

SAM MEASUREMENTS OF KRYPTON AND XENON ON MARS. P. G. Conrad¹, C. Malespin¹, H. Franz¹, M. G. Trainer¹, A. Brunner^{1,2}, H. Manning³, S.P. Schwenzer⁴, S. Atreya⁵, J. Jones⁶, P. M. Mahaffy¹, T. Owen⁷, R. O. Pepin⁸, M. H. Wong⁵, and the MSL Science Team¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771 Pamela.G.Conrad@nasa.gov, ²CRESST, Univ. of Maryland, College Park, ³Concordia College, Moorhead, MN 56562, ⁴The Open University, Milton Keynes, UK, ⁵The University of Michigan, Ann Arbor, MI, ⁶California Institute of Technology, Pasadena, CA 91106, ⁶NASA Johnson Space Center, Houston, TX, ⁷The University of Hawaii, HI, ⁸The University of Minnesota, Minneapolis, MN.

Introduction: Because of their importance to our understanding of planetary and atmospheric evolution [1], the abundances and isotopic ratios of the noble gases are an important measurement objective of the Sample Analysis at Mars (SAM) investigation on the Mars Science Laboratory mission.

SAM has conducted atmospheric enrichment experiments in which the abundances and isotopic ratios of Ar, N₂ [2, 3, 4], and Kr have been measured and we have detected and computed upper limits on the abundance of Xe as well. In this report, we focus on the Kr and Xe experiments.

Viking measured the martian atmosphere, including Kr and Xe [5]. The Viking experiments were conducted using dynamic mass spectrometry with chemical scrubbing to minimize CO and CO₂ and variable numbers of enrichment cycles to obtain the values shown in Table 1. Also shown are one SAM data set as well as values obtained from analysis of the shergottite EET (A) 79001 Lith. C—the shock melt component.

	Viking	EETA79001	SAM
Kr	300 ppb ⁵	300 ppb ⁶	263 ± 47 ppb
Xe	80 ppb ⁵	80 ppb ⁶	detected*

Table 1. Kr and Xe abundances in Mars atmosphere and in shock glass of the EETA 79001 SNC meteorite.

⁵ Owen et al. (1977)

⁶ EETA 79001 shock-glass gas Bogard & Johnson (1983)

* While we have detected Xe we are not ready to report abundances before acquiring more data.

Measurement Approach: Early in the mission, SAM measured the atmospheric volume mixing ratios and isotopic ratios of the major atmospheric constituents [2] with direct sampling of the atmosphere and SAM's quadrupole mass spectrometer (QMS) in dynamic operating mode. To measure less abundant noble gas isotopes, SAM enriches the noble gases by scrubbing CO₂ and H₂O and subsequently leaking them into the QMS while operating in a higher sensitivity semi-static mode using the getter as a pump. The complete SAM instrument suite is described in detail in [7], while semi-static mode is described in [9, 10].

The atmosphere is drawn in to an evacuated manifold system through the atmospheric inlet (lower left

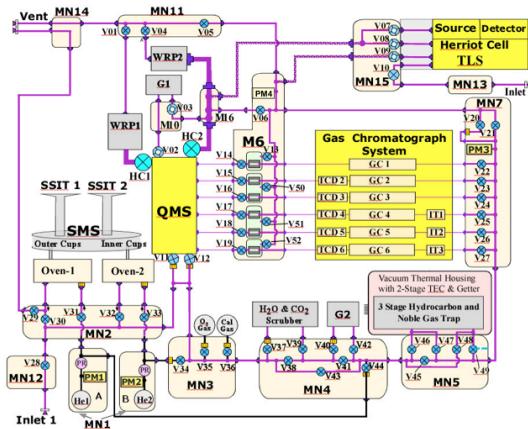


Figure 1 SAM gas flow diagram

corner of Fig. 1). Water and CO₂ are scrubbed from the atmospheric sample in manifold 4 (bottom center of Fig. 1) and then leaked into the QMS. To date, we have not yet used the chemical getters or the hydrocarbon noble gas trap for capturing the Kr and Xe. The enrichment

