11th International
Planetary Probe Workshop

IN SITU TECHNIQUES FOR MEASUREMENTS OF NOBLE GASES AND NITROGEN ISOTOPES IN PLANETARY ENVIRONMENTS: RECENT ADVANCES.

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Motivation for N and noble gas elemental abundance and isotope measurements

- Giant planet formation
- Terrestrial planetary atmosphere evolution

$^{36}Ar/^{38}Ar$ and $^{15}N/^{14}N$ as tracers of atmospheric loss

- Jupiter and sun provide primordial reservoir
- Mars measurements with enrichment techniques
- Venus measurements in future missions

Heavy noble gases give signatures of early evolutionary processes

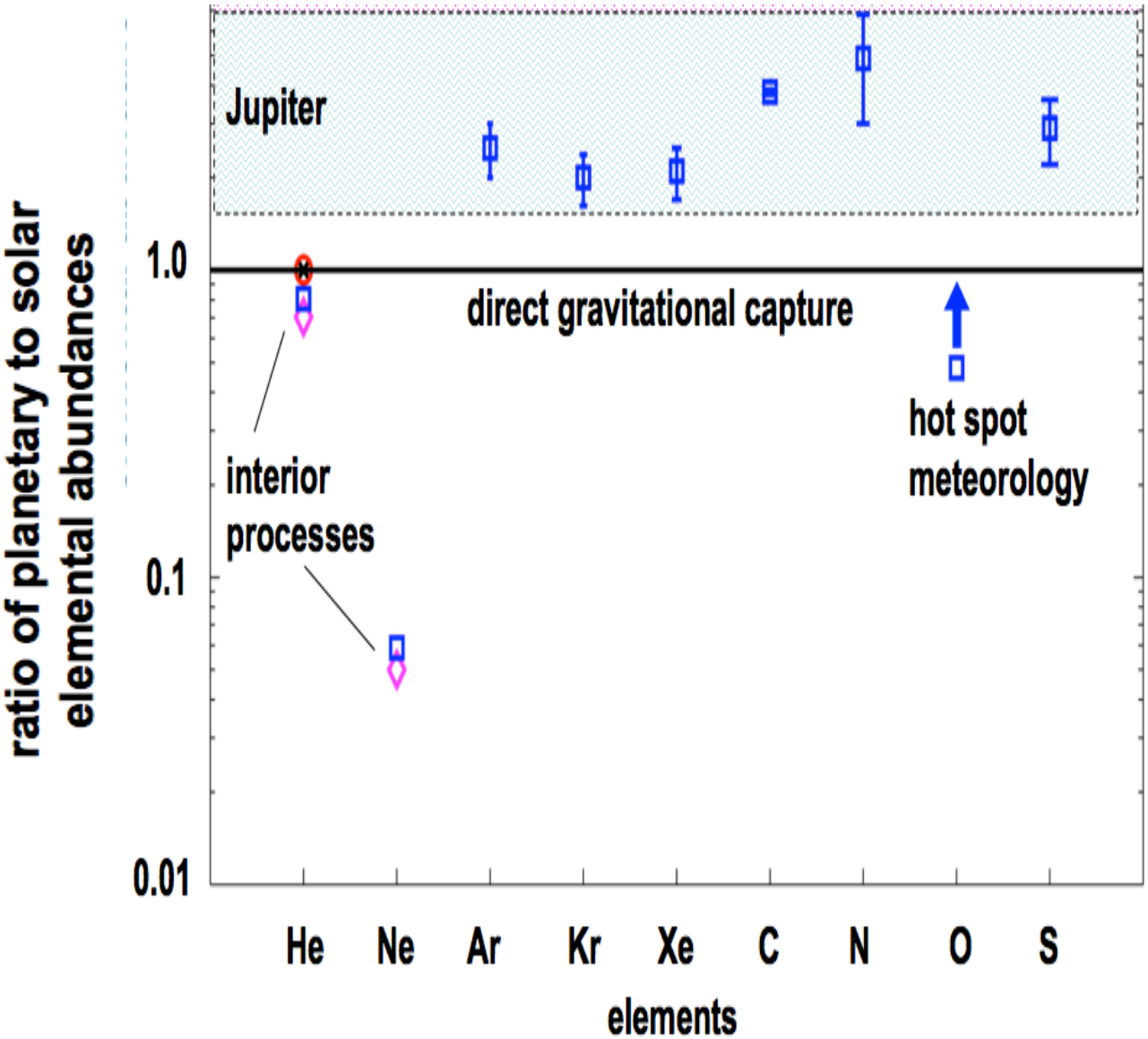
- Static mass spectrometry
- Future Mars, Venus, and cometary measurements

Chronology from spallogenic, neutron capture, and radiogenic noble gas isotopes

- Lunar radiogenic ^{40}Ar from the LADEE NMS
- First planetary K-Ar chronology experiments
- Cosmic ray exposure age from MSL APXS and SAM combined measurements

Upcoming opportunities for in situ measurements and emerging technologies

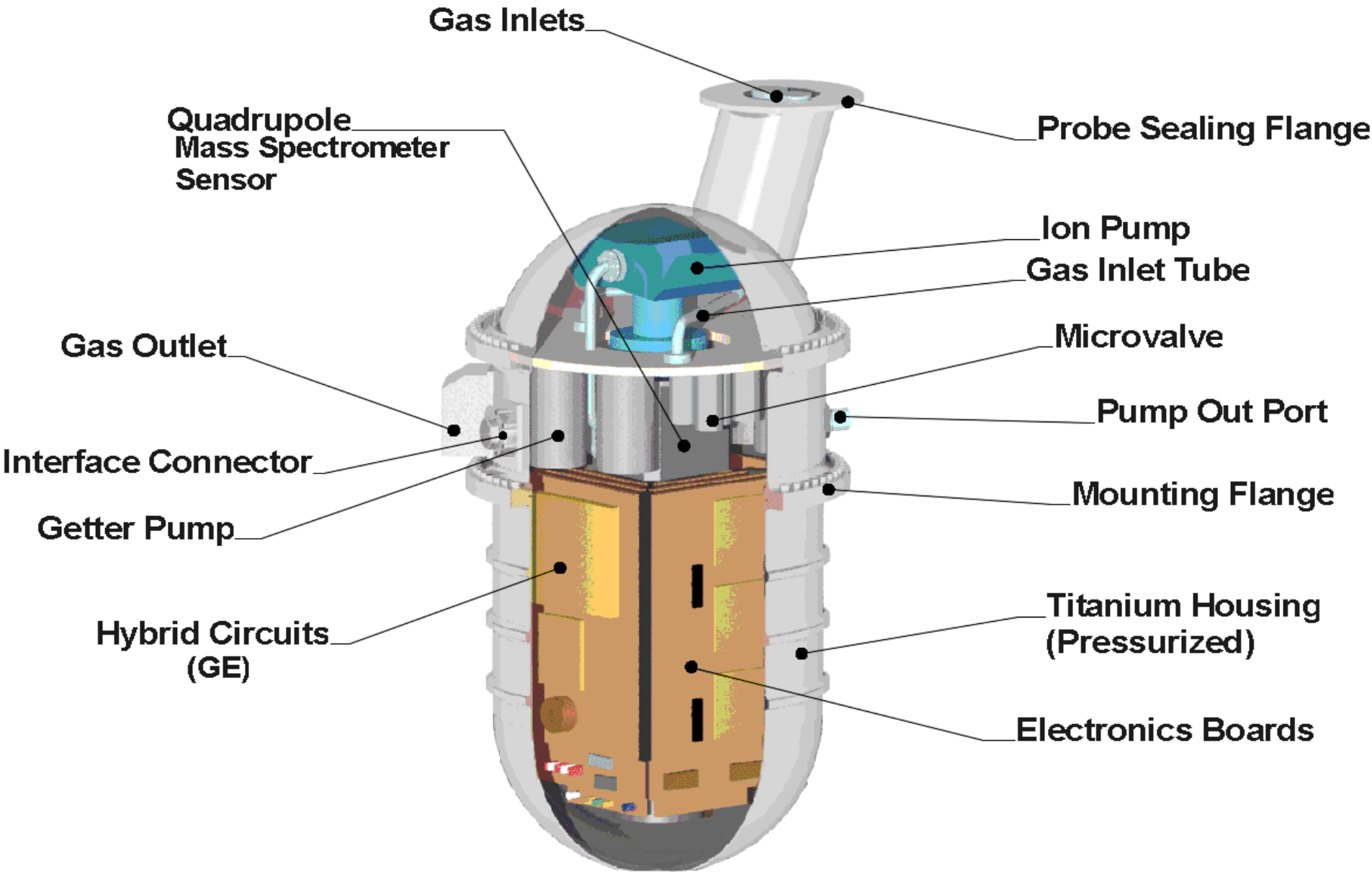
Elemental ratios of N, noble gases, & other light elements provide basis for models of giant planet formation & planetary atmosphere evolution



Elemental ratios in outer planet gas and ice giants can provide key data to constrain models of origin and evolution of the Solar System and Extrasolar Systems.

