WONG ET AL. [2013]: MARS ATMOSPHERIC NITROGEN ISOTOPES

SUPPLEMENTARY MATERIAL

1. Definitions

We define the following isotopic and ionization fractions:

- $\alpha =$ the ratio of ^{14}N/^{15}N. This is the unknown in the Mars sample.
- $\beta = \frac{\mathrm{N^{+}ions}}{\mathrm{N^{+}+N_2^{++}ions}}$ produced from N_2.
- $\gamma = \frac{\mathrm{N_2^{++}ions}}{\mathrm{N^{+}+N_2^{++}ions}}$ produced from N_2.

Then $\beta + \gamma = 1$, and β/γ is the $\mathrm{N^{+}/N_2^{++}}$ splitting fraction.

Additional definitions:

- $P(X) =$ the probability that one atom or molecule, drawn at random from a given sample, is a member of species X.
- $n(X) =$ the number of atoms or molecules of species X in the sample.

2. Distribution of N isotopes in a molecular population

For a population of nitrogen molecules, we have to determine how they are partitioned into the three isotopologues of $^{14}N_2$, $^{15}N_2$, and $^{14}N^{15}N$ (for convenience, we can also call these $^{28}N_2$, $^{30}N_2$, and $^{29}N_2$ respectively).

It is possible that there is some fractionation, so that ^{15}N is preferentially (rather than randomly) partitioned among $^{30}N_2$ and $^{29}N_2$. But we assume that N-exchange between molecules is faster than any loss mechanism that fractionates nitrogen.

The sample consists of N_2 molecules, but we can select just a single atom from this population first. The probability that we selected an atom of ^{14}N is given by

$$P(^{14}\mathrm{N}) = \frac{n(^{14}\mathrm{N})}{n(^{14}\mathrm{N}) + n(^{15}\mathrm{N})} = \frac{\alpha}{\alpha+1}. \tag{1}$$

Similarly,

$$P(^{15}\mathrm{N}) = \frac{1}{\alpha+1}. \tag{2}$$

Because this is a population of molecules, the atom we just selected actually has another atom dangling off of it. Probabilities can just be multiplied, so the probabilities for selecting the homoisotopic molecules are easily derived:

$$P(^{28}\mathrm{N}_2) = P(^{14}\mathrm{N}^{14}\mathrm{N}) = P(^{14}\mathrm{N})P(^{14}\mathrm{N}) = \frac{\alpha^2}{(\alpha+1)^2}. \tag{3}$$

$$P(^{30}\mathrm{N}_2) = P(^{15}\mathrm{N})P(^{15}\mathrm{N}) = \frac{1}{(\alpha+1)^2}. \tag{4}$$

But for the heteroisotopologue $^{29}\mathrm{N}_2$, there are two substitution sites. So,

$$P(^{29}\mathrm{N}_2) = P(^{14}\mathrm{N}^{15}\mathrm{N}) + P(^{15}\mathrm{N}^{14}\mathrm{N}) = 2P(^{14}\mathrm{N})P(^{15}\mathrm{N}) = \frac{2\alpha}{(\alpha+1)^2} \tag{5}$$

Everywhere except for Eqn. 5, we will consider $^{14}\mathrm{N}^{15}\mathrm{N}$, $^{15}\mathrm{N}^{14}\mathrm{N}$, and $^{29}\mathrm{N}_2$ to be identical. Taking the ratio of Eqns. 3 and 5 shows that $^{28}\mathrm{N}_2/^{29}\mathrm{N}_2$ is a factor of two different from $^{14}\mathrm{N}/^{15}\mathrm{N}$.

3. DETERMINATION OF SPLITTING FRACTIONS AND ISOTOPE RATIOS FROM SAM QMS DATA

In AS-DIRECT for samples at full atmospheric pressure, m/z 28 is saturated, and both m/z 28 and 29 have contributions from CO and CO_2. There are lots of counts at m/z 15, but this is largely due to a strong instrumental hydrocarbon background, making it very difficult to reliably separate the signal from the background. But there ARE counts at m/z 14 and 14.5, well above the background level.

The m/z 14/14.5 count ratio also gives the best signal/background level in enrichment experiments.

At m/z 14.5, only $^{29}\mathrm{N}_2^{++}$ is present. But at m/z 14, two sources contribute: $^{14}\mathrm{N}^{+}$ and $^{28}\mathrm{N}_2^{++}$. The $^{14}\mathrm{N}^{+}$ ions come from both $^{28}\mathrm{N}_2$ and $^{29}\mathrm{N}_2$.

