Isotopes of nitrogen on Mars: Atmospheric measurements by Curiosity's mass spectrometer

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[1] The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) measured a Mars atmospheric $^{14}N/^{15}N$ ratio of 173 ± 11 on sol 341 of the mission, agreeing with Viking's measurement of 168 ± 17. The MSL/SAM value was based on Quadrupole Mass Spectrometer measurements of an enriched atmospheric sample, with CO_2 and H_2O removed. Doubly ionized nitrogen data at m/z 14 and 14.5 had the highest signal/background ratio, with results confirmed by m/z 28 and 29 data. Gases in SNC meteorite glasses have been interpreted as mixtures containing a Martian atmospheric component, based partly on distinctive $^{14}N/^{15}N$ and $^{40}Ar/^{14}N$ ratios. Recent MSL/SAM measurements of the $^{40}Ar/^{14}N$ ratio (0.51 ± 0.01) are incompatible with the Viking ratio (0.35 ± 0.08). The meteorite mixing line is more consistent with the atmospheric composition measured by Viking than by MSL. **Citation:** Wong, M. H., et al. (2013), Isotopes of nitrogen on Mars: Atmospheric measurements by Curiosity's mass spectrometer, *Geophys. Res. Lett.*, *40*, 6033–6037, doi:10.1002/2013GL057840.

1. Introduction

[2] Isotope ratios are excellent tracers of atmospheric source and loss processes over planetary timescales. In the case of Martian oxygen and carbon, atmospheric evolution models must account for the exchange between atmospheric and surface/subsurface reservoirs [*Jakosky*, 1991; *Webster et al.*, 2013]. The potential for exchange of nitrogen between the atmosphere and surface of Mars is not currently understood, but such exchange would be very important to the study of Martian habitability that is the focus of the Mars Science Laboratory (MSL) mission [*Grotzinger et al.*, 2012].

[3] The atmospheric nitrogen isotopic ratio is difficult to measure. Very weak absorption lines are produced by the dipole forbidden vibrational-rotational transitions of ground state N_2, so the spectroscopic techniques used to measure isotope ratios in other molecules cannot be applied to molecular nitrogen. Of the 10 science instruments of the MSL payload [*Grotzinger et al.*, 2012], Sample Analysis at Mars's (SAM's) mass spectrometer provides the best capability to measure the nitrogen isotopic ratio [*Mahaffy et al.*, 2012]. Independent measurements of $^{14}N/^{15}N$ were conducted by mass spectrometers on Viking Lander 2 [*Owen et al.*, 1977; *Owen*, 1992] and the two Viking lander aeroshells [*Nier and McElroy*, 1977]. The surface and descent measurements found $^{14}N/^{15}N$ of 170 ± 15 and 168 ± 17, respectively.

2. Experiments

[4] SAM is a highly capable and configurable instrument suite for analyzing gases either directly sampled from the atmosphere or evolved from solid samples [*Mahaffy et al.*, 2012]. SAM/Quadrupole Mass Spectrometer (QMS) determines isotopic ratios based on ratios of detector counting rates. In direct atmospheric experiments, CO^+ ions (from CO_2) interfere at m/z 28 and 29 (where the N_2^+ parent ions are detected). But there is no CO^{++} contribution at m/z 14, so we can derive $^{14}N/^{15}N$ from direct atmospheric experiments using the m/z 14/14.5 count ratio. In enrichment experiments, chemical scrubbers remove CO_2, H_2O, and other species with chemical affinity to the scrubber material. The enrichment process allows determination of the isotopic ratio using m/z 28/29 and 14/29 count ratios. We further boost signal level (compared to the normal dynamic mode) using a semistatic mode, where the pumping rate out of the QMS is reduced. Figure 1 shows a mass spectrum from

