Oxidation of CO on surface hematite in high CO$_2$ atmospheres

John Lee Grenfell$^{1*}$, Joachim W. Stock$^2$, A. Beate C. Patzer$^1$, Stefanie Gebauer$^1$, and Heike Rauer$^{1,2}$

(1) Zentrum für Astronomie und Astrophysik
Technische Universität Berlin (TUB)
Hardenbergstr. 36
10623 Berlin
Germany

(2) Institut für Planetenforschung
Deutsches Zentrum für Luft- und Raumfahrt (DLR)
Rutherford Str. 2
12489 Berlin
Germany

*Corresponding Author: John Lee Grenfell
Email: lee.grenfell@dlr.de
Telephone: +49 30 314 25463
Abstract: We propose a mechanism for the oxidation of gaseous CO into CO$_2$ occurring on the surface mineral hematite (Fe$_2$O$_3$(s)) in hot, CO$_2$-rich planetary atmospheres, such as Venus. This mechanism is likely to constitute an important source of tropospheric CO$_2$ on Venus and could at least partly address the CO$_2$ stability problem in Venus’ stratosphere, since our results suggest that atmospheric CO$_2$ is produced from CO oxidation via surface hematite at a rate of 0.4 Petagrammes (Pg) CO$_2$ per (Earth) year on Venus which is about 45% of the mass loss of CO$_2$ via photolysis in the Venusian stratosphere. We also investigated CO oxidation via the hematite mechanism for a range of planetary scenarios and found that modern Earth and Mars are probably too cold for the mechanism to be important because the rate-limiting step, involving CO(g) reacting onto the hematite surface, proceeds much slower at lower temperatures. The mechanism may feature on extrasolar planets such as Gliese 581c or CoRoT-7b assuming they can maintain solid surface hematite which e.g. starts to melt above about 1200K. The mechanism may also be important for hot Hadean-type environments and for the emerging class of hot Super-Earths with planetary surface temperatures between about 600-900K.

Key words: Exoplanet, Atmosphere, Venus, CO$_2$ stability, hematite, catalysis
1. **Introduction**

Venus and Mars have maintained rich CO$_2$ atmospheres over geological periods despite loss of this molecule via photolysis. How CO$_2$ is re-generated from its photolysis products is usually termed the “CO$_2$ stability problem.” On Mars, catalytic photochemical cycles can mostly account for this re-regeneration (McElroy and Donahue, 1972; Parkinson and Hunten, 1972; Yung and DeMore 1999). On Venus, however, the situation is less clear. The effectiveness of the proposed Venus reaction cycles is not well-determined, e.g. because rate data of important chemical reactions are lacking for a CO$_2$ bathgas and are challenging to obtain under Venus conditions. Further, key intermediate species such as the chloroformyl radical, essential for the proposed chlorine catalytic cycles (Yung and DeMore, 1999; Pernice et al. 2004) have still to be detected in-situ in Venus’ atmosphere. Improved understanding of the photochemistry of CO$_2$-rich atmospheres will also aid in the future assessment of exoplanetary spectral signatures of potential biomarkers i.e. life-indicating species.

In this paper we discuss an alternative mechanism to account for the stability of hot, high-CO$_2$ atmospheres, which proceeds via oxidation of CO occurring on hematite on the planet’s surface. The basic process is well-known in the chemical industry (e.g. Strassburger, 1969). We estimate the rate of CO$_2$ production via this mechanism for a range of different planetary scenarios such as Venus, Earth, Early Earth, Mars, and hot exoplanet conditions.
762. Method

782.1 Heterogeneous catalysis on hematite

CO(g) and O\textsubscript{2}(g) adsorb quickly onto many iron-containing surfaces (Atkins, 1986) via chemisorption e.g. between the oxygen 2p orbitals of CO and the 3d orbitals of iron in the surface of hematite (e.g. Becker et al., 1996; Föhlisch et al., 2000; Reddy et al., 2004). The adsorbed species’ bonds are weakened and can react to form CO\textsubscript{2}. For CO oxidation on hematite, there are some indications that both the Eley-Rideal mechanism (ER), i.e. where an adsorbed species reacts with a gas-phase species (Atkins, 1986) and the Langmuir-Hinshelwood mechanism (LH) i.e. where both reacting species must first adsorb, can occur. The ER mechanism for CO on hematite was discussed e.g. by Halim et al., (2007), and Wagloehner et al. (2008), whereas the LH mechanism was discussed by Bergmayer and Schweiger, (2004); Kandalam et al., (2007) discussed both mechanisms. There are numerous theoretical studies which are investigating this issue (e.g. Panczyk, 2006; Bulgakov and Sadykov, 2004; Reddy et al., 2004).

