EART193 Planetary Capstone

Francis Nimmo
Atmospheres

- Atmospheres can preserve *signatures of volcanism*
- Atmospheres can *influence volcanic activity*
- Volcanic activity can have *effects on climate*
<table>
<thead>
<tr>
<th></th>
<th>Earth</th>
<th>Venus</th>
<th>Mars</th>
<th>Titan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>1 bar</td>
<td>92 bar</td>
<td>0.006 bar</td>
<td>1.5 bar</td>
</tr>
<tr>
<td>N₂</td>
<td>77%</td>
<td>3.5%</td>
<td>2.7%</td>
<td>98.4%</td>
</tr>
<tr>
<td>O₂</td>
<td>21%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>1%</td>
<td>0.01%</td>
<td>0.006%</td>
<td>-</td>
</tr>
<tr>
<td>Ar</td>
<td>0.93%</td>
<td>0.007%</td>
<td>1.6%</td>
<td>0.004%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.035%</td>
<td>96%</td>
<td>95%</td>
<td>~1ppb</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.7 ppm</td>
<td>-</td>
<td>?</td>
<td>1.6%</td>
</tr>
<tr>
<td>CO</td>
<td>0.12 ppm</td>
<td>40 ppm</td>
<td>700 ppm</td>
<td>45 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>~0.2 ppb</td>
<td>~150 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ne</td>
<td>18 ppm</td>
<td>5 ppm</td>
<td>2.5 ppm</td>
<td>0.3 ppm?</td>
</tr>
<tr>
<td>⁴⁰Ar</td>
<td>6.6x10^{16} kg</td>
<td>1.4x10^{16} kg</td>
<td>4.5x10^{14} kg</td>
<td>3.5x10^{14} kg</td>
</tr>
<tr>
<td>H/D</td>
<td>3000</td>
<td>63</td>
<td>1100</td>
<td>3600</td>
</tr>
<tr>
<td>¹⁴N/¹⁵N</td>
<td>272</td>
<td>273</td>
<td>170</td>
<td>183</td>
</tr>
</tbody>
</table>

Isotopes are useful for inferring outgassing and atmos. loss.
1. Signatures of volcanism
Signatures of volcanism

- Volcanic gases were equilibrated at conditions very different from atmospheric conditions
- So some have short residence times in the atmosphere
- These short-lived species can be used as tracers of volcanic activity
Earth

• Most common volcanic gases are $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{N}_2$, $\text{SO}_2$ and $\text{H}_2\text{S}$.

• The first three have little effect (because the atmosphere is the dominant reservoir).

• But sulphur species are important – they convert to $\text{H}_2\text{SO}_4$ aerosols, which have lifetimes of $\sim$years.

• These are good tracers for volcanic activity (e.g. ice cores).

• They also affect radiative balance (see later).
**Sulphur Cycle**

- $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}$
- $\text{O} + \text{SO}_2 \rightarrow \text{SO}_3$
- $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ (condenses)

- UV photon
- Escape

**but aerosols *cool* the atmosphere!**

- SO$_2$ is an important greenhouse gas**
- Major source of SO$_2$ is volcanic outgassing
- Applications: Earth, Venus, early Mars(?)
- Removal of SO$_2$ requires water
Venus

- D/H ratio is ~50 times Earth’s, suggesting Venus has lost a lot of H (from photodissociation of H$_2$O)
- What happened to the O?
- Either it was also lost, or it ended up bound in the crust
- Present-day survival time of H$_2$O is ~100 Myr
- So unless we are viewing Venus at a special time, there must be a present-day water source. What is it?
- $^{40}$Ar in Venus’ atmosphere suggests that the interior is only ~10% outgassed (cf. 50% for Earth’s mantle). Why the difference?
SO$_2$ on Venus

- Lifetime of SO$_2$ in Venus atmosphere is short (few Myr) (longer than on Earth – why?)
- And there are fluctuations on ~100 day periods
- So there must be a current source (cf. H$_2$O)
- Could be sign of present-day volcanism

![Graph showing mean SO$_2$ concentration at 40 mbar height](image)

40mbar height
Esposito (1984)
Titan Composition

<table>
<thead>
<tr>
<th></th>
<th>Titan</th>
<th>Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>98.4 %</td>
<td>78%</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.4 %</td>
<td>2 ppm</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>21%</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.01 ppm</td>
<td>350 ppm</td>
</tr>
<tr>
<td>Ar</td>
<td>7 ppm</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

- Obtained from UV/IR spectra, radio occultation data and *Huygens*
- Various organic molecules at the few ppm level
- Haze consists of ~1 µm particles, methane condensates plus other hydrocarbons (generated by photolysis of methane)
- Atmosphere is reducing (e.g. CO<sub>2</sub> vs. CH<sub>4</sub>). Where is the oxygen?
- Solar system C:N ratio is 4-20:1. On Earth, most of the C is locked up in carbonates; where is the C stored on Titan?
- <sup>40</sup>Ar indicates inefficient outgassing compared with Earth
Titan chemistry

- Methane lifetime \(\sim 10\) Myr – implies recharge
- Recharge requires outgassing of \(\text{CH}_4\) from interior (e.g. by "cryovolcanic" activity or clathrate decomposition)

\[
2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2
\]

After Coustenis and Taylor, *Titan*, 1999
Methane on Mars?

