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CO Oxidation and O₂ Removal on Meteoric Material in Venus' Atmosphere

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Abstract

The heterogeneous oxidation of CO by O₂ on olivine, Fe sulfate and Fe oxide particles was studied using a flow tube apparatus between 300 and 680 K. These particles were chosen as possible analogues of unablated cosmic dust and meteoric smoke in Venus' atmosphere. On olivine and Fe oxides, the rate of CO oxidation to CO₂ only becomes significant above 450 K. For iron sulfates, CO₂ production was not observed until these dust analogues had decomposed into iron oxides at ~ 540 K. The CO oxidation rate increases significantly with a higher Fe content in the dust, implying that oxidation occurs through Fe active sites (no reaction was observed on Mg₂SiO₄). The oxidation kinetics can be explained by CO reacting with chemi-sorbed O₂ through an Eley-Rideal mechanism, which is supported by electronic structure calculations. Uptake coefficients were measured from 450 to 680 K, yielding:

24 $\log_{10}(\gamma(\text{CO on MgFeSiO}_4)) = (2.9 \pm 0.1) \times 10^{-3} T(\text{K}) - (8.2 \pm 0.1);$

25 $\log_{10}(\gamma(\text{CO on Fe}_2\text{SiO}_4)) = (2.3 \pm 0.3) \times 10^{-3} T(\text{K}) - (7.7 \pm 0.2);$

26 $\log_{10}(\gamma(\text{CO on FeOOH/Fe}_2\text{O}_3)) = (5.6 \pm 0.8) \times 10^{-3} T(\text{K}) - (9.3 \pm 0.4).$

27 A 1-D atmospheric model of Venus was then constructed to explore the role of heterogeneous
28 oxidation. The cosmic dust input to Venus, mostly originating from Jupiter Family Comets, is
29 around 32 tonnes per Earth day. A chemical ablation model was used to show that ~34% of
30 this incoming mass ablates, forming meteoric smoke particles which, together with unablated
31 dust particles, provide a significant surface for the heterogeneous oxidation of CO to CO₂ in
32 Venus' troposphere. This process should cause almost complete removal of O₂ below 40 km,
33 but have a relatively small impact on the CO mixing ratio (since CO is in large excess over O₂).
34 Theoretical quantum calculations indicate that the gas-phase oxidation of CO by SO₂ in the
35 lower troposphere is not competitive with the heterogeneous oxidation of CO. Finally, the
36 substantial number density of meteoric smoke particles predicted to occur above the cloud
37 tops may facilitate the low temperature heterogeneous chemistry of other species.

38

39 *Keywords: Venus Atmosphere; Cosmic dust; Experimental techniques*

40

41 **1. Introduction**

42 The most abundant atmospheric species in Venus' atmosphere are CO₂ (96.5%) and N₂ (3.5 %)
43 (Bezard and de Bergh, 2007). Despite CO₂ undergoing photolysis, Venus has maintained its
44 CO₂-rich atmosphere over geological timescales. Photolysis occurs *via* solar ultraviolet light at
45 wavelengths below 200 nm, forming CO and atomic O. This process occurs mainly above the
46 top of the sulfuric acid cloud and haze layers (> 65 km), since these aerosols reduce the UV

47 solar flux in the lower atmosphere (Krasnopolsky, 2012). O atoms rapidly recombine to form
48 O₂. The current abundance of CO (45 ppm at the cloud tops) would be produced in only ~200
49 yrs (Taylor, 2010).

50 Curiously, the O₂ mixing ratio is much less than half that of CO, which is the value that would
51 be expected based on this simple photochemistry. Trauger and Lunine (1983) used terrestrial
52 spectroscopic observations to determine an upper limit to the mixing ratio of O₂ immediately
53 above the clouds of only 0.3 ppm, in good agreement with an earlier study (Traub and
54 Carleton, 1974). In contrast, gas chromatographic measurements by the Pioneer Venus
55 sounder probe reported O₂ mixing ratios of 44 and 16 ppm at heights of 52 and 44 km,
56 respectively (Oyama et al., 1980). This result is difficult to reconcile with the above-cloud
57 measurements, since this is where the source of the O₂ should be (Trauger and Lunine, 1983;
58 von Zahn et al., 1983; Krasnopolsky, 2012). In any case, there must be efficient routes to
59 re-oxidise CO and remove O₂; indeed, O₂ above the clouds is currently over-predicted in
60 atmospheric models by an order of magnitude relative to the upper limit (Krasnopolsky,
61 2012).

62 CO oxidation cannot occur through the spin-forbidden recombination of CO with O in the gas
63 phase, and the gas-phase reaction between CO and O₂ has an activation energy of around 200
64 kJ mol⁻¹ and is thus extremely slow except possibly close to the surface of Venus (Tsang and
65 Hampson, 1986). Instead, a chlorine-catalyzed cycle has been proposed which involves
66 formation of the ClCO intermediate followed by reaction with O₂ (Mills and Allen, 2007;
67 Krasnopolsky, 2012):





70 where R2 proceeds via the ClCO_3 intermediate (Pernice et al., 2004). This appears to be the
71 primary CO oxidation pathway above 65 km. Because the OH radical concentration ($\sim 10^3 \text{ cm}^{-3}$
72 at 70 km) is low relative to Cl ($\sim 10^{10} \text{ cm}^{-3}$ at 70 km) in Venus' atmosphere, the reaction



74 must play a secondary role (Krasnopolsky, 2012). Below the clouds ($< 38 \text{ km}$) where the
75 temperature increases above 400 K, SO_2 has been proposed as a significant oxidant (reaction
76 R4) (Fegley et al., 1997):



78 Previous attempts to understand this atmospheric CO chemistry have focused on comparing
79 these gas-phase mechanisms in atmospheric models. However, CO oxidation can also occur
80 catalytically on a surface at high temperatures in the presence of O_2 , including the proposed
81 oxidation of CO on hematite at the Venusian surface (Grenfell et al., 2010; Grenfell et al.,
82 2013). The oxidation can take place either through the Langmuir-Hinshelwood mechanism,
83 which involves both species adsorbing on the surface and then diffusing together before
84 reacting; or via the Eley-Rideal mechanism, where reaction occurs between one of the
85 reactants adsorbed on the surface and the second directly from the gas phase (Kolasinski,
86 2002). There is a large body of research from the automotive industry on CO oxidation by
87 platinum group metal-containing materials (Kašpar et al., 2003), though much less on
88 materials with base metals such as Fe which tend to be poisoned by SO_2 in vehicle exhausts
89 (Wang, 2006).

90 In this paper we consider the heterogeneous oxidation pathway of CO by O₂ on meteoric
91 material in Venus' atmosphere. This material will be both un-ablated meteoroids and the
92 meteoric smoke particles (MSPs) which form from the oxidation and subsequent
93 condensation of ablated meteoric metals. These nm-sized particles are probably composed
94 of olivines (Mg_{2-2n}Fe_{2n}SiO₄ where 0 ≤ n ≤ 1) or Fe-Mg oxides (Saunders and Plane, 2006).

95 To the best of our knowledge, there are no studies of CO oxidation on olivines in the literature.
96 However, CO₂ formation on hematite (α-Fe₂O₃) has been studied previously: in addition to a
97 low temperature (196 K) study of CO uptake on Fe₂O₃ and Fe₃O₄ (Leu et al., 1992), Grenfell
98 et al. (2013) and Grenfell et al. (2010) used the experimental work of Wagloehner et al. (2008)
99 to show that the CO oxidation data was better modelled assuming the Eley-Rideal mechanism
100 with gaseous CO molecules reacting directly with adsorbed O₂. The diffusion of adsorbed O₂
101 (or O if the molecule dissociated on the surface) on α-Fe₂O₃ was not considered to be
102 significant i.e. the O₂ was confined to the active adsorption sites (Randall et al., 1997).

103 Calculations performed by Wu et al. (2015) for CO oxidation on a graphyne-supported single
104 Fe atom found that O₂ bonds more strongly than CO to the Fe atom, resulting in the incoming
105 CO molecules reacting with adsorbed O₂ *via* the Eley-Rideal mechanism. In contrast, Khedr et
106 al. (2006) found that CO₂ formation on Fe₂O₃ nanoparticles occurred through the Langmuir-
107 Hinshelwood mechanism, with CO reacting with dissociated O₂ molecules bound on Fe active
108 sites. A theoretical study by Bulgakov and Sadykov (1996) assigned CO oxidation to the
109 existence of defect centres or centres located on stepped planes on α-Fe₂O₃ surfaces.

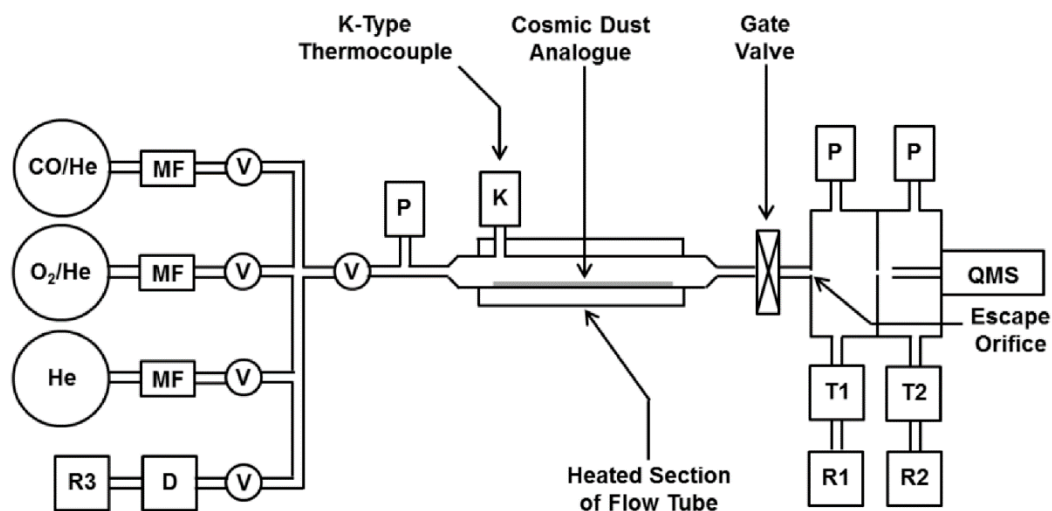
110 In the present study, meteoroids and MSPs were represented by synthetic olivine (MgFeSiO₄),
111 forsterite (Mg₂SiO₄) and fayalite (Fe₂SiO₄) analogues. In Venus' atmosphere, these particles

112 will sediment through the H₂SO₄ cloud layers between ~38 and 65 km (Knollenberg and
113 Hunten, 1980), which may chemically alter their composition through dissolution in
114 H₂SO₄/H₂O droplets and precipitation of sulfate salts on evaporation of the liquid droplets, in
115 a similar way to that proposed in Earth's atmosphere (Saunders et al., 2012). Thus, CO
116 oxidation within the H₂SO₄ clouds was explored on ferric (Fe₂(SO₄)₃) and ferrous sulfate
117 (FeSO₄) analogues. At the higher temperatures below the clouds, Fe sulfate particles will
118 decompose into Fe oxides (as demonstrated in the present study). Fe oxides were
119 represented with a synthetic goethite (FeOOH) analogue which dehydrates into hematite (α -
120 Fe₂O₃).

121 The experiments were performed using a flow tube technique combined with mass
122 spectrometry (Section 2). The mechanism with of CO oxidation was investigated (Section 3)
123 and the experimental uptake coefficients are then included in a 1D model of meteoric dust
124 transport in Venus' atmosphere in order to assess the potential impacts on CO oxidation and
125 O₂ removal (Section 4).

126 **2. Experimental Method**

127 A schematic diagram of the flow tube apparatus used to measure uptake coefficients on
128 meteoric dust analogues is shown in Figure 1. The quartz flow tube is 50 cm in length with an
129 internal diameter of 1 cm. The middle section of the flow tube (38 cm in length) was wrapped
130 in heating tape and Rockwool pipe insulation, enabling the flow tube temperature to be
131 varied between room temperature and 680 K. A K-type thermocouple located inside the
132 heated part of the flow tube was used to monitor the temperature of the dust analogue
133 surface.



134

135 **Figure 1.** Schematic diagram of the flow tube apparatus where MF denotes a

136 mass flow controller, V a 2- way valve, P a pressure gauge, K a K-type

137 thermocouple, QMS the quadrupole mass spectrometer and D, T and R are

138 diffusion, turbo and rotary pumps, respectively.