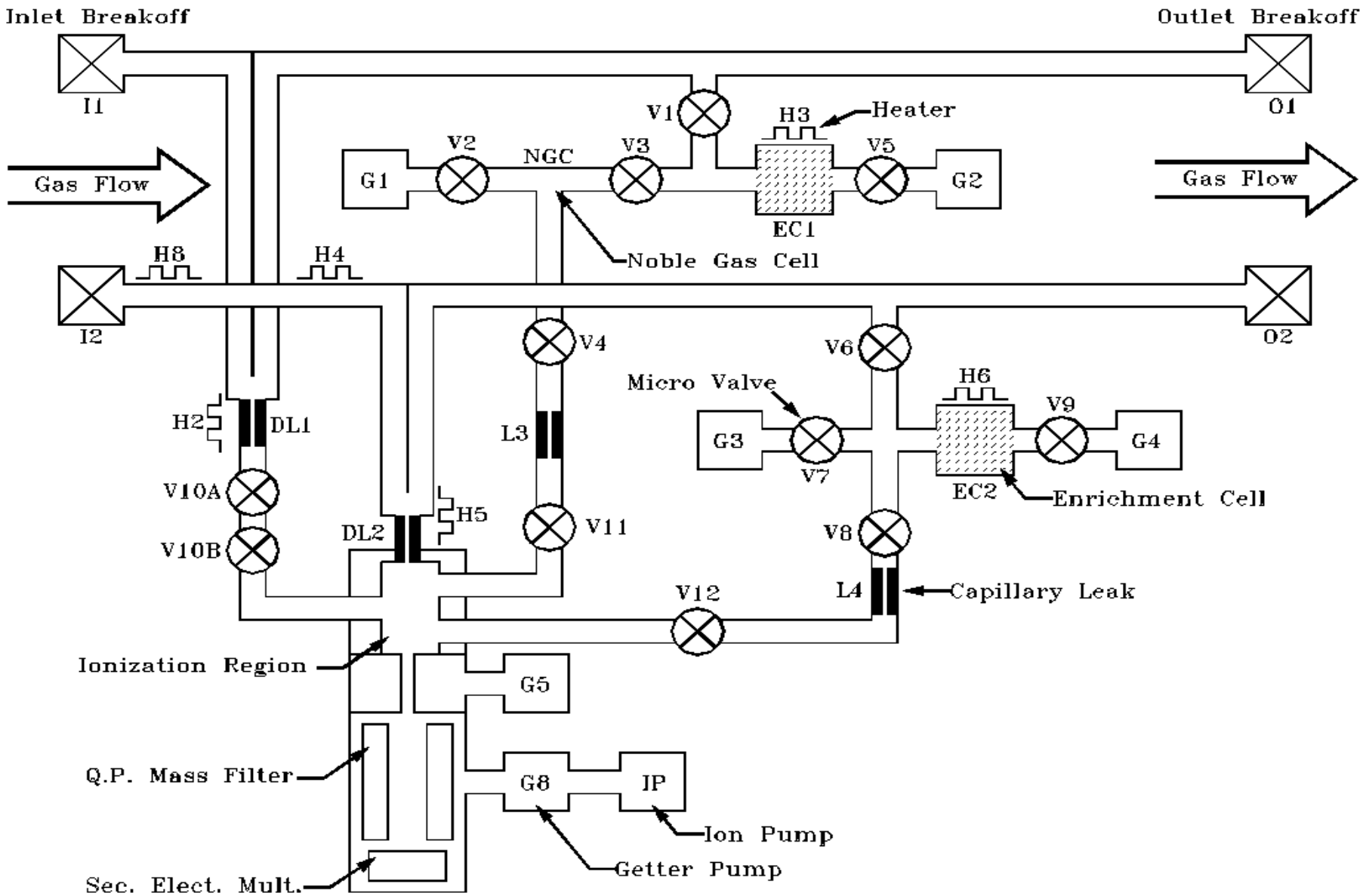
Isotope ratios of N, C, O, S, H, and the noble gases provide a reference for understanding evolution of the atmospheres of terrestrial planets and early solar system habitability
-> Venus early ocean
-> Mars persistent water with heavier atmosphere?

Galileo Probe Mass Spectrometer had an early version of an enrichment system but without “static” mass spectrometry

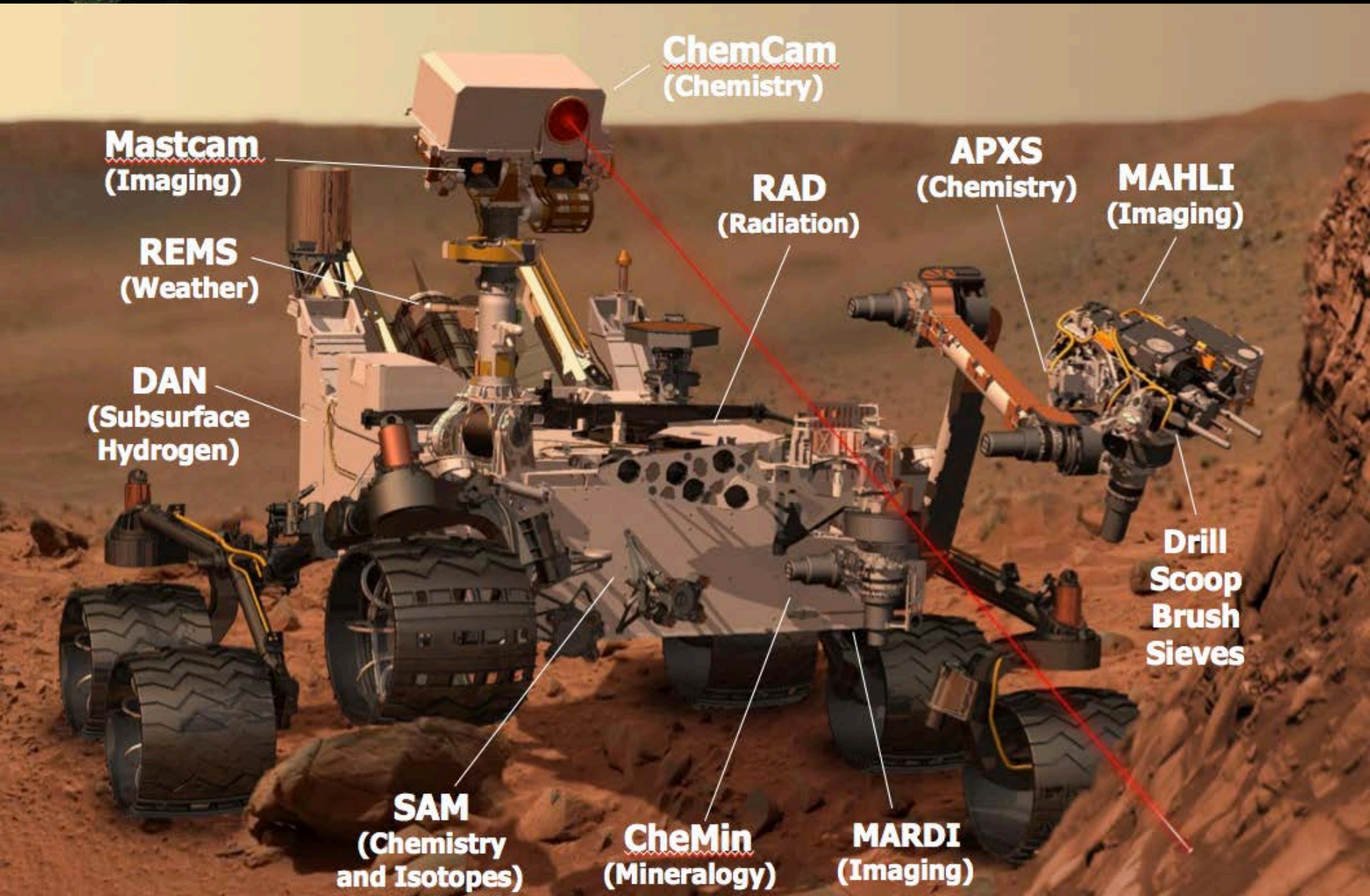


GPMS with an enrichment system but without "static" mass spectrometry

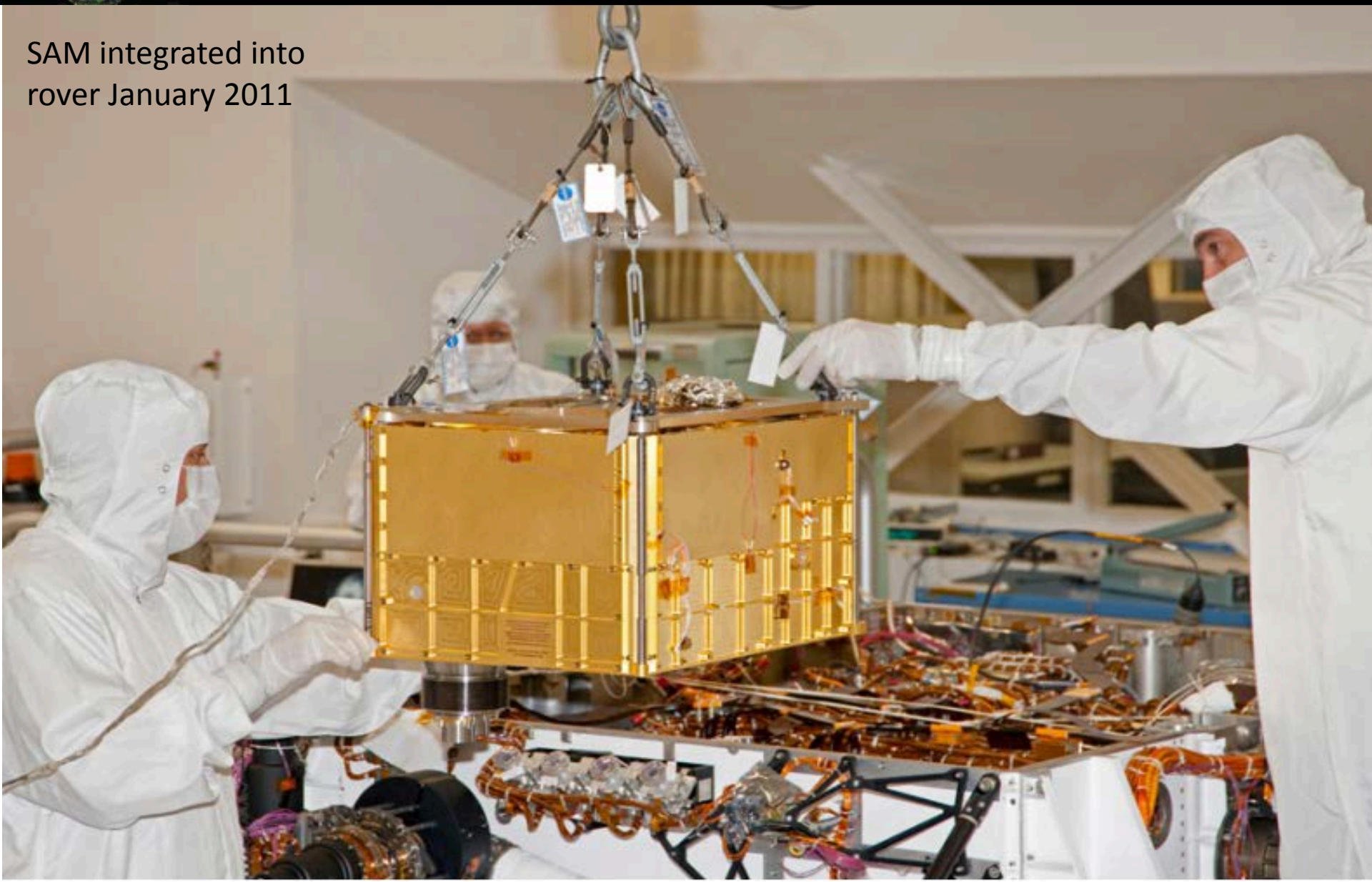
→ GPMS employed getters & a miniature ion pumps



Curiosity's primary scientific goal is to explore and quantitatively assess a local region on Mars' surface as a potential habitat for life, past or present

