_3}$, and the mass flux of FeCl_3 can be calculated using the molar mass of FeCl_3 , M_{FeCl_3} :

$$\phi_{m, \text{FeCl}_3} = \frac{\dot{m}_{\text{Fe}} M_{\text{FeCl}_3}}{4\pi (R + h)^2 M_{\text{Fe}}} \quad (5)$$

212 which can be substituted, along with Equation 3, into Equation 2:

$$\tau_{\text{FeCl}_3} = \frac{4\pi(R + h)^2 M_{\text{Fe}} w_{\text{FeCl}_3} \zeta_1}{\dot{m}_{\text{Fe}} M_{\text{FeCl}_3}} \quad (6)$$

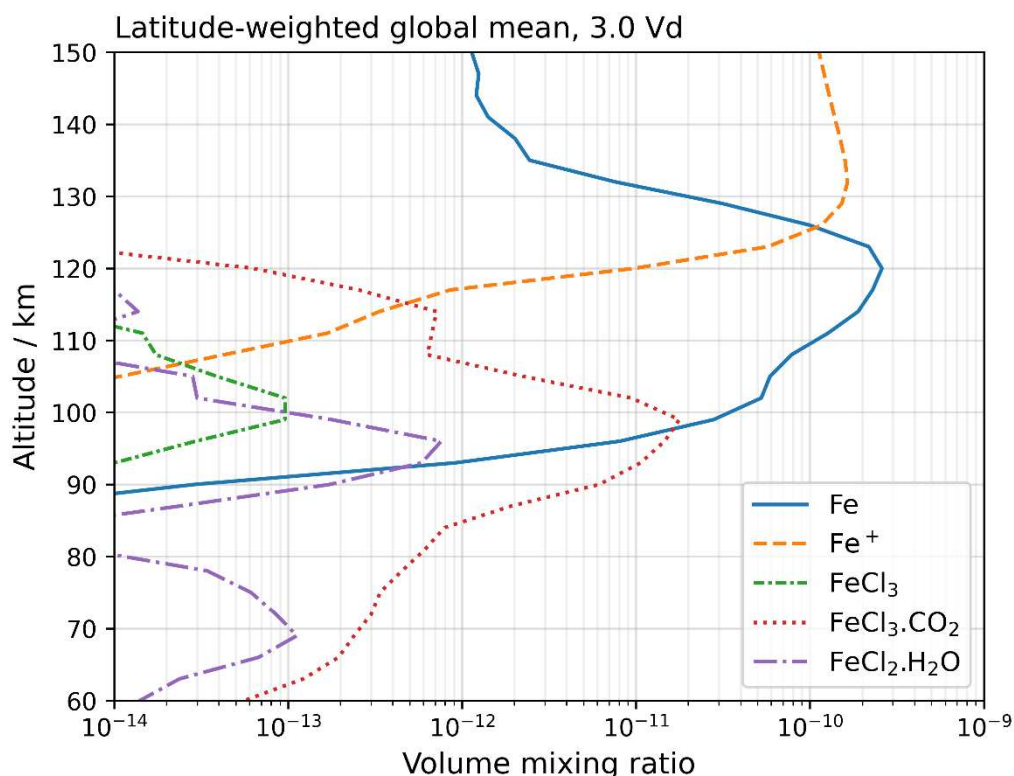
213 3. Results

214 3.1 Distribution of iron-containing species

215 A chemical network (Figure 1) for the production of iron oxide, carbonate, and chloride species from
 216 ablated Fe in the Venusian upper atmosphere was developed (see Methods section, which lists the
 217 rate coefficients and method of theoretical calculation for reactions where rate coefficients have not
 218 been measured), and then implemented in the V-PCM. The initial source of iron into the model is
 219 provided by a global flux of 4.2 tonnes per Earth day of Fe (72%) and Fe⁺ (28%), injected from 95 – 250
 220 km (maximum at 115 km) (Carrillo-Sánchez et al., 2020). The ablation is not directly modelled, and as
 221 such the Fe and Fe⁺ are added directly into the gas phase in thermal equilibrium with the surrounding
 222 atmosphere. As discussed in Section 2.1, hot ablated atoms are rapidly quenched by collision with CO₂,
 223 so this simplification is valid. A plot of the injection profile is available in Figure S10 (SI).

