

HEAVY NOBLE GAS MEASUREMENTS ON MARS WITH SAM. P. G. Conrad¹, C. Malespin¹, H. Manning², S. P. Schwenzer³, S. Atreya⁴, W. B. Brinckerhoff¹, J. Eigenbrode¹, K. Farley⁵, H. Franz¹, D. P. Glavin¹, J. Jones⁶, P. M. Mahaffy¹, T. Owen⁷, R. O. Pepin⁸, A. Steele⁹, A. Treiman⁶, M. Wong⁴, and the MSL Science Team ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771 Pamela.G.Conrad@nasa.gov, ²Concordia College, Moorhead, MN 56562, ³The Open University, Milton Keynes, UK, ⁴The University of Michigan, Ann Arbor, MI, ⁵California Institute of Technology, Pasadena, CA 91106, ⁶NASA Johnson Space Center, Houston, TX, ⁷The University of Hawaii, HI, ⁸The University of Minnesota, Minneapolis, MN, ⁹Geophysical Laboratory, Carnegie Institution of Science, Washington, DC 20015.

Introduction: Mars Science Laboratory's Sample Analysis at Mars (SAM) investigation possesses the capability to measure gases directly from the martian atmosphere as well as gases thermally evolved from rock and sediment. Such flexibility enables us to look at both crustal (or mantle) and atmospheric reservoirs of species of interest, including both reactive and inert gases. N₂ (inert in the molecular form) Ne, Ar, Kr and Xe are all important tracers of fundamental importance to our understanding of planetary accretion history and atmospheric evolution [1]. Indeed, a first order question underlying the accretionary history of planets is the source of their volatile inventories. And because some non-radiogenic atmospheric noble gases are fractionated to solar (i.e., bulk solar system), it is necessary to invoke models of accretion, hydrodynamic escape and subsequent processing to account for this fractionation. The source(s), departure and subsequent evolution of the planetary atmospheres have profound impact on the planets' potential to develop habitable environments.

Here we focus specifically on the heavy noble gases, Kr and Xe at Mars. Correlated studies of both solid samples and atmospheric reservoirs can reveal the nature of geologic processes. Advantageous for the measurements are their noble nature and that they have fewer mass interferences to confound experimental results. They may record events that hydrodynamic escape may have erased from other elements' memories. Moreover, given their association with reduced macromolecular carbon in meteorites [2,3], the heavy noble gases might also be important for understanding and distinguishing between impactor-related chondritic sources of reduced carbon and those that formed from the alteration of basalts in situ.

The heavy noble gases in martian surface rocks may include trapped components from the atmosphere and planet interior, in-situ produced isotopes arising from radioactive decay and cosmic ray irradiation, and, in the case of sedimentary rocks, a meteoritic- or interplanetary dust component. The wealth of isotopes and elemental abundances in the (Ar)-Kr-Xe system should allow us to disentangle these various sources as well as assess fractionation effects.

Xe, in particular is interesting because of its underabundance relative to chondritic values in both Earth's and Mars' atmospheres. Its nine stable isotopes afford an opportunity for very high resolution examination of mass fractionation processes [4].

Both Viking landers 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 in the table are values obtained from analysis of the shergottite EET (A) 79001 Lith. C—the shock melt component.

| | Viking | SNC's |
|--------------------------------------|-----------------------|-----------------------|
| Kr abundance | 0.3 ppm ¹ | 0.3 ² |
| Xe abundance | 0.08 ppm ¹ | 0.08 ² |
| ¹²⁹ Xe/ ¹³² Xe | 2.5 ¹ | 2.6±0.05 ³ |
| ⁸⁴ Kr/ ¹³² Xe | 11.5 | 20.5±2.5 ³ |

Table 1. Heavy noble gas abundances and isotope ratios in Mars atmosphere and SNC meteorites.

¹ Owen et al. (1977)

² EETA 79001 shock-glass gas Bogard & Johnson (1983)

³ Bogard and Garrison (1998)

Note that noble gases in martian meteorites have a variety of sources, including trapped components of the interior [6] as well as Martian atmosphere first found in lithology C of EETA79001 [7]. Besides these two unfractionated components, the nakhlite Martian meteorites contain a component with heavy noble gas (Ar/Xe and Kr/Xe) ratios fractionated compared to the Viking and EETA79001 Martian atmospheric values [6, 8, 9, 10, 11].

Chemical fractionation effects are also observed terrestrially when atmosphere is incorporated into rocks by adsorption or weathering/alteration [12, 13]. In fact, this process has also been invoked to explain the Kr and Xe characteristics of the nakhlites [10]. Therefore, we will be mindful of such chemical fractionations as we measure soil and rock samples.