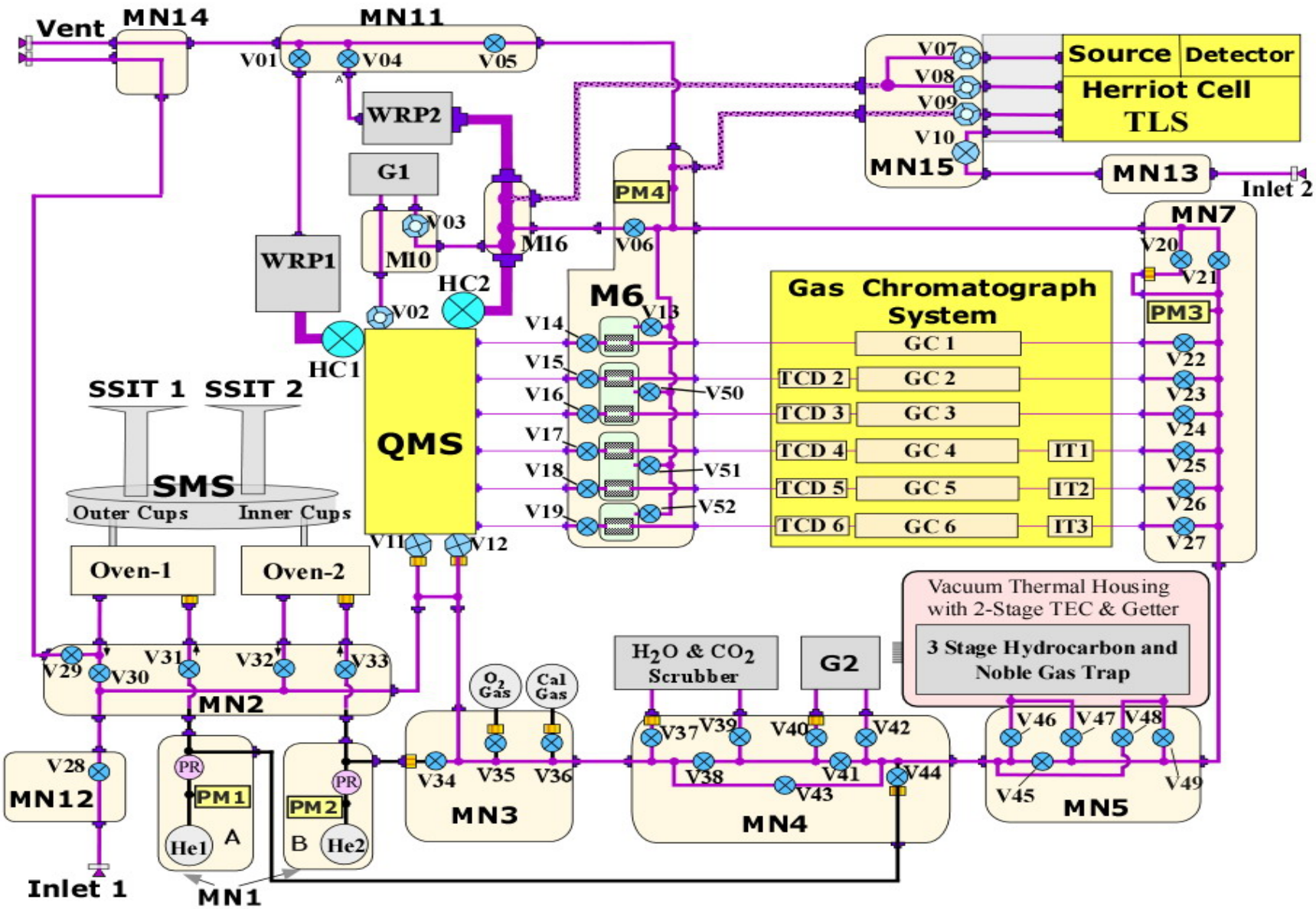


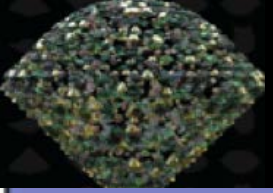
Sample Analysis Instrument Suite on the Curiosity Rover is designed to carry out a range of isotopic studies of light elements and noble gases



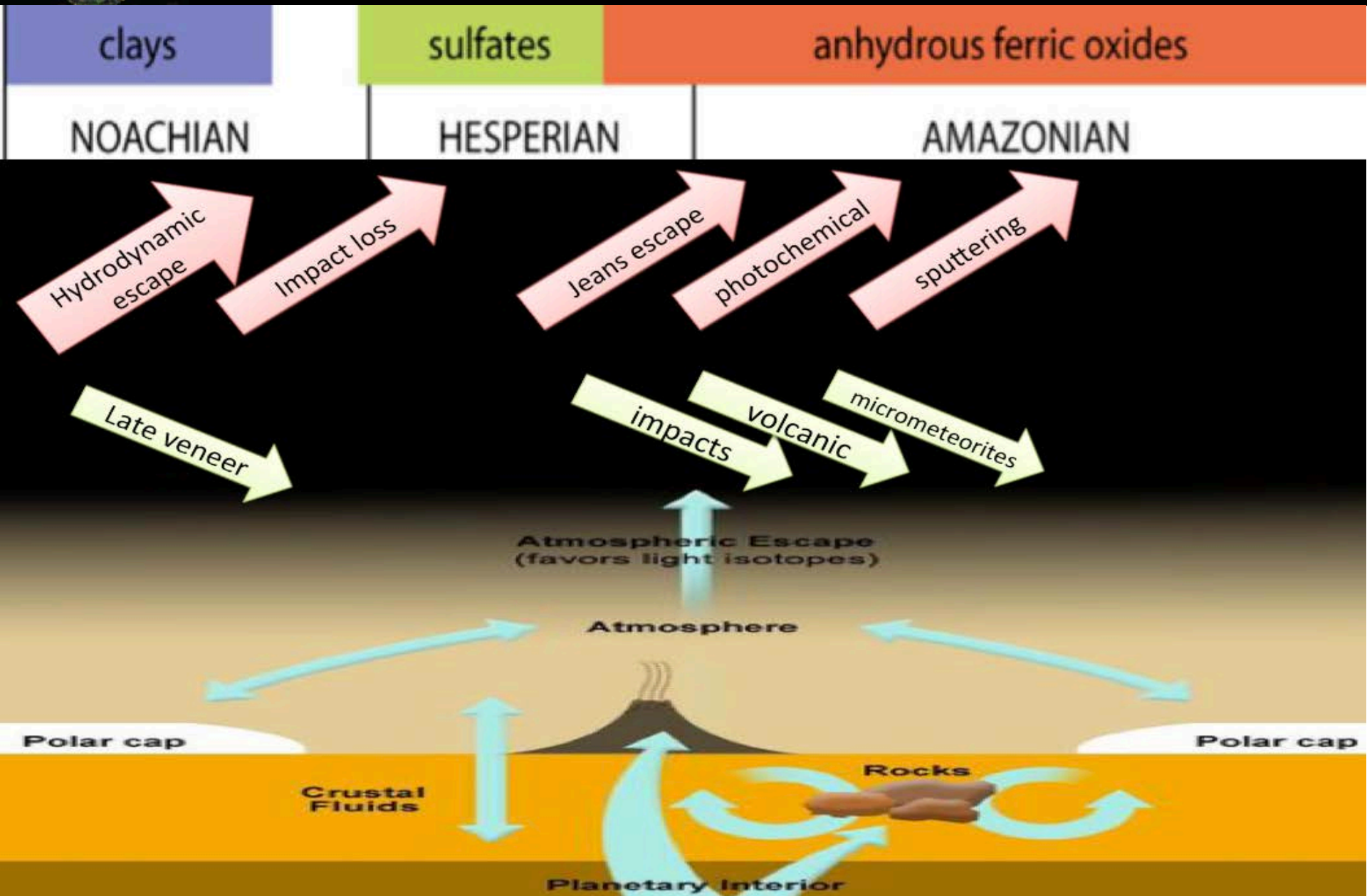
SAM integrated into rover January 2011

Gas Flow Diagram of the Sample Analysis Instrument Suite on the Curiosity Rover (QMS, TLS, GCMS, 54 valves, heaters, enrichment system)





Multiple processes contribute to the loss of planetary atmospheres but most loss process to space enrich the remaining heavy isotopes