224 Figure 2 shows the modeled mean mixing ratio profiles of key Fe-containing species after a 3.0 Venus
 225 Vd simulation. Profiles of all iron species are shown in Figure S2 (SI). Fe and Fe⁺ are the dominant
 226 species above 100 km. Fe is converted via FeO to FeCO₃, which reacts with abundant HCl and Cl to
 227 form FeCl₃. FeCl₃, clustered with CO₂, then becomes the dominant iron-containing species below 100
 228 km. The latitude-weighted global mean flux of FeCl₃ and other reservoir species (FeCl₃.CO₂ and
 229 FeCl₂.H₂O) after 3.0 Vd is -8.1×10^4 molecules cm⁻² s⁻¹ at the base of the ablation profile (95 km), which
 230 is 84% of the column-integrated iron injection rate (here, the negative sign indicates a downward flux
 231 by convention). Vertical transport slower than the formation rates above 90 km results in the
 232 accumulation of FeCl₃, FeCl₃.CO₂, and FeCl₂.H₂O in the layers seen in Figure 2. FeCl₃ formation continues
 233 in this region from Fe transported below the base of the ablation before reacting (Figure 2) and other
 234 intermediate species (Figure S2, SI), leading to complete conversion to FeCl₃ and the other reservoir
 235 species by ~75 km. Note that, while the atmosphere above 100 km reaches steady state, FeCl₃ and
 236 FeCl₃.CO₂ concentrations below 100 km are still increasing with time after 3.0 Vd and should continue
 237 to do so beyond reasonably achievable model run lengths. At altitudes near the base of the ablation,
 238 downward advection occurs predominantly on the night side of the planet. At ~±40 – 70° latitude,
 239 vertical transport increases near 85 km, transporting FeCl₃ and precursors more rapidly downwards
 240 into the clouds once they reach this region. Condensation of these species, or their uptake to cloud

241 and haze droplets, and their subsequent sedimentation will likely increase the rate of downward
 242 transport of FeCl_3 to the dynamically stable, stratified upper cloud region.



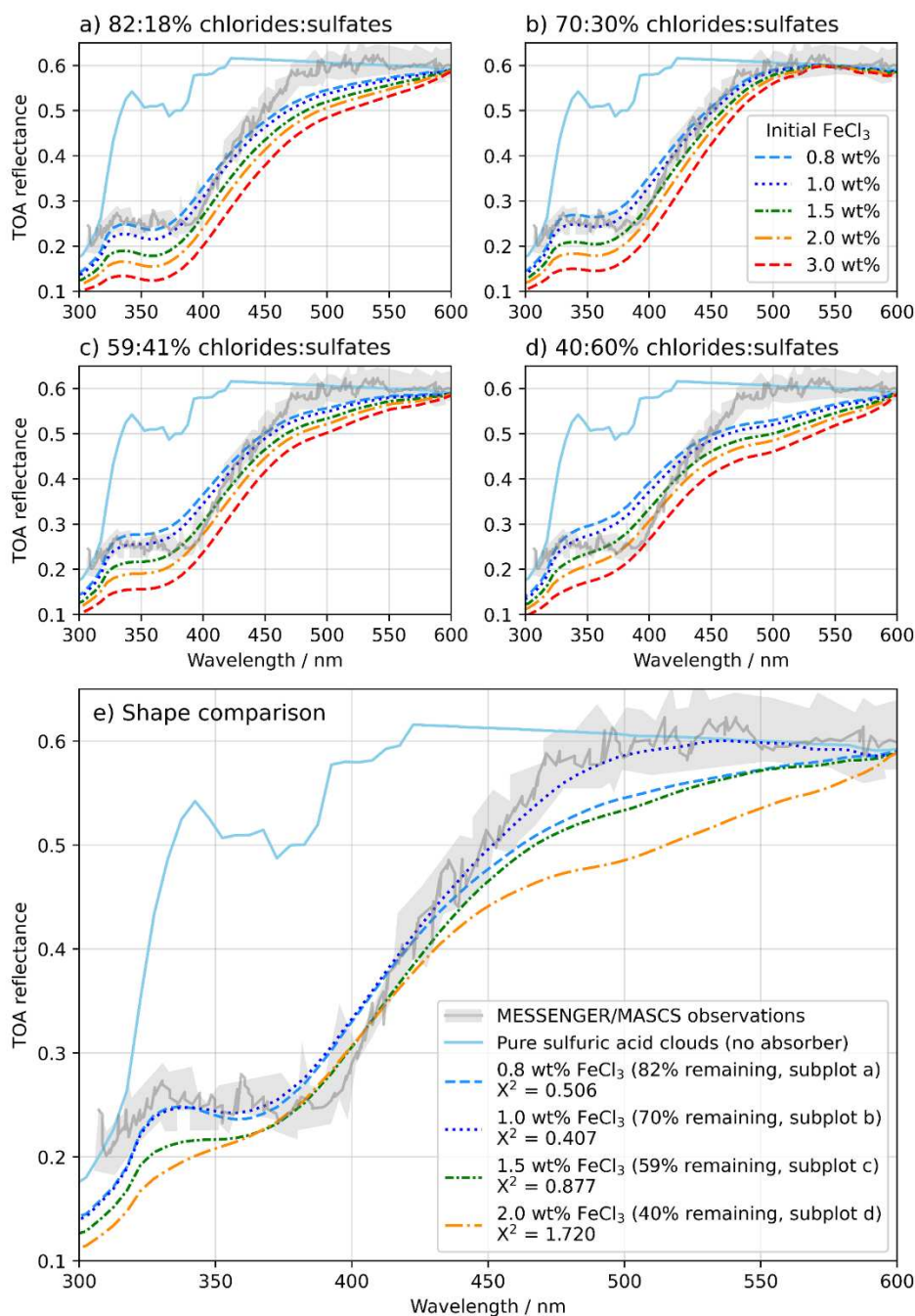
243
 244 **Figure 2.** Latitude-weighted global mean mixing ratios of meteoric Fe and Fe^+ and FeCl_3 and reservoir
 245 species modelled in the V-PCM after 3.0 Vd. Concentrations of FeCl_3 will continue to build up over time.
 246 Note that the Fe species below 100 km are likely to begin to be taken up in haze or cloud droplets (Gao
 247 et al., 2014; Karyu et al., 2024; Luginin et al., 2024; Wilquet et al., 2012), rather than remaining solely
 248 in the gas phase.

