INVESTIGATING THE ORIGIN AND EVOLUTION OF VENUS WITH IN SITU MASS SPECTROMETRY

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Venus Exploration Goals

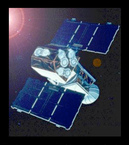
The 2010 Planetary Sciences Decadal Survey - *Visions and Voyages*[1] - highlights several scientific questions for which Venus is a fundamental exploration target.

Building New Worlds	#3: What governed the accretion, supply of water, chemistry, and internal differentiation of the inner planets and the evolution of their atmospheres, and what roles did bombardment by large projectiles play?
Planetary Habitats	#5 Did Mars or Venus host ancient aqueous environments conducive to early life, and is there evidence that life emerged?
Solar Systems Workings	#9 Can understanding the roles of physics, chemistry, geology, and dynamics in driving planetary atmospheres and climates lead to a better understanding of climate change on Earth?

- Addressing the origin and evolution of Venus' atmosphere is a long-standing high priority investigation[2]
- **Noble gas mixing ratios and isotope abundances are key** to deciphering the early and later history of planets (*see "Origin of Terrestrial Planets", above right*).
- Such studies are only possible through **in situ measurement**
- Previous attempts have been challenged by low abundances and the limitations within the harsh Venus environment

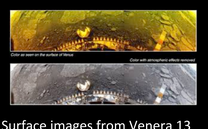
Table: Despite successful probe missions in the 1970s and 1980s, there are many gaps in our knowledge of noble gases and key stable isotopes.

Species	Previous Measurement		Spacecraft (reference)
	Value	± Error	
He	9 ppm	67%	EUVE (3); *model dependent*
$^{3}He/^{4}He$	not measured	-	-
Ne	7 ppm	43%	PV MS, Ven. 11/12 MS (4); *recommended*
$^{20}Ne/^{22}Ne$	11.8	6%	PV MS (5)
$^{21}Ne/^{22}Ne$	not measured	-	-
Ar	70 ppm	36%	PV MS & GC, Ven. 11/12 MS (4); *recommended*
^{36}Ar	31 ppm	39%	PVMS, Ven. 11/12 MS (4); *recommended*
$^{40}Ar/^{36}Ar$	1.13	15%	PV MS, Ven. 11/12 MS (6,7)
$^{36}Ar/^{38}Ar$	5.56	11%	PV MS (6)
Kr	50 or 700 ppb	50%	Ven. 11/2 MS, PV MS (4)
$^{86}Kr/^{84}Kr$	not measured	-	-
$^{82}Kr/^{84}Kr$	not measured	-	-
Xe	not measured	-	-
$^{n}Xe/^{132}Xe$	not measured	-	-
N_2	3.5%	23%	PV MS & GC, Ven. 11/12 MS (4)
$^{14}N/^{15}N$	273	17-25%	PV MS (4,8)



Extreme Ultraviolet Explorer (EUVE)

Pioneer Venus (PV) Multiprobe



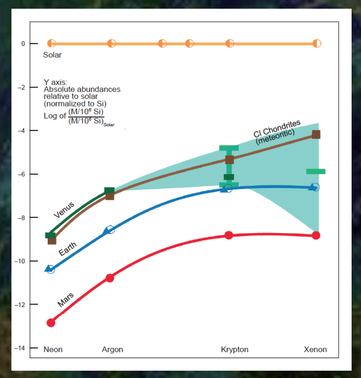
Surface images from Venera 13 (Ven11/Ven12 cameras lens caps did not deploy)

MS = Mass Spectrometer

GC = Gas Chromatograph

Origin of Terrestrial Planets

Noble gas abundances for Earth, Mars, Venus, chondrites, and the Sun

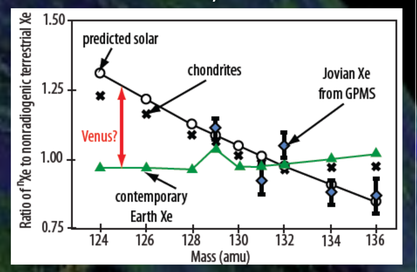


Enhanced abundances for Ne and Ar on Venus as compared to Earth and Mars may indicate loss of original atmospheres from those planets, and/or enhanced delivery of these noble gases to Venus. The poorly constrained Kr and Xe abundances (aqua region) do not allow distinction from solar system objects. From Baines et al.[9], after Pepin et al.[10]

"The [noble gas] record for Earth and Mars, particularly given the new [MSL/]SAM measurements, is quite complete. **What is missing to complete the broad history of planetary atmospheres throughout the inner solar system are accurate measurements for Venus.**"

-K. H. Baines et al. (2013)
in *Comparative Climatology of Terrestrial Planets*, Mackwell et al eds.

