

IN SITU TECHNIQUES FOR MEASUREMENTS OF NOBLE GASES AND NITROGEN ISOTOPES IN PLANETARY ENVIRONMENTS: RECENT ADVANCES. P. R. Mahaffy¹, S. K. Atreya², J. A. Cartwright³, P. C. Conrad¹, K. A. Farley³, H. B. Franz¹, J. B. Garvin¹, L. S. Glaze¹, C. Malespin¹, M. G. Trainer¹, and M. H. Wong^{2,4}, ¹Planetary Environments Laboratory/Code 699, NASA Goddard Space Flight Center, 8800 Greenbelt Rd., Greenbelt, MD 20771 (Paul.R.Mahaffy@NASA.gov), ²Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, Michigan, ³Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, ⁴Astronomy Department, University of California, Berkeley, California.

Introduction: Recent in situ experiments carried out by the mass spectrometer of the Sample Analysis at Mars (SAM) instrument suite [1] on the Mars Science Laboratory have demonstrated the utility of enrichment techniques for noble gas measurements. The long mission duration has enabled implementation and optimization of multiple such measurements. We review these measurements and the roadmap they provide for related analyses in future missions to address a variety of fundamental planetary issues.

Argon and Nitrogen to Address Atmospheric Evolution: Martian $^{36}\text{Ar}/^{38}\text{Ar}$ and $^{15}\text{N}/^{14}\text{N}$ ratios are key tracers of long term atmospheric escape since their reintroduction to surface reservoirs through e.g. crustal recycling is relatively minor once these gases are introduced to the atmosphere. Fig. 1 illustrates the precision in $^{36}\text{Ar}/^{38}\text{Ar}$ ratios achieved with an incremental enrichment method using SAM's CO_2 scrubber: the technique has provided improved precision measurements for both nitrogen [2] and argon [3] compared to meteorite and previous in situ measurements.

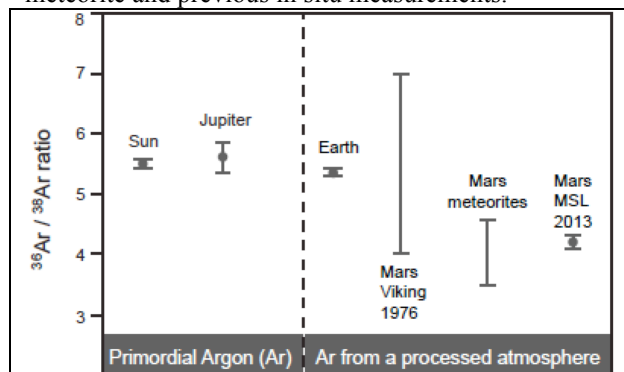


Figure 1. The $^{36}\text{Ar}/^{38}\text{Ar}$ ratio secured by incrementally adding aliquots of atmosphere to the SAM manifold with the path to the CO_2 scrubber open. After multiple volumes of gas were added the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio converged to a constant value as the signal to noise of the measurement increased. Figure is taken from [3].

Noble Gases to Secure Radiometric and Exposure Age: SAM measurements of ^{40}Ar released at $\sim 900^\circ\text{C}$ from the Gale Crater Yellowknife Bay mudstone together with the Alpha Particle Backscatter X-

ray Spectrometer enabled a determination of the K-Ar rock formation age of this sample [4]. Measurements of the cosmogenic noble gases ^3He , ^{21}Ne , and ^{36}Ar measurements established a surface exposure age of ~ 78 Myr [4]. In these experiments, both the SAM scrubber and its getters were utilized to “clean” the gas and remove substantial portions of active gases.

Krypton and Xenon and Fully Static Mass Spectrometry: Scripts for fully static atmospheric experiments that were demonstrated on the SAM flight unit during its calibration are presently being optimized for use on Mars. Fractionation in krypton and xenon isotopes presently known from SNC meteorite studies are expected to be measured for the first time with this technique by SAM.

Future Challenges for Venus and Saturn Probe Measurements: During the descent of a Venus or Saturn probe the noble gas measurements must be made much more rapidly than the experiments implemented by SAM on MSL where several hours were typically employed for each experiment sequence. These experiments will require rapid scrubbing of active gases to make an accurate measurement of the noble gases. Although this capability was demonstrated by the Galileo Probe mass spectrometer at Jupiter [5], breadboard studies are necessary to robustly simulate system performance under relevant Venus conditions.

Isotope Dilution Techniques for Precise Radiometric Dating: A dual isotope technique utilizing ^{39}Ar and ^{41}K embedded in a tracer spike has recently been developed and successfully demonstrated on a terrestrial basalt [6]. This technology is at the state where it is being proposed for flight opportunities. On Mars, this technique may eventually be able to calibrate the cratering record, which presently utilizes extrapolations from the lunar record with its ground truth from returned Apollo samples.

References: [1] Mahaffy, P. R. et al. (2012) *SSR*, 170, 401-478. [2] Wong, M. H. et al., *GRL* (2013) 40, 6033-6037. [3] Atreya, S. K., et al., *GRL* (2013) 40, 5605-5609. [4] Farley, K. A. et al., (2014) *Science* (2014) 343, 1247166 [5] Mahaffy, P. R., *JGR Planets* (2000) 105, 15061- 15071. [6] Farley, K. A. et al., (2013) *Geochim Cosmochim Acta* 110, 1.