249 3.2 Modelled reflectance

250 We assume that FeCl_3 and $\text{FeCl}_3 \cdot \text{CO}_2$, when taken up in Venusian cloud droplets, form solvated FeCl_3 .
 251 Egan et al. (2025b) showed that ferric sulfate ions ($\text{Fe}(\text{SO}_4)_2^-$) form slowly from FeCl_3 in concentrated
 252 sulfuric acid (with a chemical lifetime of several weeks to over a year at 298 K), and that somewhat
 253 different Venusian spectra measured over time (Crisp, 1986; Lee et al., 2022; Pérez-Hoyos et al., 2018)
 254 could be reproduced by varying the ratio of ferric chloride to ferric sulfate. The most complete
 255 measured Venusian reflectance spectrum was obtained by the MASCS spectrometer on the spacecraft
 256 MESSENGER during its 2007 gravity assist manoeuvre at Venus (Pérez-Hoyos et al., 2018). The
 257 spectrum has good spectral resolution down to 300 nm, making it ideal for comparison in this work.

258 Initial tests were carried out using measured spectra from Egan et al. (2025b) with varying ratios of
 259 ferric chlorides to sulfates (Figure 3). The iron species were modelled as being present in the same

concentrations in all cloud modes. The best fit results are those with a 70:30% ferric chloride to sulfate ratio (Figure 3b), which satisfactorily reproduces the shape of the absorption well throughout the wavelength range. The variation in spectral shape at 500 – 600 nm is assumed to be due to the variation in chlorination of the iron (FeCl_n^{3-n} ions) (Egan et al., 2025b; Liu et al., 2006), which causes variation in the precise shape of the absorption spectrum.



265

Figure 3. Best fit to MESSENGER observations (grey line and uncertainty region, Pérez-Hoyos et al., 2018) for different initial concentrations of FeCl_3 using spectra containing iron chloride:sulfate molar ratios of a) 82:18% b) 70:30%, c) 59:41%, d) 40:60%. The concentration in the legend refers to the

initial wt% of FeCl_3 in the sample, some fraction of which (given in subplot title) has reacted to form sulfates i.e., it is not the instantaneous ferric chloride concentration in the samples at the time the spectrum was measured. The predicted spectrum of Venus in the absence of any NUV absorber candidate (light blue line) is shown for comparison. The iron concentrations that provide the most similar value of reflectance near 365 nm are shown in subplot e to aid in comparison of shapes. The line colours are consistent in all the figure panels. The quality of the fit is calculated as $X^2 = \sum_{\lambda} \left(\frac{\text{observation} - \text{model}}{\text{observation}} \right)^2$, where the MESSENGER observations (grey line) have been interpolated to the wavelength (λ) values of the model.

3.3 Sensitivity of the reflected spectrum to cloud mode

The Venusian clouds are made up of different sizes of cloud droplets, divided into four size modes: $\sim 0.2 \mu\text{m}$ radius “mode 1” droplets throughout the cloud deck; $\sim 1.0 \mu\text{m}$ radius “mode 2” droplets in the upper and lower cloud layers, growing into a slightly larger $\sim 1.4 \mu\text{m}$ radius “mode 2'” in the middle clouds; and $3.65 \mu\text{m}$ “mode 3” droplets in the middle and lower clouds (Knollenberg & Hunten, 1980; Stolzenbach et al., 2023; Tomasko et al., 1980). Sensitivity tests were carried out to predict the effect of FeCl_3 in the different Venusian cloud modes (Figure 4). The observed reflectance spectrum (Pérez-Hoyos et al., 2018) could be reproduced with FeCl_3 in all cloud modes (Figure 3b), or else exclusively in mode 1 (Figure 4). An initial concentration of $\sim 10 \text{ wt\%}$ FeCl_3 in mode 2 was able to reproduce the strength of the absorption near 360 nm reasonably well, but the quality of the fit at long wavelengths is poor.