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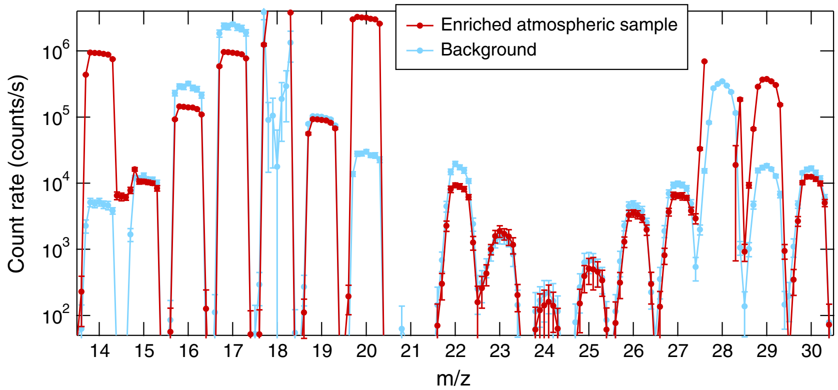

Figure 1. High-resolution mass spectrum from the enrichment experiment on sol 232. Sample spectrum is an average of data from enrichment cycle 9 (see Figure 2). Nitrogen ions are present at m/z 14, 14.5, 28, and 29. The singly ionized N_2 "parent ion" appears in the Mars data at m/z 28 (for $^{14}N^{14}N$) and at m/z 29 (for $^{15}N^{14}N$). A third parent ion, $^{15}N^{15}N$, is so rare as to produce only a small signal below the background level (difference between red and blue curves). For a comparison of the m/z 14–15 range in the direct atmospheric experiment, see *Wong et al.* [2013].

an enrichment experiment in dynamic mode, spanning the relevant m/z range for nitrogen analysis.

[5] On Jupiter, the nitrogen isotopic ratio was determined using Galileo Probe Mass Spectrometer measurements of NH_3^{++}, to avoid interferences at m/z 17 and 18 from water [*Owen et al.*, 2001; *Wong et al.*, 2004]. We use a similar approach in the MSL/SAM analysis, although there is an additional complication because the count ratio of m/z 14/14.5 includes contributions from two nitrogen daughter ions, N^+ and N_2^{++}.

[6] To extract the nitrogen isotopic ratio, we first measure a splitting fraction (derived from SAM/QMS preflight calibration data) that gives the relative contributions from these two daughter ions:

$$\beta = \frac{N^+}{N^+ + N_2^{++}} = \frac{2\left[\frac{m14}{m14.5}\right] - {}^{14}N/{}^{15}N}{2\left[\frac{m14}{m14.5}\right] + 1}, \qquad (1)$$

where the count rates at a mass/charge ratio of m/z X are represented as mX, and $^{14}N/^{15}N$ is independently measured in the calibration gas. We find $\beta = 0.404 \pm 0.033$ based on five experiments [*Wong et al.*, 2013]. The $^{14}N/^{15}N$ isotopic ratio is then derived from the splitting fraction