The probability of measuring a particular daughter ion depends on the the probability of starting with the right parent ion and the splitting fractions β and γ. At m/z 14.5,

$$P(^{29}\mathrm{N}_2^{++}) = P(^{29}\mathrm{N}_2)P(\mathrm{N}_2 \rightarrow \mathrm{N}_2^{++}) = \frac{2\gamma\alpha}{(\alpha+1)^2}. \tag{6}$$

At m/z 14, there are more terms because both singly and doubly charged ions contribute, and both $^{28}\mathrm{N}_2$ and $^{29}\mathrm{N}_2$ are parent ions:

$$\begin{aligned} P(^{28}\mathrm{N}_2^{++}) + P(^{14}\mathrm{N}^{+}) &= P(^{28}\mathrm{N}_2)P(\mathrm{N}_2 \rightarrow \mathrm{N}_2^{++}) \\ &\quad + P(^{28}\mathrm{N}_2)P(\mathrm{N}_2 \rightarrow \mathrm{N}^{+}) + P(^{29}\mathrm{N}_2)\frac{P(\mathrm{N}_2 \rightarrow \mathrm{N}^{+})}{2} \\ &= \frac{\gamma\alpha^2}{(\alpha+1)^2} + \frac{\beta\alpha^2}{(\alpha+1)^2} + \frac{\beta\alpha}{(\alpha+1)^2} \end{aligned} \tag{7}$$

Then dividing Eqn. 7 by Eqn. 6 gives the observable ratio of m/z 14/14.5 (which we denote by [m14/m14.5]):

$$\left[\frac{\mathrm{m14}}{\mathrm{m14.5}}\right] = \frac{\gamma\alpha^2 + \beta\alpha^2 + \beta\alpha}{2\gamma\alpha} = \frac{(1-\beta)\alpha^2 + \beta\alpha^2 + \beta\alpha}{2(1-\beta)\alpha}. \tag{8}$$

For a calibration experiment, where we have a known $^{14}\mathrm{N}/^{15}\mathrm{N}$ ratio α, we can solve Eqn. 8 for β to determine the N^+/m14 splitting fraction:

$$\beta = \frac{2\left[\frac{\mathrm{m14}}{\mathrm{m14.5}}\right] - \alpha}{2\left[\frac{\mathrm{m14}}{\mathrm{m14.5}}\right] + 1}. \tag{9}$$

Or, for a flight experiment, we can derive the unknown $^{14}\mathrm{N}/^{15}\mathrm{N}$ ratio with knowledge of SAM's N^+ splitting fraction β:

$$\alpha = 2(1-\beta)\left[\frac{\mathrm{m14}}{\mathrm{m14.5}}\right] - \beta. \tag{10}$$

On 2013-01-08, Jen Stern measured $\delta^{15}\mathrm{N}$ in the SAM FM cal gas cell to be -0.587 ± 0.014 per mil, or $\alpha = 272.195 \pm 0.003$. This allowed a determination of $\beta = 0.404 \pm 0.033$ from the combination of one SAM testbed experiment and four pre-flight calibration experiments. This measurement of β was presented at the 2013 LPSC [*Wong et al.* 2013].

4. NITROGEN ISOTOPIC RATIO: ERROR BUDGET

Uncertainties are discussed briefly in the main text. The uncertainties in Fig. S1 are ESTIMATES of the true errors. For simplicity, we do not present uncertainties in the uncertainty estimates, but the uncertainty estimates are judged to be accurate to within 50% of their values. The uncertainty in the correct background correction is particularly