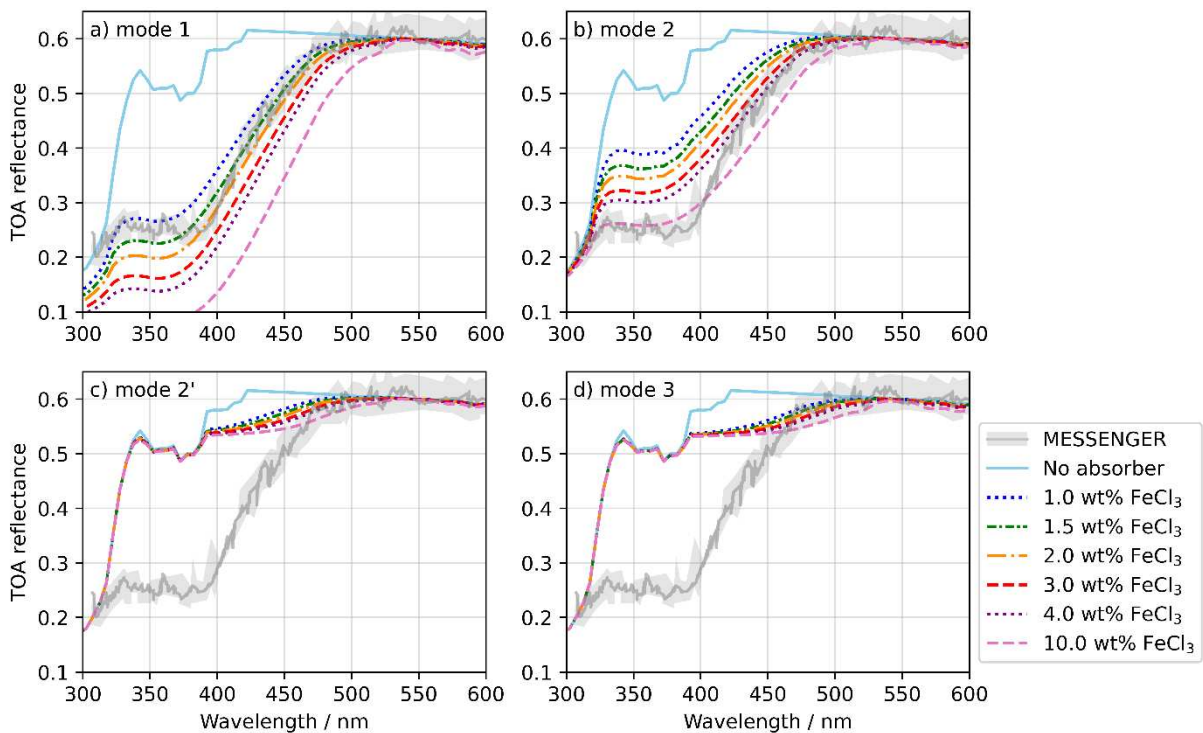


Figure 4. Comparison of the MESSENGER reflectance spectrum (grey line and uncertainty region, Pérez-Hoyos et al., 2018) with the predicted spectrum in the absence of an absorber (light blue line) and predicted spectra of different initial concentrations of FeCl_3 in a) mode 1 b) mode 2, c) mode 2', and d) mode 3.

Even high concentrations (> 10 wt% FeCl_3) in modes 2' or 3 were not able to reproduce the observed absorption. This is because both cloud modes are located too far below the cloud top to contribute a significant amount of observable absorption. The model is not sensitive to their composition with this cloud configuration, so no further conclusions can be drawn. Despite the sensitivity of the model to mode 2 in the upper clouds, only mode 1 is considered henceforth due to its dominant effect. We emphasise that the dominance of mode 1 does not preclude the presence of FeCl_3 in other cloud modes, but it is not required to explain the absorption.

3.4 Improvements to the spectral shape

The predicted absorption in Figure 4 is generally higher than observations near 300 nm when the rest of the fit is good, which may indicate that the concentration of one or more of the absorbing species (FeCl_n^{3-n} , $\text{Fe}(\text{SO}_4)_2^-$, SO_2) is over-estimated. Inspection of the wavelength regions of absorption due to ferric chloride and ferric sulfate ions reported by Egan et al. (2025b) shows that ferric sulfate absorbs at all wavelengths below 400 nm, with a peak around 290 nm and so would therefore contribute to the modeled absorption near 300 nm. The dominant effect is due to SO_2 in this region, which has historically been assumed to be the only absorbing species at these wavelengths (e.g. Crisp, 1986). The reaction of ferric chloride to form ferric sulfate depends on the chloride concentrations of the solution (Egan et al., 2025b), with high chloride concentrations shifting the reaction equilibrium to favour ferric chloride, rather than ferric sulfate species. The high gas-phase HCl concentration in the Venusian clouds ($\sim 0.1 - 0.4$ ppm, Figure S8, SI; Bertaux et al., 2007; Bézard et al., 1990; Krasnopolsky, 2010a; Mahieux et al., 2023b; Vandaele et al., 2008; Young, 1972) will maintain a higher Cl^- concentration in the droplets ($\sim 10^{-3} - 10^{-4}$ M near 90 km (~ 170 K), decreasing to 10^{-5} M near 56 km (~ 300 K) (Figure S9, SI; Williams & Golden, 1993) than was achievable in the laboratory work of Egan et al. (2025b) at 298 K and with unmeasurable but likely negligible HCl in the headspace above the samples. In addition, the V-PCM temperature of 200 – 250 K in the upper cloud region, similar to observations (Ando et al., 2020; Seiff et al., 1985; Tellmann et al., 2009) should slow the conversion of Fe chloride to sulfate by reducing the reaction rate in addition to increasing HCl solubility in the droplets. Thus, higher ferric chloride fractions are likely in the upper clouds, compared with the laboratory measurements.