139

140 Attached to the flow tube is a stainless steel and glass gas-handling line fitted with mass flow

141 (MF) controllers (MKS Instruments, 20, 100 and 200 sccm). Pressure was measured by a

142 Baratron gauge (MKS, 0-1000 Torr) just upstream of the flow tube. Downstream, the flow

143 tube is coupled to a double differentially pumped vacuum chamber equipped with a

144 quadrupole mass spectrometer (QMS) (VG Quadrupoles, SXP Elite). The entrances to the first

145 and second differentially pumped chambers are separated by flanges with orifices of 0.3 and

146 1.2 mm diameter, respectively.

147 Of the meteoric material analogues used in this study, four were synthetic: MgFeSiO₄;

148 Mg₂SiO₄; Fe₂SiO₄; and FeOOH. Each of the metal silicate analogues were prepared using

149 sol-gel techniques by mixing solutions in stoichiometric amounts under stirring at room

150 temperature of magnesium chloride (MgCl_2) (Aldrich), ferrous (II) ammonium sulphate
151 ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$) (Sigma-Aldrich) and sodium orthosilicate (Na_4SiO_4) (Alfa Aesar). These
152 solutions were stirred at room temperature for 7 days to allow the reaction to go to
153 completion. Metal-salt by-products were removed from all of the synthetic analogues by
154 repeated dialysis using a soxhlet apparatus with the particles held in water permeable tubing
155 (Snakeskin, 7000 MWCO) for 12-16 hours. The products were then stored in a desiccator.
156 Goethite (FeOOH) was produced by stirring a solution of 0.1 mol l^{-1} each of $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2$ and
157 NaOH for 3 days with a flow of compressed air bubbling through the reacting solution. The
158 purified goethite product of this reaction was dehydrated by annealing at 573 K for 24 hours
159 to produce hematite (Fe_2O_3). These syntheses provide large quantities (10s g) of appropriate,
160 well-characterised analogues for bulk surface science work. Further details of the preparation
161 and characterisation of these amorphous materials with large specific surface areas are
162 provided in James et al. (2016). In order to explore the effect of the chemical alteration of
163 MSPs in the sulfuric acid clouds and haze layers in Venus' atmosphere, the dust analogues
164 ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) (BDH Chemicals Ltd.) and ferrous sulfate heptahydrate (FeSO_4) (Arcos
165 Organics) were used.

166 The physical and chemical characterisation of all the analogues used in this study (both before
167 and after each experiment) were explored using several techniques (see Table 1). Morphology
168 and elemental composition were obtained using transmission electron microscopy (TEM)
169 combined with energy-dispersive X-ray spectroscopy (EDX) (FEI Tecnai F20 200 kV FEGTEM
170 fitted with a Gantan Orius SC600 CCD camera and an Oxford Instruments X-Max 80 mm^2 SDD
171 EDX). These results were combined with the crystal structure analysis, obtained by X-ray
172 diffraction (XRD) (Bruker, D8 Advance with a $\text{Cu K}\alpha$ X-ray source), to constrain the nature of

173 each analogue. The XRD analysis also showed that the metal-silicate analogues were
 174 amorphous. The dust specific surface area, $a_{(BET)}$, was obtained *via* the Brunauer-Emmet-
 175 Teller (BET) isotherm (Micrometrics, ASAP 2020). The bulk density of each analogue (i.e. the
 176 density of the dust analogue particles in air) was measured by placing a known mass of sample
 177 in a measuring cylinder, so that the volume accessible to the gas in the flow tube could be
 178 calculated. The flow tube geometry was also used to estimate the surface area of the 0.5 g
 179 sample of each dust analogue exposed to the gas flow, where the dust was spread uniformly
 180 along the bottom of the flow tube. This yielded a minimum dust surface area, $a_{(GEO)}$, assuming
 181 no porosity and a flat surface. The validity of these $a_{(GEO)}$ values in relation to a realistic,
 182 textured surface is discussed in Section 3.3.

183

184 Table 1. BET surface area, $a_{(BET)}$, bulk mass densities and the geometric surface area
 185 $a_{(GEO)}$ (0.5 g sample in the flow tube) for each cosmic dust analogue.

Cosmic Dust Analogue	$a_{(BET)} / \text{m}^2 \text{g}^{-1}$	Bulk Density / g cm^{-3}	$a_{(GEO)} / \text{cm}^2$
Mg_2SiO_4	102.2±5.1	0.82±0.03	17.0
MgFeSiO_4 (300 K)	358.1±16.1	0.88±0.03	16.6
(heated to 656 K)	156.9±4.87		
Fe_2SiO_4 (300 K)	244.3±2.3	0.72±0.03	17.9
(heated to 683 K)	208.2±2.1		
$\text{FeOOH}/\text{Fe}_2\text{O}_3$ (unheated)	41.4±0.4	0.78±0.03	16.7
(heated to 495 K with CO and O ₂)	93.9±2.8		
(heated to 550 K with CO and O ₂)	104.9±3.0		
(heated to 636 K with CO)	34.4±0.2		
$\text{Fe}_2(\text{SO}_4)_3$ (unheated)	8.4±0.1	0.80±0.03	17.2
(heated to 698 K)	16.9±0.2		
FeSO_4 (unheated)	45.6±0.1	1.06±0.04	15.7
(heated to 689 K)	5.9±0.1		

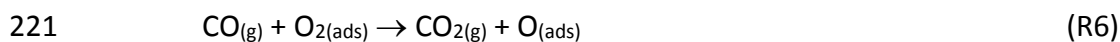
186 CO (>99.0 %, SAFC) and O₂ (>99.999 %, BOC) were each diluted in He (CP grade, BOC) to a
187 mixing ratio of 0.0134 using standard manometric techniques. In a typical experiment,
188 8.4 and 4.2 sccm of the CO/He and O₂/He gas mixtures, respectively, were introduced into
189 the flow tube simultaneously to provide a 2:1 ratio consistent with the stoichiometry of the
190 overall $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ reaction. In some experiments this ratio was varied in order to
191 investigate the kinetic order dependence and a balancing He flow was then used to maintain
192 constant pressure.

193 In a typical experiment, 0.5 g of a particular dust analogue was evenly distributed into the
194 heated section of the flow tube before degassing by pumping overnight. The flow tube was
195 heated to the selected temperature and allowed to stabilise for at least 30 minutes. The CO,
196 O₂ and CO₂ mass traces were then monitored for approximately 2 minutes to obtain
197 background counts, before introducing the CO and O₂ flows into the flow tube. Here, the
198 pressure inside the flow tube rose to ~10 Torr; at this relatively low pressure, diffusion of
199 reactants through the gas phase does not kinetically limit the uptake process. Once the mass
200 traces had stabilised, the data was collected for a minimum of 5 minutes before terminating
201 the gas flow. After the mass traces decreased to a minimum they were once again monitored
202 for background correction. The uptake of CO and O₂ onto the flow tube walls was determined
203 by repeating all the experiments with the same procedure, but without a dust sample in the
204 flow tube. Once background corrected, the empty flowtube data was subtracted from the
205 background corrected dust data to determine the changes to the CO, O₂ and CO₂ caused by
206 CO oxidation on the dust analogue. After each experiment, the sample was recovered for
207 compositional, structure and BET analysis.

208

209 3. Results and Discussion

210 The proposed mechanism for the heterogeneous oxidation of CO on these dust samples is
211 shown by reactions R5 to R7. The evidence supporting this mechanism is presented in the
212 following sub-sections. The subscripts *g* and *ads* denote molecules in the gas phase and
213 adsorbed to the dust surface, respectively. Based on a review of the literature (see Section 1),
214 adsorption of O₂ at these elevated temperatures most likely involves chemisorption to an Fe
215 active site. Once bound, the O₂ molecules remain confined to these surface sites (e.g. Randall
216 et al. (1997)), until reaction with gas-phase CO molecules through the Eley-Rideal mechanism
217 (reactions 6 and 7). The CO molecules remove each O atom in succession, with reaction 6
218 being the overall rate-determining step. Electronic structure calculations are presented in
219 Section 3.6 to support this mechanism and interpret the experimental observations.

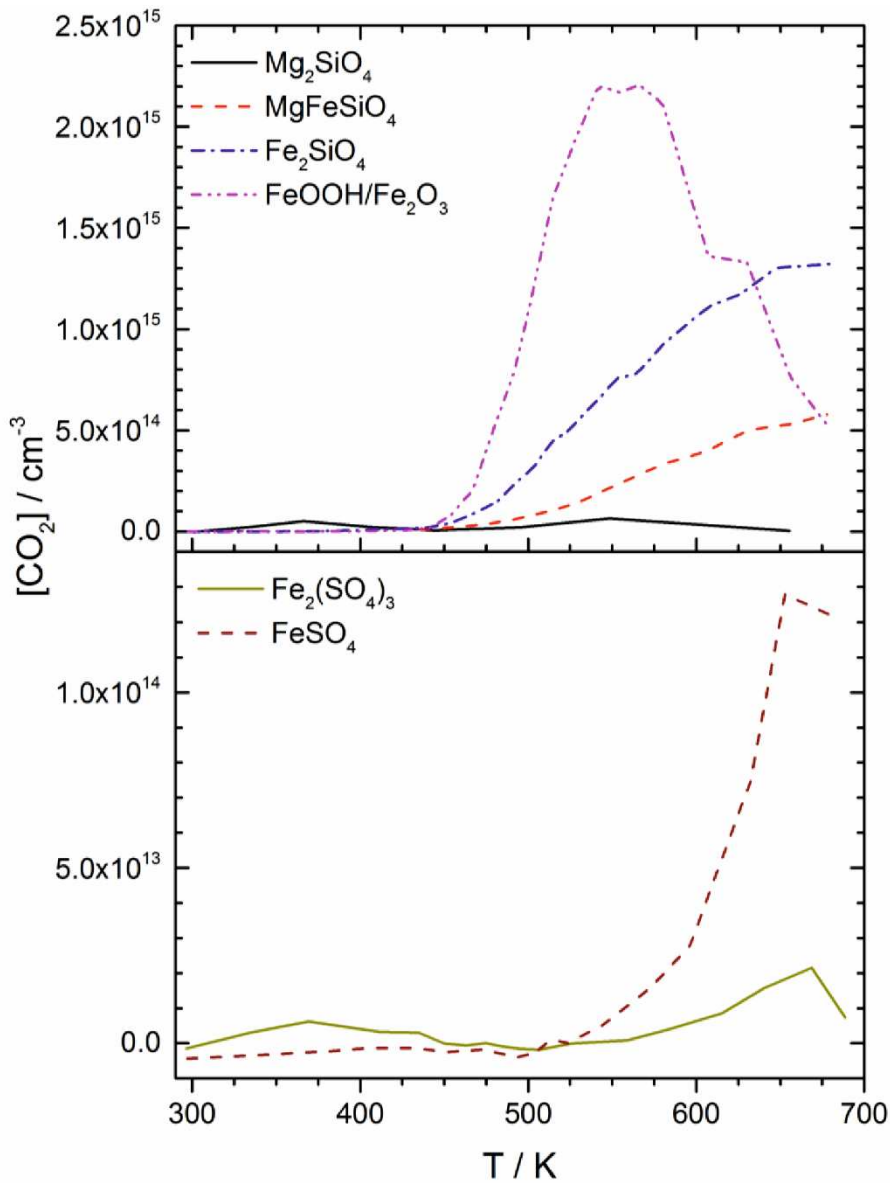


223

224 3.1. Fe Active Site Dependence

225 Figure 2 illustrates the concentration of CO₂ downstream of the flow tube as a function of
226 temperature, for 0.5 g of each of the analogue dust samples. On MgFeSiO₄ and Fe₂SiO₄, the
227 CO₂ mass trace became detectable above the noise at ~450 K, and appears to plateau around
228 680 K. About 50% less CO₂ is produced on MgFeSiO₄ compared with Fe₂SiO₄, and none was
229 detected on Mg₂SiO₄. This implies that the surface reaction is governed by the availability of
230 Fe active surface sites. The amount of CO₂ formed on the FeSO₄ and Fe₂(SO₄)₃ samples is

231 approximately 1 and 2 orders of magnitude smaller, respectively, than that formed on
232 Fe_2SiO_4 . These differences could be due to the smaller BET surface areas of the sulphate
233 particles (Table 1), and a lower oxidation efficiency of the Fe^{3+} ions in $\text{Fe}_2(\text{SO}_4)_3$.



234

235 **Figure 2.** The CO_2 concentration produced from each dust analogue, as a

236

function of temperature in the flow tube.

