# MSL/SAM Measurements of Nitrogen and Argon Isotopes in the Mars Atmosphere


**Michael H. Wong**
mike.wong@umich.edu
Univ. Michigan (AOSS Department)
UC Berkeley (Astronomy Department)

**Sushil K. Atreya**
University of Michigan

**Paul R. Mahaffy**
NASA GSFC

**Melissa Trainer**
NASA GSFC

**Heather Franz**
NASA GSFC

**Jennifer Stern**
NASA GSFC

**Tobias Owen**
University of Hawai'i

**Chris McKay**
NASA ARC

**John Jones**
NASA JSC

**Heidi Manning**
Concordia College

**Rafael Navarro-González**
Universidad Nacional Autónoma de México

**Charles Malespin**
NASA GSFC



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## Overview

We report on three QMS (part of MSL/SAM) measurements of the martian atmosphere in the first 100 sols. Consistent results are obtained for the isotopic ratios of $^{14}N/^{15}N$ and $^{40}Ar/^{36}Ar$, although these measurements are still preliminary. An enrichment experiment will permit better measurements of minor isotope ratios by scrubbing $CO_2$ from the sample [1]. Table 1 summarizes our preliminary nitrogen and argon isotope measurements and upper limits.

*Information in this poster supercedes the accepted conference abstract*, which gave only the dependence of $^{14}N/^{15}N$ on the relative contribution of $^{14}N^+$ and $^{14}N^{14}N^{++}$ to the m/z 14 signal. Here, we derive the martian $^{14}N/^{15}N$ ratio, and we limit the discussion of argon, which is discussed in other LPSC papers [2, 5, 8].

## Measurements

The analysis described here uses QMS unit scan and fractional scan modes [1]. Details of the analysis methods are given in [2]. Both $^{14}N^+$ and $^{14}N^{14}N^{++}$ contribute to m/z 14, while only $^{15}N^{14}N^{++}$ contributes to m/z 14.5 (Fig. 1). For molecular nitrogen, the primary ion at mass-to-charge ratio m/z 28 is confused by $CO_2$ and CO contributions. The m/z 15 signal is not significantly above the background, so we do not measure $^{15}N^+$ or $^{15}N^{15}N^{++}$ (Figs. 2, 3). Different behavior at m/z 13.5 and 14.5 clearly demonstrates that the half-integer data are not contaminated by signal at the adjacent integer masses.

Experiments in Table 1 each followed a different measurement sequence, with varying durations of background and sample scans, fractional and unit scans, volume expansions, and ionization filament current levels [1, 2]. The best MSL $^{14}N/^{15}N$ ratio is an average of all three experiments, and the best MSL $^{40}Ar/^{36}Ar$ ratio is the measurement from Sol 77 data, which allowed the best characterization of background levels.

## Calibration/analysis

Uncertainties in the values listed in Table 1 include statistical noise, background uncertainty, uncertainty from time-variation in the signal, and uncertainty in the $^{14}N^+/^{14}N^{14}N^{++}$ splitting fraction. Systematic sources of error are still being discovered and characterized, so these estimates are preliminary. Large increases in the contrast between sample signal and background levels are anticipated with the SAM enrichment experiments [1].

Retrieval of the $^{14}N/^{15}N$ ratio from the signals at m/z 14 and 14.5 depends on the relative contributions of $^{14}N^+$ and $^{14}N^{14}N^{++}$ to m/z 14. We define the fraction $\beta$ = m14($N^+$)/m14(all), and the isotopic ratio $\alpha = {}^{14}N/{}^{15}N$. Then we can find $\beta$, which is characteristic of the SAM QMS, from calibration runs with known values of $\alpha$:

$$\beta = \frac{2\left[\frac{m14}{m14.5}\right] - \alpha}{2\left[\frac{m14}{m14.5}\right] + 1}$$

Figure 4 shows values of $\beta$ derived from multiple calibration experiments with the flight unit before launch, and the testbed in early 2013. The mean value of $\beta$ is 0.404 ± 0.033, from the average of five experiments (Table 2). With $\beta$ known for the SAM QMS, observed m14/m14.5 on mars can then be related to the isotopic ratio $\alpha$:

$$\alpha = 2(1-\beta)\left[\frac{m14}{m14.5}\right] - \beta$$

Mars values derived with this expression for $\alpha$ are given in Table 1. The derivation of the relations for $\alpha$ and $\beta$ is too involved for this poster, but is available upon request.

