Neutral Mass Spectrometry for Venus Atmosphere and Surface

Paul Mahaffy
NASA Goddard Space Flight Center
Code 915, Greenbelt, MD 20771
Paul.R.Mahaffy@NASA.gov
Why such divergent evolution in terrestrial planets?

90 bar CO₂
730 K
H₂SO₄ clouds
100,000 x drier than Earth
D/H 160 x Earth
(Venus once wet?)
Thermochemistry below clouds

1 bar N₂, O₂
300 K in San Francisco
Receives ½ the solar radiation of Venus
H₂O clouds
Oceans, Life

7 mbar CO₂
~210 K
H₂O and CO₂ ice clouds
D/H 5 x Earth
Photochemistry at surface

How unique is our solar system?
Motivation for improved mass spectrometer measurements at Venus
• to address fundamental issues of terrestrial planetary formation and evolution

The assignment
• to make precise (better than 1 %) measurements of isotope ratios and accurate (5-10%) measurements of abundances of noble gas
• to obtain vertical profiles of trace chemically active gases from above the clouds all the way down to the surface

The challenge for Venus probe mass spectrometry
• 4 orders of magnitude pressure differential on track from above clouds to surface
• trace species measured to parts per billion
• 9 orders of magnitude difference between atmospheric pressure at surface and ion source pressure in mass spectrometer
• 500 degree temperature gradient from atmosphere above clouds to surface
• cloud droplets and aerosols that can clog mass spectrometer inlet systems and mask real vertical variations due to their condensation on surfaces
• a fast ride to the surface with an entry probe
Topics

Near term Venus science goals for chemical and isotopic measurements

Where have the Venus missions, to date, left us with respect to these goals?
  • noble gas elemental and isotopic composition
  • cloud chemistry
  • surface science

The challenge of Venus mass spectrometry and future directions
Space Studies Board SSE Strategy – July 2002

• The first billion years of solar system history
  1. What processes marked the initial stages of planet and satellite formation?
  2. How long did it take Jupiter to form and how did the formation of the gas and ice giants differ?
  3. What was the rate of decrease of impacts by comets, asteroids, and other objects and how did it affect the emergence of life?

• Volatiles and organics: the stuff of life
  1. What is the history of volatile material, especially water, in our solar system?
  2. What is the nature and history of organic material in our solar system?
  3. What planetary processes affect the evolution of volatile on planets?

• The origin and evolution of habitable worlds
  1. Where are zones in our solar system where life can exist and what are the processes for producing and sustaining habitable planets?
  2. Does (or did) life exist beyond the Earth?
  3. Why did Mercury, Venus, Earth, and Mars diverge so much in their evolution?
  4. What hazards do solar system objects present to Earth?

• How planets work
  1. How do the processes that shape planets today operate and interact?
  2. What does our solar system tell us about other solar systems?
Decadal Study Recommendations for Venus

Profile
Venus In Situ Explorer

Mission Type: Lander
Cost Class: Medium

Priority Measurements:
- Determine elemental and mineralogical surface compositions.
- Measure the composition of the atmospheres, especially trace gases and their isotopes.
- Undertake high-precision measurements of noble gases and light stable isotopes.
- Assess processes and rates of atmosphere-surface interaction.
- Search for evidence of volcanic gases in inner-planet atmospheres.
Science measurement objectives of VISE are as follows:

- Determine the composition of Venus’ atmosphere, including trace gas species and light stable isotopes
- Accurately measure noble-gas isotopic abundance in the atmosphere
- Provide descent, surface, and ascent meteorological data
- Measure zonal cloud-level winds over several Earth days
- Obtain near-IR descent images of the surface from 10-km altitude to the surface
- Accurately measure elemental abundances & mineralogy of a core from the surface
- Evaluate the texture of surface materials to constrain weathering environment.
Motivation for noble gas measurements at Venus

Noble gas elemental ratios and isotopic fractionation constrain models of atmospheric formation and evolution
Inner planet noble gas elemental abundances do not match those of the sun or various types of chondrites.

The $^{36}\text{Ar}/^{84}\text{Kr}$ ratio at Venus may be much more solar like than Earth or Mars.

However - great uncertainty in Kr and Xe elemental abundances.

Xenon Isotopic Composition

Mars and Venus vs. the Sun and chondrites.

The Martian values are established from SNC meteorite analysis.

The fractionation in Venus is unknown.