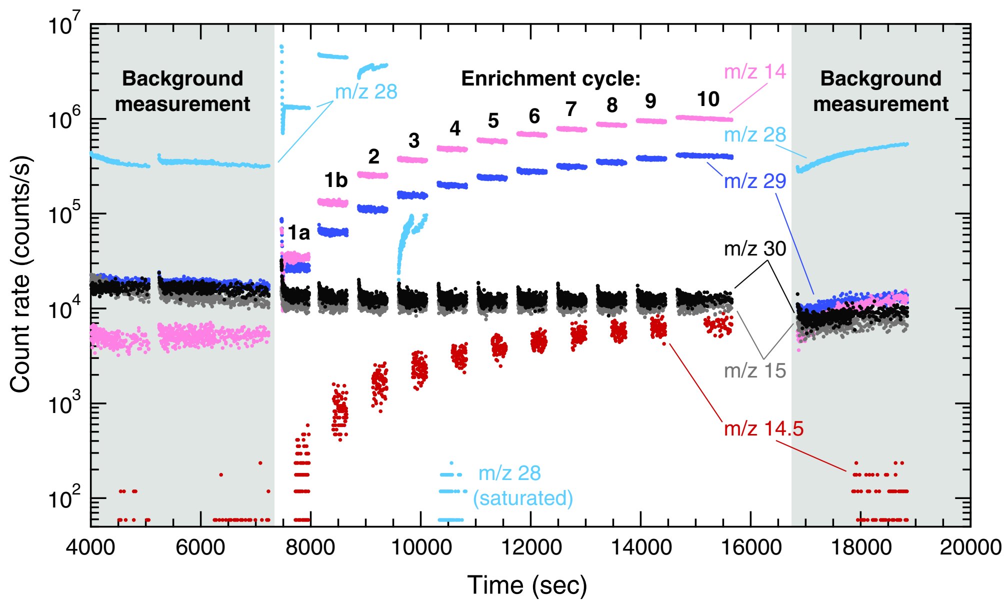

Figure 2. Visual narrative of the sol 232 enrichment experiment. Parent and daughter nitrogen ions are shown as colored points. Background measurements (shaded) are used to characterize the background signal that must be subtracted from the data before calculating count ratios. Detector corrections have been applied to the data (see supporting information). In each of 10 enrichment cycles, an atmospheric sample was introduced, and CO_2 and H_2O were removed by chemical scrubbers [*Mahaffy et al.*, 2012]. The enriched sample from one cycle was then combined with a new injection of Mars atmosphere and scrubbed to produce the next sample. Signal at m/z 28 decreases in enrichment cycle 2 and later due to detector saturation at high source pressures.

Table 1. Mars Nitrogen Isotopic Ratios Measured in Atmospheric N_2

MSL Sol[a]	$^{14}N/^{15}N$	$\delta^{15}N$(‰)[b]	Count Ratio	Limiting S/BG[c]	Experiment Type
341 (night)	173 ± 11	572 ± 82	m14/m14.5	≤ 388	Enrichment (MSL/SAM, semistatic mode)
341 (night)	175 ± 21	554 ± 187	m28/m29	3.4	Enrichment (MSL/SAM, semistatic mode)
232 (night)	178 ± 12	528 ± 103	m14/m14.5	≤ 97	Enrichment (MSL/SAM, dynamic mode)
232 (night)	179 ± 11	519 ± 91	m28/m29	≤ 13	Enrichment (MSL/SAM, dynamic mode)
19 (night)	150 ± 60	813 ± 725	m14/m14.5	2	Direct atmospheric (MSL/SAM)
45 (night)	151 ± 27	798 ± 324	m14/m14.5	9	Direct atmospheric (MSL/SAM)
77 (night)	169 ± 19	611 ± 183	m14/m14.5	8	Direct atmospheric (MSL/SAM)
278 (day)	173 ± 27	572 ± 245	m14/m14.5	14	Direct atmospheric (MSL/SAM)
284 (night)	172 ± 38	582 ± 345	m14/m14.5	17	Direct atmospheric (MSL/SAM)
292 (night)	177 ± 14	537 ± 123	m14/m14.5	20	Direct atmospheric (MSL/SAM)
321 (day)	167 ± 14	628 ± 140	m14/m14.5	12	Direct atmospheric (MSL/SAM)
Testbed[d]	270 ± 28	8 ± 104	m14/m14.5	≤ 33	Testbed enrichment TID 50765
Comparison measurements					
Viking aeroshell mass spec	168 ± 17	619 ± 182	m28/m29	< 50	Viking, 125 km [*Nier and McElroy*, 1977]
Viking lander mass spec	165 ± 17	649 ± 183	m28/m29?[e]	?[e]	Viking, surface [*Owen et al.*, 1977]
Viking lander mass spec	170 ± 15	600 ± 155	m28/m29?[e]	?[e]	Viking, surface [*Owen*, 1992]

[a]MSL landing occurred on sol 0 at 15:03 local mean solar time or UTC 2012-08-06 05:17.