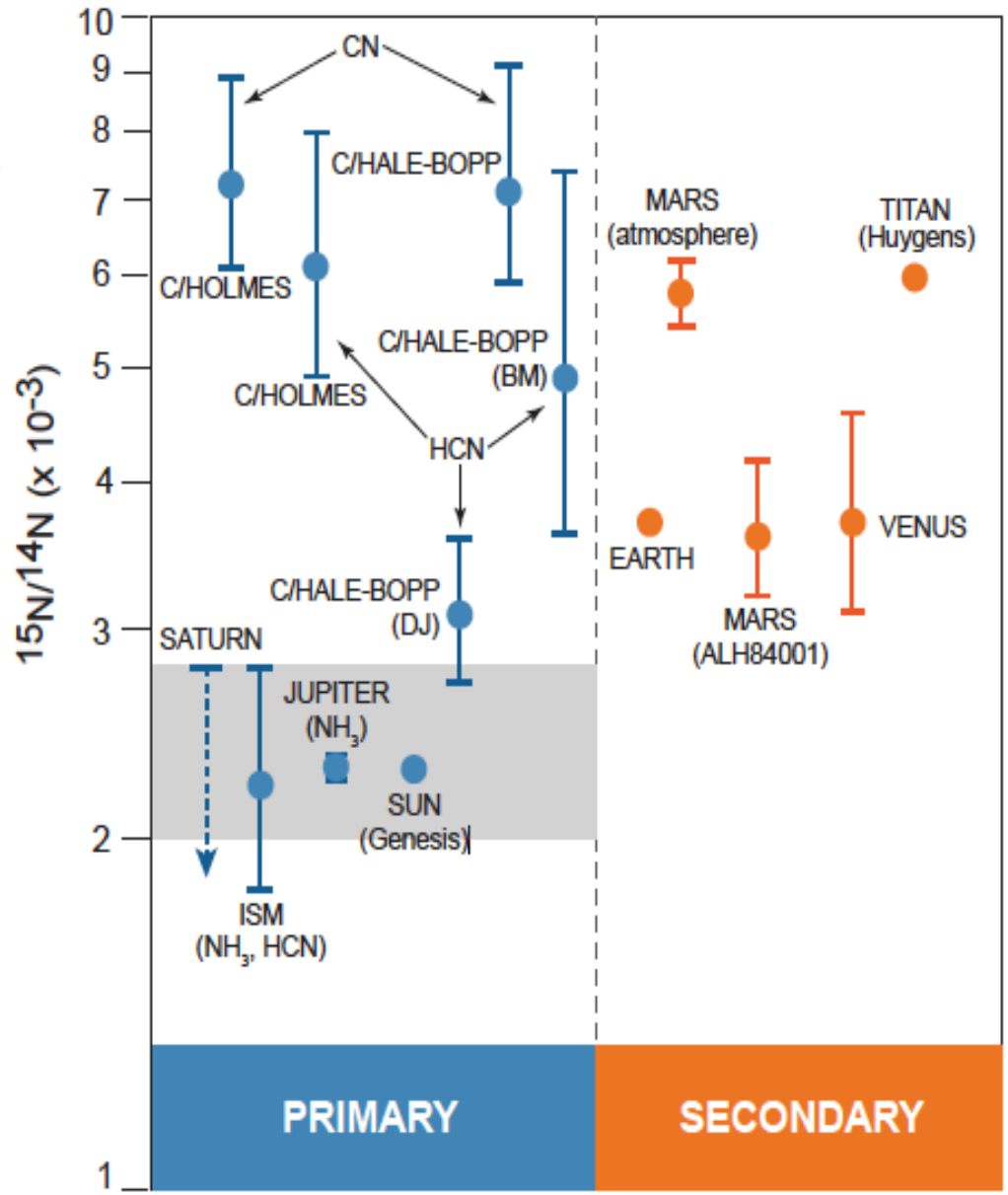


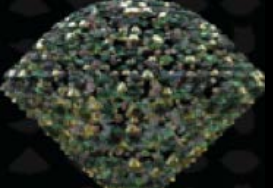
$^{15}N/^{14}N$ attributed to atmospheric loss on Mars

Measured at Jupiter and Mars but not Venus

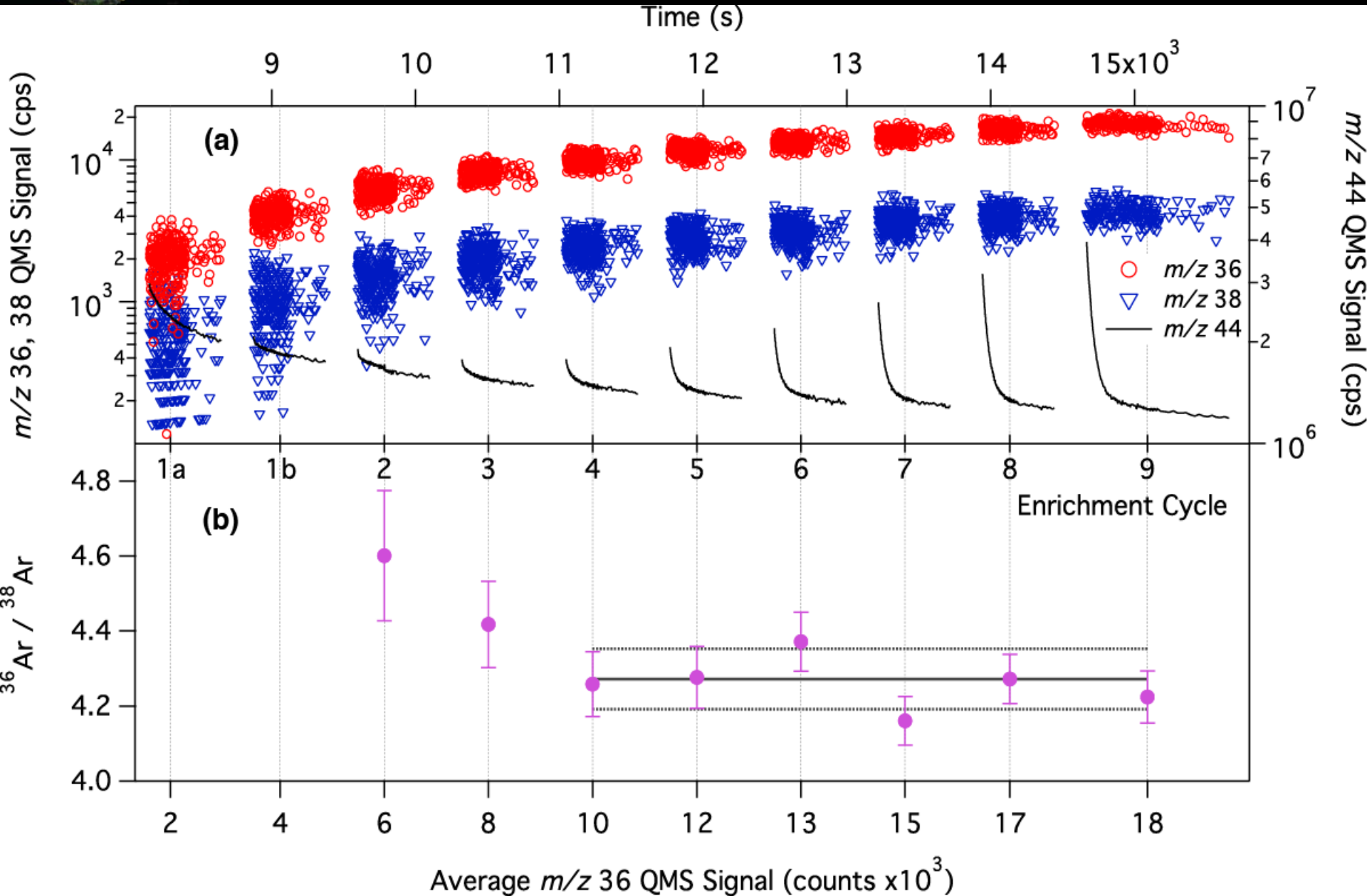
$^{15}N/^{14}N$ and atmospheric loss on Venus

- Jovian ratio (from Galileo Probe MS) and new solar (Genesis) values represent average protosolar value
- Other possible primary sources for planetary atmospheres are comets
- high martian value attributed to extended period of atmospheric escape
- does terrestrial value represent different source or vigorous escape?
- N not effectively fractionated in rich CO_2 atmosphere
  - ➢ heavy N → intense hydrodynamic escape prior to enrichment CO2 in the Venus atmosphere followed by runaway greenhouse and loss of oceans
  - ➢ if similar to Earth contribution from a common primary source must be considered
- $^{15}N/^{14}N$ measurements by mass spectrometer realized by chemical separation of CO_2 and N_2

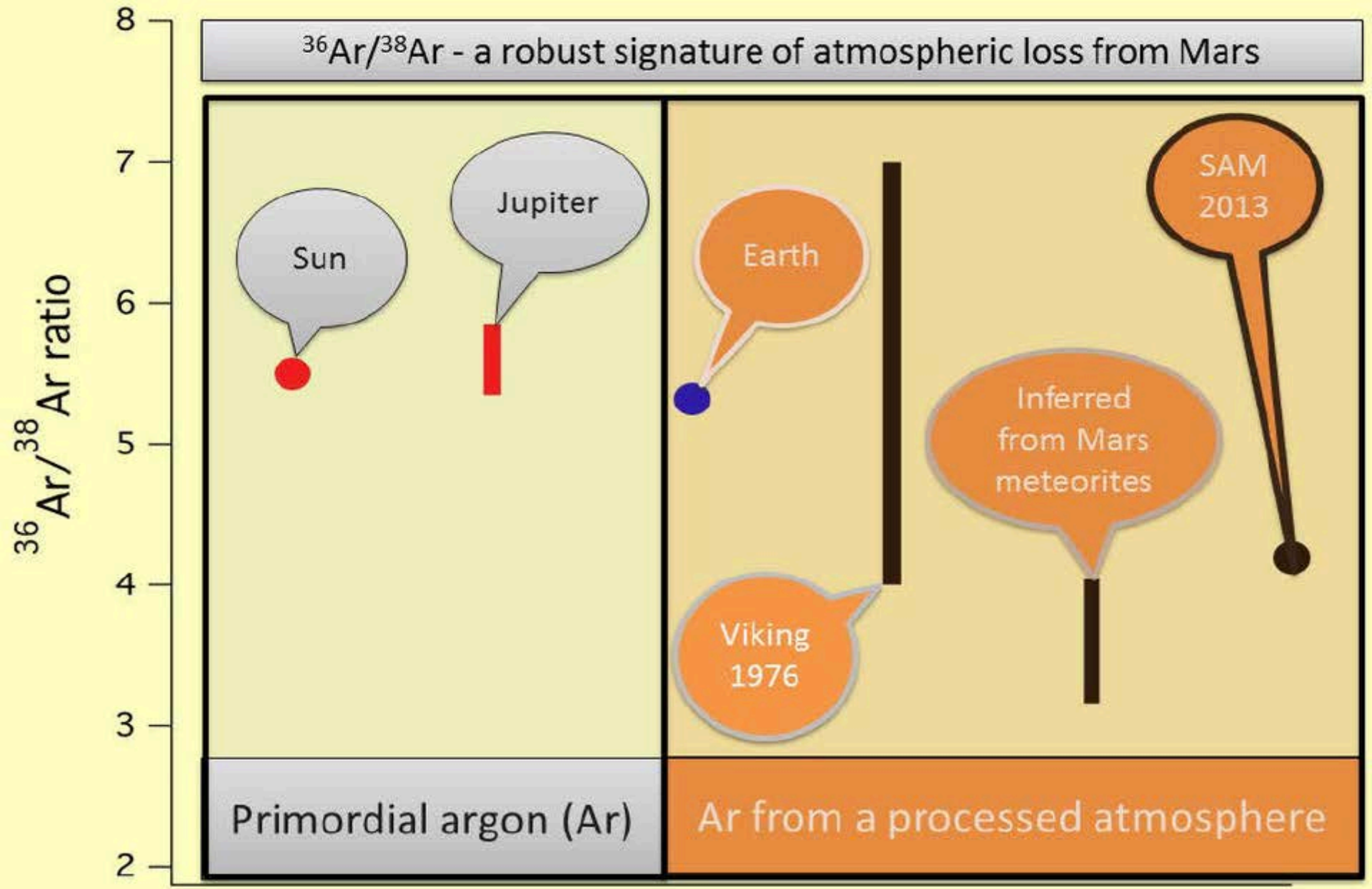


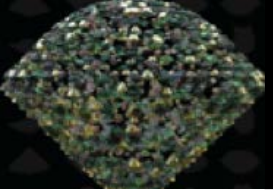


On Curiosity at night there is ample time and power to make extended measurements



Isotopes of C, O, N, H in carbon dioxide, water, nitrogen, and noble gases provide key signatures of atmospheric loss