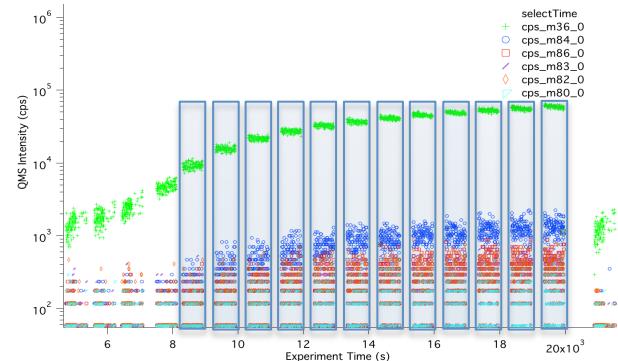


Figure 2 The enrichment experiment over time (x axis). Y axis is the relative intensity in counts per second (cps). Note, for example ⁸⁴Kr in blue open circles, increasing with successive enrichments and leveling off in the last two cycles at 18K to 20K seconds. Enrichment cycles are highlighted with pale gray rectangles over each one for clarity.

cycle is repeated several times (Fig. 3), and during each cycle, the data are obtained with a vector scanning algorithm that is designed to cycle scans for masses of interest to maximize the number of data points for the avail-

able time while skipping scans for masses that are not important to a given experiment.

Results: In two separate enrichment experiments, we obtained data on ^{86}Kr , ^{84}Kr , ^{83}Kr , ^{82}Kr , ^{80}Kr and total Xe. There were insufficient counts to obtain isotopic information on the Xe isotopes, and we refrain from calculating abundance until we improve the Xe sensitivity further by invoking the hydrocarbon noble gas trap.

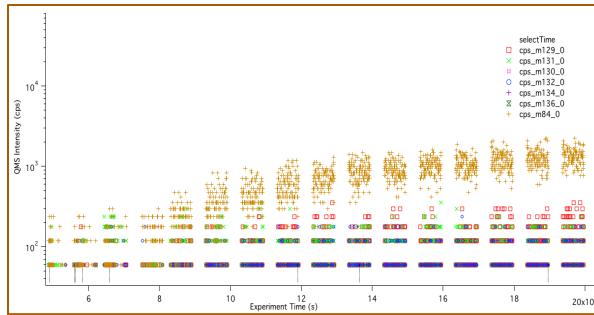


Figure 3 The six most abundant Xe isotopes show only a very modest enrichment relative to ^{84}Kr (gold crosses).

The results for the first enrichment experiment reveal Kr isotopic ratios consistent with the solar wind and with extraterrestrial regolith as compiled by Pepin et al [8].

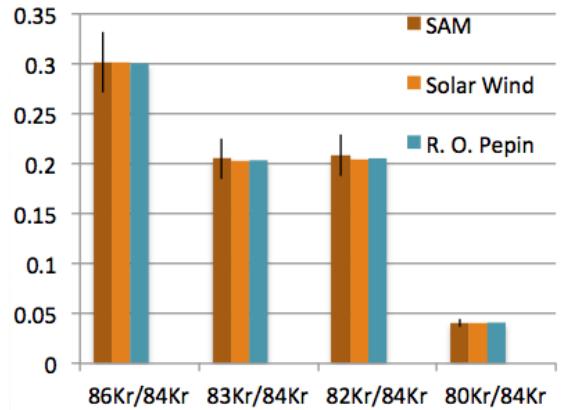


Figure 4 SAM measurements compared to solar values (red) and to lunar & meteorite regolith [8].