Figures 1a-c illustrates the various steps in the mechanism adopted in our work for the oxidation of CO on hematite. Hematite particles consist of a bulk (dark shading) and surface (light shading) region. Active adsorption sites (“holes”) exist on the surface (Randall et al., 1997; Wagloehner et al., 2008; Bergmayer et al., 2004), some of which may be occupied by trapped oxygen atoms, which can originate either via diffusion from the crystal bulk, through the lattice to the surface region (e.g. Kandalam et al., 2007; Randall et al., 1997) or from the atmosphere directly via dissociative adsorption of e.g. O\textsubscript{2}(g) or/and CO\textsubscript{2}(g). Migration across the surface is not
considered to be significant for CO oxidation on hematite because adsorbed species are confined to the active sites (Randall et al., 1997).

The first step (Figure 1a) involves O$_2$ adsorption. This process is suggested to involve the radical anion reactive intermediates O$^-$ or O$_2^-$ with different adsorbed states depending on how the O$_2$ approaches the surface e.g. perpendicularly, sideways or obliquely (Kandalam et al., 2007; Bergermayer and Schweiger, 2004). Also important is the number of surface iron atoms, with which the adsorbed O$_2$ can interact (Bulgakov and Sadykov, 1996). The next step (Figure 1b) involves gaseous CO removing the adsorbed oxygen atom. The final step (Figure 1c) involves desorption of the CO$_2$ product leaving behind an active site occupied with an adsorbed oxygen atom.

Details of the individual mechanism steps are, however, not certain. The theoretical study of Kandalam et al. (2007), for example, suggested that a CO molecule first adsorbs onto hematite, weakening an Fe-O bond near the crystal surface. Then, a second CO molecule adsorbs and forms CO$_2$ by breaking the weakened Fe-O bond. Further reaction rate data are needed, however, to assess this particular mechanism. In our study we focus on the ER mechanism illustrated in Figure 1a-c, for which detailed kinetic data are available (Wagloehner et al., 2008).

2.2 Experimental data for oxidation of CO on hematite

Obtaining experimental rate data is challenging mainly because the morphology and size-distribution of the hematite crystal, hence the CO oxidation rate, can vary from experiment to experiment (Lin et al., 2005; Kwon et al., 2007). Such chemical rates are determined by passing carrier gases containing typically a few
126percent of CO and/or O\textsubscript{2} over hematite powder then measuring the conversion rate of
127CO into CO\textsubscript{2} based on mass spectroscopy, for a range of temperatures and pressures.
128Typical data suggests between (10-100)% conversion of the CO by mass into CO\textsubscript{2} per
129second at normal laboratory flow rates of about 1 litre per minute, typically with
130(0.1-1.0)g powdered hematite at (400-700)K (e.g. Tripathi et al., 1999; Khedr et al.,
1312006; Li et al., 2003; Khoudiakov et al., 2004; Randall et al. 1997). The overall rate
132constant (k\textsubscript{i}) features the well-known Arrhenius dependence upon temperature, such
133that k\textsubscript{i}= A\textsubscript{i}\exp(-E_{a,i}/(RT)) where A\textsubscript{i} denotes the pre-exponential constant; E\textsubscript{a,i} is the
134activation energy; R is the gas constant and T denotes the temperature.
135In our study we use the detailed kinetic data based on the investigation of
136Wagloehner et al. (2008), which consists of the following rate expressions (see also
137Figures 1a-c):
138\[ R_1 = A_1\exp(-E_{a,1}/RT) [O_2] \theta_2^2 \]
139\[ R_2 = A_2\exp(-E_{a,2}+\alpha_2\theta_5)/(RT)\theta_3^2 \]
140\[ R_3 = A_3\exp(-E_{a,3}/RT)[CO] \theta_0 \]
141\[ R_4 = A_4\exp(-E_{a,4}-\alpha_4\theta_3)/(RT)\theta_{CO2} \]
142\[ R_5 = A_5\exp(-E_{a,5}/RT)[CO_2] \theta_5 \]
143\[ R_6 = A_6\exp(-E_{a,6}+\alpha_6\theta_5)/(RT)\theta_{CO2} \]
144Where R\textsubscript{i} denotes the reaction rate of reaction, i (mol m\textsuperscript{-3} s\textsuperscript{-1}), [X] is the gas phase
146concentration of species X, (mol m\textsuperscript{-3}); \theta\textsubscript{X}, the fractional coverage of hematite surface
147by species X; \alpha\textsubscript{X}, a constant and \theta\textsubscript{\ast}, the fractional coverage of unoccupied, active sites
148on the hematite surface. The quadratic theta terms in R\textsubscript{1} and R\textsubscript{2} arise because we
149follow the arguments of Wagloehner et al. (2008), who assumed the adsorbing O\textsubscript{2}
150binds to two active sites. All rates are multiplied by the surface area of hematite per
151unit volume.