237

238 CO₂ production on FeSO₄ and Fe₂(SO₄)₃ is not apparent until around 540 K. From 450 to 540 K,
239 a small drop in the CO mass trace was detected in the experiments with FeSO₄ in the flow
240 tube, indicating adsorption of CO although no CO₂ production was observed. The onset of CO₂
241 production coincides with the decomposition of the sulfates to oxides. This was shown by a
242 colour change in the dust samples (turquoise green to pale yellow for FeSO₄; ivory to pale
243 caramel for Fe₂(SO₄)₃). XRD analysis confirmed that FeSO₄ had partly decomposed to Fe oxides
244 (including α-Fe₂O₃), and SO₂ production was observed from 540 K when CO₂ became
245 detectable. This process is hypothesised to occur through the following reactions:

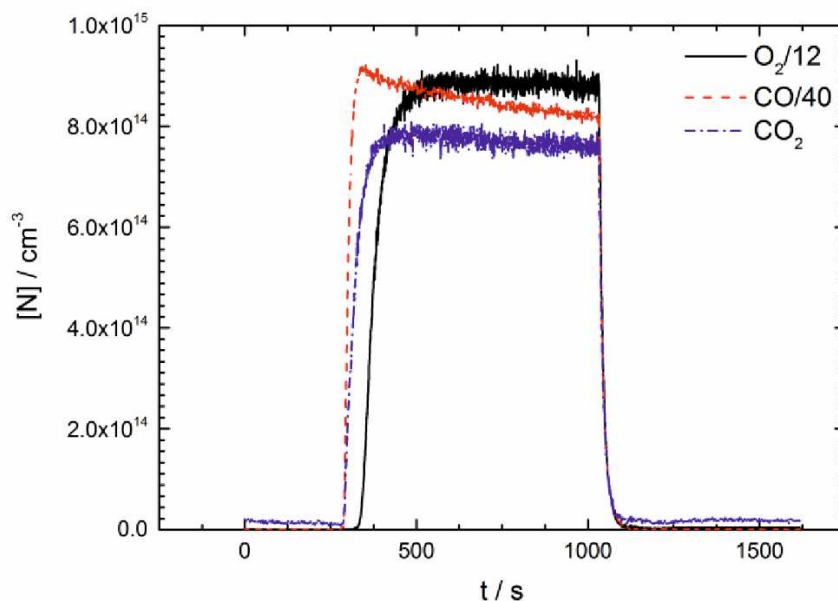


248 CO oxidation on FeOOH is complex as FeOOH dehydrates to hematite (α-Fe₂O₃) at elevated
249 temperatures (Cornell and Schwertmann, 2003), so hereafter this dust analogue will be
250 referred to as FeOOH/Fe₂O₃. Overall, a faster rate of CO oxidation was detected on
251 FeOOH/Fe₂O₃ compared to Fe₂SiO₄ (Figure 2), despite FeOOH having a BET surface area, $a_{(\text{BET})}$,
252 ~ 6 times smaller than Fe₂SiO₄ (Table 1). The temperature at which the CO₂ mass trace became
253 detectable above the noise was similar to that of Fe₂SiO₄ and MgFeSiO₄. The CO oxidation
254 rate peaks at ~ 550 K; the decrease at higher temperatures is probably due to sintering of the
255 dust causing the observed reduction of the BET surface area.

256 3.2. O₂ Uptake to Fe Active Sites

257 A key observation in these experiments was a delay in the O₂ mass trace despite the O₂/He
258 and CO/He gas mixtures being introduced to the dust analogue at the same time (Figure 3).
259 This delay, which was typically around 5 s on Fe₂SiO₄, implies that O₂ molecules are

260 preferentially and rapidly adsorbed on the Fe active sites, and hence O₂ does not emerge at
261 the downstream end of the flow tube until all these sites have been occupied (this is modelled
262 in Section 3.3). The delay in O₂ has also been observed by Wagloehner et al. (2008) and Wu
263 et al. (2015) for CO oxidation by O₂ on α -Fe₂O₃ and pure Fe, respectively. Note that the rapid
264 uptake of O₂ to the empty Fe active sites indicates that O₂ adsorption is not the rate-
265 determining step in the CO oxidation mechanism under these experimental conditions. Since
266 the distance between adjacent surface Fe atoms on these dust minerals (4.82 Å for Fe₂SiO₄
267 (Hazen, 1977); 6.50 Å for FeSO₄ (Anderson et al., 2007); 3.01 Å for FeOOH and 5.03 Å for α -
268 Fe₂O₃ (Cudennec and Lecerf, 2005)) are much larger than the O-O bond distance (1.21 Å), it
269 seems unlikely that an adsorbed O₂ would stretch across adjacent Fe atoms and dissociate.



270

271 **Figure 3.** O₂, CO and CO₂ in a typical experiment on Fe₂SiO₄ indicating the delay
272 in the O₂ mass trace with respect to CO and CO₂.

273

274 3.3. Surface Area Available for CO Oxidation

275 The rate of uptake of a gas to a solid surface is characterised by the uptake coefficient, γ ,
276 defined as the probability that a collision will result in the loss of a molecule from the gas
277 phase. In this experimental set-up, γ can be calculated from the expression:

$$278 \quad \gamma = \frac{4F}{\bar{c}\alpha_s} \ln\left(\frac{[N_0]}{[N_\tau]}\right) \quad (1)$$

279 where F is the total flow rate through the flow tube (in $\text{cm}^3 \text{s}^{-1}$); \bar{c} is the molecular mean speed
280 (cm s^{-1}); α_s the surface area available for uptake (cm^2); and $[N_0]$ and $[N_\tau]$ are the
281 concentrations of species N upon entering and exiting the flow tube, respectively (τ is the
282 residence time of the species N in the flow tube). $[N_0]$ and $[N_\tau]$ were taken as the CO mass
283 signals in the experiments without and with dust, respectively. F was obtained by correcting
284 the calibrated mass flow controller settings for the experimental temperature and pressure.

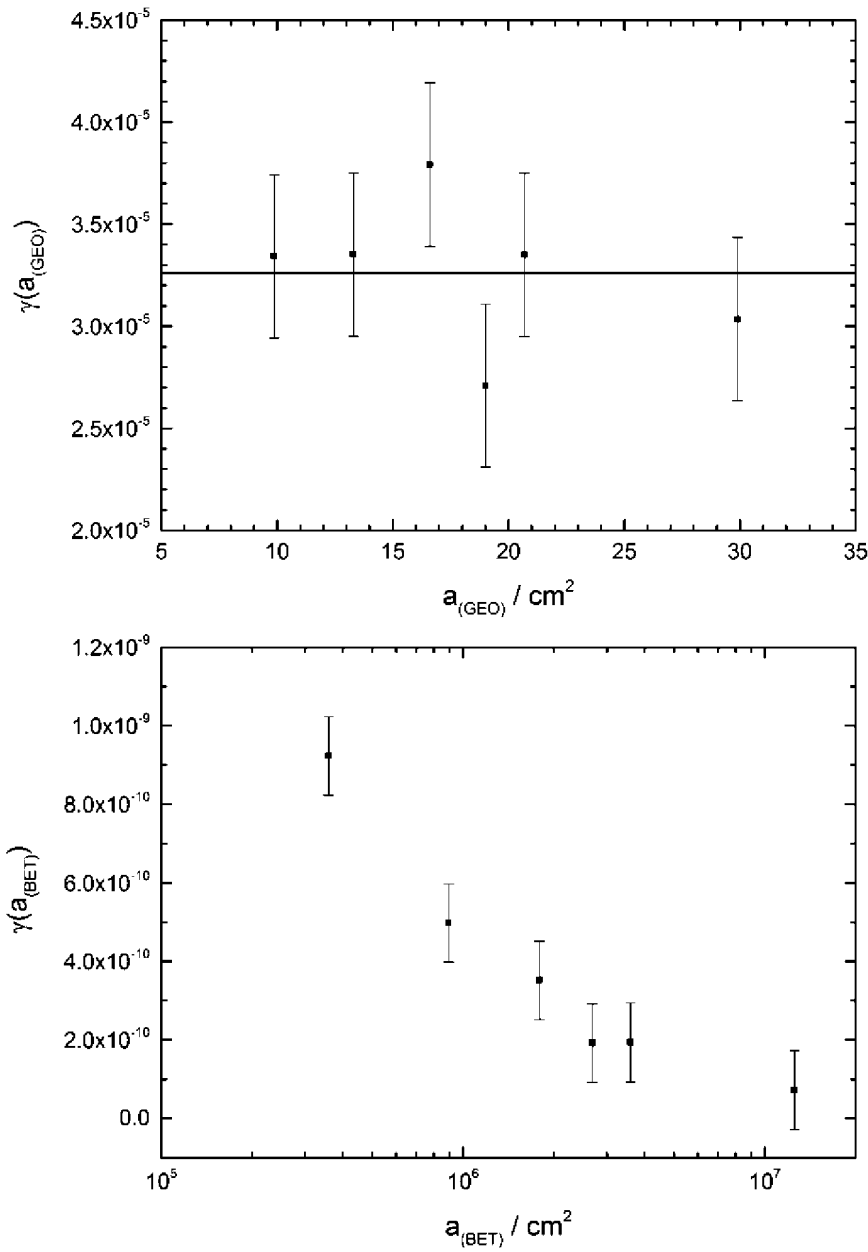
285 One potential complication with this technique is knowing the fraction of the dust surface
286 area which is available for the uptake of O_2 and CO. At one extreme, if the gas is readily taken
287 up then it will only be the particles in the uppermost layers of the sample which will be directly
288 involved. At the other extreme, an unreactive gas will penetrate throughout the sample and
289 be exposed to the full surface area of the dust analogue particles.

290 Possible values of α_s range from the geometric surface area, $a_{(GEO)}$ (the surface area of the
291 dust sample inside the heated region of the flow tube if a smooth ideal surface is assumed –
292 see Table 1), to the surface area given by the Brunauer-Emmet-Teller isotherm, $a_{(BET)}$.
293 Measured values of $a_{(BET)}$ with respect to temperature (to account for thermal processing of
294 the dust analogues) are listed in Table 1. It should be noted that annealing MgFeSiO_4 in an

295 oven at 1027 K for 48 hours did not reduce the surface area by more than the factor of 2
296 shown in Table 1 for 30 mins at 656 K.

297 $a_{(GEO)}$ and $a_{(BET)}$ were varied by varying the sample mass of $MgFeSiO_4$ from 0.1 to 3.5 g at 490
298 K (at which temperature the BET surface area was not significantly different than that
299 measured before exposure to high temperatures). The results are plotted in Figure 4 with the
300 error in γ calculated from the error in the CO_2 concentration which was taken as one standard
301 deviation of the mean between repeats. The upper plot shows there is no variation in $\gamma(a_{(GEO)})$
302 with respect to $a_{(GEO)}$. Taking the assumption that $a_s = a_{(BET)}$, the number of active sites for CO
303 oxidation should increase linearly with the available mass. The lower panel shows a physically
304 unreasonable variation of $\gamma(a_{(BET)})$ with the total available surface area (hence no fit was
305 applied to Figure 4b). This suggests that the surface area available for CO oxidation is
306 significantly less than $a_{(BET)}$, and is much closer to $a_{(GEO)}$. A similar result was obtained with the
307 $FeOOH/Fe_2O_3$ dust.

308



309

310 **Figure 4.** The uptake coefficient, γ , of CO on MgFeSiO₄ at 490 K as a function of dust surface
 311 area. The top panel shows γ calculated using the geometric surface area, $a_{(GEO)}$, which yields
 312 an upper limit; the bottom panel shows γ calculated using the BET surface area, $a_{(BET)}$, which
 313 yields a lower limit for γ .

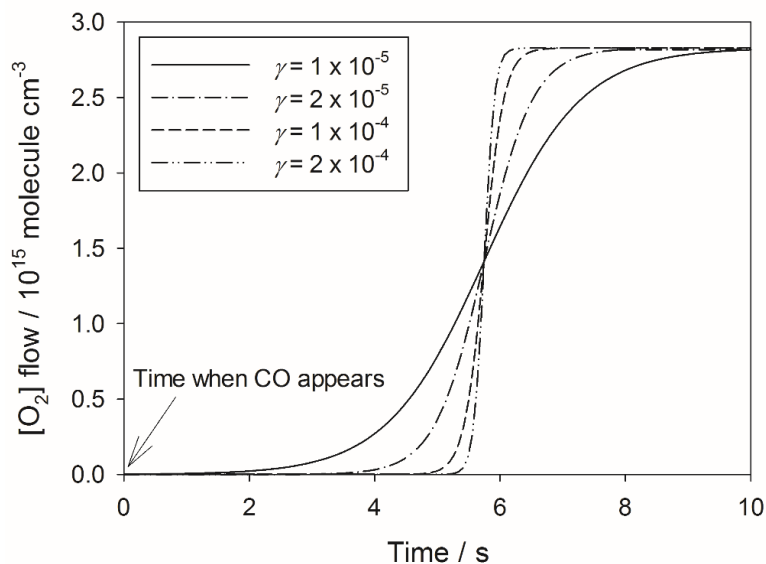
314

315 The available surface area can also be estimated from the observed delay in the O₂ signal
316 when the CO and O₂ flows are first switched on simultaneously (see Section 3.2 and Figure 3).
317 The observed O₂ signal delay indicates that the O₂ molecules were taken up on the surface
318 but, after some time, the surface reached an equilibrium between uptake of O₂ and
319 production of CO₂, the latter reactivating available surface sites. The amount of O₂ which was
320 required to saturate the surface was calculated from the O₂ mixing ratio in the gas flow and
321 the flow rate through the reactor. This amount of saturated O₂ was converted into a surface
322 density based on the value of $a_{(GEO)}$ for the analogue being used. Assuming that only a single
323 O₂ molecule occupied each Fe active site on the analogue surface, the adjustment required
324 to get the available reactive surface area, a_r , from $a_{(GEO)}$ was obtained by taking the ratio of
325 the surface densities of O₂ to Fe for each analogue.