## Discussion

MSL/SAM results for both the $^{40}Ar/^{36}Ar$ isotope ratio and the $^{40}Ar/^{14}N$ ratio are significantly different from the Viking measurements [2]. These ratios should not vary in time, so it is likely that systematic errors affect one or both retrievals [5]. The difference with respect to Viking has implications for analyses of gas inclusions in meteorites which use the $^{40}Ar/^{14}N$ ratio and N isotopes to indicate the degree of mixing between the martian atmosphere and internal gas component due to the shock of impact ejection (Fig. 5). Nitrogen isotopic ratios in martian meteorites imply a Mars atmospheric $\delta^{15}N > 290‰$ [7], consistent with our results. The SAM measurements, once confirmed by further laboratory testing and the enrichment experiment, will provide new constraints on the evolution of the atmosphere of Mars [8].

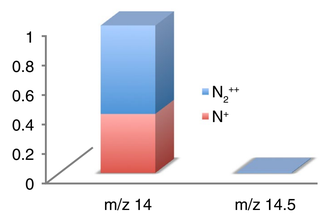


**Fig. 1:** Nitrogen ions contributing to m/z 14 and 14.5. The objective is to determine the $^{14}N/^{15}N$ isotopic ratio from the data. If the fraction of the signal at m/z 14 from $N^+$ is known, then the ratio of the remaining signal at m/z 14 to the signal at m/z 14.5 gives the isotopic ratio.

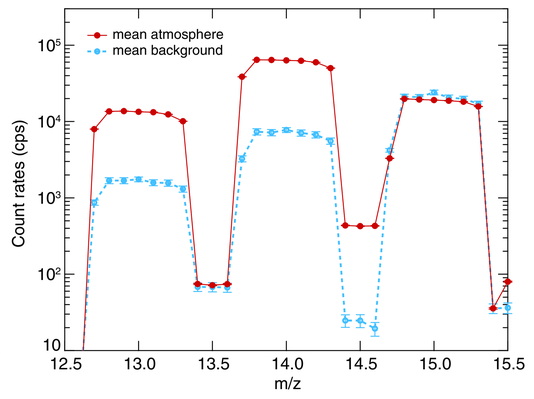


**Fig. 2:** SAM/QMS spectrum at 0.1-Da resolution, acquired on Sol 77 of the MSL mission. Background and atmosphere spectra are averages of many scans, and statistical uncertainties in these averages are plotted as error bars.