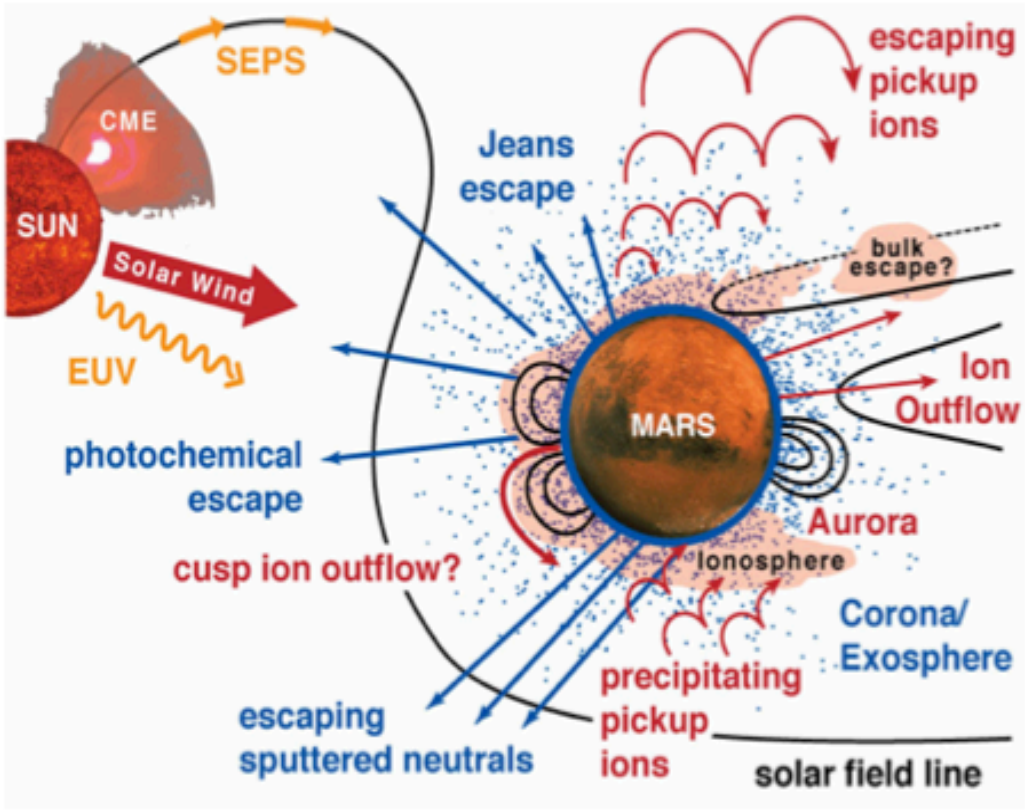
All isotopes measured on mars point to atmospheric loss. Additional isotope ratios can be secured with SAM from thermally evolved gas

Isotopes	Mars value ‰	SAM suite instrument	Reference
$\delta^{38}Ar_{Sun}$	310 ± 31	QMS	Atreya et al. (2013, *GRL*)
$\delta^{40}Ar_{Earth}$	5419 ± 1013	QMS	Mahaffy et al. (2013, *Science*)
$\delta^{15}N_{Earth}$	572 ± 82	QMS	Wong et al. (2013, *GRL*)
$\delta^{13}C_{VPDB}$	45 ± 12	QMS	Mahaffy et al. (2013, *Science*)
$\delta^{13}C_{VPDB}$	46 ± 4	TLS	Webster et al. (2013, *Science*)
$\delta^{18}O_{SMOW}$	48 ± 5	TLS	Webster et al. (2013, *Science*)
δD_{SMOW}	4950 ± 1080	TLS	Webster et al. (2013, *Science*)

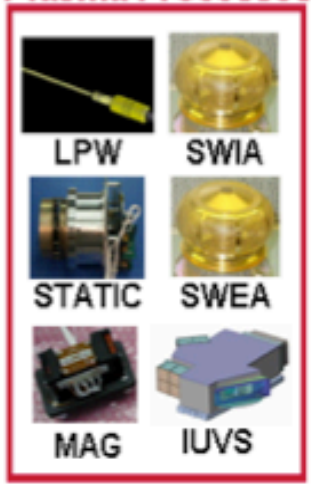
MAVEN Will Measure the Drivers, Reservoirs, and Escape Rates

CU/LASP • GSFC • UCB/SSL • LM • JPL

Solar Inputs



Plasma Processes



Neutral Processes

- MAVEN will determine the present state of the upper atmosphere and today's rates of loss to space.
- Essential measurements allow determination of the net integrated loss to space through time.

Nucleogenic & cosmogenic noble gas production

Cosmogenic noble gas production from the top 750-1000 g/cm^2

- Include **^{3}He**, ^{13}C, ^{15}N, ^{20}Ne, **^{21}Ne**, ^{22}Ne, ^{36}Cl, ^{36}Ar, ^{38}Ar from nuclear spallation of O, Na, Mg, Al, Si, Cl, Ca, and Fe
- Calculated from GEANT simulations of nuclear spallation reactions
- Current Mars atmosphere ~20 g cm^{-2} → surface production similar to the moon
- **^{36}Ar** produced by capture of thermal neutrons by ^{35}Cl
- Lunar samples used to secure averaged GCR flux
- Production rates typically picomole gm^{-1} Myr^{-1}

Radiogenic isotopes

- Include ^{40}Ar from ^{40}K and ^{129}Xe from ^{129}I
- Lower production rates but throughout the crust

First *in situ* rock formation age experiment on another planet

^{40}Ar discovered in 1938 by geophysicist Lyman Aldrich & mass spectrometer guru Al Nier

Radioactive decay equation

$$N = N_0\, e^{-\lambda t}$$

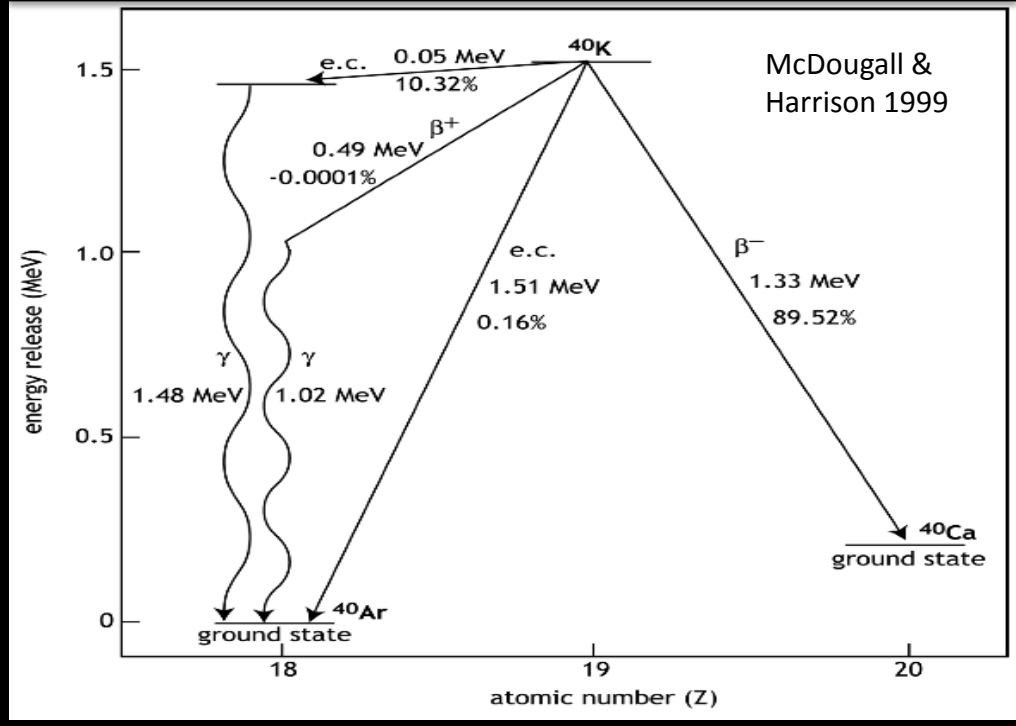
Or with a daughter nuclide D

$$t = \frac{1}{\lambda} \ln\left(\frac{D}{N} + 1\right)$$

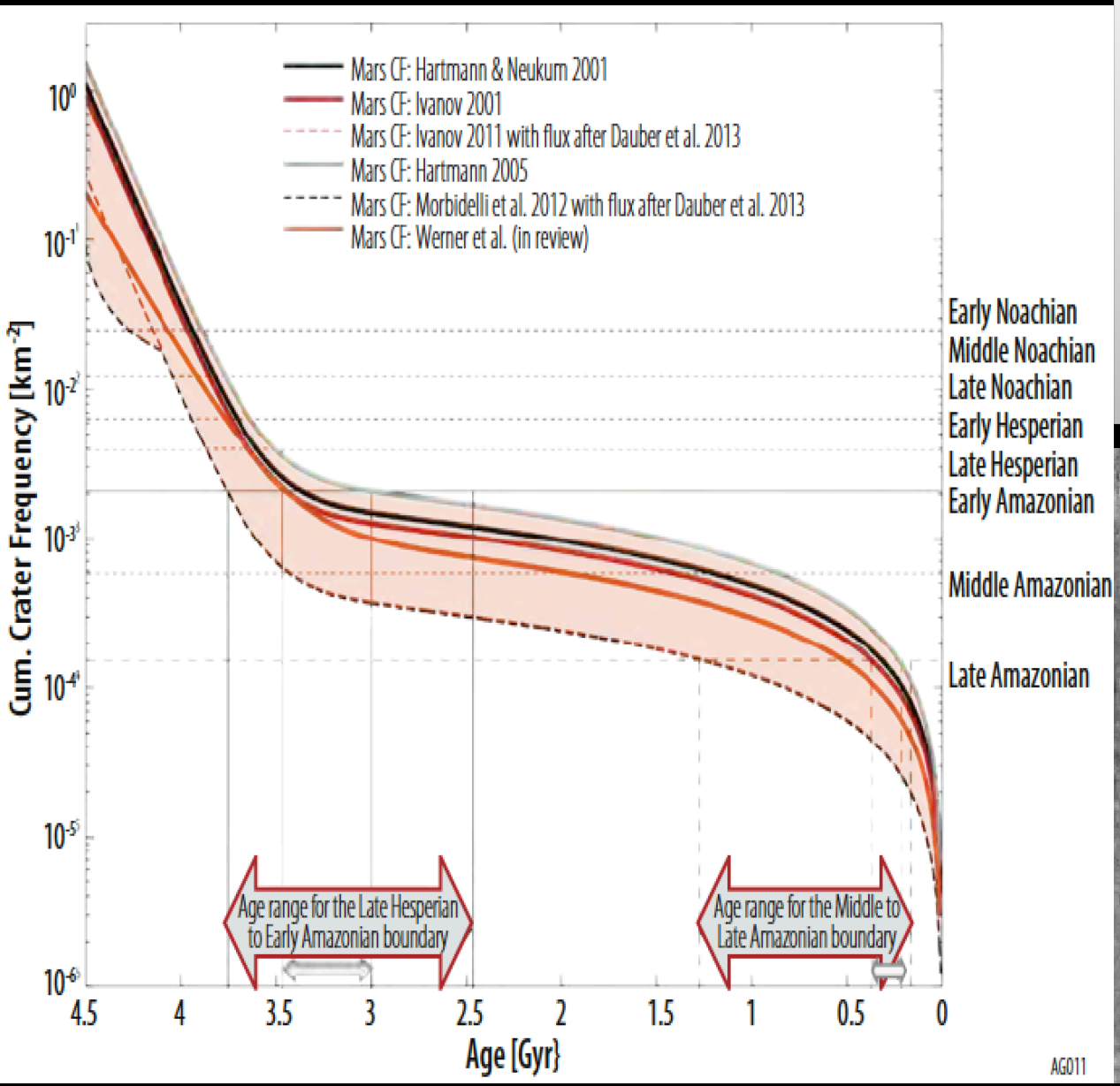
For the 2 daughter K-Ar-Ca system age equation is

$$t = \frac{1}{(\lambda_{Ar} + \lambda_{Ca})}\, ln\left[\left(\frac{40Ar}{40K}\right)\left(\frac{(\lambda_{Ar} + \lambda_{Ca})}{\lambda_{Ar}}\right) + 1\right]$$