• Exciting because methane is produced on Earth mainly by biology (though there are also non-biological sources e.g. serpentinization)

• But the observations don’t make much sense
  – Methane’s lifetime against photodissociation is 300 years, but variability is seen on yearly timescales
  – Mixing in Mars’ stratosphere should be rapid, but large spatial variations in CH4 were seen

• Zahnle et al. (2012) argue that it is all just interference from terrestrial methane (hard to remove)

• Curiosity rover reports methane detection (Webster et al. 2015) but there are contamination issues . . .
2. Influence on volcanic activity
Volcanism on Venus

- Surface is hot (450°C) and pressure is high (40-100 bars)
- Less cooling of lava in the near surface, but more at the surface (because of atmosphere) – effects aren’t very large
- Exsolution of volatiles suppressed by high $P$
- Pyroclastic flows probably rare, eruption columns don’t reach as high as on Earth

West Mata volcano, 1.2 km depth
Resing et al. (2011)

Head & Wilson (1986)
3. Effect on climate
Effect on climate

- Individual volcanic eruptions can have short-term climatic effects
- Overall degree of volcanic activity can have climatic effects on ~Gyr timescales
Short-term effects

- Sulphur aerosols block direct sunlight
- This overwhelms the greenhouse gas effect
- Occurs for eruptions which reach stratosphere

Robock (2000)

El Chichon eruption  Pinatubo eruption  Robock (2000)
\( T_{eq} \) and greenhouse

<table>
<thead>
<tr>
<th></th>
<th>Venus</th>
<th>Earth</th>
<th>Mars</th>
<th>Titan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar constant ( S ) (Wm(^{-2}))</td>
<td>2620</td>
<td>1380</td>
<td>594</td>
<td>15.6</td>
</tr>
<tr>
<td>Bond albedo ( A )</td>
<td>0.76</td>
<td>0.4</td>
<td>0.15</td>
<td>0.3</td>
</tr>
<tr>
<td>( T_{eq} ) (K)</td>
<td>229</td>
<td>245</td>
<td>217</td>
<td>83</td>
</tr>
<tr>
<td>( T_s ) (K)</td>
<td>730</td>
<td>288</td>
<td>220</td>
<td>95</td>
</tr>
<tr>
<td>Greenhouse effect (K)</td>
<td>501</td>
<td>43</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>Inferred ( \tau_s )</td>
<td>136</td>
<td>1.2</td>
<td>0.08</td>
<td>0.96</td>
</tr>
</tbody>
</table>

\[
T_{eq} = \left( \frac{S \,(1-A)}{4 \varepsilon \sigma} \right)^{1/4}
\]

\[
T_s^4 = T_{eq}^4 \left( 1 + \frac{3}{4} \tau_s \right)
\]

Recall that \( \tau = \int \rho \alpha \, dz \)

So if \( \alpha = \text{constant} \), then \( \tau = \alpha \times \text{column density} \)

So a (wildly oversimplified) way of calculating \( T_{eq} \) as \( P \) changes could use:

\[
\tau = \alpha \frac{P}{g}
\]

Example: water on early Mars
Early Mars was Wet

Hematite “blueberries” (concretions?)
SO$_2$ on Mars

• Halevy et al. (*Science* 2007) proposed that early volcanic output of SO$_2$ on Mars could increase the temperature (greenhouse gas) and help stabilize liquid water at the surface

• But they did not include the cooling effect of aerosols, which is a more important effect (Tian et al. 2010)
Ingassing and surface interactions

- Plate tectonics can take volatiles (e.g. water) and redeposit them in the deep mantle.
- Reactions can remove gases e.g. oxygen was efficiently scavenged on early Earth (red beds) and Mars.
- A very important reaction is the Urey cycle:
  \[ MgSiO_3 + CO_2 \rightarrow MgCO_3 + SiO_2 \]
- This proceeds faster at higher temperatures and in the presence of water (+ and - feedbacks).
- Causes removal of atmospheric CO$_2$ on Earth and maybe Mars (but where are the carbonates?)
- Reverse of this cycle helped initiate runaway greenhouse effect on Venus.
Rampino & Caldeira (1994)

• How were temperatures suitable for liquid water maintained 4 Gyr B.P.?
• Presumably some greenhouse gas (CO$_2$?)
• Urey cycle as temperature stabilizer
Magma oceans

- Magma oceans can arise in 4 ways:
  - Close-in, tidally-locked exoplanets (hemispheric)
  - Extreme greenhouse effect (e.g. steam atmosphere)
  - Gravitational energy (giant impacts) (Earth)
  - Early radioactive heating ($^{26}$Al) (Mars?)

- Some volatiles (e.g. $\text{H}_2\text{O}$, $\text{CO}_2$) are quite soluble in magma

- Magma oceans can store volatiles for later, long-term release
Venus: recent outgassing & climate

- Venus was resurfaced \(~0.5\) Gyr ago, probably involving very extensive outgassing
- How has atmosphere evolved since then?

(Taylor *Planetary Atmospheres* Fig 9.8, after Bullock (1997))
• Ice-albedo feedback (runaway)
• Several occurrences (late Paleozoic last one)
• Abundant geological & isotopic evidence
• Details are open to debate (ice-free oceans?)
• How did it end?
# Gas properties

<table>
<thead>
<tr>
<th></th>
<th>Atomic mass</th>
<th>Solidification temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
<td>4.2</td>
</tr>
<tr>
<td>Ne</td>
<td>20.2</td>
<td>27</td>
</tr>
<tr>
<td>O₂</td>
<td>32.0</td>
<td>54</td>
</tr>
<tr>
<td>N₂</td>
<td>28.0</td>
<td>63</td>
</tr>
<tr>
<td>Ar</td>
<td>40.0</td>
<td>87</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.0</td>
<td>90.5</td>
</tr>
<tr>
<td>Kr</td>
<td>83.3</td>
<td>121</td>
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<tr>
<td>Xe</td>
<td>131.3</td>
<td>166</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.0</td>
<td>195</td>
</tr>
<tr>
<td>NH₃</td>
<td>17.0</td>
<td>195</td>
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