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# In situ measurement of atmospheric krypton and xenon on Mars with Mars Science Laboratory

P.G. Conrad [a,*], C.A. Malespin [a,b], H.B. Franz [a,c], R.O. Pepin [d], M.G. Trainer [a], S.P. Schwenzer [e], S.K. Atreya [f], C. Freissinet [a], J.H. Jones [g], H. Manning [h], T. Owen [i], A.A. Pavlov [a], R.C. Wiens [j], M.H. Wong [f], P.R. Mahaffy [a]

[a] Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA
[b] Universities Space Research Association (USRA), Columbia, MD, USA
[c] CRESST, UMBC, NASA GSFC, Greenbelt, MD 20771, USA
[d] University of Minnesota, Minneapolis, MN 55455, USA
[e] The Open University, Department for Environment, Earth and Ecosystems, Walton Hall, Milton Keynes MK6 3AQ, United Kingdom
[f] Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI 48109-2143, USA
[g] XI-3, ARES, NASA/JSC, Houston, TX 77058, USA
[h] Concordia University, Moorhead, MN 56562, USA
[i] University of Hawaii, Honolulu, HI 96822, USA
[j] Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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ABSTRACT

Mars Science Laboratory's Sample Analysis at Mars (SAM) investigation has measured all of the stable isotopes of the heavy noble gases krypton and xenon in the martian atmosphere, *in situ*, from the Curiosity Rover at Gale Crater, Mars. Previous knowledge of martian atmospheric krypton and xenon isotope ratios has been based upon a combination of the Viking mission's krypton and xenon detections and measurements of noble gas isotope ratios in martian meteorites. However, the meteorite measurements reveal an impure mixture of atmospheric, mantle, and spallation contributions. The xenon and krypton isotopic measurements reported here include the complete set of stable isotopes, unmeasured by Viking. The new results generally agree with Mars meteorite measurements but also provide a unique opportunity to identify various non-atmospheric heavy noble gas components in the meteorites. Kr isotopic measurements define a solar-like atmospheric composition, but deviating from the solar wind pattern at $^{80}$Kr and $^{82}$Kr in a manner consistent with contributions originating from neutron capture in Br. The Xe measurements suggest an intriguing possibility that isotopes lighter than $^{132}$Xe have been enriched to varying degrees by spallation and neutron capture products degassed to the atmosphere from the regolith, and a model is constructed to explore this possibility. Such a spallation component, however, is not apparent in atmospheric Xe trapped in the glassy phases of martian meteorites.

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## 1. Introduction

The noble gases are key indicators of planetary evolution. Krypton and xenon are especially useful with their large numbers of stable isotopes; six and nine respectively, making them ideal for tracking source reservoirs and for understanding the evolution of planetary interiors and atmospheres. Many of the isotopes are formed or fractionated by distinct mechanisms, so their enrichment or depletion can be informative with regard to source: $^{129}$Xe is produced by decay of $^{129}$I, a now extinct radioactive nuclide with a half-life of 15.7 Myr. Isotopes $^{131}$Xe, $^{132}$Xe, $^{134}$Xe and $^{136}$Xe are produced by actinide fission. Radiogenic $^{129}$Xe and $^{136}$Xe can be used (along with other noble gas isotopes) to test hypotheses for atmospheric formation and loss: their $^{129}$I and $^{244}$Pu parent species abundances at the time of Earth and Mars' formation are constrained by their radiogenic daughters in the atmospheres. Comparison of planetary interior values (trapped in mantle phases of igneous rocks) with atmospheric abundances and solar wind abundances can reveal how long ago $^{129}$Xe and $^{136}$Xe were degassed (Podosek and Ozima, 2000). Excess $^{129}$Xe relative to $^{130}$Xe in Mars' atmosphere relative to interior components supports the hypothesis that Mars degassed soon after planetary

* Corresponding author.
*E-mail address:* Pamela.G.Conrad@nasa.gov (P.G. Conrad).

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accretion, while fractionation of Xe isotopes in the martian atmosphere may indicate substantial loss of atmosphere in a very early hydrodynamic escape phase (Pepin, 1991, 2000).

Previous to MSL, what we knew about martian noble gases was based on the noble gas measurements of Viking (Owen and Biemann, 1976; Owen et al., 1976, 1977) and the analyses of meteorites ejected from Mars. These meteorites: shergottites (Treiman and Filiberto, 2015), nakhlites (Treiman, 2005), chassignites (Treiman et al., 2007), ALH84001 (Treiman, 1998) and the basaltic breccia NWA7034 (Agee et al., 2013) are petrologically distinct from primitive chondritic meteorites, and the compositional similarity of gases trapped in their impact melt inclusions to Mars' atmospheric values is what identified them as martian (Bogard and Johnson, 1983; Pepin, 1985; Wiens and Pepin, 1988). But martian meteorites all contain more than one noble gas component, and measurements therefore return a composite of unfractionated or fractionated martian atmosphere, martian interior gases, fission and cosmogenic additions, and terrestrial contamination.