[b]$\delta^{15}N$ (‰) = $1000(R/R_{AIR} - 1)$, where $R = {}^{15}N/{}^{14}N$ in the sample, and $R_{AIR} = 0.003676$ [*Coplen et al.*, 2002].

[c]Signal to background level (S/BG) is "limiting" because it refers to the count rate with the poorest S/BG (e.g., m/z 14 in the case of the m/z 14/14.5 ratio). The "≤" symbol means that the S/BG level changes over the course of the experiment, and the best S/BG ratio over the full experiment range is reported.

[d]Testbed experiment is listed to confirm SAM accuracy with a gas sample of known isotopic composition ($\delta^{15}N$ = 0‰, $^{14}N/^{15}N$ = 272). Analysis method is the same as for flight data.

[e]Viking lander mass spectrometer publications do not describe count ratios used for isotopic determination or S/BG levels in the data. Experiments used enriched atmospheric samples.

β and the flight m/z 14/14.5 count ratio (see supporting information):

$$^{14}N/^{15}N = 2(1-\beta)\left[\frac{\text{m14}}{\text{m14.5}}\right] - \beta. \tag{2}$$

[7] Additional count ratios can be used to measure nitrogen isotopes in the enrichment experiments. Measurement of the $^{14}N/^{15}N$ ratio directly from the parent ions is difficult because the signal level is very high at m/z 28 over most of the enrichment experiment; in fact, Figure 2 shows that the m/z 28 signal is near saturation in the first enrichment cycle (labeled 1a and 1b). The m/z 28 counting rate decreases in enrichment cycles 2–4 due to saturation, with 0 counts/s in the subsequent cycles. The isotope ratio can also be derived from m/z 14/29 data, but different voltage frequencies used above and below m/z 20 [*Mahaffy et al.*, 2012] introduce complications that have not yet been fully resolved.

3. Results

[8] Table 1 lists nitrogen isotopic results from SAM up through MSL sol 360 (Planetary Data System release 4). Uncertainties include all sources of error (see supporting information). Specifically, we include uncertainties from detector corrections, background subtraction, statistical noise, and splitting fractions. SAM background corrections are significant, so the limiting S/BG level is listed as a measure of the confidence in each measurement. Where known, S/BG levels from other instruments are also given for comparison.

[9] The most reliable MSL/SAM measurement of $^{14}N/^{15}N$ comes from m/z 14/14.5 in the semistatic enrichment experiment, where a S/BG ratio of 388 was achieved. Results at low S/BG have much more scatter than results at S/BG >50 (see supporting information), suggesting that imperfect background corrections dominate the uncertainty in the direct atmospheric measurements. The largest single source of uncertainty in the isotopic ratio is the uncertainty in β (equation (1) and Figure S1). The range of $^{14}N/^{15}N$ ratios derived from MSL/SAM data falls completely within the error bars of Viking measurements.

4. Discussion

[10] Nonterrestrial nitrogen isotopic ratios in Martian meteorite samples have been interpreted as tracers of atmospheric gas, trapped within the meteorites at their time of ejection from Mars [*Bogard and Johnson*, 1983]. Figure 3 compares laboratory analyses of gases evolved from meteorite samples to in situ measurements of the Mars atmosphere by Viking and MSL. Selected step-heating gas releases in the terrestrial laboratory experiments can be used to define mixing lines between the compositional measurements. The choice of steps for analysis (black symbols and references in figure caption) was intended to eliminate contributions from terrestrial air or organic contamination. For comparison, we also show meteorite data (red symbols) and linear fits based on the total gas released in each experiment. These total gas release data are free from uncertainties introduced by subjective interpretation of stepped heating data. The mixing line slope is not significantly affected by uncertainties in cosmic ray exposure ages [*Nyquist et al.*, 2001; *Schwenzer et al.*, 2007].