^{40}K half life 1.249x10^{9} years

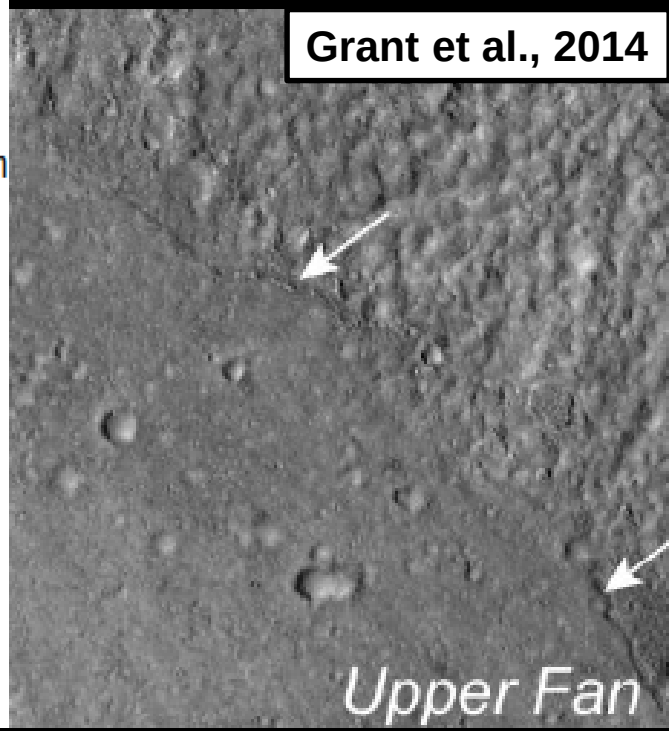


Crater densities used to estimate ages of geological units on Mars – model comparison Stephanie Werner/U. Oslo



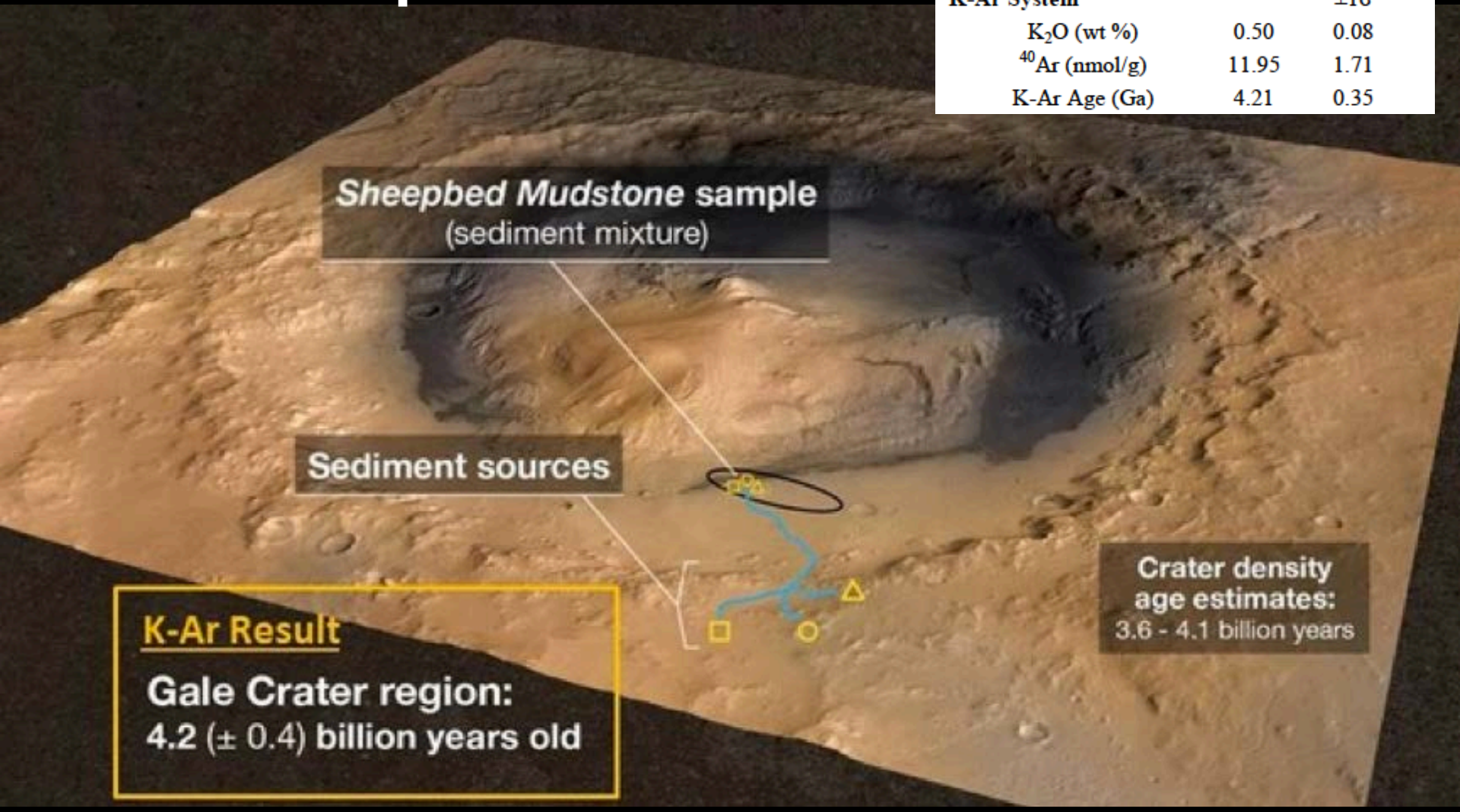
Potential error sources for absolute age determination

- **Chronology calibration based on lunar record with ground truth samples**
- **Resurfacing**
- **Early (>3.5 Gyr) cratering flux recently revisited (e.g. Morbidelli 2010)**



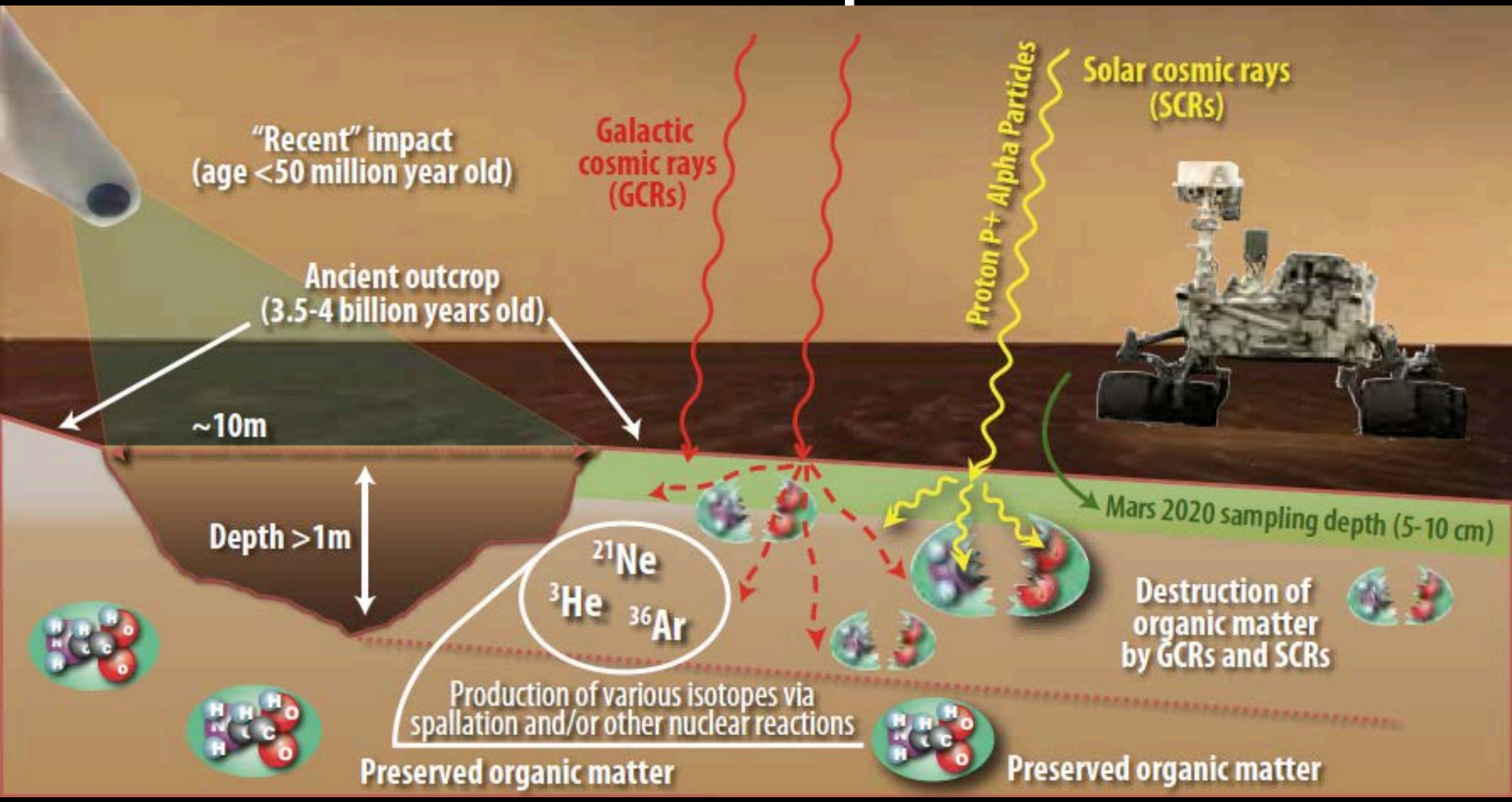
First *in situ* rock formation age experiment on another planet

