Surface-Atmosphere Interactions on Venus: A Review

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Outline

• overview of atmosphere-surface environment

• major processes
  • reactions with CO₂
  • reactions with S gases
  • surface redox conditions
  • low radar emissivity regions

• measurement requirements
Main Questions

• *to what extent is atmospheric chemistry controlled by surface mineralogy?*

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\[
\text{mineral A + gas (CO}_2\text{,SO}_2\text{,etc) } \leftrightarrow \text{ mineral B } \pm \text{ mineral C}
\]
Overview: Atmosphere

- extreme near-surface conditions
  - 0 km: 740 K, 95 bar
  - 12 km: 650 K, 45 bar
  - reactive species

- composition below ~20 km is poorly known

<table>
<thead>
<tr>
<th>gas</th>
<th>abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>96.5%</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.5%</td>
</tr>
<tr>
<td>CO$^a$</td>
<td>15 ± 10 ppm</td>
</tr>
<tr>
<td>SO$_2$$^a$</td>
<td>130 ± 50 ppm</td>
</tr>
<tr>
<td>H$_2$O$^a$</td>
<td>30 ± 15 ppm</td>
</tr>
<tr>
<td>H$_2$S$^a$</td>
<td>3 ± 2 ppm</td>
</tr>
<tr>
<td>OCS$^a$</td>
<td>4.4 ± 1 ppm</td>
</tr>
<tr>
<td>S$_{1-8}$$^a$</td>
<td>20 ppb</td>
</tr>
</tbody>
</table>

$^a$ altitude dependent
Overview: Atmosphere

- *composition below ~20 km is poorly known*
- 50% of atmospheric mass below Maxwell Montes
Overview: Surface

- XRF elemental analyses consistent with ~ basalt

- in contact with reactive species at high P, T
  - chemical weathering is dominant (low surface winds, dry)
  - mineral A + gas (CO$_2$, SO$_2$, etc) $\leftrightarrow$ mineral B $\pm$ mineral C

XRF analyses of Venusian surface at $\sim$ 1 km altitude
Reactions with CO$_2$: carbonate formation?

- “Urey reaction” as plausible buffer:
  \[ \text{CaCO}_3(\text{calcite}) + \text{SiO}_2(\text{quartz}) = \text{CaSiO}_3(\text{wollastonite}) + \text{CO}_2 \]
- at equilibrium: CO$_2$ $\sim$ 90 bar at 740 K

- evidence for carbonates on Venus:
  - formation driven by high CO$_2$ pressure
    - Mg$_2$SiO$_4$ + CO$_2$ = MgSiO$_3$ + MgCO$_3$
  - flow features from carbonatite magmas $\rightarrow$
  - responsible for 1-5% XRF mass deficits?

Treiman (2009)
Reactions with CO$_2$: carbonate formation?

- evidence **against** carbonates on Venus:
  - too dry
  - carbonate buffer results in climate instability
    - calcite + quartz = wollastonite + CO$_2$
    - *most* carbonates react with 130 ppm SO$_2$ to form sulfates

climate evolution since 0.5 Ga event

CaSO$_4$ on CaCO$_3$ crystal

*Bullock & Grinspoon (2001); Fegley & Prinn (1989)*
Reactions with S gases: Weathering

- SO₂ is important for chemical weathering
  - Ca-silicates + SO₂ → CaSO₄ (anhydrite)
- surface basalts show high S content
  - incomplete sulfurization of Ca
  - S content correlates with physical weathering

Zolotov & Volkov (1992); Venera 13 and Venera 14 panoramas
Reactions with S gases: Sulfur Cycle

- $\text{SO}_2$ is removed from lower atmosphere by weathering
  - re-supplied from volcanic outgassing? (cf. Esposito 1984, etc)
  - what is the atmospheric sulfur abundance near the surface?

*after Fegley et al (1995)*
Reactions with S gases: Sulfur Cycle

• OCS, $\text{H}_2\text{S}$ abundances increase with depth
  • oxidation products of iron sulfides $\rightarrow$ iron oxides?

Reactions with S gases: Sulfur Cycle

- iron in silicates is susceptible to oxidation and/or sulfurization
  - which phases are stable? what is surface redox?

*after Fegley et al (1995)*
Surface Redox Conditions: 0 km altitude

- Oxygen fugacity calculated using $\text{CO} = 15 \pm 10$ ppm
- Sulfur fugacity calculated using $\text{SO}_2 = 130 \pm 50$ ppm, $S_3 = 0.02-0.08$ ppb
- Evidence for MH from Venera color imagery

*modified after Fegley (1997), Figure 2a*
Surface Redox Conditions: 5 km altitude

- assumptions diverge!
- equilibrium among C-O-S gases is unlikely
- redox conditions from lower altitudes prevail if mixing rate > rate of chemistry

(modified after Fegley (1997), Figure 2b)
While we’re up here at 5 km…

• what is responsible for low-radar emissivity?
  • altitude correlation suggests $T$-dependent chemical process

• dielectric loading in surface rock
  (e.g. Fe$_3$O$_4$, FeS$_2$, etc; Klose et al 1992)

• ferroelectric minerals
  (e.g. perovskites; Shepard 1994)

• metallic compound vapor deposition
  (e.g. Te, PbS; Bracket et al. 1995, Schaefer & Fegley 2004)
Summary

• carbonates are scarce if present, are not buffering CO$_2$
  • potentially more abundant beneath the surface

• sulfurization is the dominant weathering process
  • formation of anhydrite from calcium silicates, carbonates

• magnetite-hematite likely coexist at surface
  • plausibly regulating surface redox conditions (Zolotov 2007)
  • system is probably too oxidizing/sulfur-poor for pyrite (Fegley 1997)

• HCl (0.5 ppm), HF (5 ppb) do appear to be buffered by surface minerals
Measurement Requirements

- surface materials: **mineralogy**
  - carbonates and sulfates
  - Fe-bearing phase(s)
  - low radar emissivity substance

- **near-surface** (<12 km) atmosphere: **redox conditions**
  - CO, SO$_2$, H$_2$O,
  - OCS, H$_2$S

- **reaction kinetics**