If fractionation on Venus was found to be similar to Earth and Mars, then fractionation could have occurred in planetesimals prior to their incorporation in planets from Owen and Bar-Num, Orig. of Life and the Evolution of the Biosphere, 31, 435, 2001.
Current status of noble gas measurements at Venus

Xe – no isotope information, upper limit on abundance
Kr – no isotope information, great uncertainty in abundance
Present state of the art in Venus noble gas measurements

### Noble gas abundance

<table>
<thead>
<tr>
<th>Noble gas abundance</th>
<th>Previous measurements</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>12 (+24,-8) ppm</td>
<td>extrapolated from meas. &gt; 130 km</td>
</tr>
<tr>
<td>Ne</td>
<td>7 ± 3 ppm</td>
<td>4 MS measurements</td>
</tr>
<tr>
<td>Ar</td>
<td>70 ± 25 ppm</td>
<td>3 MS and 2 GC measurements</td>
</tr>
<tr>
<td>Kr</td>
<td>0.4 ± 0.14</td>
<td>Venera 11 and 12 reproduced measurements</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>PV Probe Hoffman analysis</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>PV Probe Donahue analysis</td>
</tr>
<tr>
<td>Xe</td>
<td>0.12 upper limit</td>
<td>PV Probe Donahue analysis</td>
</tr>
</tbody>
</table>

### Noble gas isotope ratio

<table>
<thead>
<tr>
<th>Noble gas isotope ratio</th>
<th>Previous measurement</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{He}/^4\text{He}$</td>
<td>---</td>
<td>$^3\text{He}$ predicted at low ppb level – methane or H$_2$ could give H$_3^+$ interference with HD</td>
</tr>
<tr>
<td>$^{20}\text{Ne}/^{22}\text{Ne}$</td>
<td>11.8 ± 0.7</td>
<td>Potential interference from $^{40}\text{Ar}^{++}$ at 20 Da and CO$_2^{++}$ at 22 Da</td>
</tr>
<tr>
<td>$^{20}\text{Ne}/^{21}\text{Ne}$</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>$^{36}\text{Ar}/^{38}\text{Ar}$</td>
<td>5.56 ± 0.62</td>
<td>PV Probe Donahue analysis</td>
</tr>
<tr>
<td></td>
<td>5.08 ± 0.05</td>
<td>Venera 11/12 MS</td>
</tr>
<tr>
<td>$^{40}\text{Ar}/^{36}\text{Ar}$</td>
<td>1.03 ± 0.04</td>
<td>PV Probe Donahue analysis</td>
</tr>
<tr>
<td></td>
<td>1.19 ± 0.07</td>
<td>Venera 11/12 MS</td>
</tr>
<tr>
<td>Kr isotopes</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Xe isotopes</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

Target accuracy <5-10%

Target precision <1-2%

Key future measurements → Kr and Xe abundance and isotopic distribution
Approach for future noble gas measurements at Venus

Wide dynamic range mass spectrometer
Dedicated noble gas processing unit to optimize all noble gas measurements including Xe and Kr
Predicted signal with direct sampling at Venus with no enrichment or saturation of CO₂
Dynamic range possible with small quadrupole mass spectrometer
Galileo Probe use enrichment but NOT static MS
Enrichment techniques – the Galileo Probe Neutral Mass Spectrometer approach
Xenon Isotopic Fractionation at Jupiter from the Galileo Probe Mass Spectrometer

U-Xe [Pepin, 1992]

CI chondrites

Jovian xenon
A proposed measurement protocol for Venus noble gas and $^{15}\text{N}/^{14}\text{N}$ measurement

- sample a volume of Venus atmospheric gas
- chemically remove CO$_2$ as gas is sampled
  
  \[(\text{CaO (s)} + \text{CO}_2\text{(g)} \rightarrow \text{CaCO}_3\text{(s)}\)

- $({^{15}\text{N}}/^{14}\text{N})_\text{N}_2$ with dynamic MS to obtain $^{15}\text{N}/^{14}\text{N}$
- chemically remove N$_2$ and other active gases with a getter
- cryogenically remove Kr and Xe (on high surface area trap)
- $^{38}\text{Ar}/^{36}\text{Ar}$ and $^{36}\text{Ar}/^{40}\text{Ar}$ with static MS
- cryogenically remove Ar
- residual $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{3}\text{He}/^{4}\text{He}$ with static MS
- release Kr and Xe
- all Kr and Xe isotopes with static MS
Motivation for trace gas measurements at Venus

Vertical profiles through the clouds and down to the surface enable cloud chemistry and atmosphere/surface interactions to be studied.
Gases and reactions expected to be important for cloud chemistry

SO$_2$, H$_2$O, SO$_3$, SO, OCS

SO$_2$ + $\frac{1}{2}$ O$_2$ + H$_2$O + M $\rightarrow$ H$_2$SO$_4$  \hspace{1cm} \text{net reaction}