Three cases are considered to examine the effect of sulfur-containing species near 300 nm: mode 1 contains some concentration of ferric chloride and ferric sulfate in a 70:30% ratio as measured in Egan

322 et al. (2025b) (Figure 5a); mode 1 contains some concentration of ferric chloride, and the formation of
323 ferric sulfate is negligible in the optically relevant upper cloud region (Figure 5b); and mode 1 contains
324 a 70:30 ratio of ferric chloride to ferric sulfate, but the atmospheric SO₂ mixing ratio throughout the
325 atmosphere (~150 ppm below the cloud deck and 0.01 - 1 ppm above the clouds, Figure S7, SI; Belyaev
326 et al., 2012; Bertaux et al., 1996; Bézard et al., 1993; Encrenaz et al., 2012; Gel'man et al., 1979; Jessup
327 et al., 2015; Krasnopolsky, 2010b; Mahieux et al., 2023a; Marcq et al., 2008; Na et al., 1994; Oyama et
328 al., 1980; Sandor et al., 2010) is decreased by a factor of 10, in line with below-cloud concentrations
329 adopted by current photochemistry models (e.g., Krasnopolsky, 2012; Stolzenbach et al., 2023; Winick
330 & Stewart, 1980).

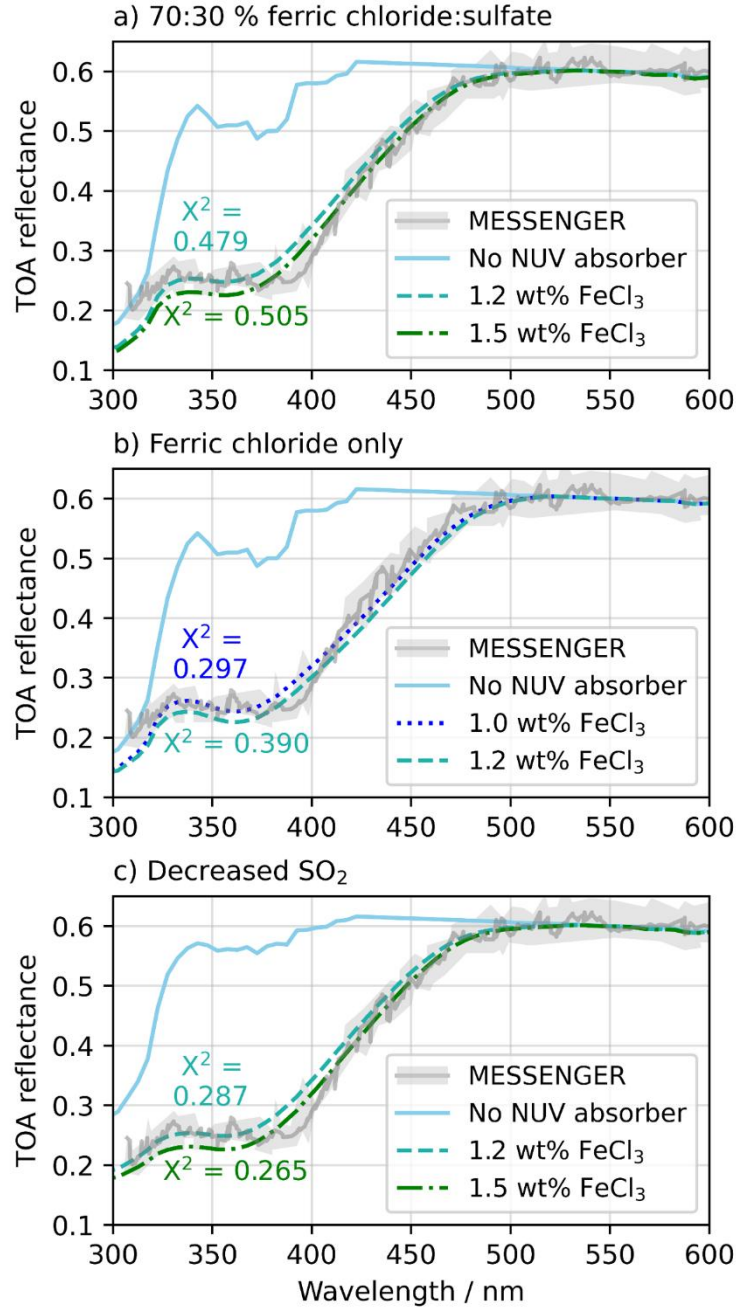


Figure 5. Modelled reflectance for varying initial concentrations of FeCl_3 in mode 1 using a) measured spectra containing 70:30% ferric chloride:sulfate (Egan et al., 2025b), b) reconstructed spectra containing only iron chloride contributions, or c) measured spectra as in a) but with the gas phase SO_2 mixing ratio decreased by a factor of 10 (light blue solid line). Different initial concentrations of FeCl_3 are compared to observations from MASCS/MESSENGER (grey line and uncertainty region, Pérez-Hoyos et al., 2018). The quality of the fit is calculated as $X^2 = \sum_{\lambda} \left(\frac{\text{observation} - \text{model}}{\text{observation}} \right)^2$, where the MESSENGER observations (grey line) have been interpolated to the wavelength (λ) values of the model.