[11] There is a clear disagreement between the Ar/N measurement by MSL/SAM of 0.51 ± 0.01 [*Mahaffy et al.*, 2013] and by multiple Viking instruments of 0.35 ± 0.08 [*Oyama and Berdahl*, 1977]. All of the meteorite mixing lines are consistent with Viking composition and inconsistent with MSL.

[12] Three possible explanations for the disagreements can be considered: that the MSL composition is wrong, that the Viking composition is wrong, or that the Martian atmospheric composition is variable. Internal and peer reviews

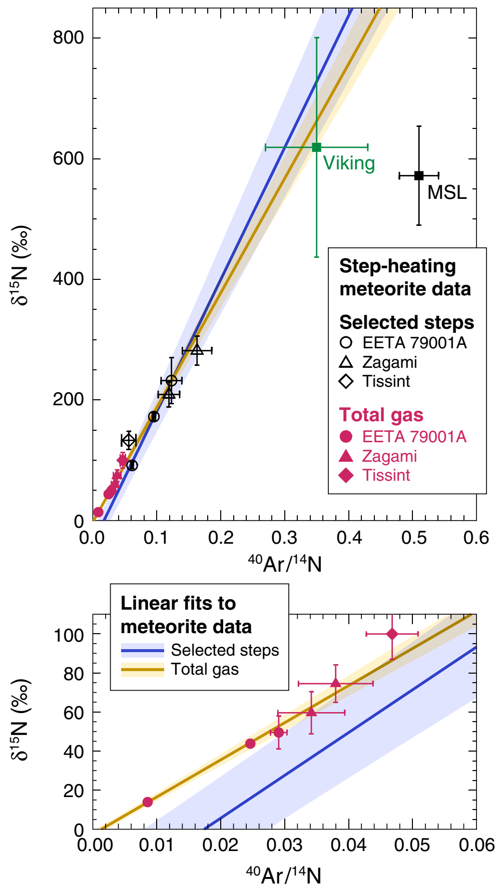

Figure 3. Pseudo-three-isotope plots at two different magnifications (comparing ^{14}N, ^{15}N, and ^{40}Ar) showing Mars meteorite and atmosphere measurements and linear fits. The meteorite data suggest mixing between at least two components: Martian atmosphere and terrestrial atmosphere. Black meteorite data include only selected temperature steps in stepped heating gas release experiments. Red data points include the total gas released at all temperatures. Meteorite data are from *Becker and Pepin* [1984, EETA 79001A samples C1 and C2], *Wiens et al.* [1986, sample C3], *Marti et al.* [1995, Zagami], *Chennaoui Aoudjehane et al.* [2012, Tissint], and *Avice* [2012, Tissint]. Viking Ar/N ratio is from *Oyama and Berdahl* [1977], and Viking $\delta^{15}N$ is from *Nier and McElroy* [1977]. MSL values are from SAM/QMS measurements, with $\delta^{15}N$ described in this work, and Ar/N is from *Mahaffy et al.* [2013]. Linear fits included uncertainties in both Ar/N and $\delta^{15}N$, following the method of *York et al.* [2004], assuming uncorrelated errors.

of the MSL/SAM data argue against the first possibility at this time [*Mahaffy et al.*, 2013]. Similarly, the Viking composition seems highly robust, with good agreement among multiple instruments. The MSL $^{14}N/^{15}N$ ratio falls easily within the error bars of the Viking measurements by both lander and aeroshell mass spectrometer experiments. So the primary disagreement is with the Ar/N ratio. This ratio was repeatedly measured by both the Viking lander mass spectrometer [*Owen et al.*, 1977] and the gas exchange experiment [*Oyama and Berdahl*, 1977]. Unfortunately, Viking flight data are no longer available, so we cannot repeat the same validation we applied to the MSL data. Therefore, the possibility that Viking Ar/N measurements were erroneous can only be speculation.