\text{Photolysis of SO}_2 \rightarrow \text{SO} + \text{O}

**Elemental sulfur**

SO + SO $\rightarrow$ SO$_2$ + S
S + S + M $\rightarrow$ S$_2$ + M
S$_2$ + S$_2$ + M $\rightarrow$ S$_4$ + M
S$_4$ + S$_4$ + M $\rightarrow$ S$_8$ + M

**Other possible species**

NO, Cl$_2$, S$_2$Cl$_2$ etc
Reactions that may be important for surface/atmosphere interaction

Volcanoes likely source of SO₂
Weathering of surface minerals may buffer atmospheric gases

\[
\text{CaCO}_3(s) + \text{SO}_2(g) \rightarrow \text{CaSO}_4(s) + \text{CO}(g)
\]
Calcite anhydrite
(time constant ~ 2 M yr – Fegley & Prinn, 1989)

\[
\text{CaCO}_3 \ (s) + \text{SiO}_2 \ (s) = \text{CaSiO}_3 \ (s) + \text{CO}_2 \ (g)
\]
Calcite quartz wollastonite
(source of calcite – Fegley & Treiman, 1992)

Trace species of interest that reflect the oxidation state near the surface

\[
\text{H}_2\text{S}, \text{SO}_2, \text{OCS}, \text{O}_2, \text{CO}, \text{H}_2\text{O}
\]

Oxidation state determines Fe mineralogy

\[
\text{Fe}_3\text{O}_4(s) + \text{O}_2 = \text{Fe}_2\text{O}_3 \ (s)
\]
magnetite hematite
Past and future Venus mass spectrometer experiments need to address the difficult sampling issues.
Sampling issues

- 4 orders of magnitude pressure differential on track from above clouds to surface
- Trace species measured to parts per billion
- 9 orders of magnitude difference between atmospheric pressure at surface and ion source pressure in mass spectrometer
- 500 degree temperature gradient from atmosphere above clouds to surface
- Cloud droplets and aerosols that can clog mass spectrometer inlet systems and mask real vertical variations due to their condensation on surfaces
### Example Venus mass spectrometer experiments

<table>
<thead>
<tr>
<th>Mission (Team, Date)</th>
<th>Mass Spectrometer</th>
<th>Altitude (Pressure)</th>
<th>Inlet type</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Venera 9 &amp; 10 (Surkov, von Zahn, 1975)</td>
<td>monopole</td>
<td>63-34 km (130 mbar to 6 bar)</td>
<td>3 porous plugs</td>
<td>instrument measured primarily background signal throughout descent</td>
</tr>
<tr>
<td>PV-Large Probe (Hoffman, 1978)</td>
<td>magnetic sector</td>
<td>62 km to surface</td>
<td>pinched Ta tube (3 inlets)</td>
<td>50 km to 29 km inlet was blocked and instrument measured outgassing from H$_2$SO$_4$ droplets</td>
</tr>
<tr>
<td>Venera 11 &amp; 12 Lander (Grechnev, 1978)</td>
<td>Bennett RF</td>
<td>23 km to surface</td>
<td>1 m x 5 mm inlet pipe &amp; pulsed microvalve</td>
<td>possible inlet tube memory effects, Ar isotopes in &quot;static&quot; mode, Kr detected but isotopes NOT resolved</td>
</tr>
<tr>
<td>PV-Orbiter (Niemann, Kasprzak, 1978-1992)</td>
<td>Quadrupole MS</td>
<td>orbiter (upper atmosphere)</td>
<td>source open to ambient</td>
<td>14 years of data neutral scale heights (CO$_x$, CO, N$_2$, O, N, and He) O escape (thermospheric measurements gave no information on heavy noble gas isotopes)</td>
</tr>
<tr>
<td>PV-Multiprobe Bus (von Zahn, 1978)</td>
<td>Magnetic Sector</td>
<td>entry to 0.01 mbar</td>
<td>open with differential P</td>
<td>entry measurements (upper limit on $^{36}$Ar and $^{40}$Ar), identified He homopause at 137 km</td>
</tr>
</tbody>
</table>

### Atmospheric sampling approach

- short inlet lines heated above ambient to vaporize condensates
- chemically inert materials in inlet
- adequate aerosol traps and baffles
- multiple inlet leaks
- redundant inlet lines
The future of Venus exploration?
• near term objectives from the planetary science community are clearly recommended to NASA in the Decadal Study Report
• the probe/measurement technology is ready for noble gas and trace species measurements
• NASA Discovery & New Frontier Missions may enable some of these recommendations to be realized
• future Venus detailed cloud investigations, long term surface packages and sample return clearly require advanced technology support