326 In the case of Fe₂SiO₄, the surface density of adsorbed O₂ is 54 times larger than that of Fe
327 active sites (Hazen, 1977). This implies, as expected, that the rough surface area provided by
328 an assemblage of particles provides a considerably larger reactive surface area a_r , which we
329 define as $a_r = 54a_{(GEO)}$. For a 0.5 g sample of Fe₂SiO₄, $a_{(GEO)}$ is 17.9 cm² and so a_r is 967 cm².
330 Note that this is much smaller than $a_{(BET)} = 1.2 \times 10^6$ cm² (Table 1). The surface density of Fe
331 active sites in the synthesized MgFeSiO₄ analogue is not known, and so it was assumed here
332 that the closest distance between two Fe active sites on the surface is the same as that for
333 Fe₂SiO₄ i.e. a_r for MgFeSiO₄ was taken as $54a_{(GEO)}$, which is possibly a lower limit.

334 The O₂ time delay for FeSO₄ was below that of the QMS time resolution (0.6 s), giving a lower
335 limit for $a_r(FeSO_4)$ of $17a_{(GEO)}$. The O₂ time delay on FeOOH/Fe₂O₃ varied between 2 and 121 s
336 depending on T , so that a_r varied between $16a_{(GEO)}$ to $928a_{(GEO)}$. A possible explanation for this
337 variation in a_r is that the crystal structure of this dust analogue changes as FeOOH dehydrates

338 to $\alpha\text{-Fe}_2\text{O}_3$ with respect to time and temperature (Cornell and Schwertmann, 2003). Note that
 339 these values of a_r for $\text{FeOOH}/\text{Fe}_2\text{O}_3$ dust are a relatively small increase in a_s compared to the
 340 upper limit given by $a_{(BET)}$, suggesting that that the increase from a_s to a_r is likely due to surface
 341 roughness and the CO oxidation occurring in the few uppermost layers of the particles.
 342 Using a_r , we can now estimate a lower limit to the uptake coefficient for O_2 on olivine, $\gamma(\text{O}_2)$.
 343 A kinetic uptake model of the flow tube was constructed with $a_r = 967 \text{ cm}^2$ (see above). The
 344 radius of each adsorption site was set equal to 3 \AA , roughly half the distance between adjacent
 345 surface Fe atoms in Fe_2SiO_4 (Hazen, 1977). Figure 5 shows the modelled O_2 concentration in
 346 the downstream flow for a range of $\gamma(\text{O}_2)$, plotted as a function of time after CO first appears
 347 (see the figure caption for experimental details). This figure demonstrates that $\gamma(\text{O}_2)$ must be
 348 larger than 2×10^{-5} in order to explain the observed time delay of 5 s.



349
 350 **Figure 5.** Modelled concentration of O_2 exiting the flow tube as a function of time after CO
 351 first appears, for a range of $\gamma(\text{O}_2)$ on Fe_2SiO_4 . Conditions: $T =$ at 500 K; pressure = 10 torr;
 352 total flow = $12.2 \text{ cm}^3 \text{ s}^{-1}$; O_2 mixing ratio = 0.0165.

353

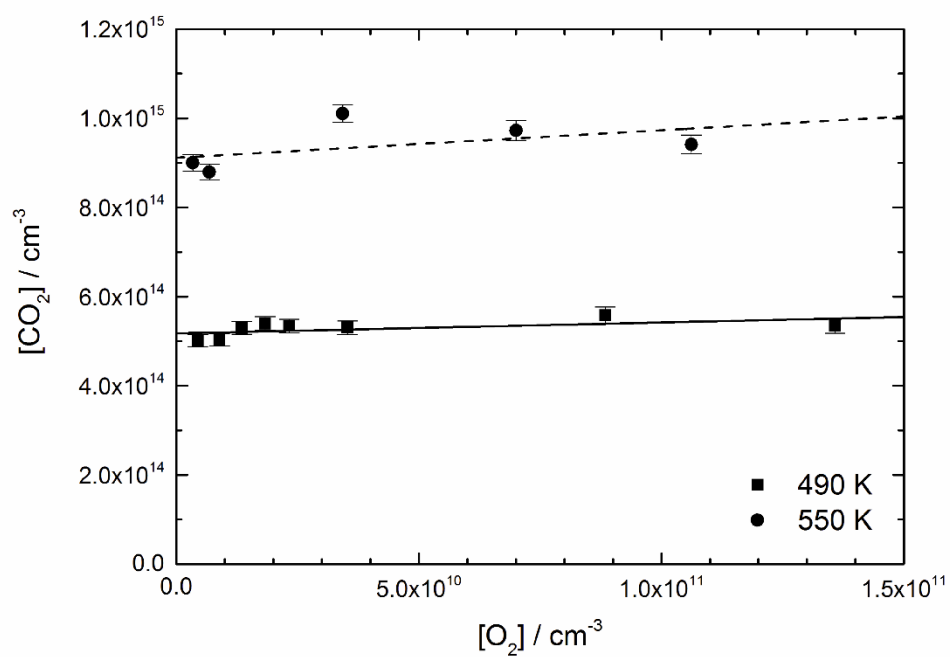
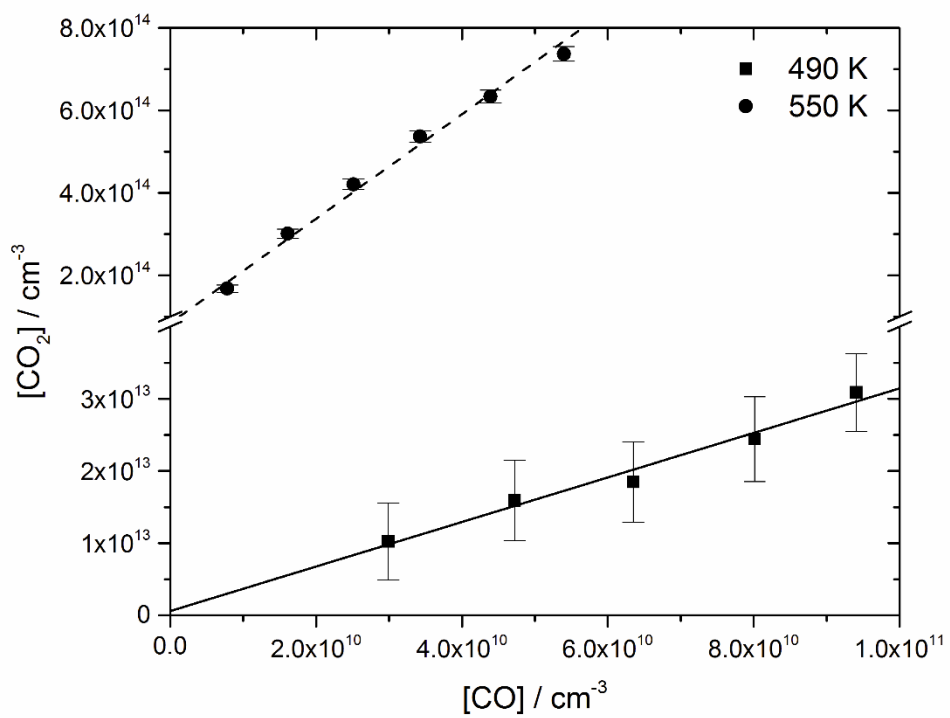
354 Another consequence of the surface being saturated with chemisorbed O₂ molecules is that
355 the incoming CO molecules would be unable to adsorb and diffuse across the dust analogue
356 surface. Thus, the CO oxidation was assumed to follow the Eley-Rideal (reaction without prior
357 accommodation of one of the reactants on the surface) rather than the Langmuir-
358 Hinshellwood surface mechanism. This is in agreement with the recent work of Grenfell et al.
359 (2013) and Wu et al. (2015).

360

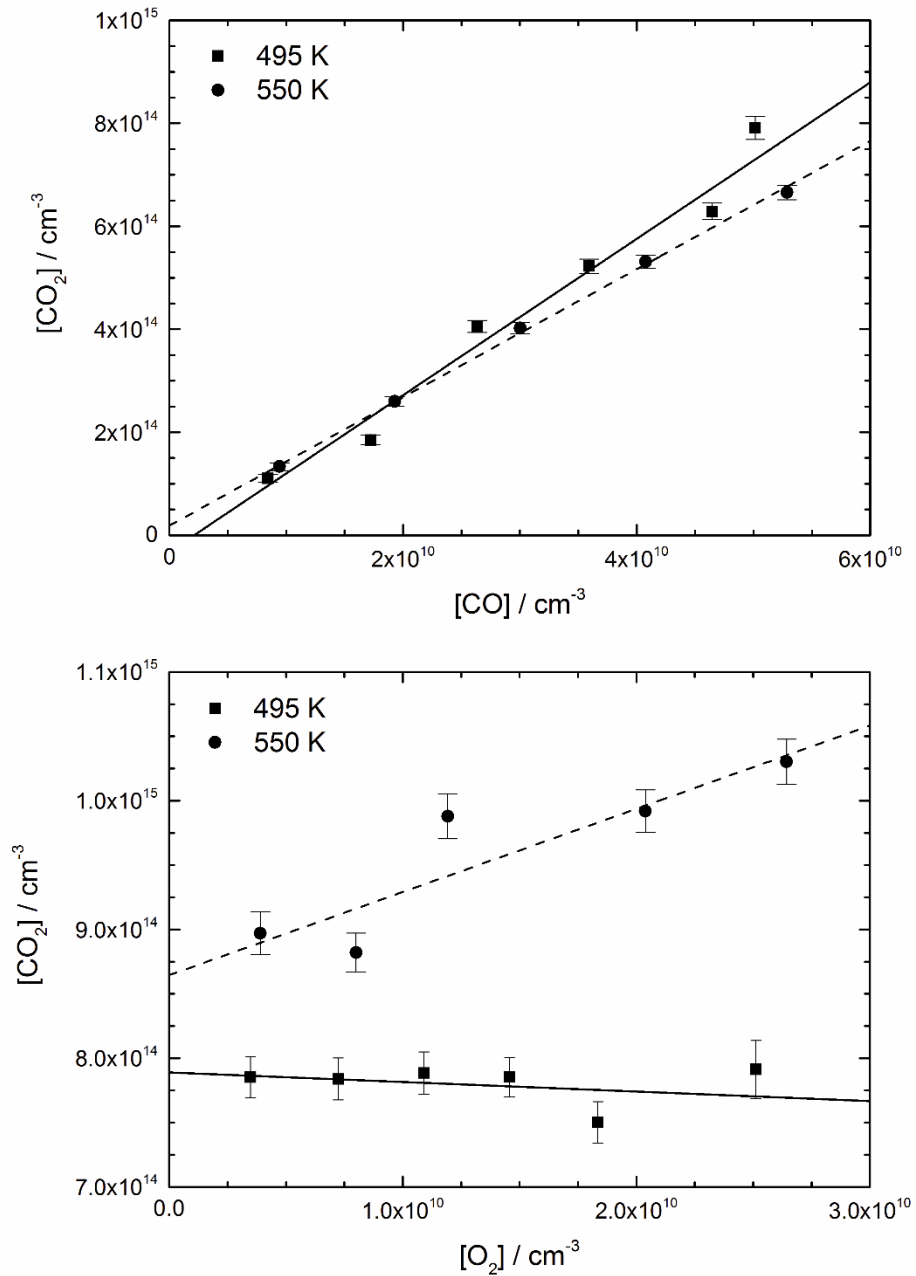
361 *3.4. CO Oxidation as the Rate Determining Step*

362 As discussed earlier in Section 3, the reaction of CO with adsorbed O₂ is assumed to be the
363 rate-determining step in the overall oxidation of CO. Further evidence for this was obtained
364 by examining the kinetic order dependence of CO₂ formation on [CO] and [O₂]. This was
365 explored on MgFeSiO₄ at 490 and 550 K (Figure 6), and on FeOOH/Fe₂O₃ at 495 and 550 K
366 (Figure 7) with the error taken as one standard deviation of the mean CO₂ concentration
367 between repeats. Both dust samples (at all temperatures) showed a first-order dependence
368 on CO (note the break in the ordinate axis of the CO plot in Figure 6). For O₂, the slopes are
369 close to zero within error, indicating that the O₂ dependence is zeroth order on MgFeSiO₄ at
370 both temperatures, and on FeOOH/Fe₂O₃ at 495 K. The same kinetic order behaviour for CO
371 and O₂ has been observed previously on superfine maghemite (γ -Fe₂O₃) nanoparticles at
372 517 K (Li et al., 2003). The change in kinetic behaviour with respect to O₂ on FeOOH/Fe₂O₃ at
373 550 K could be due to the dust analogue having full transformed to α -Fe₂O₃.