[13] There is currently no satisfactory mechanism that could explain a variable Ar/N ratio in the Martian atmosphere. Adsorbed CO_2 and H_2O in the regolith make up a large volatile reservoir that exchanges over time with the atmosphere and polar caps [e.g., *Fanale et al.*, 1982; *Fanale and Jakosky*, 1982]. Nitrogen and argon are not thought to participate in this cycle, although these gases do adsorb onto Martian soil [*Ballou et al.*, 1978]. A previously unknown surface-atmosphere exchange mechanism would need to involve very large column density changes: a release of up to 1 kg m^{-2} Ar or sequestration of up to 0.7 kg m^{-2} N_2, prior to 2012. Column density changes might be thermally driven by global warming of 0.65 K since Viking [*Fenton et al.*, 2007], or related to a reduction of polar cap mass [*Malin et al.*, 2001], but MSL measurements from early spring to late summer on Mars do not support any variation in Ar/N [*Atreya et al.*, 2013; *Trainer et al.*, 2013].

[14] Heavy nitrogen in the atmosphere of Mars is enriched relative to both the protosolar isotopic ratio and the ratio in the terrestrial and Venusian atmospheres (Table 2), as well as to the primordial Mars atmosphere as suggested by the meteorite ALH84001 with $\delta^{15}N = 4 \pm 2$ ‰ [*Marti and Mathew*, 2000]. The enrichment of ^{15}N is due to preferential escape of ^{14}N from the Martian atmosphere [e.g., *McElroy et al.*, 1976; *Fox and Dalgarno*, 1983; *Fox and Hać*, 1997; *Chassefière and Leblanc*, 2004]. Some models of sputtering and photochemical escape of nitrogen to space suggest that exchange with surface/interior reservoirs is needed to buffer the nitrogen against excessive fractionation due to escape [*Jakosky et al.*, 1994; *Zent et al.*, 1994], leading to a loss of ~90% of atmospheric nitrogen over time [*Jakosky and Phillips*, 2001]. The detailed history and mechanisms of exchange between atmosphere and surface/interior are poorly understood for nitrogen, compared to similar processes that fractionate atmospheric carbon and oxygen [*Webster et al.*, 2013], via exchange between polar ices, carbonates, and regolith adsorption [*Jakosky*, 1991; *Fanale et al.*, 1992].

[15] SAM may provide insight into these processes by investigating nitrogen-containing compounds in solid samples. Reduced and oxidized compounds have tentatively been identified in evolved gases, including N, NO, HCN, CN, and CH_3CN [*Stern et al.*, 2013; *Navarro-González et al.*, 2013]. The origin of the detected nitrogen could include terrestrial sources within the SAM instrument or the Curiosity sample chain, exogenous nitrogen delivered by meteorites, or indigenous Martian inorganic and organic matter. Exchange between solid and atmospheric reservoirs

Table 2. Solar System Nitrogen Isotopic Ratios

Measurement	$^{14}N/^{15}N$	$\delta^{15}N$ (‰)	Reference
Protosolar/primordial			
Sun (Genesis)	441 ± 5	–383 ± 8	*Marty et al.* [2011]
Jupiter	434 ± 7.5	–373 ± 11	*Owen et al.* [2001]
Interstellar medium	450 ± 98	–395 ± 168	*Dahmen et al.* [1995]
Secondary atmospheres			
Mars (MSL)	173 ± 11	572 ± 82	(This work)
Titan	183 ± 5	487 ± 42	*Niemann et al.* [2005]
Venus	272 ± 54	0 ± 250	*Hoffman et al.* [1979]
Earth	272	0	

could occur as organic surface nitrogen is photolytically or radiolytically decomposed to N_2 or oxidized to inorganic nitrogen in the form of nitrates, which are also converted to N_2 by the current impact flux [*Manning et al.*, 2008].

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