The second enrichment experiment was conducted after an evolved noble gas experiment [9], and though the scrubbers were cleaned and getters reactivated, the data are noisier, suggesting the system was not as pristine. The ratios are relatively close but with greater scatter, particularly in the trace $^{80}\text{Kr}/^{84}\text{Kr}$ value. The two experiments were conducted differently in that the second one had a much longer data integration—1122.8 s compared to 564.1 s, although the samples were scrubbed for the same length of time.

With regard to Xe, while it was detected, the count rates for ^{129}Xe , ^{132}Xe and ^{131}Xe were quite low at $200\text{-}300 \text{ counts s}^{-1}$, so these data should be interpreted cautiously. In Fig. 5, note that ^{129}Xe is qualitatively at

a higher count rate average than are the ^{132}Xe and ^{131}Xe , which would be consistent with both observations of the Martian atmosphere from Viking [5] and in Martian meteorites [6], including the Nakhrites and ALHA84001, which have a fractionated heavy noble gas signature [11]. Less abundant Xe isotopes were not detected above the noise threshold. It could be that we need to capture the Xe on the chilled hydrocarbon noble gas trap to obtain higher counts, however it is also possible that the Xe is somehow retarded by the scrubber. Future experiments are planned.

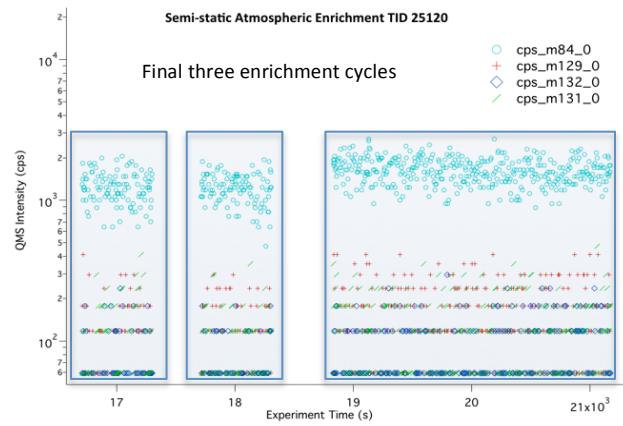


Figure 5 ^{132}Xe , ^{131}Xe and ^{129}Xe , compared to ^{84}Kr . The counts in the last three enrichment cycles are highlighted with gray boxes.

Results from both atmospheric and solid sample noble gas experiments can be calibrated to the known isotopic compositions of noble gases in the SAM calibration gas cell on Mars. Details of SAM calibration, including that of the noble gases are in [10].

Summary: SAM measurements of Kr reproduce the atmospheric results from Viking and contribute the first in situ measurement of atmospheric Kr isotopic ratios at Mars showing good agreement with meteorite data. While Xe was detected and ^{129}Xe was more abundant than ^{132}Xe and ^{131}Xe , we await improvements in sensitivity before reporting ratios and total abundance for Xe.

As SAM continues to develop its atmospheric enrichment experiment to include the HCNG trap or perhaps move closer to full static conditions, we will refine measurements of both atmospheric and thermally evolved (from solid samples) Kr and Xe.

References:

- [1] Pepin, R.O. (1991) Icarus 92, 2-79. [2] Mahaffy, P. R., et al. (2013) *Science* 341.6143: 263-266., [3] Atreya, S. K., et al. (2013) *Geophys Res Lett* 40.21: 5605-5609. [4] Wong, M. H., et al. *Geophys Res Lett* (2013). [5] Owen, T. et al. (1977) *JGR* 82, 4635-4639. [6] Bogard and Johnson (1983) *Science*, 221: 651-654. [7] Mahaffy, P.R. et al (2012) *Space Sci Rev.* 170, 401-478. [8] Pepin, R. O., et al. (1995) *Geochim et Cosmochim Acta* 59.23: 4997-5022. [9] Farley, K. A., et al. (2013) *Science* 342 [10] Franz et al., *Planet. Space Sci.* in review.[11] Bogard, D. D. et al. (2001) *Space Sci. Rev.*, 96, 425-458.