CARBON DIOXIDE WITHIN VENUS AND THE EARTH

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ABSTRACT

The maximum inventories of CO₂ and H₂O in the terrestrial and Venus mantles are calculated on the basis of shock wave data for magnesite and dunite to be <10⁸ times the observed atmospheric inventories. The CO₂ fugacity determined for the buffer reaction MgCO₃ plus SiO₂ going to MgSiO₃ plus CO₂ yields values which increase from 10⁶ to 10⁸ times the lithostatic pressure, going from 35 to 800 km depths in the earth. The major uncertainties in the fugacity calculations arise from lack of knowledge of effective activities. The calculated fugacity of CO₂ and water brought to the surface from hypothetical mantle reservoirs on Earth and Venus indicate that, in the case of the Earth, the cool and dry atmosphere is strongly depleted in both CO₂ and H₂O compared to the low velocity zone. In contrast to the Earth, on Venus, the 750 K surface temperature and 90 bar CO₂ surface pressure is in equilibrium and probably in communication with an assumed upper mantle CO₂ reservoir.

INTRODUCTION

Because data prescribing atmospheric composition and thermal state of a planetary atmosphere such as that of Venus can and have been readily obtained from earth-based and space craft spectral and radiometry observations (e.g. Hunten [1]; Hoffman et al [2]), the question of what these data tell us about the total planet volatile content and the composition of the solid planet has been continually raised. Mueller and Sassen [3] point out that, of the terrestrial planets with atmospheres i.e. Venus, Earth and Mars, only Venus has a sufficiently high surface temperature ~750 K such that reactions involving interaction of CO₂ with crustal silicates will occur rapidly compared to geological time scales. Previously, Adamski and Draper [4], Lewis [5], Mueller and Kiedbough [6], Walker [7] and recently Lewis and Kreitzendahl [8] have discussed, and rather convincingly demonstrated the possibility that reactions such as:

\[
\begin{align*}
\text{CaCO}_3 + \text{SiO}_2 & \rightleftharpoons \text{CaSiO}_3 + \text{CO}_2 \quad (1) \\
\text{MgCO}_3 + \text{SiO}_2 & \rightleftharpoons \text{MgSiO}_3 + \text{CO}_2 \quad (2) \\
\text{CaMg(CO}_3 \rightleftharpoons \text{CaSiO}_3 + 2 \text{CO}_2 \quad (3)
\end{align*}
\]

\[
\begin{align*}
\text{calcite} & \text{quartz} & \text{vollastonite} & \text{gas} \\
\text{magnesite} & \text{quartz} & \text{muscovite} & \text{gas} \\
\text{dolomite} & \text{quartz} & \text{diopside} & \text{gas}
\end{align*}
\]

\(177\)
\[
\text{MgSiO}_3 + \text{CaO} + \text{SiO}_2 + \text{CaMgSi}_2\text{O}_6 + \text{CO}_2
\]
constitute calcium quartz diopside fayalite

provides a CO\textsubscript{2} partial pressure which is an excellent fit to the observed value of 90 bar or 9 MPa at the average Venus surface temperature of 750 K. Moreover, Lewis and Kieffer [8] point out that at 750 K the equilibrium reaction such as:

\[
\text{Ca}_2\text{MgSi}_2\text{O}_6(\text{OH})_2 + 3 \text{MgSiO}_3 + 2 \text{NaCaSi}_2\text{O}_6 + \text{SiO}_2 + \text{H}_2\text{O}
\]
creoolite diopside quartz fayalite