152In addition we parameterised the diffusion rates of O-atoms from the internal
153hematite bulk to the surface ($R_{\text{out}}$) and from the surface back into the bulk ($R_{\text{in}}$) based
154on rate data from Randall et al. (1997), using:

$$R_{\text{in}} = R_{\text{out}} = A_{\text{diffusion}} e^{-E_{\text{diffusion}}/(RT)}$$

155

1582.3 Computational details

159

160The chemical rate expressions discussed in section 2.2 were integrated using
161the FACSIMILE program, in which non-linear, time-dependent chemical reactions are
162treated as source terms and solved as a system of differential equations using Gear’s
163method (Gear et al. 1985). The differential equation system contains eight rate
164equations, i.e. $R_1-R_6$, $R_{\text{in}}$ and $R_{\text{out}}$, as discussed in section 2.2 for the variables: $O_2(g)$,
165$CO(g)$, $CO_2(g)$, $\theta^*$, $\theta_0$, $\theta_{CO}$, and $\theta_{CO2}$. The solution of this system with appropriate
166initial values yields their temporal development approaching the equilibrium situation.
167Wagloehner et al. (2008) assumed constant coverages of $\theta_0 = 0.6$, $\theta_{CO2} = 0.4$,
168and $\theta_* = 4 \times 10^{-4}$ in their kinetic modelling experiment, which was sufficient to
169reproduce their laboratory-observed $CO_2$ formation rate. In our study, however, since
170we wish to apply our model flexibly to a range of planetary environments, we
171modified the Wagloehner et al. concept so that surface coverage is not considered as
172given, fixed values, but instead is calculated variably in our model. With our variable
173scheme, our modelled results were consistent with the observed CO oxidation rates of
174Wagloehner et al. (T=265°C, P=1bar, 0.5g hematite sample with surface area of
taking a hematite active site surface density of $3.7 \times 10^{18}$ m$^{-2}$ based on Iwamoto et al. (1978). Results from our interactive model, showing CO and CO$_2$ concentrations for the above-mentioned observed laboratory conditions of the Wagloehner et al. study, are shown in Figure 2a, whereby CO is completely oxidised into CO$_2$ on hematite within timescales of a few hours. Figure 2b shows surface coverage variables calculated in our model for the laboratory conditions. Results imply that our interactive $\theta_O$ and $\theta_{CO_2}$ values differ from the prescribed values used by Wagloehner et al. by about 50% mainly because, we are modelling a mass-isolated box, whereas the Wagloehner et al. experiment featured a constant supply of reagant gas being pumped over the hematite surface.

To be applied to planetary atmospheres, we consider a local volume element located at the surface of the planet with – where possible – observed values for the prevailing chemical and physical conditions i.e. the hematite surface coverage, the temperature, the pressure, the atmospheric CO(g) and O$_2$(g) content. We assume zero atmospheric CO$_2$ at the initial time of the integration. Starting with zero particle coverage, we solve the differential equations by forward time integration until the CO$_2$ concentration reaches a steady-state value (c.f. Figures 4a, 4b). To calculate the global CO$_2$ production, the resulting CO$_2$ production rate ($R_3$, mol m$^{-3}$ s$^{-1}$) is multiplied by the surface area of the planet assuming a smooth sphere.

2.4. Boundary Conditions for the Planetary Scenarios

The various conditions of the seven planetary scenarios conditions are summarised in Table 1. For modern Venus, several studies have suggested the presence of hematite on the surface (e.g. Fegley et al., 1995; Klingelhöfer and Fegley,
However, some works have questioned whether magnetite may be more stable at the surface (Wood, 1996), with hematite favoured near mountain tops (Fegley et al., 1997). Other works suggested that hematite could be present in a nano-phase form on Venus (Straub et al., 1991; Straub and Burns, 1990).

In the following we assume a 1% surface coverage of hematite, which is the lower limit suggested by Klingelhöfer and Fegley (2000) and an amount of observed O$_2$(g) equal to the upper limit of (3x10$^{-7}$) volume mixing ratio (vmr) in Venus’ atmosphere (Trauger and Lunine, 1983).

3. Results

Table 2 shows the global rate of CO$_2$ production in 10$^{15}$ g yr$^{-1}$ (i.e. petagrammes (Pg) CO$_2$ per Earth year) for the seven planetary scenarios. The results suggest that on modern Venus the proposed hematite mechanism produces about 0.4 Pg CO$_2$/yr at its surface with the assumed 1% hematite coverage.