The SAM Experiments: The complete SAM instrument suite consists of a quadrupole mass spectrometer (QMS), gas chromatograph (GC) and tunable laser spectrometer (TLS) with supporting subsystems that include sample manipulation (SMS) and gas proc-

essing (SMS) systems. The suite is described in detail in [14]. The QMS can be operated both dynamically and statically, the latter mode being employed for noble gas experiments.

Atmospheric Measurements. The SAM noble gas experiment ingests the gas sample through an atmospheric inlet. The sample is pulled into the CO₂ scrubber and then into a getter for removal of active gases, with the exception of CH₄. The scrubbed gas is leaked into the QMS for measurement of the lighter noble gases, Ne and Ar. The Xe and Kr are enriched by leaking the scrubbed gas directly onto a cooled hydrocarbon/noble gas (HC/NG) trap for separation from the Ar and Ne. Once the SAM manifolds are pumped out, only the Xe and Kr remain and then can be released from the trap or undergo additional enrichment cycles. One of the two getters is used as a pump to leak small amounts of the Xe and Kr into the QMS for measurement. The gas pressure is gradually increased until there are sufficient counting statistics to measure the trace abundances of the lighter Xe isotopes 124 and 126.

Preliminary calculations have been done to estimate the sensitivity of SAM to Ar at a variety of emission levels over a range of pressures. From these calculations, estimates are derived for the sensitivity of SAM to Xe and Kr using a 50 μ A emission level [15]. These estimates are shown in table 2.

| | Residual PP in QMS (torr) | S _i $\frac{\text{cps}}{\text{atom cc}}$ | I _{it} (cps) |
|------------------------|---------------------------|--|-----------------------|
| Xe | 5.7x10 ⁻⁹ | 1.07x10 ⁻² | 1.96x10 ⁶ |
| Kr | 2.13x10 ⁻⁸ | 6.67x10 ⁻³ | 4.57x10 ⁶ |
| ^{124, 126} Xe | 5.7x10 ⁻¹² | 1.07x10 ⁻² | 1.95x10 ³ |

Table 2. Summary of Kr and Xe showing values calculated after 7 torr of Martian atmosphere have traveled through SAM scrubber, getter, and HCNG trap. S_i= sensitivity to the species of interest, I_{it}= total ion rate ⁻s.

Note that the predicted sensitivities are a best case scenario for one enrichment cycle and assume total removal of reactive gases. The actual separation is unlikely to be 100% efficient, so it is possible two or more enrichment cycles may benefit the signal to noise contrast.

Evolved Noble Gas Experiments. SAM can accept solid samples from Curiosity's sample distribution system directly into sample cups in the SAM SMS. Each sample is about 75 mm³ \pm 12.6. The samples are then pyrolyzed at programmable temperature ramp and maximum (with a limit of 1000 $^{\circ}$ C). The evolved gases are then conducted on a path similar to that of the atmospheric noble gas experiment. One challenge for analyzing these gases is the limited temperature range accessible with the SAM ovens. While some phases (e.g., sulfates, halides) will likely release all of their noble gases below 1000 $^{\circ}$ C as they break down, others will not.

Note that the first SAM solid sample evolved gas analyses at Gale Crater have revealed sediment and dust compositions that are consistent with a chlorate or perchlorate type oxidant, and consistent with Viking and Phoenix observations. If the rock samples to be acquired at Gale also exhibit evidence of oxidizing components, the putative oxidant could be useful in facilitating the release of the Kr and Xe as is done in terrestrial laboratories. This might suggest adjustment to the experiment to exploit the use of the oxidant, but care must be taken to avoid release of CO₂, that can confound the measurement of the light noble gases.

Results from both atmospheric and solid sample noble gas experiments can be calibrated to the known Xe isotopic composition of Xe gas in the SAM calibration gas cell in SAM on Mars.

Summary: The utility of Kr and Xe measurement are severalfold: (i) We hope to improve upon the atmospheric measurements from Viking (and refinements of those measurements using martian meteorites); (ii) We hope to measure minor isotope abundances to determine the influence on the atmosphere of impact vaporization of spallogenic Kr and Xe isotopes; (iv) If spallogenic contributions to the atmosphere are small, then mass fractionation of Xe could be more precisely determined; and (v) A better mass fractionation determination will result in a better estimation of the fission Xe component in the martian atmosphere.

SAM provides an opportunity to measure both atmospheric Kr and Xe and that thermally evolved from solid samples, both without the interference of terrestrial contamination. The static operation, chemical scrubbing and gettering will facilitate the separation and then trapping of Kr and Xe for analysis on Mars with the potential to inform our continued quest for understanding of the accretionary and evolutionary processes that affect the development of habitable planets.

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