provides a reasonably low value for the inferred H\textsubscript{2}O mole fraction of \(10^{-3}\) which is both observed and arguments concerning the strong lithosphere of the planet (Weernin [9] require). Experimental studies of the stability relations of carbonate-bearing and ferromagnesian peridotites – CO\textsubscript{2}-H\textsubscript{2}O systems at (Earth) upper mantle temperature and pressure (Green and Boetcher [10]). Bagnoli [11], Wyllie [12] suggest that the regions between 90 and 140 and 75 to 100 km depth below shielded and oceanic contain (CaMgSi\textsubscript{2}O\textsubscript{6})\textsubscript{2} in equilibrium with a CO\textsubscript{2}-rich vapor. Moreover, strong support for the idea of a heavily carbonated Earth mantle can be derived from the ubiquitous occurrence of highly compressed, CO\textsubscript{2}-charged vesicles observed in minerals in every occurrence of olivine-bearing nodules including the eclogitic and kimbleritic xenoliths (Moore [13]) and Moore et al [14]). Although direct observation of carbonates in mantle-derived inclusions have been made (McCreesh and Wood [16]) the question of how deeply within the earth and other planetary mantles volatile bearing minerals can exist which hold CO\textsubscript{2} and H\textsubscript{2}O in their lattices is not clear. Laboratory phase equilibrium studies of high pressure water-bearing ferromagnesian phases and their occasional occurrence in kimberlites (Akagi and Mitomo [17]), Aoki et al [18], McCreesh et al [19]) allow a considerable volatile budget in the upper mantle of the Earth. On the other hand systematic chemical analysis of mantle-derived ultramafic nodules from alkali basalts seem to indicate a systematic decrease of H\textsubscript{2}O content with depth of origin below continents (Jagnit et al [20]).

Since the Earth’s crust contains approximately the same quantity of CO\textsubscript{2} (5 X 10\textsuperscript{24} g) (Ronov and Varshabovskiy [21]) as is present in the Venus atmosphere and convincing evidence has been, in the case of Venus, the atmosphere is in chemical equilibrium with the surface rocks, it is useful to try to estimate what the maximum content of CO\textsubscript{2} in the Venus mantle could be. Because of the similarity in gross planetary structure between the Earth and Venus, (Ringwood and Anderson [22]) such an estimate will be virtually the same for the Earth. Rock wave data for (\text{MgO}=55, \text{FeO}=17%) \text{SiO}_2(\text{fayalite}) and \text{MgCO}_3(magnesite) are used in this estimate. The latter and therochemical and phase data are also used to calculate the CO\textsubscript{2} fugacity in the earth (and presumably also) in the Venus mantle. In this paper we accept the numerous suggestions summarized above that the Venus atmosphere is in equilibrium with the surface rocks and ask the question of whether the Venus atmosphere is also in equilibrium with conditions in the upper mantle. We demonstrate, that in the contrast to the earth, which has a cool lithosphere which effectively detaches the atmosphere from the underlying hot and volatile-rich upper mantle, the upper mantle of Venus, like the surface could apparently be in chemical equilibrium with the atmosphere. The low water \textit{content} of the atmosphere could well reflect a similar lack of low-velocity zone like the Earth and thus be devoid of a water-bearing vapor phase.
The shock wave data for Norbeck dunite, (MgO,33FeO,45)2SiO4 (McQueen et al [23]) and MgCO3 (magnesite) of Kalashnikov et al. [24] and serpentine (McQueen and Marsh, unpublished; Marsh [25]) and planetary interior models giving density versus pressure e.g. Zharkov and Troubyay [26], provide a simple framework for estimating the maximum CO2 and H2O contents of the Earth's and Venus's lower mantle (Fig. 1). These data imply maximum MgO3 and Mg3Si2O6 (ringwoodite) contents of 0.36 and 0.16 (mass fraction) respectively and when compared to the visible crustal and/or atmospheric inventories are potentially 1012 larger. These and similar values which can be inferred for CO2 and H20 inventories from other volatile-bearing minerals should be taken only as upper limits (Table 2).

![Diagram](image)

Fig. 1 Pressure-density relations for the mantle of the Earth and Venus (Zharkov and Troubyay [26]) in relation to Yaginota data for magnesite (MgO) (Kalashnikov et al. [24]), serpentine (Mg3Si2O6) (McQueen and Marsh, unpublished; Marsh [25]) and dunite (MgO,5FeO,45)2SiO4 (McQueen et al [23]).
TABLE 1 \( \text{CO}_2 \) Inventories of Earth and Venus

<table>
<thead>
<tr>
<th></th>
<th>Earth</th>
<th>Venus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>crustal carbonates (a)</td>
<td>0.00051 ( \times 10^{-7} ) gram</td>
</tr>
<tr>
<td></td>
<td>in ( \text{MgCO}_3 ) in mantle (maximum)</td>
<td>0.36 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>Atmosphere (b)</td>
<td>0.00047 ( \times 10^{-7} ) gram</td>
<td>0.41 ( \times 10^{-7} )</td>
</tr>
<tr>
<td></td>
<td>in ( \text{MgCO}_3 ) in mantle (maximum)</td>
<td></td>
</tr>
</tbody>
</table>