Figure 3 presents an overview of the atmospheric CO$_2$ budget on Venus and implies that the hematite mechanism could be of central importance in the troposphere. Escape rates in Figure 3 are based on Lammer et al. (2008). Boxes marked HOx, SOx and ClOx in the stratosphere of Figure 3 represent the contribution from photochemical catalytic cycles involving hydrogen, sulphur-, and chlorine oxides respectively. Values are calculated from the model study of Yung and DeMore (1999) (chapter 8 and references therein) and have been averaged from 60km up to the stratopause. Figure 3 suggests that potentially fast CO$_2$ production from SOx and ClOx may offset loss of CO$_2$ via photolysis hence address the stability problem.

However, there are some important caveats. Firstly, SOx values are uncertain due to
poorly-defined fluxes of sulphur-containing compounds from the troposphere to the stratosphere. Secondly, ClOx values are uncertain since reactive chlorine intermediates required for such cycles have not been observed in-situ. Mills and Allen (2007) discuss these issues in the context of the ongoing stability problem on Venus. At the surface, the volcanism contribution in Figure 3 is based on Fegley and Prinn (1989) who suggested that CO\textsubscript{2} emissions from volcanoes on Venus are weaker than on Earth, which emits <0.5 Pg/yr CO\textsubscript{2} (Gerlach 1991).

To address whether our mechanism at the surface is able to address the CO\textsubscript{2} stability problem in the stratosphere, Figure 3 shows the global mean rates of Eddy diffusion, as calculated via the diffusion equation:

\[
\text{Flux} = -K\left(\frac{dn}{dz} + \frac{n}{H} + \frac{1}{T}(\frac{dT}{dz}) n \right)
\]

In the above, we consider a 1km thick layer at the tropopause located at a height of 60km. K represents the Eddy diffusion coefficient, taken to be (0.8-10)x10\textsuperscript{4} cm\textsuperscript{2} s\textsuperscript{-1} (Yung and DeMore, 1982), which is the main source of uncertainty in the calculation. Remaining variables were calculated from the Venus International Reference Atmosphere (VIRA) database (Seiff, 1983); n is the number density of CO\textsubscript{2} taken to be 4.71x10\textsuperscript{18} molecules cm\textsuperscript{-3} at 60km, H is the scale height with the value 6km at 60km; T is the temperature taken to be 234K at 60km. Results suggest that Eddy diffusion is fast and does not limit the supply of CO\textsubscript{2} from the troposphere.

Figures 4a-b are similar to Figures 2a-b but for modern Venus. Figure 4a implies that CO is reduced, being converted into CO\textsubscript{2}(g), which rises as shown in Figure 4a, and also into CO\textsubscript{2}(ads) which rises as shown in Figure 4b. For Venus conditions, the fractional coverage of vacant active sites (“holes”) on the hematite
surface increases to about 0.5 (Figure 4b) compared with \( \sim 10^{-5} \) for the laboratory conditions (Figure 3b). This was due to the higher Venus temperatures, which enabled adsorbed species to escape more easily from the hematite surface.

We performed a sensitivity study, varying the boundary conditions in our model. Lowering atmospheric oxygen in the Venus run by a factor of 10,000 had only a small impact on the results, since the supply of adsorbed oxygen atoms was still saturated via diffusion from the bulk crystal. Changing the assumed hematite surface coverage for Venus impacted the CO\(_2\) production rate linearly.

Table 2 shows surface coverage data and resulting global CO\(_2\) production rates (Pg/yr) for the seven planetary scenarios. These results suggest that on modern Earth, modern Mars, and the Early Earth scenarios, the hematite mechanism is not important due to a slowing in the temperature-dependent chemical rates. For the hypothetical Super-Earth scenario, however, the hematite mechanism could be quite important. Finally, for the recently discovered hot exoplanets Gliese 581c and CoRoT-7b, the hematite mechanism could be important, especially at higher surface pressures, as suggested by the high CO\(_2\) production in Table 2 for the Gliese 581c scenario (with 93 bar surface pressure) with the much lower production for the CoRoT-7b scenario (with 0.1 bar surface pressure), assuming that the surface is not too hot to melt hematite or convert all hematite into magnetite, which is more stable at warm temperatures.

In summary, the catalytic formation of CO(g) into CO\(_2\)(g) on hematite surfaces can play an important role in some planetary atmospheres. However, the efficiency of the process depends critically on the surface temperature and the amount of surface hematite.