374



377 **Figure 6.** Dependence of CO₂ formation on CO (top – note the break in the ordinate axis) and
378 O₂ (bottom) for MgFeSiO₄ at 490 K and 550 K. The lines are linear regression fits to the data
379 at 490 K (solid) and 550 K (dashed).



380

381

382

383 **Figure 7.** Dependence of CO₂ formation on CO (top) and O₂ (bottom) for
 384 FeOOH/Fe₂O₃ at 495 K and 550 K. The lines are linear regression fits to the data
 385 at 490 K (solid) and 550 K (dashed).

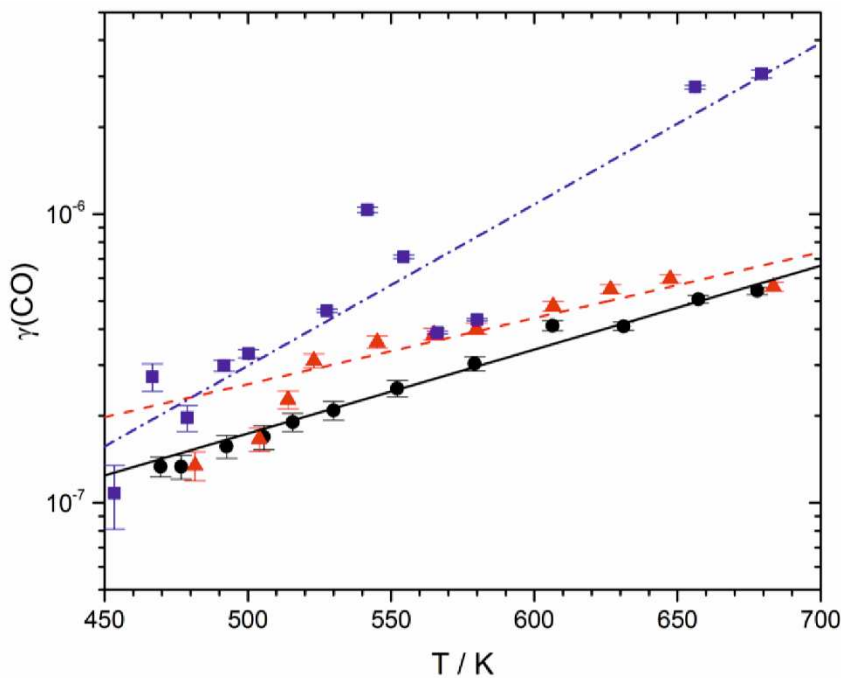
386 *3.5. Temperature dependence of uptake*

387 For each dust where significant uptake was observed, the uptake coefficient was calculated
 388 using equation 1 with α_s taken as α_r for that dust analogue (Section 3.3). Figure 8 shows that
 389 $\gamma(\text{CO})$ increases exponentially with temperature. Because CO₂ production was not observed
 390 until FeSO₄ had decomposed into Fe oxides (section 3.1), FeSO₄ is excluded from Figure 8.
 391 MgFeSiO₄ has a similar slope but lower $\gamma(\text{CO})$ compared to Fe₂SiO₄. Regression fits though
 392 each data set between 450 and 700 K yield:

393 $\log_{10}(\gamma(\text{CO on MgFeSiO}_4)) = (2.9 \pm 0.1) \times 10^{-3} T(\text{K}) - (8.2 \pm 0.1);$

394 $\log_{10}(\gamma(\text{CO on Fe}_2\text{SiO}_4)) = (2.3 \pm 0.3) \times 10^{-3} T(\text{K}) - (7.7 \pm 0.2);$

395 $\log_{10}(\gamma(\text{CO on FeOOH/Fe}_2\text{O}_3)) = (5.6 \pm 0.8) \times 10^{-3} T(\text{K}) - (9.3 \pm 0.4).$



396

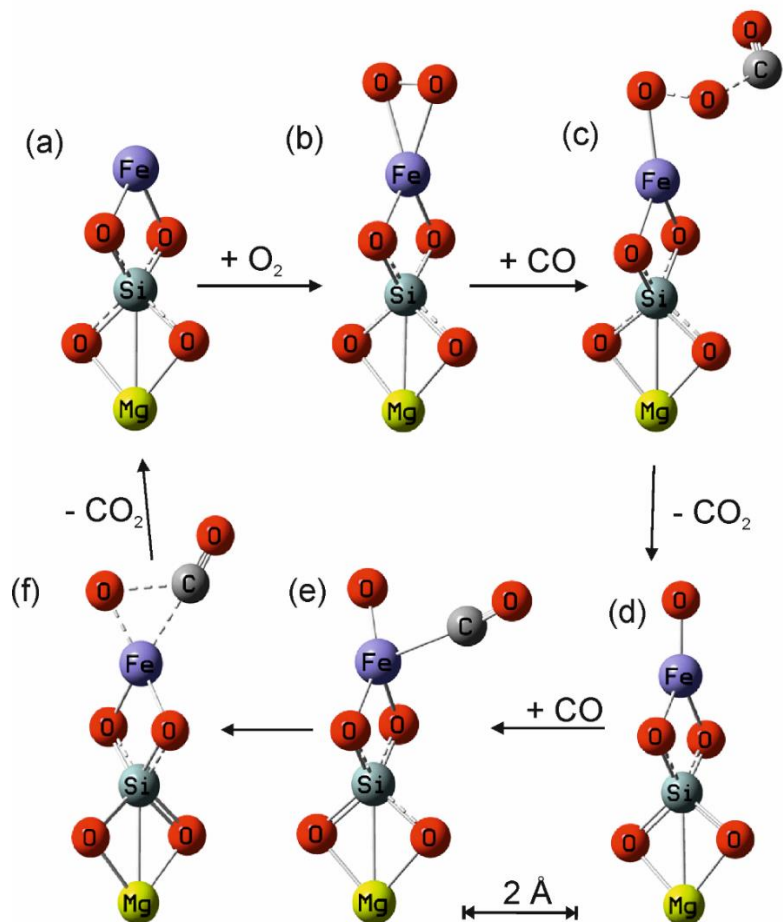
397 **Figure 8.** CO uptake coefficient, $\gamma(\text{CO})$, with respect to temperature for MgFeSiO_4
398 (circles, solid line), Fe_2SiO_4 (triangles, dashed lines) and $\text{FeOOH}/\text{Fe}_2\text{O}_3$ (squares, dash-
399 dot line).

400 *3.6 Electronic structure calculations*

401 We now use quantum theory calculations to examine the heterogeneous reaction mechanism
402 postulated from the experimental results. The hybrid density functional/Hartree-Fock B3LYP
403 method was employed together with the 6-311+G(2d,p) triple zeta basis set, which is a
404 reasonably large, flexible basis set with both polarization and diffuse functions added to the
405 atoms. We have used this level of theory previously for calculations on Fe- and Mg-containing
406 oxides, hydroxides and silicates (Saunders and Plane, 2011; Rapp et al., 2012). The expected
407 uncertainty in the calculated reaction enthalpies is $\pm 20 \text{ kJ mol}^{-1}$ at this level of theory. The
408 calculations were performed using the Gaussian 09 suite of programs (Frisch et al., 2009).

409 The Eley-Rideal mechanism supported by the calculations is illustrated in Figure 9. We first
410 consider the binding of O_2 with exposed surface sites i.e., to either the Fe or Mg end of an
411 FeMgSiO_4 unit, followed by reaction with CO. While this is clearly an approximation of the
412 surface, it yields useful insights into the reaction mechanism. For each molecule the geometry
413 was first optimised, and then vibrational frequencies calculated to determine the zero point
414 energy correction. The most stable form of FeMgSiO_4 (Figure 9(a)) has quintet spin multiplicity
415 (Saunders and Plane, 2011) because of the presence of the Fe atom. We therefore considered
416 all possible spin multiplicities of the species involved in O_2 uptake and subsequent reaction.
417 The results for the most stable spin states are reported here.

418 O₂ binds much more strongly to the Fe end of the molecule (binding energy = 146 kJ mol⁻¹),
419 compared with the Mg end (66 kJ mol⁻¹). This is consistent with the observed rate of CO₂
420 production depending on Fe active sites (Section 3.1). Note that the strong O₂-Fe binding
421 energy ensures that O₂ will adsorb at temperatures as high as 700 K. CO can then attack the
422 adsorbed O₂ (Figure 9(b)) via the transition state (Figure 9(c)) to yield CO₂ and the single
423 adsorbed O in Figure 9(d). Finally, a second CO removes this O via the transition state in Figure
424 9(e), which then releases the Fe active site for further uptake of O₂. The transition state for
425 attack by the first CO (Figure 9(c)) is 113 kJ mol⁻¹ above the reactants O₂FeMgSiO₄ + CO. In
426 contrast, the energy barrier for the gas-phase reaction CO + O₂ → CO₂ + O is 203 kJ mol⁻¹. This
427 explains why the heterogeneous reaction is significantly faster, and the positive temperature
428 dependence of $\gamma(\text{CO})$ (Figure 8). The presence of this barrier also supports the conclusion that
429 CO reacting with adsorbed O₂ is the rate determining step, so long as there is significant O₂ to
430 pre-adsorb onto the surface. There is no barrier for the reaction OFeMgSiO₄ + CO: the
431 transition state in Figure 9(f) is 3.6 kJ mol⁻¹ below the energy of the reactants, because the
432 reaction first involves formation of an O(CO)FeMgSiO₄ complex (Figure 9(e)), followed by
433 rearrangement to the CO₂ + FeMgSiO₄ products. A final point is that CO binds much less
434 strongly to FeMgSiO₄ than O₂: the binding energies are 110 compared with 146 kJ mol⁻¹. This
435 explains why the reaction involves gas-phase CO reacting with adsorbed O₂, in agreement
436 with the finding of Leu et al. (1992) who measured negligible uptake of CO on metal oxides
437 including Fe₂O₃ in the absence of O₂.



438

439 **Figure 9.** Electronic structure calculations at the B3LYP/6-311+g(2d,p) level of theory,
 440 illustrating the oxidation of CO by O₂ on FeMgSiO₄: (a) FeMgSiO₄, quintet spin multiplicity; (b)
 441 O₂ adsorbed on the Fe active site, septet spin multiplicity; (c) transition state for CO₂
 442 formation in the rate-determining step, septet spin multiplicity; (d) singly bound O, quintet
 443 spin multiplicity; (e) addition of CO to form a weakly-bound complex, quintet spin multiplicity;
 444 (f) transition state for formation of a second CO₂ molecule, quintet spin multiplicity, which
 445 regenerates the Fe active site (a).