Sample Mass		0.135 ± 0.018 g
K-Ar System		±1σ
K_2O (wt %)	0.50	0.08
^{40}Ar (nmol/g)	11.95	1.71
K-Ar Age (Ga)	4.21	0.35



Conclusion – rock sediment that washed down from the rim of Gale Crater was formed ~4.2 billion years ago – this consistent with crater densities

First cosmic ray exposure age experiment on another planet



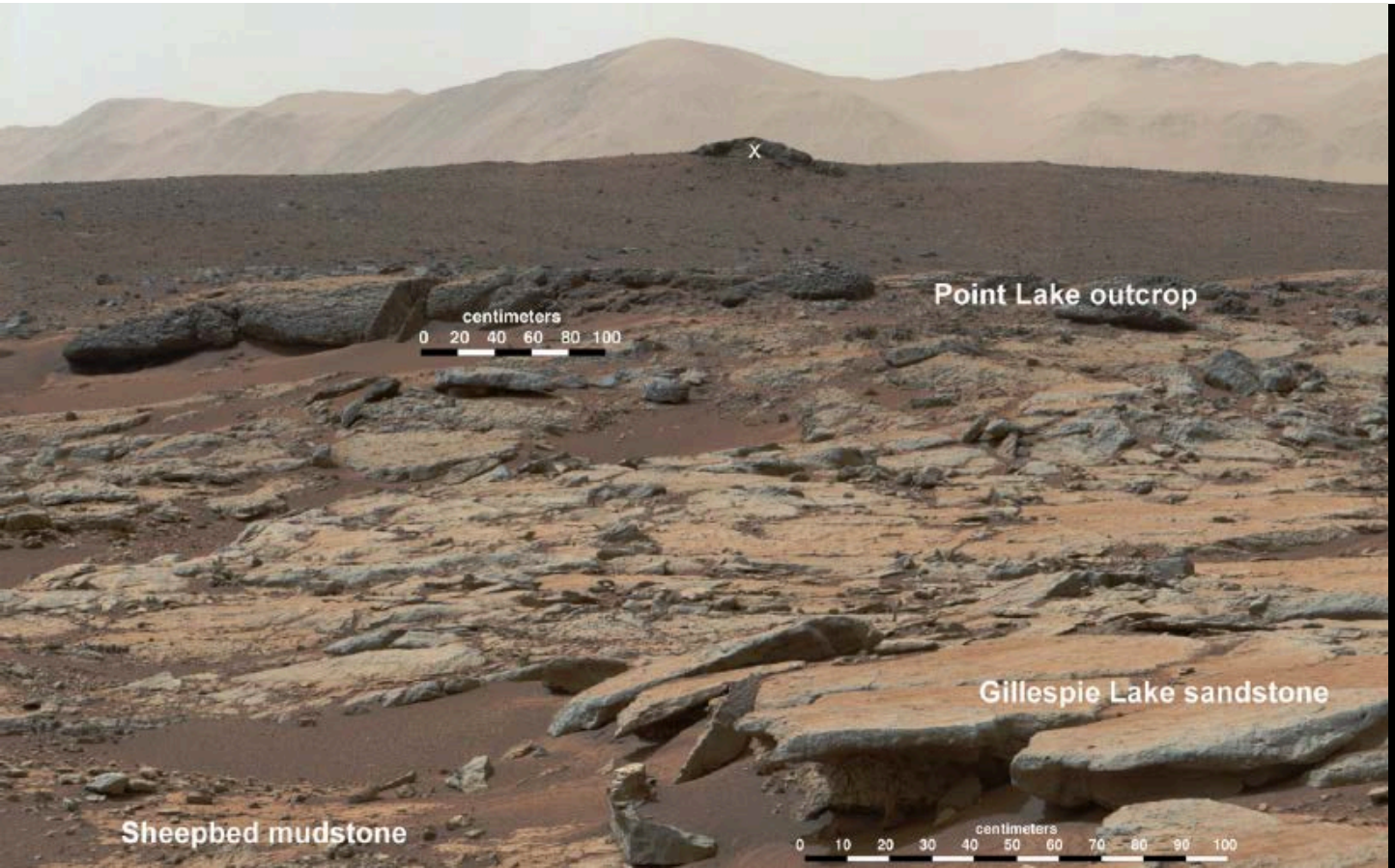
Cosmic ray exposure determination important to understand extent of transformation of organic compounds and possible destruction of biosignatures

First in situ planetary cosmic ray exposure age experiment

Cosmogenic Isotopes

Isotope	pmol/g	±	PR (pmol g^{-1} Ma^{-1})[A] Surface	2m Average	Exposure Age[B] (Ma)	±
^{3}He	33.7	6.9	0.466	0.254	72	15
^{21}Ne	4.49	1.52	0.054	0.034	84	28
^{36}Ar	55.6	16.8	0.714	1.029	78	24

Notes: elemental composition from APXS measurement of Cumberland drill tailings. [A]Model isotope production rate (*47*). [B]Surface exposure age assuming no erosion.



Since near surface cosmic radiation exposure for 10's or 100's of millions of years can transform organics – this has implications for preservation of organic molecules and potential biosignatures

Ratios of noble gases can discriminate between the end members of continuous vs. rapid erosion – Figures from Farley et al. 2014

SAM result → $^{36}Ar/^{3}He = 1.7 \pm 0.5$ and $^{36}Ar/^{21}Ne = 12 \pm 5$

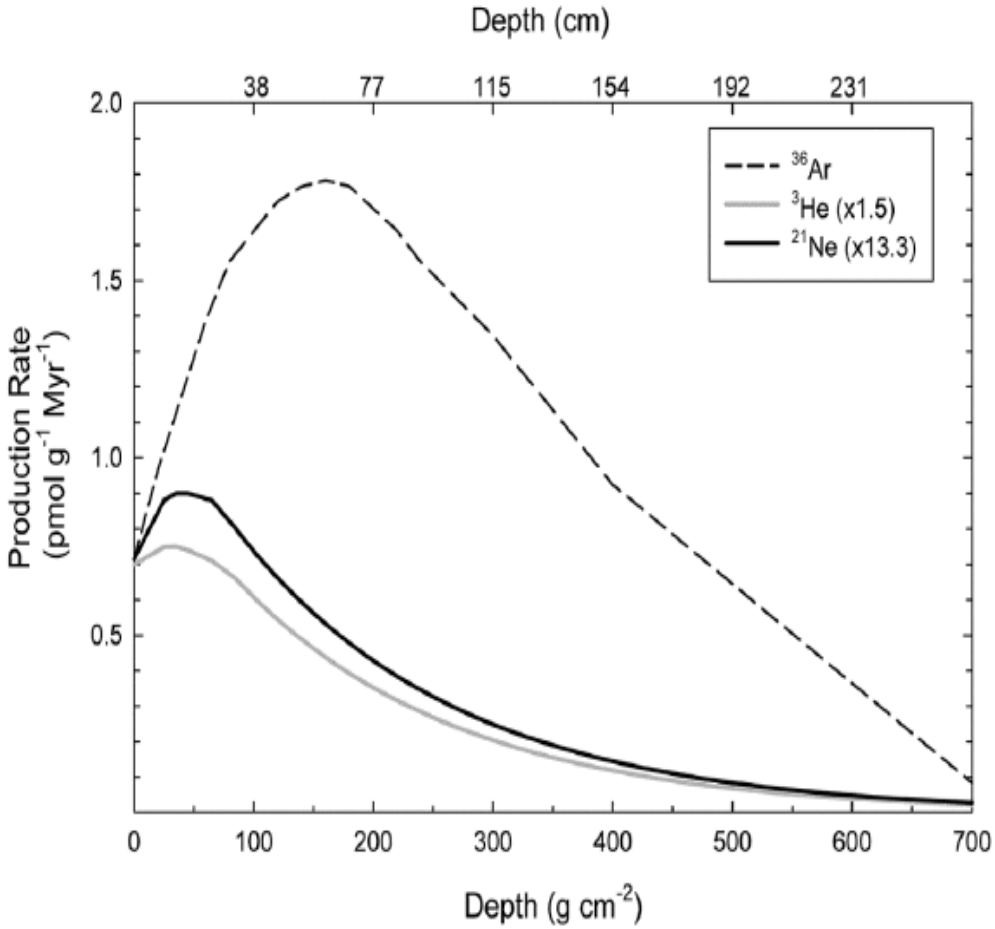
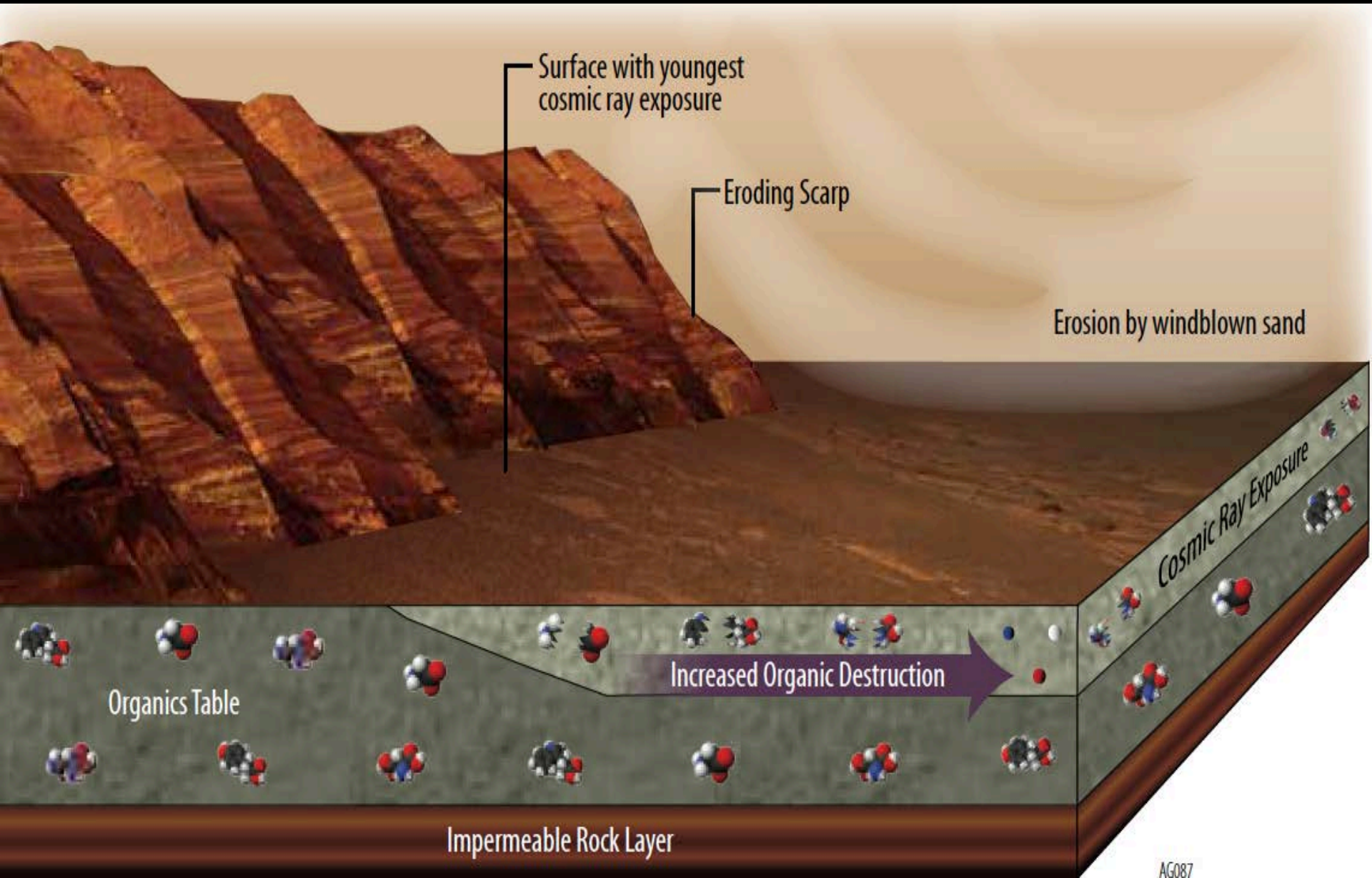