4. Conclusions
Oxidation of CO on surface hematite may address at least partly the long-standing CO$_2$ stability problem in Venus’ atmosphere - our results imply that CO$_2$ is generated from CO oxidation via the hematite mechanism at about 45% (see Figure 2) of its rate of mass loss via photolysis in the Venusian stratosphere.

As Early Venus warmed, the hematite mechanism increased, contributing a positive feedback to Venus’ climate, which could have played an important role in the well-known runaway climate scenario.

The hematite mechanism may also play an important role in stabilising the CO$_2$ atmospheres of hot Super-Earths with surface temperatures in the range of 600-900 K. For cooler environments, such as on Earth, Early Earth, or Mars, strongly temperature-dependent rates virtually switch off the hematite mechanism, whereas in very hot environments the mechanism may also play an important role.

O$_2$ and N$_2$O are central biomarkers whose atmospheric responses have been recently studied in a wide range of Earth-like scenarios (e.g. Segura et al., 2003; Grenfell et al., 2007). Both species can adsorb onto hematite and other transition metal surfaces, undergoing significant chemical change at temperatures typically in the range of hot Super-Earths and maybe at even somewhat cooler conditions. For example, O$_2$ undergoes dissociative adsorption on hematite, N$_2$O adsorbs then decomposes to release O$_2$. Such effects are currently not considered in models of Earth-like atmospheres.

Acknowledgement

We are grateful to Steffen Wagloehner and to Philip von Paris for useful discussion. This research has been supported by the Helmholtz Gemeinschaft through the research alliance “Planetary Evolution and Life”.
References

Atkins, P. W., 1986. Physical Chemistry, 3rd edition, Oxford University Press.

Becker, U., Hochellajr, F., Edoardo, I., 1996. The electronic structure of hematite (001) surfaces: Applications to the interpretation of STM images and heterogeneous surface reactions, Amer. Minerol. 81, 1301-1314.

Bergermayer, W., Schweiger, H., 2004. Ab-initio thermodynamics of oxide surfaces: O$_2$ on Fe$_2$O$_3$ (001), Phys. Rev. 69, 195409, 1-12.

Bulgakov, N. N., Sadykov, V. A., 1996. Surface energies of hematite faces and heats of oxygen adsorption: calculations by modified semi-empirical interacting bonds method, reaction Kin. And Cat. Lett., 58, 397-402.

Clarke, F. W., 1924. The data of geochemistry, US Geol. Survey. Bull. 770.

Encrenaz, Th., Bézard, B., Greathouse, T. K., Richter, M.J., Lacy, J.H., Atreya, S.K., Wong, A. S., Lebonnois, S., Lefèvre, F., Forget, F., 2004. Hydrogen Peroxide on Mars: Evidence for Spatial and Seasonal Variations, Icarus 170, 424-429.

Fegley, B., Prinn, R. G., 1989. Estimation of the rate of volcanism on Venus from reaction rate measurements, Nature, 337, 55-57.
Fegley, B., Lodders, K., Treiman, A. H., Klingelhöfer, G., 1995. The rate of pyrite decomposition on the surface of Venus, Icarus, 115, 159-180.

Fegley, B., Zolotov, M. Y., Lodders, K., 1997. The oxidation state of the lower atmospheres of Venus, Icarus, doi: 10.1006/icar.1996.5628.

Föhlisch, A., M. Nyberg, J. Hasselstrm, O. Karis, L.G.M. Pettersson, Nilsson, A., 2000. How Carbon Monoxide adsorbs in different sites, Phys. Rev. Lett. 85, 15, 3309.

Gear, C. W., Gupta, G. K., Leimkuhler, B., 1985. Automatic integration of Euler-Lagrange equations with constraints, J. Comput. Appl. Math., 12-13, 77-90.

Grenfell, J.L., Stracke, B., von Paris, P., Patzer, B., Titz, R., Segura, A., Rauer, H., 2007. The Response of Atmospheric Chemistry on Earth-like Planets around F, G and K Stars to Small Variations in Orbital Distance, Plan. Spa. Sci., 55, 661-671.

Gerlach, T. M., 1991. Etna’s greenhouse pump, Nature, 315, 352-353.

Halim, K. S. A., Khedr, M. H., Nasr, M. I., El-Mansy A. M., 2007. Factors affecting CO oxidation over nanosized Fe₂O₃, Mat. Res. Bull. 42 4, 731-741.

Iwamoto, M., Yoda, Y., Yamazoe, N., Seiyama, T., 1978. Bull. Chem. Soc., Jpn., 51, 3492765.
Kandalam, A., P. Jena, S. Khanna, B. Chatterjee, B. V. Reddy, 2007. Oxidation of CO on various Fe$_2$O$_3$ surfaces: a theoretical study, Amer. Phys. Soc. Meeting, March 13-17, abstract W11.003.