446

447 We now use electronic structure theory to examine two aspects of the possible role of SO₂ in
 448 CO oxidation below the clouds on Venus. Firstly, “poisoning” of these dust catalysts by SO₂

449 binding to the Fe-active sites. In fact, SO₂ also binds much less strongly than O₂, with a binding
450 energy of only 115 kJ mol⁻¹, so that adsorbed SO₂ should be displaced by O₂. The second role
451 of SO₂ is as a gas-phase oxidant of CO in the high temperatures of the Venusian troposphere
452 (Krasnopolsky, 2013). Reaction 4 has been studied in a shock tube between 1770 and 2450 K
453 (Bauer et al., 1971). However, a subsequent theoretical study (Bacskey and Mackie, 2005)
454 found that the reaction barrier on the singlet potential energy surface, calculated at a high
455 level of theory, was 245 kJ mol⁻¹; that is, considerably larger than the activation energy of 202
456 ± 4 kJ mol⁻¹ measured in the shock tube study. In fact, complex kinetics were observed in the
457 flow tube, which Bauer et al. (1971) postulated was due to vibrationally excited SO₂. Bacskey
458 and Mackie (2005) (and earlier theoretical work) demonstrated that trace impurities in the
459 CO₂ could also have been responsible. Since previous theoretical work has focused on
460 temperatures well above 1000 K, we determined the transition state for the reaction in order
461 to calculate an Arrhenius expression for the rate coefficient, k_4 , over the 300 – 800 K
462 temperature range applicable to Venus, where the temperature ranges from ~400 to 740 K
463 between 40 km and the surface (Krasnopolsky, 2012). The transition state geometry was first
464 optimized at the B3LYP/6-311+g(2d,p) level for rotational constants and vibrational
465 frequencies. An accurate barrier height of 249 kJ mol⁻¹ was then determined at the complete
466 basis set CBS-QB3 level of theory (Frisch et al., 2009), which is in excellent agreement with
467 Bacskey and Mackie (2005). The resulting expression calculated using Transition State Theory
468 is $k_4(300-800\text{ K}) = 9.4 \times 10^{-13} \exp(-256\text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It should be noted that
469 k_4 is predicted to be ~4 orders of magnitude smaller at a temperature of 620 K (typical of the
470 lower troposphere around 15 km altitude), than extrapolating from the shock tube result
471 above 1770 K adopted in the model of Krasnopolsky (2013). Of course, the reverse reaction

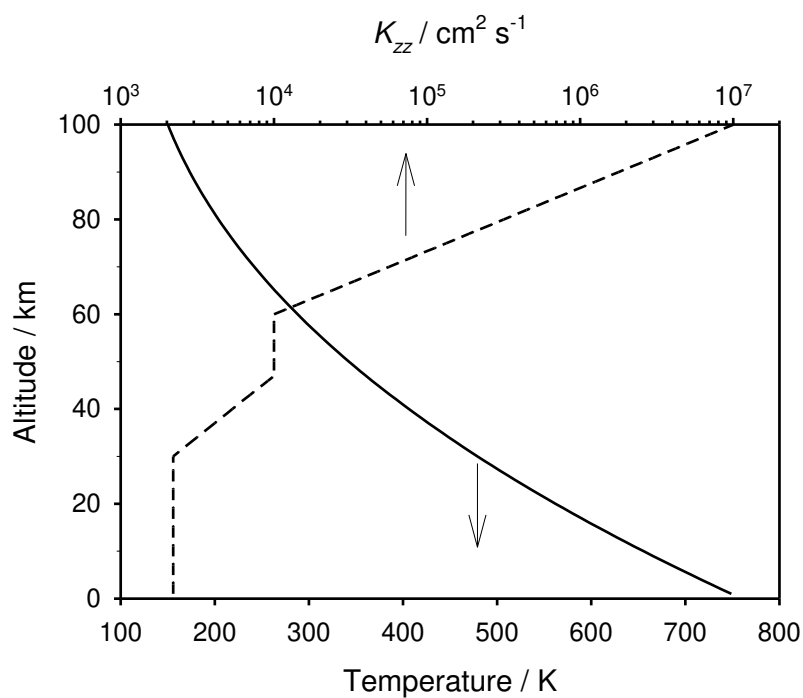
472 between CO₂ and SO to form SO₂ + CO, which nearly balances in that model, will be reduced
473 by the same factor.

474

475 4. Atmospheric Implications

476 4.1 Modelling the cosmic dust abundance

477 To study the impact of heterogeneous CO oxidation on meteoric particles in Venus'
478 atmosphere, a 1D model was constructed for the conditions of the dayside. The vertical
479 profiles of temperature, eddy diffusion coefficient (K_{zz}) and pressure were based on
480 Krasnopolsky's 1D model (Krasnopolsky, 2007;2012). The profiles of T and K_{zz} are illustrated
481 in Figure 10.



482

483 **Figure 10.** Vertical profiles of temperature and eddy diffusion coefficient (K_{zz}).

484

485 The major sources of cosmic dust particles in the inner solar system are the asteroid belt,
486 Jupiter Family comets (JFCs), and Halley Type/Oort Cloud comets. In the Zodiacal Cloud Model
487 (ZCM) developed by Nesvorný et al. (2010), sub-mm particles from these sources are
488 launched and tracked as their orbits evolve under the influence of solar radiation pressure,
489 Poynting-Robertson drag and planetary perturbations. Observations of infra-red emission
490 from the Zodiacal Cloud, measured by the Infrared Astronomical Satellite (IRAS), indicates
491 that the majority (>80%) of the IR emission is produced by particles originating from Jupiter
492 family comets (Nesvorný et al., 2010; Nesvorný et al., 2011).

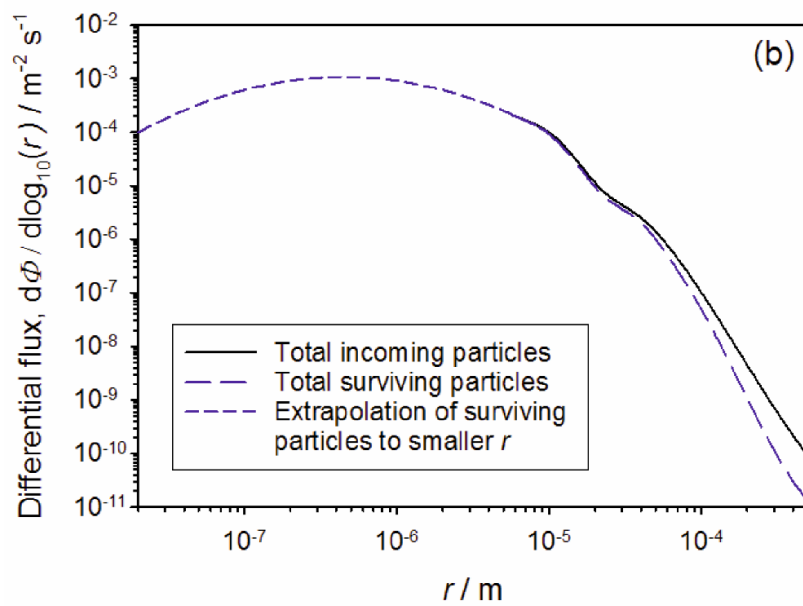
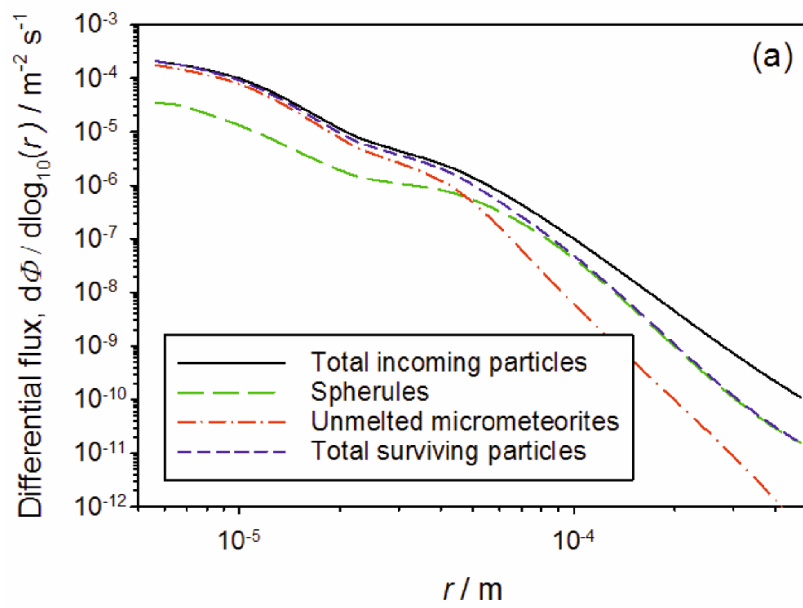
493 Here we use a specific version of the ZCM model that was calibrated on several constraints
494 using the methods from Nesvorný et al. (2010; 2011). The size distribution of cosmic dust
495 particles was assumed to be represented by a broken power law with a differential index -2
496 to -3 below the break diameter D_{break} , and a differential index -4 to -5 above D_{break} . While this
497 is arguably a crude approximation of the real size distribution, it is a good starting point to
498 explore the dependence on D_{break} . The Long Duration Exposure facility (LDEF) results
499 suggested that $D_{\text{break}} \sim 200 \mu\text{m}$ for particles accreted by the Earth (e.g. Love and Brownlee
500 (1993)). The Planck telescope, on the other hand, reported weak emission of the Zodiacal
501 Cloud at sub-mm wavelengths (Ade et al., 2014), which has been used to suggest $D_{\text{break}} \lesssim 30$
502 μm (e.g., Fixsen and Dwek (2002)). Note that changes of the assumed size distribution arise
503 because the orbital dynamics/collisional destruction of cosmic particles and their accretion
504 by planets are size dependent.

505 For the present study, the IRAS observations were used to calibrate the total population of
506 particles in the model, assuming the LDEF size distribution. Particles of different sizes were
507 released from the different sources (e.g., JFCs, asteroids) and their orbits were followed with

508 an N-body code. These integrations accounted for the gravity of all planets, solar pressure,
509 and Poynting-Robertson drag. We used a collisional model where particles were assumed to
510 be destroyed by collisions with other particles in the Zodiacal cloud if they spend a
511 characteristic time, τ , in space. The parameter τ was taken as a function of the particle size
512 and orbit (Nesvorný et al., 2011). The accretion probability of particles on planets was
513 computed with the standard Öpik code (e.g., Greenberg (1982)). The LDEF ZCM with
514 $D_{\text{break}} \sim 200 \mu\text{m}$ was found to reproduce the LDEF measurement of the size distribution of
515 accreted particles.

516 We have recently combined the mass/velocity/radiant distributions of these cosmic dust
517 populations from the ZCM with the Chemical Ablation MODel (CABMOD) (Vondrak et al.,
518 2008), in order to estimate the injection rates of Na and Fe into the Earth's upper atmosphere,
519 as well as the flux of cosmic spherules to the surface (Carrillo-Sánchez et al., 2016). By
520 comparing these parameters to lidar observations of the vertical Na and Fe fluxes, and the
521 measured cosmic spherule accretion rate at South Pole, the absolute contributions from JFCs,
522 the asteroid belt and Halley Type/Oort Cloud comets can be determined for the terrestrial
523 atmosphere and hence in the ZCM (Carrillo-Sánchez et al., 2016). The ZCM can then be
524 applied to Venus. We find that Venus and Earth have similar accretion influx in cosmic
525 particles and that the velocity distribution of accreted particles by both planets is also
526 similar. The total mass of un-ablated cosmic dust into Venus' atmosphere is 32 metric tonnes
527 per earth day (t d^{-1}), with 86% of the mass from JFC particles, 12% from Halley Type/Oort
528 cloud comets, and 2% from the asteroid belt.

529



530

531 **Figure 11.** (a) Differential flux of cosmic dust particles into Venus' atmosphere, showing the
 532 total flux made up of particles from Jupiter family comets, the asteroid belt, and Halley type
 533 comets (black line); particles which form cosmic spherules (green line); particles which do
 534 not melt and form micrometeorites (red line); and total surviving particles (blue line). (b)
 535 Total incoming particles (black line) and surviving particles (blue line), extrapolated to
 536 smaller particle sizes using the parameterisation in eqn. 2.

537 Figure 11(a) illustrates the differential flux of particles from these sources into Venus'
538 atmosphere. The modelled differential flux can be fit to the following parameterisation of
539 particle radius r (in m):

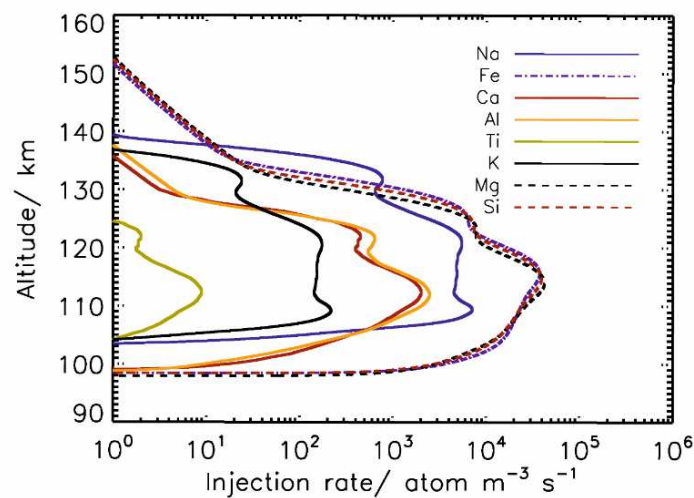
$$540 \quad d\phi / d\log_{10}(r) / \text{particle m}^{-2} \text{ s}^{-1} = 10^{\alpha} \quad (2)$$

541 where $\alpha = -9168.23 - 13841.3x - 8641.28x^2 - 2848.13x^3 - 521.647x^4 - 50.0844x^5 - 1.91675x^6 +$
542 $7.203504 \times 10^{-3}x^7$, and $x = \log_{10}(r)$. Figure 11(b) shows this parameterisation extrapolated from
543 the particle size range in the ZCM (5 - 500 μm) down to 20 nm. The gradual fall-off in the
544 differential flux of particles $< 5\mu\text{m}$ is expected because solar radiation pressure ejects very
545 small particles from the solar system (Nesvorny et al., 2010). Note that the sharpness of the
546 fall off is uncertain; however, as discussed below, the modelling results of particle number
547 distribution in the atmosphere are not sensitive to the degree of fall off. The dust is assumed
548 to have a density of 2200 kg m^{-3} (Han et al., 2011), and was segregated into 45 size bins
549 increasing geometrically in particle radius from 0.016 to 512 μm .