(a) Konov and Taraschevsky [22]
(b) Pollack and Black [31]

Of the disproportionation reactions listed in the Introduction, reaction #2 is most amenable to calculating the approximate range of \( \text{CO}_2 \) fugacity in the Earth's and Venus's interior on account of:

a) High temperature thermochemical data are available for the low pressure phases corresponding the upper mantle assemblage \( \text{MgSiO}_3 \) enstatite, \( \text{SiO}_2 \) (quartz), \( \text{MgCO}_3 \) (magnesite) and \( \text{CO}_2 \) (gas).

b) High temperature thermochemical data are also available for the high temperature assemblage \( \text{SiO}_2 \) (stishovite) and may be inferred for the low-mantle phase \( \text{MgSiO}_3 \) (perovskite) using the data of Liu [27] and Yagi et al [23]. The shock wave data for \( \text{MgCO}_3 \) (Kalashnikov [24]) and \( \text{CO}_2 \) (Zubarev and Talagia [29]) do not indicate a phase change in these materials.

c) Free energies at high pressure may be calculated for the solid phase using the equations of state parameters for \( \text{SiO}_2 \), \( \text{MgSiO}_3 \) and \( \text{MgCO}_3 \) listed in Table 2 and pressure-density relations of Fig. 2.

TABLE 2 Equation of State Parameters Used in Free-Energy Calculations

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ambient Density (Mg/cm(^3))</th>
<th>Bulk Modulus, ( K ) (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MgCO}_3 ), magnesite</td>
<td>2.975</td>
<td>110.7</td>
<td>4</td>
</tr>
<tr>
<td>( \text{SiO}_2 ), quartz</td>
<td>2.648</td>
<td>37.5</td>
<td>4.4</td>
</tr>
<tr>
<td>stishovite</td>
<td>4.29</td>
<td>272</td>
<td>8.9</td>
</tr>
<tr>
<td>( \text{MgSiO}_3 ), enstatite</td>
<td>3.19</td>
<td>105</td>
<td>5.0</td>
</tr>
<tr>
<td>petrosvite</td>
<td>4.09</td>
<td>260</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yagi et al [41]</td>
</tr>
</tbody>
</table>
Fig. 2 Pressure-density equation of state used to calculate CO₂ fugacity in the terrestrial and Venus mantle.

Actually MgSiO₃ is known to disproportionate above 10 GPa and 1300 K to Mg₂SiO₄ plus stilpnomelane and this assemblage in turn transforms Mg₂SiO₄ (optimal) plus stilpnomelane at 4/6 GPa and to the ilmenite structure at 1/8 GPa and finally to the perovskite phase at 22 GPa (Liu [27] and Yagi et al [28]). For simplicity and on account of the lack of appropriate free energy data, we have approximated these transformations by assuming transformation to stilpnomelane and MgSiO₃ (perovskite) to occur at 15 GPa in the present calculations.

Using the approach of Ostrovsky and Kishenko [30] and Satz [31], the free-energy activity relation for Eq. 2 is written as:

$$\Delta G_0 = \frac{\Delta V^0}{V_0} \Delta P + \frac{\Delta V}{V_0} \Delta P - RT \ln \frac{f_{CO_2}}{f^0_{CO_2}}$$

(6)

where $\Delta G_0$ is the change in free energy at ambient pressure and high temperature, $\Delta V$ is the change in molar volume of the condensed species in Eq. 2, $V_{CO_2}$ is the specific volume of the CO₂ and the $\Delta$'s are the effective activities. Using the relation of the variation in Gibbs free energy of CO₂ with pressure at constant temperature,

$$\Delta G = RT \ln f_{CO_2} = \frac{P}{V_0} \Delta V - f_{CO_2}$$

(7)

where $f_{CO_2}$ is the fugacity of CO₂ and assuming

$$f_{CO_2} = f^0_{CO_2}$$

(8)

yields from Eq. (6).
\[
\ln f_{CO_2} = \left[ -\frac{1}{1+(X\Pi)} \right] \left( \Delta G^0 + \frac{P}{T} \frac{d \Delta G^0}{dP} + RT \ln \left( \frac{MgSiO_3}{MgCO_3 \cdot SiO_2} \right) \right)
\]