The best fit results are for initial concentrations of 1.2 – 1.5 wt% FeCl_3 if ferric sulfate is formed (with improvement to the spectral shape from 300 – 350 nm if the atmospheric SO_2 is decreased), or 1.0 – 1.2 wt% FeCl_3 if the reaction to form sulfate is negligible in the upper clouds. The best fit FeCl_3 concentration in the absence of ferric sulfate is slightly higher than the equivalent FeCl_3 concentration in the 70:30 % $\text{FeCl}_3:\text{Fe}(\text{SO}_4)_2^-$ case due to the small contribution of ferric sulfate to the absorption at 300 – 400 nm. The refractive indices used for both cases are available in the SI (Table S6 and Figure S11).

4. Discussion

Examination of Figure 5 shows that the best fit initial concentration of FeCl_3 in mode 1 is 1.2 – 1.5 wt% FeCl_3 when partial conversion to ferric sulfate is assumed (resulting in an instantaneous concentration of approximately 0.85 – 1.0 wt% FeCl_3). The agreement of the measured spectrum (Figure 5a) with observations is excellent above 320 nm, and slightly too high below 320 nm, where the SO_2 contribution may be too high. Decreasing the gas-phase SO_2 by a factor of 10 throughout the atmosphere (Figure 5c), representing the possibility of historical errors in the measurement of SO_2 or wide variation in concentrations between measurements in different parts of the atmosphere (e.g., Belyaev et al., 2012; Jessup et al., 2015; Marcq et al., 2008; Sandor et al., 2010) improves the agreement of the spectral shape in this region. The removal of the ferric sulfate contribution similarly decreases the absorption below 320 nm – though the high SO_2 absorption is still dominant in this region – and the observed spectrum can be matched well with 1.0 – 1.2 wt% of FeCl_3 . The minor difference in the FeCl_3 concentration providing the best fit for spectra containing ferric sulfate contributions and the best fit concentrations for pure ferric chloride spectra are likely due to a combination of uncertainty in the estimated concentrations of the measured spectra, and the contribution of the ferric sulfate to the absorption below 400 nm.

Assuming a purely meteoric source of vapourised Fe above the upper clouds, the required residence time of FeCl_3 , τ_{FeCl_3} , in the upper cloud region (the only cloud region which the TOA reflectance model is sensitive to), can be estimated using Equation 6 (Section 2.3), with the height of injection of iron taken to be 100 km, the base of the injection profile; the column mass density of mode 1 particles above 60 km calculated to be $231 \mu\text{g cm}^{-2}$ from the V-PCM cloud model (Figure S6, SI); and the Fe mass input rate from meteoric ablation 4.2 ± 2.4 tonnes per Earth day (t d^{-1}) (Carrillo-Sánchez et al., 2020). If the formation of ferric sulfate is assumed to be negligible in the upper clouds and haze (i.e., the chemical lifetime of FeCl_3 in the upper clouds and haze exceeds the dynamical lifetime), ~ 1.1 wt% FeCl_3 in mode 1 would be sufficient to explain the absorption, requiring a residence time of 2800 years. If ferric sulfate formation cannot be neglected, an initial FeCl_3 concentration of ~ 1.4 wt% is required,

requiring 3400 years to accumulate sufficient iron. Additional loss processes of iron species, either chemical or dynamical, will require higher initial FeCl_3 concentrations, indicating either an additional source or a method of reforming FeCl_3 below the cloud top. The 58% uncertainty in the iron flux into the Venusian atmosphere ($31 \pm 18 \text{ t d}^{-1}$, approximately 13% of which ablates) introduces significant uncertainty in these values, as does the inability to run the chemical model to steady state due to the prohibitively long model run time that would be needed. While a residence time of several thousand years may seem high, we note that the reported iron bulk mass loading of $0.21 \pm 0.06 \text{ mg m}^{-3}$ in the cloud layer measured by the Venera 12 descender (Petryanov et al., 1981) is comparable to the total mode 1 mass loading in the upper clouds, and recent reanalysis of Pioneer Venus Large Probe descent data identified $1.1 \pm 0.2 \text{ mg m}^{-3}$ of $\text{Fe}_2(\text{SO}_4)_3$ (equivalent to $0.31 \pm 0.06 \text{ mg m}^{-3} \text{ Fe}$) in the lower cloud (Mogul et al., 2025). Iron mass loadings, and therefore residence times, significantly higher than required to account for only a small percentage of the mode 1 cloud particles are therefore clearly feasible in the Venusian clouds.