550 *4.2 Meteoric ablation and the formation meteoric smoke particles*

551 In order to determine the fraction of these dust particles that will ablate, we used CABMOD
552 (Vondrak et al., 2008) to treat meteoric ablation in Venus' atmosphere starting at 500 km. For
553 a given meteoroid mass, velocity and entry angle, CABMOD predicts the ablation rate of
554 individual meteoric elements through sputtering (i.e. through inelastic collisions with
555 atmospheric molecules), and by evaporation of atoms and oxides once the particle melts. The
556 cosmic dust particles were taken to have an olivinic composition, as determined by the
557 analysis of Comet 81P/Wild 2 dust samples (Zolensky et al., 2006; Gainsforth et al., 2015),
558 with an Fe:Mg ratio of ~ 0.6 . According to the olivine phase diagram, the particles should then

559 melt at 1750 K (Vondrak et al., 2008). Figure 12 shows the predicted elemental injection rates
 560 integrated over the mass and velocity distributions ($10 - 84 \text{ km s}^{-1}$) predicted by the ZCM. The
 561 most volatile elements, Na and K, are released about 10 km higher than the main constituents
 562 Fe, Si and Mg. The peak ablation rate occurs at an altitude of $\sim 115 \text{ km}$, which is 20 km higher
 563 than in the Earth's atmosphere (Vondrak et al., 2008). Out of the 32 t d^{-1} of cosmic dust that
 564 enters the atmosphere, 11 t d^{-1} ablates (i.e. vaporizes), 8 t d^{-1} forms cosmic spherules (i.e. the
 565 particles melt but do not completely ablate and then solidify), and 13 t d^{-1} remains as
 566 unmelted micrometeorites. Figure 11 shows that significant ablation only occurs for particles
 567 larger than $r = 15 \text{ }\mu\text{m}$, and that spherules become the major form of residual meteoroids for
 568 $r > 50 \text{ }\mu\text{m}$, although most of these larger particles enter at high enough speeds to ablate
 569 completely.



570
 571 **Figure 12.** Injection rate profiles for individual elements from meteoric ablation in Venus'
 572 atmosphere.

573

574 The ablated constituents – principally Fe, Mg and Si atoms – will become oxidized by reactions
575 with O₃, O₂, CO₂, and H₂O to form metal oxide, hydroxide, carbonate and silicate molecules,
576 which then polymerize into meteoric smoke particles (MSPs) (Plane et al., 2015). These sub-
577 nm-sized particles rapidly coagulate into larger particles (Saunders and Plane, 2006). In the
578 present study, particle growth through coagulation was treated using a semi-implicit, volume-
579 conserving model fitted to growth rates measured in the laboratory (Saunders and Plane,
580 2006). Growth occurs through a number of discrete size bins where the first bin size ($r_1 = 0.20$
581 nm) corresponds to the radius of a single monomer. Growth is then assumed to be dominated
582 by Brownian diffusion-coagulation where collisions between pairs of particles result in
583 coalescence, maintaining spherical morphology and compact structure (particle density =
584 2200 kg m⁻³). The collision rate coefficients (or kernels) for Brownian coagulation of these
585 small particles are calculated using the expression for the free molecular regime (Knudsen
586 number, $K_n \gg 1$), interpolated into the transition regime for larger particles (Fuchs, 1964).
587 The flux of dust particles of different sizes being transported vertically by eddy diffusion and
588 sedimentation is given by:

$$589 \quad \phi_i = -K_{zz} \left\{ \frac{\partial N_i}{\partial z} + \left(\frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H} \right) N_i \right\} + w_i N_i \quad (3)$$

590
591 where ϕ is the vertical flux of particles in dust size bin i , K_{zz} is the eddy diffusion coefficient, z
592 is the altitude coordinate, N_i is the dust number density, H is the atmospheric scale height,
593 and w_i is the sedimentation velocity. w_i can be determined from a form of Stokes' law which
594 describes a spherical particle falling through a stationary fluid (Jacobson, 2005):

$$595 \quad w_i = \frac{2(\rho_{dust} - \rho_{air})}{9\mu} g r_i^2 C_{scf} \quad (4)$$

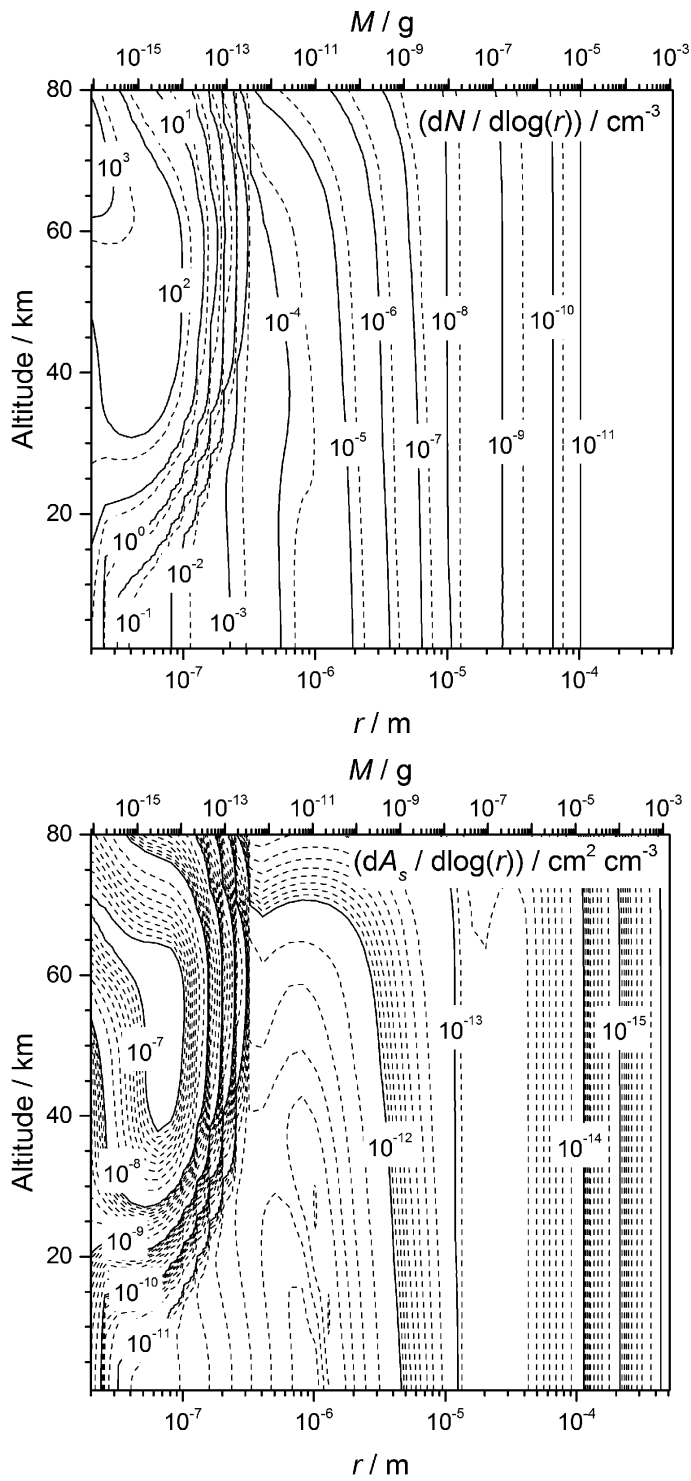
596 where ρ_{dust} and ρ_{air} are the dust and air density; μ is the dynamic viscosity of CO₂ at
 597 temperature T ; g is the gravitational constant (8.87 m s⁻² for Venus); r_i is the particle radius
 598 and C_{scf} is the Cunningham slip correction factor which takes into account the non-continuum
 599 effects of drag on small particles. C_{scf} is estimated from equation 5, where λ is the mean free
 600 path of the CO₂ molecules, and A_1 , A_2 and A_3 are dimensionless coefficients (Kasten, 1968).

$$601 \quad C_{scf} = 1 + \frac{\lambda}{r_i} \left(A_1 + A_2 \exp\left(\frac{-A_3 r_i}{\lambda}\right) \right) \quad (5)$$

602 Equation 3 was solved using a time-implicit integration scheme (Shimazaki, 1985). Figure 13
 603 shows the resulting size distributions of particle number density (N) and volumetric surface
 604 area (A_s), as a function of height between the surface and 80 km. Most of the available surface
 605 area for heterogeneous chemistry is between 40 and 70 km, and is provided by small particles
 606 ($r < 0.2 \mu\text{m}$). The highest values of A_s are therefore located in the same atmospheric region as
 607 the cloud layer on Venus (Knollenberg and Hunten, 1980). The dust number density and
 608 surface area decrease in the troposphere because of coagulation, which is exacerbated by the
 609 increasingly slow rate of sedimentation as the atmospheric density increases.

610 Knollenberg and Hunten (1980) used a particle size spectrometer on the Pioneer Venus
 611 sounder to determine a particle number density of 20 particles cm⁻³ with a mean radius of
 612 0.1 μm in the lower haze layer around 35 km, although the instrument could actually only
 613 measure particles larger than $r = 0.3 \mu\text{m}$. The present model predicts a total of 117 smoke
 614 particles cm⁻³ at 35 km. However, these coagulated smoke particles have a mean radius of
 615 only 0.04 μm , and the concentration of smoke particles with $r > 0.1 \mu\text{m}$ is 1.8 cm⁻³ (1.6×10^{-4}
 616 cm⁻³ for $r > 0.3 \mu\text{m}$), which would have been undetectable with the particle spectrometer.

617 To test the sensitivity of the aerosol model to the degree of fall-off in the differential flux of
618 small meteoroids, the extrapolated flux in Figure 11(b) was reduced by a factor of 100 for all
619 incoming particles $< 5 \mu\text{m}$. In fact, this makes essentially no difference to the particle number
620 and surface area densities in Figure 13. The reason is that it is only particles $> 5 \mu\text{m}$ that ablate,
621 and it is this ablated vapour that then produces the MSPs which contribute most of the
622 available surface area for chemistry. This is evident in Figure 13: most of the surface area is
623 carried by particles smaller than $0.2 \mu\text{m}$, which first appear via coagulation around 70 km.



624

625 **Figure 13.** A plot of the size distribution of dust particle number density, N , (top panel) and

626 volumetric surface area, A_s , (bottom panel) as a function of altitude.