Kasting, J. F., Catling, D., 2003. Evolution of a habitable planet, Ann. Rev. Astron. Astrophys. 41, 429-463.

Kharecha, P., Kasting, J., Siefert, J., 2005. A coupled atmosphere-ecosystem model of the early Archean Earth. Geobiol., 3, 53-76.

Khedr, M. H., Halim, K. S. A., Nasr, M. I., El Mansy, A. M., 2006. Effect of temperature on the catalytic oxidation of CO over nano-sized iron-oxide Materials science and engineering, doi: 10.1016/j.msea.2006.05.119.

Khoudiakov, M. M. C. Gupta, S. Deevi, 2004. Au/Fe$_2$O$_3$ nanocatalysts for CO oxidation by a deposition-prepitation technique, Nanotech., 15, 987-990.

Klingelhöfer, G., Fegley, B., 2000. Iron mineralogy of Venus’ surface investigated by Mossbauer spectroscopy, Icarus, 147, 1-10.

Krasnopolsky, V. A., 2007. Chemical kinetic model for the lower atmosphere of Venus, Icarus, 191, 25-37.
Kwon, S. C., Fan, M., Wheelock, T. D., Saha, B., 2007. Nano- and micro-oxide catalysts for controlling the emission of carbon monoxide and methane, Separation and Purif. Tech., 58, 40-48.

Lammer, H., Kasting, J. F., Chassefiere, E., Johnson, R. E., Kulikov, Yu.-N., Tian, F., 2008. Atmospheric escape and evolution of terrestrial planets and satellites Spa. Sci. Rev. 139 399-436.

Léger, A., Rouan, D., Schneider, J., Barge, P., Fridlund, M., and 145 co-authors, 2009. Transiting exoplanets from the CoRoT space mission. VIII. CoRoT-7b: the first Super-Earth with measured radius, Astron. Astrophys., 506, 287-392.

Li, P., Miser, D. E., Rabiei, S., Yadav, R. T., Hajaligol, M. R., 2003. The removal of carbon monoxide by iron oxide nanoparticles, Appl. Catat. B., 43, 151-162.

Lin, H. Y., Chen, Y. W., Wang, W. J., 2005. Preparation of nanosized iron oxide and its application in low temperature CO oxidation, J. Nanop. res., 7, 249-263.

McElroy, M. B., Donahue, T. M., 1972. Stability of the Martian atmosphere, Science, 317, 986-988.

Mills, F. P., Allen, M., 2007. A review of selected issues concerning the chemistry in Venus’ middle atmosphere, Plan. Spa. Sci., 55, 1729-1740.
Mori, K., Hidaki, R., Kawai, Y., 1981. The behavior of softening and melting of hematite pellet and sinter during heating in a reducing atmosphere, Trans. Iron Steel Inst. Jpn, 22, 3, 198-206.

Owen, T., Biemann, K., Biller, J. E., Lafleur, A. L., Rushneck, D. R., Howarth, D.W., 1977. The composition of the atmosphere at the surface of Mars, J. Geophys. Res., 82, 4054635-4639.

Panczyk, T., 2006. Sticking coefficient and pressure dependence of desorption rate in the statistical rate theory approach to the kinetics of gas adsorption. Carbon monoxide adsorption/desorption rates on the polycrystalline rhodium surface, Phys. Chem. Phys., 8, 3782-3795.

Parkinson, T. D., Hunten, D. M., 1972. Spectroscopy and aeronomy of O$_2$ on Mars, J. Atmos. Sci., 29, 1380-1390.

Pernice, H., Garcia, P., Willner, H., Francisco, J. S., Mills, F. P., Allen, M., Yung, Y. L., 2004. Laboratory evidence for a key intermediate in the Venus atmosphere: Peroxychloroformyl radical, PNAS, 101, no. 39.

Randall, H., Doepper, R., Renken, A., 1997. Modeling CO oxidation on silica-supported iron oxide under transient conditions, Ind. Eng. Chem. Res., 36, 2996-3001.

Reddy, B. V., Khanna, S. N., 2004. Stimulated NO reduction and CO oxidation by iron oxide clusters, Phys. Rev. Lett. 93, 6068301, 1-4.
Roatsch, T., Basilevsky, A. T., Shalygin, E. V., Titov, D., Markiewicz, W. J., Scholten, F., Kreslevsky, M. A., Jaumann, R., 2008. Geologic interpretation of the NIR images taken by the Venus Monitoring Camera, 37th COSPAR Meeting, July 27-2008, Montreal Canada, p. 2623, paper number C33-0026-08.