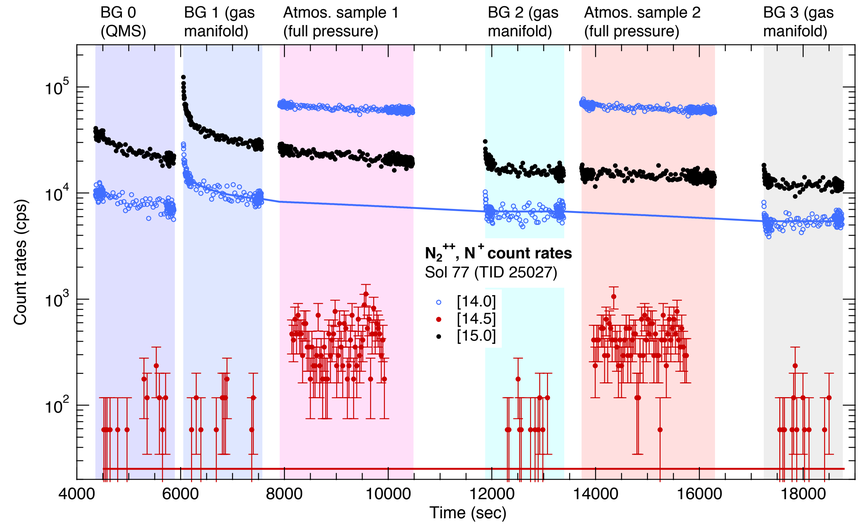


**Fig. 3:** SAM/QMS background and atmosphere scans for Sol 77, with both fractional and unit scan data plotted [2]. Error bars for m/z 14.5 are based on Poisson detector noise; this noise component is < 1% for the higher counting rates at m/z 14 and 15. The m/z 15 signal is not significantly above the background level. Continuous blue and red lines indicate background corrections for m/z 14 and 14.5. For mass 14, a time-varying background can be measured. For mass 14.5, any time variation is smaller than the uncertainty in the mean value of the background level, so a constant background correction is used. Several measurements of 0 counts/sec were included in the m/z 14.5 background level, and are not shown on this logarithmic plot.

| MSL Sol | $^{14}N/^{15}N$ | $\delta^{15}N$ (‰) | $^{40}Ar/^{36}Ar$ |
|---|---|---|---|
| 19 | 150 ± 51 | 813 ± 620 | 217 ± 80 |
| 45 | 151 ± 25 | 798 ± 299 | 2020 ± 460 |
| 77 | 169 ± 16 | 611 ± 151 | 1900 ± 300 |
| (Viking) | 170 ± 15 | 600 ± 155 | 3000 ± 500 |
| **Best MSL:** | **163 ± 13** | **669 ± 133** | **1900 ± 300** |

**Table 1:** Early Mars atmospheric nitrogen and argon isotopic ratios from SAM/QMS. Viking data from [3]. For nitrogen, the best MSL result is from an average of data from the three direct atmospheric measurements. Error bars include uncertainty in the splitting fraction $\beta$. For argon, the best MSL result is based on Sol 77, and includes a careful assessment of background correction uncertainty. The Sol 19 Ar isotopic ratio is skewed by terrestrial contamination due to trapped gas in the system.

| Experiment TID | $\beta$ ($N^+$/m14) | $\alpha$ ($^{14}N/^{15}N$) |
|---|---|---|
| 30066 | 0.369 ± 0.144 | 257 ± 65 |
| 21976 | 0.442 ± 0.084 | 300 ± 64 |
| 21548 | 0.401 ± 0.031 | 271 ± 16 |
| 21559 | 0.393 ± 0.035 | 268 ± 18 |
| 50733 | 0.445 ± 0.074 | 293 ± 40 |
| **All TIDs:** | **0.404 ± 0.033** | |

**Table 2:** Summary of pre-flight SAM/QMS nitrogen calibration experiments, except for TID 50733 which was done on the SAM testbed at NASA GSFC in February 2013. The SAM splitting fraction $\beta$ in bold is an average of all experiments. The uncertainty is the standard deviation among all experiments. Values of $\alpha$ ($^{14}N/^{15}N$) reported in the table were derived from the data using Eqn. 2, with $\beta$ = 0.404 ± 0.033. As a successful check on the method's validity, these values match the independently-measured value of $\alpha$ = 272.195 ± 0.003, within stated uncertainties.

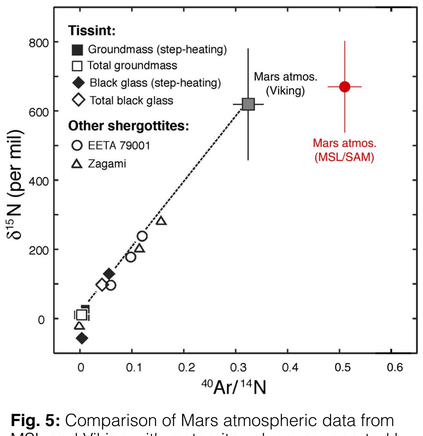


**Fig. 5:** Comparison of Mars atmospheric data from MSL and Viking with meteorite values, as reported by Chennaoui Aoudjehane et al. [5]. Volatile composition in samples from the meteorites lie along a mixing line connecting the Viking atmospheric composition to presumed martian mantle composition (or with Earth air). However, the SAM $^{40}Ar/^{14}N$ ratio [2, 9] shifts the martian atmospheric composition off of this meteoritic mixing line.