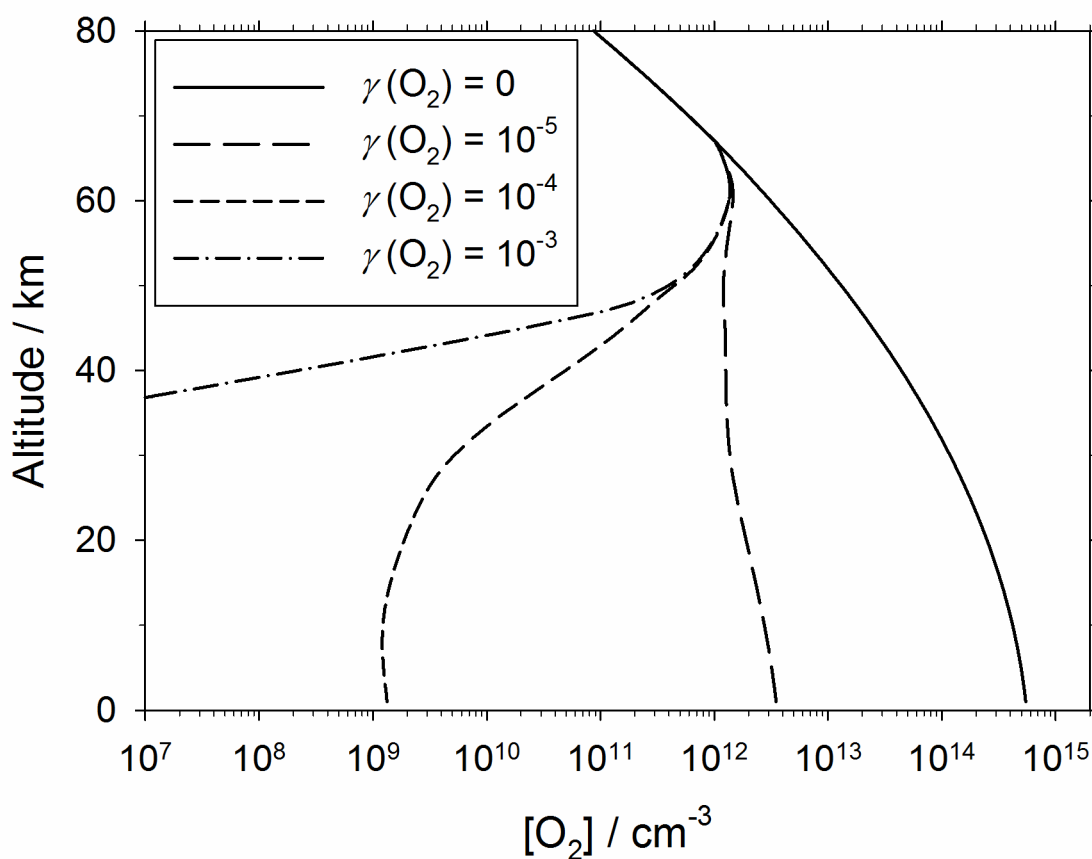
627

628 4.3 Oxidation of CO

629 The CO mixing ratio as a function of height z in the model was initially set to a polynomial
630 functional fit to various literature sources (Hedin et al., 1983; Krasnopolsky, 2012;2013):
631 $\log_{10}(\chi(\text{CO})/\text{ppm}) = 0.96 + 0.026z - 5.0 \times 10^{-4} z^2 + 3.7 \times 10^{-6} z^3$, where z is in km. The O₂ mixing
632 ratio in the model is fixed to 0.7 ppm above 67 km, so that the column abundance above the
633 cloud tops (67 km) is $6 \times 10^{17} \text{ cm}^{-2}$, which is just over 50% of the upper limit determined by
634 Trauger and Lunine (1983). The reason for fixing the O₂ above the cloud tops is that the
635 heterogeneous removal on meteoric smoke is only significant at the higher temperatures in
636 the troposphere below 40 km. Between 67 km and the surface the O₂ density was initially set
637 to the value at 67 km ($1.0 \times 10^{12} \text{ cm}^{-3}$). The SO₂ mixing ratio is set to 130 ppm up to the cloud
638 base at 48 km (Bezard et al., 1993).

639 For the CO uptake kinetics, the temperature-dependent expression for $\gamma(\text{CO on MgFeSiO}_4)$
640 was used (Section 3.5). This means that CO oxidation only becomes significant at
641 temperatures above about 400 K. We assume here that any chemical processing of the small
642 meteoric dust particles which sediment slowly through the H₂SO₄ clouds, thereby reducing
643 their catalytic activity by forming Fe sulphates, is reversed at the higher temperatures below
644 the clouds where the particles will convert into Fe₂O₃ which is catalytically active (section 3.1).
645 $\gamma(\text{O}_2)$ was varied from 1×10^{-5} (just below the lower limit from the laboratory investigation in
646 Section 3.3 – see Figure 5) to 1×10^{-3} , with no temperature dependence. As discussed in
647 Section 3.4, the rate determining step in the experimental measurements of CO oxidation was
648 the reaction of CO with an adsorbed O₂ molecule. Note, however, that the laboratory
649 measurement of $\gamma(\text{CO})$ was under conditions where the rate was independent of [O₂]. In an
650 O₂-poor region of the atmosphere the rate of O₂ uptake could become rate-determining and

651 therefore control the CO oxidation rate, especially since CO has been found to bind poorly to
652 Fe₂O₃ in the absence of O₂ (Leu et al., 1992). In the model, the rate of CO oxidation was
653 therefore set to whichever was slower: either twice the rate of O₂ uptake (since each O₂
654 oxidizes 2 CO), or the uptake rate of CO. The vertical continuity equations for CO, O₂ and CO₂
655 were then solved between 0 and 90 km, and the concentrations of these species fixed above
656 90 km (where heterogeneous uptake is unimportant because of a relatively small A_s and low
657 temperatures).



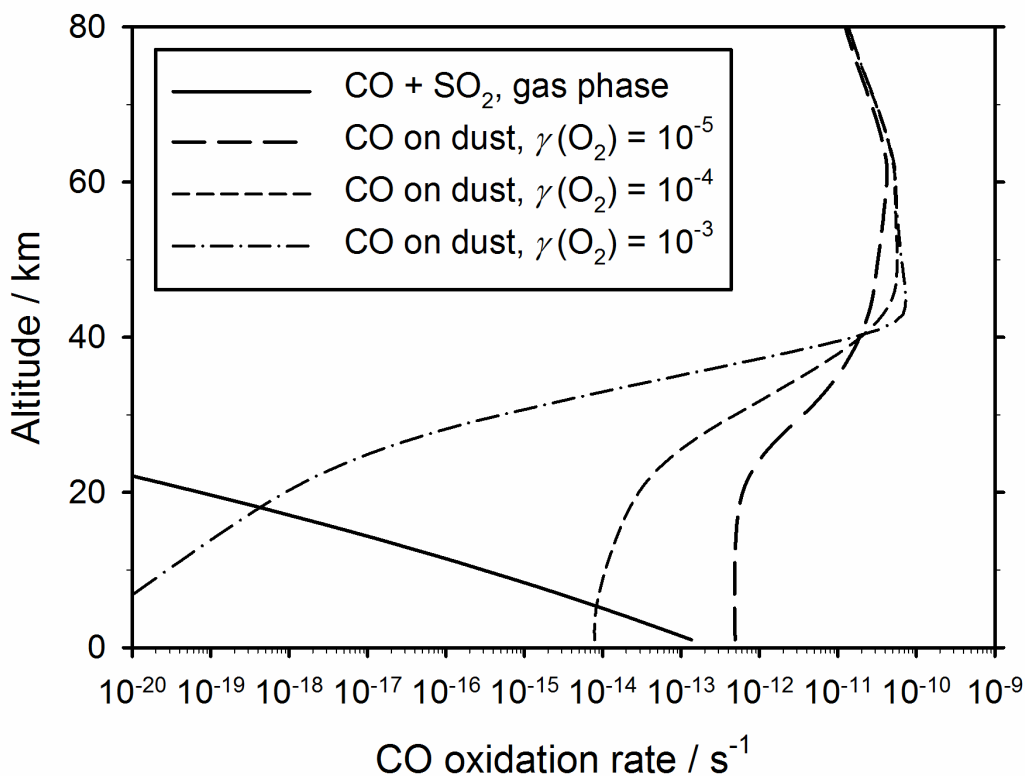
658
659 **Figure 14.** Modelled profiles of the O₂ density, for different values of $\gamma(\text{O}_2)$. Note that the O₂
660 concentration is fixed above 67 km.
661

662 Figure 14 shows the modelled O₂ density after the model has reached steady-state, for a
663 range of $\gamma(\text{O}_2)$. As discussed in Section 3, the lower limit for $\gamma(\text{O}_2)$ deduced from the flow tube
664 experiments is 2×10^{-5} , which would reduce O₂ by more than 1 order of magnitude below
665 45 km. If γ is only a factor of 5 larger, the reduction would be at least 3 orders of magnitude
666 larger below 30 km. If $\gamma(\text{O}_2)$ is $> 10^{-4}$ then there is sufficient meteoric dust to remove O₂ almost
667 completely below 40 km, because the rate of uptake is fast enough to compete with the
668 downward transport of O₂ from higher altitudes by eddy diffusion. Note that there is a
669 decrease of O₂ between 40 and 67 km, which occurs because of more rapid downward
670 transport of O₂ from the region where it is produced photochemically to the region below 40
671 km where O₂ is depleted by heterogeneous CO oxidation. However, the decrease is
672 insufficient to account for the over-prediction of O₂ that has been noted in models with full
673 chemistry (Krasnopolsky, 2012), rather than prescribed O₂ above 67 km as in the present
674 model.

675 Figure 15 shows the corresponding CO oxidation rates for the same range of $\gamma(\text{O}_2)$. The rates
676 all decrease below ~ 40 km because of the smaller available dust surface area (Figure 13). Note
677 that the CO oxidation rate is higher at lower $\gamma(\text{O}_2)$, because the O₂ below 40 km is less
678 depleted (Figure 14). However, Figure 15 shows that even at the highest value of $\gamma(\text{O}_2)$, the
679 heterogeneous oxidation rate is still faster above 20 km than the gas-phase SO₂ oxidation rate
680 calculated using the theoretical rate coefficient k_4 derived in Section 3.5. The rate coefficient
681 for the gas-phase reaction between CO and O₂ has been measured reliably at temperatures
682 above 1500 K, yielding the Arrhenius expression $k(\text{CO} + \text{O}_2) = 4 \times 10^{-12} \exp(-200 \text{ kJ mol}^{-1}/ RT)$
683 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Tsang and Hampson, 1986). Extrapolating down to temperatures below
684 750 K indicates that this gas-phase CO oxidation reaction is a factor of 40 slower than the

685 heterogeneous oxidation (for $\gamma(\text{O}_2) = 10^{-4}$) 5 km above the planet's surface, and insignificant
 686 at higher altitudes.

687 Krasnopolsky (2012) has modelled the gas-phase chemistry of CO between 47 and 112 km.
 688 Compared with Figure 2 in his paper, the heterogeneous oxidation of CO below 60 km is
 689 significantly faster than the reactions with Cl (reaction 1) and OH (reaction2). However, at 70
 690 km these reactions are 2500 and 20 times faster than the heterogeneous reaction,
 691 respectively. Since most of the CO in Venus' atmosphere is produced by photolysis of CO_2
 692 above 70 km (Krasnopolsky, 2012), this means that heterogeneous oxidation of CO at lower
 693 altitudes is relatively unimportant.



694

695 **Figure 15.** The rate of CO oxidation through heterogeneous reaction on dust, modelled for
 696 three values of $\gamma(\text{O}_2)$, compared with the gas-phase oxidation by SO_2 .

697

698 5. Conclusions

699 The kinetics of CO oxidation on a selection of dust particles which are possible analogues of
700 meteoric material in Venus' atmosphere (Mg_2SiO_4 , MgFeSiO_4 , Fe_2SiO_4 , $\text{FeOOH}/\text{Fe}_2\text{O}_3$,
701 $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4) were studied over an appropriate temperature range (300 - 680 K). The
702 reaction appears to follow the Eley-Rideal surface mechanism with O_2 chemisorbed onto Fe
703 active sites (no measurable CO_2 was formed on Mg_2SiO_4). The CO oxidation reaction step was
704 found to be rate determining on all of the Fe-bearing dust except for $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 ,
705 where the two Fe sulfates had to first decompose into Fe oxides at around 540 K before CO
706 oxidation could occur.

707 A 1-D atmospheric model of Venus was then constructed to explore the role of heterogeneous
708 oxidation. The cosmic dust input to Venus, mostly originating from Jupiter Family Comets, is
709 found to be ~ 32 tonnes per Earth day. A chemical ablation model was then used to show that
710 $\sim 34\%$ of this incoming mass ablates, forming meteoric smoke particles. Above Venus' clouds,
711 the temperature is too low for catalysis by olivinic smoke surfaces to be significant; however,
712 below 40 km, together with unablated dust particles, smoke provides a significant surface for
713 the heterogeneous oxidation of CO to CO_2 , and the corresponding removal of O_2 . Although
714 this process has a minor effect on CO because it is in large excess over O_2 (by a factor > 50),
715 substantial removal of O_2 below 40 km is predicted.

716 Theoretical calculations indicate that the oxidation of CO by SO_2 in Venus' lower troposphere
717 is about 4 orders of magnitude slower than previous work which extrapolated from a high-
718 temperature shock tube study, and so this reaction is not competitive with the heterogeneous
719 oxidation of CO measured in this study.

720 In conclusion, this study appears to be the first attempt to quantify the surface area of
721 meteoric smoke particles and unablated micro-meteorites available in Venus' atmosphere for
722 heterogeneous chemistry. Here we have focused on a high-temperature process (CO
723 oxidation), which should occur in the troposphere below 40 km. However, other surface-
724 catalyzed processes involving acidic gases and photochemical radicals, which occur on smoke
725 analogues at temperatures below 300 K (Frankland et al., 2015; James et al., 2017) , may be
726 important even above the clouds, where a significant surface area of meteoric smoke is
727 predicted to be available (Figure 13). It is also worth noting that it may be possible to observe
728 the smoke particles in this region by optical extinction from satellite-borne spectrometers, as
729 in the terrestrial mesosphere (Hervig et al., 2009). Finally, the present study demonstrates
730 the importance of laboratory measurements for quantifying the kinetics of heterogeneous
731 processes in models.

732

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740

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