Robert, F., Chaussidon, M., 2006. A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts, Nature, 443, 969-972.

Segura, A., Krelove, K., Kasting, J. F., Sommerlatt, D., Meadows, V., Crisp, D., Cohen, M., Mlawer, E., 2003. Ozone concentrations and ultraviolet fluxes on Earth-like planets around other stars, Astrobiology 3, 689-708.

Seiff, A., Hunter, D. M., Colin, F., Donhave, T. M., Moroz, T. I., 1983. Venus, U. Arizona Press, Tucson, 215.

Selsis, F., Kasting, J. F., Levrard, B., Paillet, J., Ribas, I., Delfosse, X., 2007. Habitable planets around the star Gliese 581? Astron. Astrophys. 476, 1373-1387.

Strassburger, J. H., 1969. Blast furnace: Theory and practice, Taylor and Francis, ISBN 0677104200.

Straub, D. W., Burns, R. B., 1990. NASA Washington, Reports of Planetary Geology, 432, 207-209.

Straub, D. W., Burns, R. B., Pratt, S. F., 1991. Spectral signature of oxidized pyroxenes: implications to remote sensing of terrestrial planets, J. Geophys. Res. 4718, 819-18,830.
Trauger, J. T., Lunine J. I., 1983. Spectroscopy of molecular oxygen in the atmospheres of Venus and Mars, Icarus, 55, 272.

Tripathi, A. K., Kamble, V. S., Gupta, N. M., 1999. Microcalorimetry, adsorption and reaction studies of CO, O\(_2\) and CO+O\(_2\) over Au/Fe\(_2\)O\(_3\) and polycrystalline gold catalysts, J. Cat., 187, 332-342.

Udry, S., Bonfils, X., Delfosse, X., Forveille, T., Mayor, M., Perrier, C., Bouchy, F., Lovis, C., Pepe, F., Queloz, D., Bertaux, J.-L., 2007. The HARPS search for southern extrasolar planets, XI. Superearths (5 and 8 M\(_{\oplus}\) in a 3-planet system, Astron. Astrophys. 469, L43-L47.

Wagloehner, S., Reichert, D., Sorzano, D.L., Balle, P., Geiger, Kurerti, S., 2008. Kinetic modelling of the oxidation of CO on Fe\(_2\)O\(_3\) catalyst in excess of O\(_2\), J. Cat., 260, 305-314.

Wood., J. A., 1996. Must the surface of Venus contain hematite? LPS XXVII, 1451.

Yung, Y. L., DeMore, W. B., 1982. Photochemistry of the stratosphere of Venus: implications for atmospheric evolution, Icarus, 51.

Yung, Y. L., W. B. Demore, 1999. Photochemistry of planetary atmospheres, Oxford University Press.
Figure Captions

Figure 1a: Hematite mechanism step 1: adsorption and desorption of $O_2(g)$ on the hematite surface.

Figure 1b: Hematite mechanism step 2: reaction and reverse reaction of $CO(g)$ with $O_2(ads)$ on the hematite surface.

Figure 1c: Hematite mechanism step 3: desorption and adsorption of $CO_2(g)$ on hematite surface.

Figure 2a: Model concentrations to reproduce Earth laboratory conditions ($T=265^\circ C$, $P=1\text{bar}$, 0.5g hematite, initially 50% $O_2(g)$ $7x10^{-3}$ vmr, $CO(g)$, fill-gas $N_2$).

Figure 2b: Fractional coverage of hematite surface by $O(ads)$, $CO_2(ads)$, and active sites (“holes”) under laboratory conditions (see section 3).

Figure 3: Planetary budget of atmospheric $CO_2(g)$ on modern Venus in petagramme ($Pg$) $CO_2$/Earth year. $HO_x(g)$, $SO_x(g)$ and $NO_x(g)$ denote catalytic cycles arising from hydrogen, sulfur, and nitrogen oxides respectively. *Assuming $3x10^{-7}$ vmr $O_2(g)$ and 1% hematite surface coverage.

Figure 4a: Model concentrations for modern Venus scenario (see Table 1) with $O_2(g)=3x10^{-7}$ volume mixing ratio (vmr).