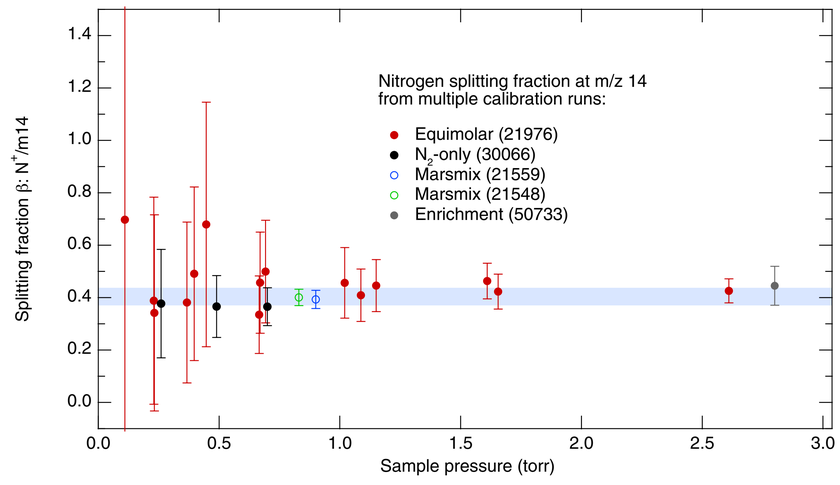


**Fig. 4:** Values of the splitting fraction $\beta$ measured in one SAM testbed experiment (TID 50733) and four pre-flight calibration experiments. Shaded bar gives the five-experiment average of $\beta$ = 0.404 ± 0.033. *X*-axis gives sample pressure for experiment 21976, which had an equimolar mixture of four gases including $N_2$. Sample pressures for other experiments have been roughly scaled to match $N_2$ partial pressures in TID 21976 for accuracy, although no dependence of $\beta$ on pressure is found. The lack of pressure dependence, especially within single experiments, shows that the measurement is not biased by an inaccurate background correction.

## References


[1] Mahaffy, P.R. et al. (2012) *SSR* 170, 401–478.

[2] Franz, H. et al. (2013a) *LPS* XLIV, Poster 2057 (Tuesday T615, Loc #232).

[3] Owen, T. (1992) In *Mars*, pp. 818–834.

[4] Wong, M.H. et al. (2013b) *LPS* XLIV, Poster 1697 (Tuesday T616, Loc #206).

[5] Atreya, S.K. et al. (2013) *LPS* XLIV, Poster 2130 (Tuesday T616, Loc #230).

[6] Chennaoui Aoudjehane, H. et al. (2012) *Science*, 338, 785–788.

[7] Bogard, D.D. et al. (2001) *Chron. Evol. Mars* 96, 425–458.

[8] Jones, J.H. et al. (2013) *LPS* XLIV, Abstract 2781 (Monday M102, 11:30am).

[9] Mahaffy et al. (2013) *Science*, submitted.


## Abbreviations

MSL = Mars Science Laboratory.

SAM = Sample Analysis at Mars instrument suite.

TLS = SAM Tunable Laser Spectrometer.

QMS = SAM Quadrupole Mass Spectrometer.

BG = Background.

Da = Dalton, unit of mass such that a $^{12}C$ atom has a mass of 12 Da.

m/z = Mass to charge ratio. For example, ions of both $^{14}N^+$ and $^{14}N^{14}N^{++}$ appear at m/z 14 in the QMS data.

$\alpha$ = Nitrogen isotopic ratio, $^{14}N/^{15}N$.

$\beta$ = Splitting fraction, ratio of signal from $^{14}N^+$ to total signal at m/z 14.