An elementally unfractionated martian atmospheric component was first found in shock melt inclusions in the shergottite EETA 79001 (Bogard and Johnson, 1983; Becker and Pepin, 1984; Wiens et al., 1986; Swindle et al., 1986), establishing the link between the SNC meteorites and Mars. The Xe composition was found to be isotopically distinct from all other known xenon reservoirs, especially in its high $^{129}Xe/^{132}Xe$ ratio and enhanced $^{134}Xe/^{132}Xe$ and $^{136}Xe/^{132}Xe$ ratios (Swindle et al., 1986). This atmospheric component was refined using a range of shock melts from four different shergottites, resulting in a recommended $^{129}Xe/^{132}Xe$ ratio of $2.60 \pm 0.05$ for Mars' atmosphere (Bogard and Garrison, 1998). Most recently, a martian brecciated meteorite (NWA7034, 'Black Beauty') (Agee et al., 2013) was shown to contain dominantly unfractionated martian atmosphere (Cartwright et al., 2014), providing evidence that this component is not unique to the shergottites. Elementally fractionated Martian atmospheric component(s) are found in the nakhlites and ALH84001 (Swindle, 2002) and the Martian interior component was first identified in the Chassigny meteorite (Ott, 1988).

Terrestrial air can introduce both unfractionated and fractionated contamination to meteorites, with the latter mimicking interior signals (Mohapatra et al., 2009) or completely masking martian signatures (Schwenzer et al., 2013). Disentangling those components is key to understanding processes such as planetary formation. It also provides insights into surface–atmosphere interaction and ejection history, but only at the precision with which the individual components are known and understood. Precise *in situ* measurements of Xe and Kr in Mars' atmosphere are not hampered by complications introduced by "contaminating" noble gases.

## 2. Experimental

Previously, we reported measurements of the stable isotopes of argon: $^{40}Ar/^{36}Ar = 1.9 \pm 0.3 \times 10^3$ and $^{36}Ar/^{38}Ar = 4.2 \pm 0.1$ (Atreya et al., 2013; Mahaffy et al., 2013). The $^{40}Ar/^{36}Ar$ ratio used dynamic mass spectrometry to directly measure these masses. To obtain the ratio of $^{36}Ar$ to $^{38}Ar$, it was necessary to develop a semi-static enrichment experiment to reach sufficiently high signal-to-noise (S/N) and background contrast for measurement of $^{38}Ar$, the least-abundant Ar isotope (Atreya et al., 2013). However, while semi-static experiments provided moderate S/N and low enough background contrast to also enable Kr isotope measurements, they were unable to enrich the Xe signals to the extent necessary for precise isotopic measurement. That required development of a fully static mass spectrometry experiment (Table 1).

**Table 1**
Semi-static and static SAM experiments on Mars.

| Experiment ID | Solar longitude | Sol |
|---|---|---|
| Semi-static enrichment mass spectrometry | | |
| 25111 (Kr) | 358 | 341 |
| 25269 (Kr) | 336 | 976 |
| Static mass spectrometry | | |
| 25253 (Xe) | 301 | 915 |
| 25269 (Xe) | 336 | 976 |

### 2.1. Static mass spectrometry

The relevant components of the SAM suite are described in Mahaffy et al. (2012). Gas is ingested, flowing through both zeolite (Linde 13x) and magnesium sulfate chemical scrubbers, effectively removing >95% of the $CO_2$ and $H_2O$, and weakly adsorbing all other active gases. The post-scrubber gas mix is enriched in $N_2$, Ar, Kr, and Xe, which then flows over a cooled hydrocarbon (HC) trap to efficiently trap out Xe, allowing other gases to pass. The HC trap consists of three adsorbents in series, Tenax® TA, silica beads, and carbosieve®. The approach and scripting were validated in the SAM high fidelity test bed at Goddard Space Flight Center.

The tunable laser spectrometer (TLS), which has been evacuated prior to atmospheric ingestion, is used as a storage volume so that gases not trapped out on the HC trap, particularly Kr, are collected here for later analysis.

The enrichment flows gas over the scrubbers and trap for 5400 s, after which the HC trap and TLS are closed off from the rest of the SAM manifolds. The manifolds are evacuated, and the scrubbers activated to clean them of adsorbed gas.

Xe-enriched gas collected on the trap is slowly released into the quadrupole mass spectrometer (QMS) in a semi-static scanning mode, where the conductance out to the pump is throttled to increase the S/N in the MS. Once the majority of the gas has been released into the manifold, the valve to the pump is closed, and the remaining gas is scanned in fully static mode. The low abundance of Xe allows fully static mode without increasing the pressure inside the mass spectrometer to a saturated level. The masses of interest (the nine stable Xe isotopes) are scanned. Once analysis of Xe is complete, the manifolds and MS are evacuated prior to releasing the Kr-enriched gas from the TLS. The QMS is returned to semi-static mode for analysis of Kr; static mode being too risky because of the high Ar partial pressure in the gas. Because Kr and Xe cannot be scanned at the same time in this method a direct measurement of the $^{84}Kr/^{132}Xe$ elemental ratio could not be obtained, nor could $^{84}Kr/^{36}Ar$ since the enrichment of $^{36}Ar$ saturates the detector.

### 2.2. Data processing

Experimental Kr and Xe data were corrected for detector dead time, mass discrimination (Appendix A1), quadrupole mass spectrometer (QMS) tuning effects, and instrument background, as discussed in Franz et al. (2014). Because the background as well as analytic signal grew with time during the semi-static and static QMS modes utilized for Kr and Xe measurements, background models were based on tracer $m/z$ representative of the instrument background. For Kr, a tracer of $m/z$ 12 was used in experiment ID #25111 and $m/z$ 79 in ID #25269. For Xe, $m/z$ 127 was used as the tracer in both ID #25253 and ID #25269. The background model is implemented by scaling the trend exhibited by the tracer $m/z$ based on the relative proportions of the analyte and tracer $m/z$ during the background region prior to introduction of Xe or Kr gas to the manifold. Uncertainties in the background model were computed from the difference in isotope ratios derived with the