The altitude range over which the absorber is present is uncertain. Cloud top reflectance measurements, such as those used in this study, are not sensitive to the lower altitudes of the cloud deck, leaving the concentration of the absorber unconstrained in this region. Bertaux et al. (1996) reported that the ultraviolet spectrometers on Vega 1 and 2 descent probes returned absorption spectra they attribute to lower cloud particles, suggesting the UV absorber is present throughout the cloud deck. In this case, FeCl_3 could be present throughout the clouds deck in either mode 1 or multiple modes. This would require a greater iron column mass within the clouds, so a method of reforming FeCl_3 from $\text{Fe}_2(\text{SO}_4)_3$ in the lower clouds would be required. However, comparison of the visible and ultraviolet radiometers on the Pioneer Venus descent probes led Pollack et al. (1979) to tentatively conclude that visible absorption occurs only near the cloud tops. This may indicate the presence of more than one species contributing to the absorption at the cloud tops, or a change in composition through the cloud deck. Due to the limitations of the retrieval sensitivity in the lower clouds, we can draw no robust conclusions on this matter. However, a layer of FeCl_3 in the upper clouds above an iron sulphate reservoir (either $\text{Fe}_2(\text{SO}_4)_3$ or other forms (Jiang et al., 2024; Mogul et al., 2025)) in the lower clouds would be consistent with the Pioneer Venus radiometry and gas chromatograph reanalysis.

Previous work has also reported a good fit for 1 wt% FeCl_3 in sulfuric acid (Krasnopolsky, 2017; Zasova et al., 1981), though their reported best fit was for the mode 2 cloud droplets. While the model is sensitive to the mode 2 contribution, we found that higher concentrations ($\sim 10 \text{ wt\%}$, Figure 4) were required in mode 2 to provide the observed absorption. While mode 1 was found to be the dominant contributor to the absorption, the precise concentrations in each mode that best reproduce the absorption will vary based on the precise treatment of cloud modes. The clouds adopted throughout

this work are constrained to the standard cloud model measured by the Pioneer Venus Large Probe Cloud Particle Size Spectrometer (LCPS) (Knollenberg & Hunten, 1980), and particles are constrained to the altitude bands of the different cloud layers. More recent studies (e.g. Luginin et al., 2024; Luginin et al., 2016; Satoh et al., 2015; Wilquet et al., 2009) have reported both smaller and larger modal sizes in the upper haze layer and upper clouds, indicating probable bimodality. The adoption of these changes to the cloud model would be expected to subtly change the best fit concentrations in the different cloud modes, though testing this hypothesis is beyond the scope of this study.

While mode 1 particles in the upper clouds are stable against sedimentation (Stolzenbach et al., 2023), local variations in vertical winds will likely transport the particles throughout the atmosphere in less than the timescale discussed above. Some recycling of ferric sulphate into NUV-absorbing species is therefore expected: Jiang et al. (2024) reported that iron sulfate minerals can form from ferric chloride in the cloud droplets, and absorb in the near-UV. If this occurs in the upper cloud layer, the reaction of the FeCl_3 to form sulfate species would no longer be a sink with regard to the near-UV absorber. Furthermore, any iron-containing cloud droplets that sediment to the bottom of the cloud deck will evaporate (Titov et al., 2018), leaving residual nano-sized iron sulfate/oxide particles (Frankland et al., 2017) which can then react with atmospheric HCl at elevated tropospheric temperatures below the cloud base to reform FeCl_3 once again. Such small particles are not expected to be able to sediment far in the high pressure conditions of the troposphere, but the reactions could occur either while in the atmosphere or at the surface if sedimentation does occur. Reanalysis of measurements from the Pioneer Venus Large Probe Neutral Mass Spectrometer detected 16 ± 3 wt% $\text{Fe}_2(\text{SO}_4)_3$ in the aerosols of the lower clouds (Mogul et al., 2025), and chemical modelling of the lower haze region measured by the Pioneer Venus Large Probe (Knollenberg & Hunten, 1980) predicted FeCl_2 and FeS_2 below the main cloud deck (Woitke et al., 2025), both of which may provide an iron reservoir for the reformation and recirculation of FeCl_3 .

Transport and recycling of iron chloride can explain the large-scale inhomogeneities of the observed absorption (Lee et al., 2015; Markiewicz et al., 2007; Titov et al., 2012; Titov et al., 2008), with regions of higher or lower FeCl_3 concentration resulting from the upwelling of recycled material from the lower clouds. The reaction of ferric chloride to ferric sulfate is expected to depend on temperature and HCl concentration, and Jiang et al. (2024) found the formation of iron sulfate minerals depended strongly on water availability, making the UV-brightness or -darkness of upwelled material dependent on the local conditions in the atmosphere. The meteoric input provides a small but continuous source of fresh FeCl_3 entering the clouds from above. In contrast, recycling of iron in the lower atmosphere would produce an intermittent source of FeCl_3 from below the cloud top; upwelling of particles from a locally warm or HCl-poor region of the atmosphere would produce a region of droplets with lower ferric

chloride concentration, while upwelling from a locally cold or HCl-rich part of the atmosphere would produce a region of droplets with higher ferric chloride concentration. As such, we would not expect a simple correlation of stronger absorption with either atmospheric upwelling or downwelling, as either may produce higher- or lower-concentration regions of FeCl_3 .