Fractionation of Xe isotopes in the Solar System



The heavy noble gas Xe with its 9 isotopes provides the best record of early planetary processes. If Venus' Xe is mass fractionated as it is on Earth and Mars, this would support a common source of volatiles for the inner solar system.[11] If Venus' Xe is not mass fractionated (as on Jupiter) this would suggest early atmospheric loss for Earth and Mars.[9]

Instrumental Techniques used on Jupiter and Mars can be adapted for Venus

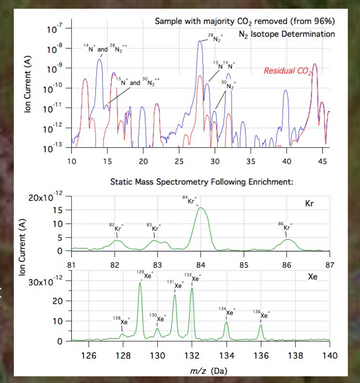
Enrichment

- Enrichment of trace noble gases is needed to enhance the signal and secure the required measurements with adequate precision
- Galileo Probe Mass Spectrometer (GPMS) demonstrated comprehensive analysis of noble gases in Jupiter's atmosphere by ingesting and processing atmospheric gas during a brief residence time, consistent with the Pioneer Venus and Venera Probes (~1 hr.)
- The groundbreaking GPMS measurements were acquired with < 10 minutes of MS time:[12,13]

Galileo Probe Entry into Jupiter's Atmosphere: December 7, 1995	**Galileo Probe Mass Spectrometer** Two Enrichment Cells (EC) were used to secure measurements of noble gas mixing ratios and isotope abundances	
	EC1	EC2
Sample into GPS	0.89 - 2.85 bar	8.89 - 9.56 bar
Initial Process time (Major gas)	11.4 min (H_2)	4.5 min (H_2)
GPS Element for purification	Getter	Getter
Trap material for Heavy Noble Gas	Carbosieve	Carbosieve
Temperature for trapping HNG	5°C – 15°C	10°C – 15°C
MS Integration time for HNG	7.8 min	7.4 min

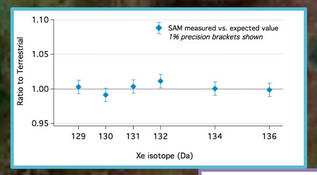
Static Mass Spectrometry

- Static mass spectrometry, in which the mass spectrometer is isolated from the pump and only reactive species are pumped with a chemical getter, is the preferred method for laboratory analysis of noble gases.
- SAM has demonstrated high sensitivity using static MS and semi-static MS.[14,17]
- The enrichment in noble gas atoms in the analyzer enables the quantitative determination of isotopic ratios with excellent precision in a short amount of time:



Laboratory tests with a gas enrichment breadboard system and commercial MS show successful enrichment and measurement of a Venus-like gas mixture, with 100 ppb each of Kr and Xe. The bottom two spectra were captured in static MS mode during a 3-minute integration period.

Static mode performance of the SAM QMS during calibration demonstrates isotopic measurements of Xe achieved in ~ 30 seconds.[14]

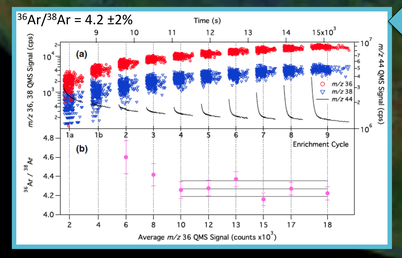


The approach of atmospheric enrichment and static MS has been successfully performed on Mars by SAM, as highlighted in a recent press release - 01 April 2015.

In the news

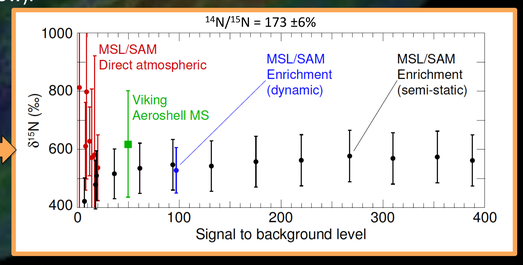
Curiosity Sniffs Out History of Martian Atmosphere
NASA - 16 hours ago
NASA's Curiosity rover is using a new experiment to better understand the history of the ...

The Mars Science Laboratory (MSL) Sample Analysis at Mars (SAM) Quadrupole MS benefits from improvements to the enrichment process, pumping throughput, and instrument sensitivity over GPMS and Pioneer Venus MS.[14] Strategic enrichment of trace isotopologues with semi-static MS has allowed sub-picomole to nanomole abundances to be measured on Mars (see Ar and N_2 below).



The SAM QMS made the first measurements of $^{36}Ar/^{38}Ar$ on Mars by scrubbing CO_2 and progressively enriching the abundance of Ar in the sample. This measurement provides excellent evidence that "Mars" meteorites are indeed of Martian origin, and it points to a significant loss of argon of at least 50% and perhaps as high as 85-95% from the atmosphere of Mars in the past 4 billion years. From Atreya et al.[15]

These same enrichment runs in the SAM QMS secured high precision N_2 isotope values and improvements over previous measurements with Viking or SAM without enrichment. In semi-static mode the pumping rate out of the QMS is reduced and the nitrogen signal to background level is enhanced by orders of magnitude. From Wong et al.[16]



Summary

- Understanding Venus' origin and evolution is a high priority goal both for Venus exploration and for understanding the history of the inner solar system.
- Noble gases and their isotopes provide insight into how the terrestrial planets formed and major geologic events throughout their evolution.
- Accurate measurements of noble gases on Venus are needed to complete this picture for the inner solar system.
- This can be accomplished as part of an in situ atmospheric investigation using flight-proven technology and demonstrated enrichment techniques.
- Successful missions, such as GPMS at Jupiter and MSL/SAM at Mars, provide guidance towards the best instrumental approaches to adapt for a future in situ Venus mission.

Acknowledgments

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Background image: Hemispheric View of Venus with Magellan MIDRs Centered at 90° East Longitude. Credit: NASA/JPL/USGS, 1998-06-04.