Fig. 3. Depth dependence of cosmogenic isotope production rates modeled for a rock of Cumberland mudstone chemistry on Mars. ^{3}He and ^{21}Ne are spallation isotopes, while ^{36}Ar is produced by capture of cosmogenic neutrons. Note the multiplicative factors applied to ^{3}He and ^{21}Ne. A mudstone bulk density of 2.6 g/cm^{3} was assumed to convert overburden mass to linear depth.

Fig. 2. Mars Hand Lens Imager (MAHLI) image of brushed, gray bedrock outcrop of Sheepbed mudstone near the Cumberland drill hole. Protrusion of nodules (9) results from eolian scouring of rock surface, creating wind-tails. Preference for steep faces of wind-tails on NE side suggests long-term averaged paleowind direction from NE to SW. This is a portion of MAHLI image 0291MH0001970010103390C00, acquired on Sol 291. Illumination from the top/upper left.

SAM noble gas measurements are pointing toward the best locations to search for minimally transformed organic compounds



SAM's commanding language allows us great flexibility in generation of new sequences on Mars as we make discoveries – we keep a duplicate SAM operational at NASA Goddard to test these scripts

Improved precision for future planetary in situ chronology experiments now seems within reach

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- ID-KArD: Proof of Concept
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- The Team
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Nate Jacobson (GRFC)

http://www.gps.caltech.edu/~jac/IDKArD/

Isotope dilution technique developed by Farley, Cartwright, and others demonstrated to improve precision of K-Ar dating

Unique Features:

The ID-KArD technique has two unique features that remove the need for a sample weight measurement and high temperatures for analysis.

To lower the temperature for sample heating, we are using a lithium-borate flux agent (ultra purity, 50% $LiBO_2$, 50% $Li_2B_4O_7$), which allows for the isotopic homogenisation of K and Ar in the sample and the spike glass, and fusion temperatures of 950-1000 ^{o}C.

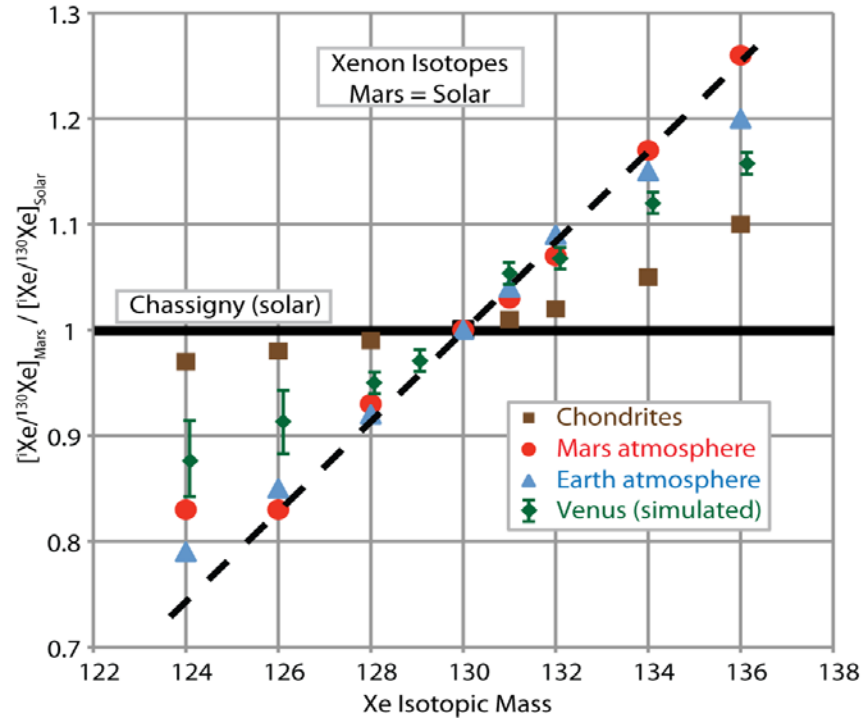
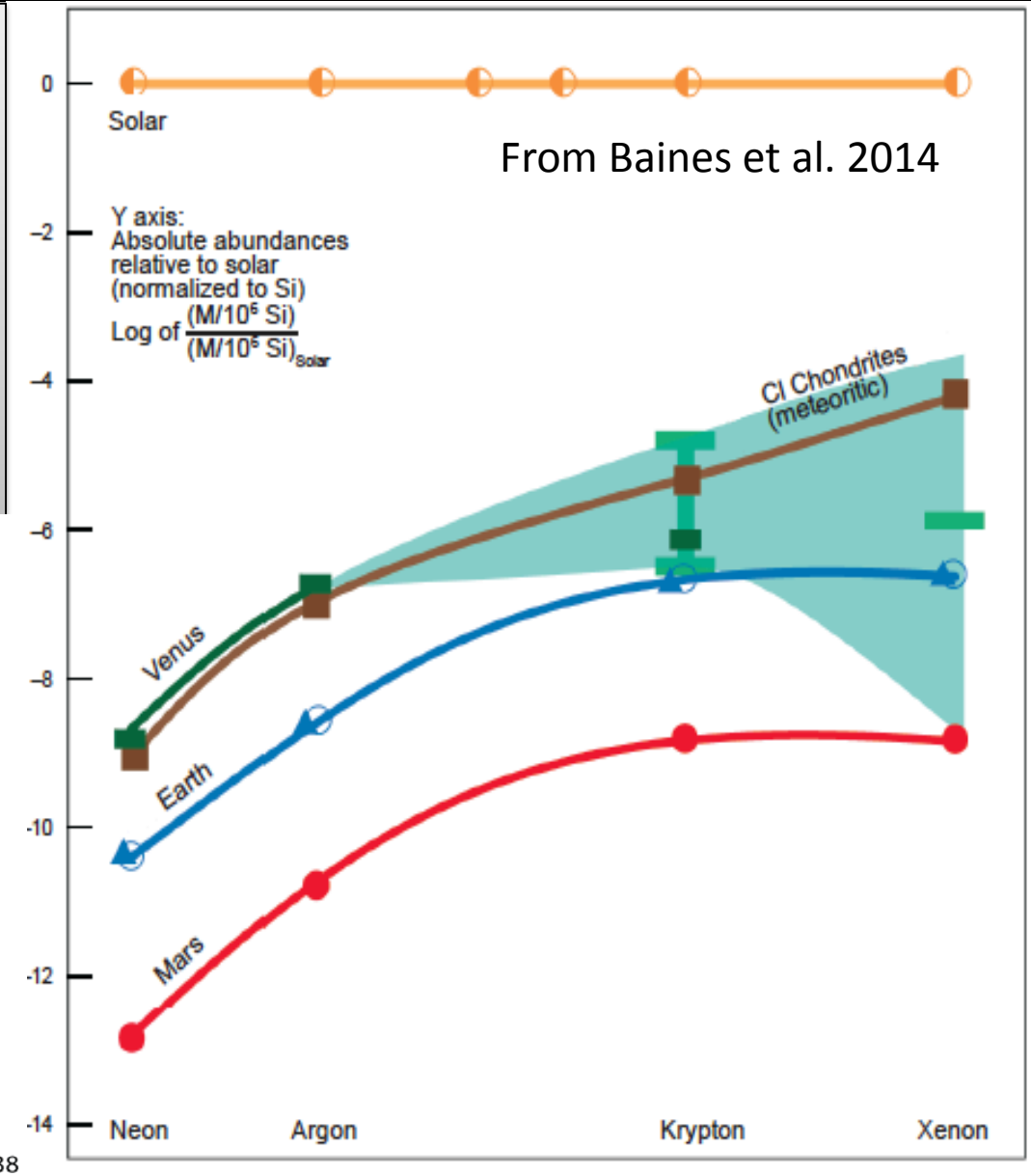
Lithium borate flux

SEM image of spike glass fragment

We are using a doubly-spiked synthesised glass to act as a tracer, which is isotopically enriched in ^{41}K (>95%). By neutron- irradiating this glass, we convert any trace ^{39}K present into ^{39}Ar. Thus, the $(^{39}Ar/^{41}K)_{spk}$ ratio is known. The glass has been synthesised in-house in the petrology labs at Caltech.

Future challenges for N and noble gas elemental and isotope ratio measurements include Decadal Study targets Venus and Saturn

Large uncertainties in Venus noble gas measurements – just an upper limit for Xe from Pioneer Venus MS measurements

In situ measurements utilizing enrichment techniques can address this record

The heavy Xe noble gas with its 9 isotopes provides the best record of early planetary processes