Unlike for Mars and Earth (Carrillo-Sánchez et al., 2020; Crismani et al., 2017; Gómez Martín et al., 2017; Grebowsky et al., 2017; Plane, 2003a; 2018a; Plane et al., 2015), no reliable measurements of meteoric metal fluxes have been made in the Venusian atmosphere, so uncertainties in the meteoric input are large ($31 \pm 18 \text{ t d}^{-1}$) (Carrillo-Sánchez et al., 2020). Of the major meteoric metals, the atomic Na layer should be the most straightforward to observe in Venus's upper atmosphere because of the relatively high abundance of injected Na (Carrillo-Sánchez et al., 2020) and its strong optical transition at 589 nm (the terrestrial Na layer has been observed using both solar-pumped resonance fluorescence (Fan et al., 2007) and stellar occultation (Fussen et al., 2010)). The differential ablation of Fe to Na in Venus' atmosphere produces a relative elemental injection ratio of 4.5 (Carrillo-Sánchez et al., 2020), from which an estimate of the Fe layer abundance could be obtained (assuming similar rates of removal of both metals). Note that the relative Na to Fe flux produced by ablation in the Earth's upper atmosphere has been measured directly using co-located Na and Fe lidars (Huang et al., 2015); this data was then used to determine the relative contributions of cosmic dust particles from Jupiter Family Comets, the main asteroid belt, and Long Period Comets (Carrillo-Sánchez et al., 2016).

The 58% uncertainty on meteoric input means that the available iron flux may differ significantly from the values adopted in this work, thereby increasing or decreasing the required iron residence time. Measurements of meteoric metals in the Venusian atmosphere are therefore vitally important for constraining the achievable atmospheric FeCl_3 concentration and consequently its contribution to the NUV absorption.

5. Conclusions

We present radiative transfer modelling of Venus in the near-UV and visible wavelength range, including absorption by FeCl_3 measured in sulfuric acid (Egan et al., 2025b) in the different cloud modes. The best agreement of the shape and strength of the absorption predicted with the retrieved spectrum from the MASCS spectrometer on the MESSENGER spacecraft (Pérez-Hoyos et al., 2018) is for 1.0 – 1.2 wt% FeCl_3 in the mode 1 cloud droplets. The spectrum can also be reproduced by the inclusion of FeCl_3 in all cloud droplets, but mode 1 alone is the dominant contribution. The residence lifetime of iron in the clouds required for a purely meteoric source of iron to produce sufficient FeCl_3 to explain the absorption is probably between 2800 and 3400 years. The required concentration of iron in the upper clouds is lower than the observed iron mass loadings in the lower clouds (Mogul et

al., 2025; Petryanov et al., 1981), suggesting, in the absence of a known alternative source of iron into the clouds, that long residence times are expected in the cloud deck.

Reformation of FeCl_3 from other iron species in the clouds or deep atmosphere (Jiang et al., 2024; Mogul et al., 2025; Woitke et al., 2025) is likely required to increase the effective chemical lifetime of FeCl_3 or other absorber candidates to a scale comparable with the required residence time. Such reformation may explain the inhomogeneity of the observed absorption, with local variations in temperature, water availability, and HCl concentration changing the rate of formation and loss of FeCl_3 , and producing regions of locally FeCl_3 -rich or -poor droplets. Further work is required to explore these processes of conversion and/or reformation of FeCl_3 in the clouds and lower atmosphere. In the present study, we have presented a chemical scheme for the initial production of FeCl_3 from meteoric Fe atoms and atmospheric HCl and Cl, probably of volcanic origin. The chemical scheme has been implemented in the V-PCM PCM (e.g., Garate-Lopez & Lebonnois, 2018; Martinez et al., 2024; Martinez et al., 2023; Stolzenbach et al., 2023), and the dominant Fe species below 100 km was found to be $\text{FeCl}_3\cdot\text{CO}_2$, which would be taken up into the cloud droplets as FeCl_3 .

The excellent spectral agreement of the FeCl_3 , the reasonable predicted concentrations of FeCl_3 compared to the observed iron mass loading, and the proposed mechanism for forming FeCl_3 above the clouds, make FeCl_3 the most promising candidate for the cause of the Venusian unknown UV absorption.

Acknowledgements

We thank the UK Science and Technology Research Council for funding this study (project ST/T000279/1). JVE acknowledges funding for a PhD studentship from the UK Engineering and Physical Sciences Research Council (EP/S023593/1). Aurélien Stolzenbach acknowledges the support of project PID2021-126365NB-C21 funded by the Agencia Estatal de Investigación (MCIN/AEI/10.13039/501100011033/) and FEDER.

We would also like to thank an anonymous reviewer for providing the simplified Kooij forms of reaction rates 5 and 9 in Table 1.

Conflicts of interest

The authors declare there are no conflicts of interest for this manuscript.

Open Research

Data to reproduce all figures in the main paper and Supplementary Information is available at Zenodo, via <https://doi.org/10.5281/zenodo.17487186> (Egan, 2025).

504 The Venus Climate Database (2023) is available at <http://www-venus.lmd.jussieu.fr/>.

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