In order to obtain a value for \( \Delta G^0 \) at temperatures as high as 3100 K, which is the temperature assumed for the Earth's core-mantle interface, the standard Gibbs free-energy data for the species in Eq. 2 (Bolt et al. [32]) were extrapolated via a quadratic curve. The energy of transition at the standard pressure for the low to high pressure assemblage was assumed to be 102 kJ/mol. Examples of the Gibbs-free-energy data are shown in Fig. 4. The temperature, T, depth (h) curve for the Earth employed is the one suggested by Sato [31]:

\[
T(K) = -1482 + 1472 \ln f_{CO_2} (h + 19)
\]

and is shown in Fig. 3 as comparison to thermal models for the Earth beneath the ocean and continents proposed by Stacey [33] and the thermal model assumed in the present paper for Venus. Using the equations of state of Table 2, (Fig. 2) and assumed values of \( \frac{\Delta H_{SO_2}}{\Delta H_{CO_2}} \) varying from 200 to 2000, yield the upper and lower 30% MJ curves shown in Fig. 5. In general we expect fugacities which are appreciably lower than the actual pressures. This seems to be the case for depths of as great as 800 km or pressures of 29 GPa for the calculation shown in Fig. 5 with an assumed activity ratio of 3000.

Fig. 3 Temperature versus depth curves for the Earth under oceans (a) and continents (c) and for Venus.
Fig. 4 Gibbs free-energy (with respect to oxides at one bar) versus temperature data (Rubie et al. [32]) used to extrapolate to higher temperatures for thermochemical calculations.
Fig. 5 Calculated $\log_{10}$ of CO$_2$ fugacity and ambient pressure (P) versus depth for the Earth.

Given a range of fugacities as a function of depth for the Earth which also possibly is applicable to Venus, it is useful to examine how these translate into partial pressures of CO$_2$. For this purpose we employ the recent pressure, volume and temperature data of Sheanov and Shaulovich [34] which provide actual measurements to 1 GPa (10 kbar). At a temperature of 975 K and 1 GPa a molar volume of 34.15 cm$^3$/mole was measured; this yields a fugacity of 0.26 GPa. Thus, at least for the upper mantle we can infer, that if the CO$_2$ fugacity is buffered by a reaction like that of Eq. 1, the fugacity is $\frac{1}{4}$ of the pressure. The calculation summarized in Fig. 5 thus predicts, that if a carbonate phase is present in the mantle of the Earth and probably Venus a substantial CO$_2$ partial pressure will result.

ARE THE MANTLES OF EARTH AND VENUS IN CHEMICAL EQUILIBRIUM WITH THEIR ATMOSPHERES?

One approach toward answering the above question is to consider whether either a CO$_2$ or H$_2$O reservoir which has been hypothesized to be present in the terrestrial or Venus's upper mantle has a fugacity such that it is in equilibrium with an overlying atmosphere after correcting for temperature and pressure. We shall assume the fugacity of both H$_2$O and CO$_2$ in the upper mantle of the Earth and Venus and determine whether these hypothetical reservoirs are in equilibrium with their atmospheres at their respective surfaces. The variation of fugacity with pressure
at constant temperature is given by
\[
d\ln f_p = -\Delta_{\text{H}}^{\text{m,ref}} \frac{\partial p}{\partial T} + \Delta_{\text{H}}^{\text{m}} \right.dh
\]
where \( M \) is the molecular weight of the species.
\[
d \ln f_p = \frac{M}{N} \right.dh
\]
where \( N \) is taken to be a function of either \( T \) or \( h \) in a planetary model.. The variation of fugacity with temperature at constant pressure is given by
\[
d \ln f_p = -\frac{H}{RT} \frac{\partial T}{\partial T}
\]
where \( H \) is the high temperature enthalpy and \( \Delta_{\text{H}}^{\text{m,ref}} \) is the enthalpy of a low pressure:

\[
\text{standard state such that the fugacity equals the partial pressure.}
\]
Approximating the term \( H - \frac{\Delta_{\text{H}}^{\text{m,ref}}}{T} \) where \( \Delta_{\text{H}}^{\text{m,ref}} \) is the specific heat at constant pressure, and
Integrating Eq. (13) assuming \( \Delta_{\text{H}}^{\text{m,ref}} = \text{constant} = \Delta_{\text{H}}^{\text{m}} \), where \( N \) is a dimensionless
number representing the degrees of freedom of the specie of interest, yields
\[
d \ln f_p = -\frac{N}{T} \frac{\partial T}{\partial T}
\]
Combining Eqs. (12) and (15) to get the variation of fugacity wiz pressure and
temperature going from the surface condition, state 1, to the mantle, state 2,
yields
\[
\ln f_p = \ln f_1 = \frac{M}{N} \int_{T_1}^{T_2} \frac{\partial h}{\partial T} + N \ln \left( \frac{T_2}{T_1} \right)
\]
Using the variation of \( \frac{\partial h}{\partial T} \) with depth given in Zharov and Trubitsyn [26] and a
mean value of \( N \) of 4.5 for both \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), permitting to the temperature range of
interest, the fugacity specified by Eq. (15) for \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) when taken from a mantle reservoir at a pressure of 1 GPa and 973 K and brought to the surface of
either the Earth or Venus at their respective surface temperatures is given in
Table 3.

<table>
<thead>
<tr>
<th>Volatile</th>
<th>Fugacity (GPa) in mantle</th>
<th>Fugacity (Mpa) brought no Earth's surface (at1,7=300K)</th>
<th>Partial Pressure (Mpa) on Earth's surface</th>
<th>Fugacity (Mpa) brought to Venus's surface (h=1,7=300K)</th>
<th>Partial Pressure (Mpa) on Venus's surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>0.26(a)</td>
<td>0.06(c)</td>
<td>0.000034(d)</td>
<td>14(c)</td>
<td>5(d)</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.44(b)</td>
<td>0.44(c)</td>
<td>&lt;0.001(d)</td>
<td>42(c)</td>
<td>&lt;0.05(d)</td>
</tr>
</tbody>
</table>

(a) Shashov and Shmulovich [35]
(b) Burdumy et al. [41]
(c) Calculated, this work
(d) Mueller and Saxena [3]; Pollack and Black [37]
As is evident from Table 3, on the Earth if CO₂ and H₂O is present as a vapor phase, and if the partial pressure is approximately equal to the upper mantle pressure a much higher surface atmospheric pressure, specifically 0.05 and 0.44 MPa is required to be in equilibrium with these gases in the Earth’s mantle. This result is really in qualitative accord with geological observations in that both CO₂ and H₂O are the major terrestrial volcanic gases and kimberlite pipe appear to have been explosively driven up through the terrestrial crust by CO₂ and H₂O vapor when these are expelled.

In the case of Venus, the theoretical surface fugacity of H₂O in equilibrium with a mantle reservoir is 42 MPa. This result can be interpreted two ways, one, following the ideas of Walker [7] and Anspach and Anderson [22], suggest that Venus has a similar endowment of volatiles as the Earth and is indeed presently still losing what was initially a large reservoir of H₂O via degassing from the interior. The second hypothesis, which is preferred, is that H₂O is not present in appreciable quantities in the interior of Venus and that the lack of equilibration is not significant. Moreover a water-depleted planet as suggested by Lewis and Kreissendahl [8] is possibly the simplest explanation of the lack of water in the atmosphere and the persistence of spectacular topographic relief (Pettenegil et al [35]; Weaverman [37]) and gravity anomalies (Phillips [36]) on a planet with similar rock types and surface gravity as the Earth and yet with much higher surface temperatures. In the case of CO₂ it is clear that not only does this gas appear to be in equilibrium with the surface rocks but the present calculations demonstrate that the surface partial pressure is in equilibrium with a possible major mantle reservoir. Uncertainties of even several hundred degrees in mantle temperature will not change this conclusion appreciably. This result implies that unlike the Earth, Venus does not have a lithosphere which seals the hot and volatile-rich interior from the atmosphere. In the case of Venus then, the atmospheric composition and state may be in equilibrium with the mantle and thus provide a chemical indicator of the composition state of the planetary interior.

ACKNOWLEDGMENTS

I have benefited from discussion of this work with E. Stolper, A. Thompson, R. Waldon, G. Archenho and M. Satz. Supported under NASA Grant NGR-05-029. Contribution 9310, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

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