Figure 4b: Fractional coverage of hematite surface by $O(ads)$, $CO_2(ads)$ and active sites (“holes”) for modern Venus scenario as for Figure 4a.
O$_2$(g) adsorbs to active sites

CO(g) reacts with O(ads)

CO$_2$ desorbs

521
522Figure 1b
523
524
525Figure 1c
526
527
528
529
530Figure 2a
531
Figure 2b

Laboratory Control: Concentrations

Laboratory Control: Hematite Surface

Active sites

Coverage (O, CO2)

Oxygen
Carbon dioxide

Time (s)
Figure 3

VENUS

\[ \text{CO}_2 + \text{hv} \rightarrow \text{HO}_x + 0.9 \]
\[ \text{HO}_x \rightarrow \text{ClO}_x + 0.01 \]
\[ \text{SO}_x \rightarrow 2.9? \]
\[ \text{ClO}_x \rightarrow +1.1? \]

Eddy Diffusion (10^6-10^7)

SEE TEXT

~60km

Clouds

Volcanism

<<0.5

Equilibrium chemistry?

Mineral reactions?

Hematite = 0.4*

this work

Surface

escape (of O)

<-1.1x10^-4

Volcanic activity

<+0.5

Eddy Diffusion (10^6-10^7)

SEE TEXT

~60km

Clouds

Volcanism

<<0.5

Equilibrium chemistry?

Mineral reactions?

Hematite = 0.4*

this work

Surface

escape (of O)

<-1.1x10^-4
Venus: Concentrations

- O2
- CO2
- CO

Hematite Surface

576
577 Figure 4b

578
579
580
Table 1: Input data for planetary scenarios considered.

| Scenario       | Hematite (% coverage at surface) | $T_0$ Surface (K) | $P_0$ Surface (bar) | $[CO]_0$ surface volume mixing ratio | $[O_2]_0$ surface volume mixing ratio | Mean Planetary Radius (R) (km) |
|----------------|----------------------------------|-------------------|--------------------|--------------------------------------|--------------------------------------|---------------------------------|
| Modern Earth   | 2.6 (Clarke, 1924)               | 288               | 1.0                | 1.25x10^-7 (Yung and DeMore 1999)     | 0.21                                 | $R_{Earth} = 6371.009$          |
| Modern Venus   | 1.0- (Klingelhöfer and Fegley, 2000) | 735               | 93 (Seiff et al. 1983) | 1.5x10^-5 Krasnopolsky (2007)         | <3x10^-7 Trauger and Lunine (1983)   | 6051.8                          |
| Modern Mars    | 3.0 (Encrenaz et al. 2004)       | 220               | 5.6x10^4 (Yung and DeMore 1999) | 17x10^-4 (Owen et al. 1977)           | 1.3x10^-3 (Owen et al. 1977)         | 3389.5                          |
| Hot Archean    | 2.6 (Robert and Chaussion 2006)  | 343               | 1.0                | 8.0x10^-3 (Kasting and Catling, 2003) | ~10^-12 times modern (Kharecha et al. 2005) | $R_{Earth}$                     |
| Hot Super-Earth | 1.0##                            | 800##             | 1.0##              | As for Venus                         | As for Venus                         | $2.0R_{Earth}$                  |
| Gliese 581c    | 1.0##                            | 1000              | 93##               | As for Venus                         | As for Venus                         | $1.5R_{Earth}$                  |
| CoRoT-7b       | 1.0##                            | 1000              | 0.1##              | As for Venus                         | As for Venus                         | $1.68R_{Earth}$                 |

# = mass hematite in Earth’s crust; ## no observations exist – sensitivity value only; ### assuming an Earth composition.
Table 2: Fractional coverage of hematite with O-atoms, CO$_2$-atoms, and vacant active sites, resulting CO$_2$ production for the hematite mechanism at the planet surface for the seven scenarios.

| Scenario     | $\theta$$_O$ | $\theta$$_{CO2}$ | $\theta$$_{active sites}$ | CO$_2$ (Pg/yr) |
|--------------|--------------|------------------|---------------------------|----------------|
| Laboratory   | 0.88         | 0.12             | 1.30x10$^{-5}$            | not applicable |
| Venus        | 0.49         | 1.11x10$^{-4}$   | 0.49                      | 0.38           |
| Earth        | 1.00         | 3.56x10$^{-12}$  | 1.62x10$^{-10}$           | 2.49x10$^{-13}$|
| Mars         | 8.07x10$^{-4}$ | 6.1x10$^{-20}$   | 1.00                      | 9.84x10$^{-21}$|
| Early Earth  | 0.50         | 1.42x10$^{-3}$   | 0.50                      | 1.18x10$^{-16}$|
| Super-Earth  | 0.50         | 1.06x10$^{-4}$   | 0.50                      | 0.19           |
| Gliese 581c  | 0.34         | 2.84x10$^{-3}$   | 0.66                      | 1099           |
| CoRoT-7b     | 0.34         | 3.06x10$^{-6}$   | 0.66                      | 1.48           |