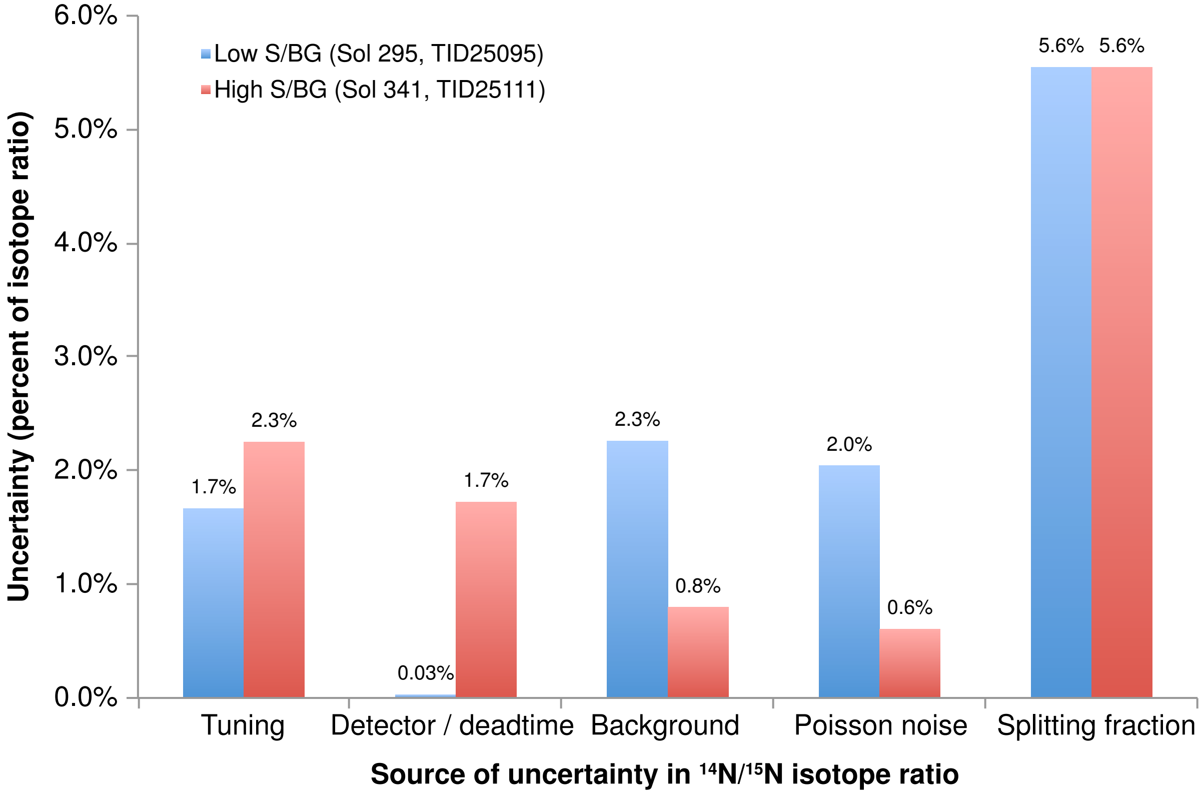

Figure S1. Error budget for the $^{14}N/^{15}N$ isotope ratios measured by MSL/SAM. Typical high and low S/BG cases are shown (see Table 1 in the main text).

difficult to estimate, since it is not possible to simultaneously measure both background and sample.

The individual sources of error evaluated for these measurements are:

- Tuning: QMS peak shapes are flat-topped functions, but are not perfectly flat. The most reliable number to use for count ratios is the peak counting rate at for each mass to charge ratio, but due to instrument tuning constraints, the peak shape functions sometimes have offset in their maxima. For example, Fig. 1 in the main text shows the peak counts/sec for m/z 14 occurs at m/z 13.8 rather than m/z 14.0. We use peak shape templates to normalize m/z 14 data to the peak counts/sec; without this adjustment, tuning errors are approximately twice as large. An accurate tuning correction for the m/z 14.5 data is not available because the wings of the peak are hidden by signal from m/z 14 and 15. Tuning variation is currently being characterized by the team, and depends on factors such as instrument temperature. Tuning variation is not apparently correlated to count rates.

- Detector/deadtime: Detector effects are corrected to remove nonlinearity from the signal at high counting rates. For low count rates, the correction is extremely small. For count rates over a million counts/sec, the correction becomes significant at the 1-5% level.

- Background: Background corrections are challenging, and the SAM team continues to refine our methods for this correction. We have estimated the background correction uncertainty by comparing alternate corrections using different tracer masses and fitting techniques. The bar graph clearly shows that background uncertainty is reduced in the enrichment run with high S/BG.

- Noise: Noise in the SAM QMS follows a Poisson distribution, as expected for counting detectors [*Bevington and Robinson* 1992]. The relative contribution from this uncertainty source is reduced at higher count rates (because the uncertainty on a single measurement is the square root of the counts per integration period), and also reduced by taking measurements over a longer time period. For this error budget, we show the uncertainty due to errors following a precise Poisson distribution. Errors calculated self-consistently from the data are not significantly larger, unless time-variable effects are significant.

- Splitting fraction: The uncertainty in β is not affected by data considerations such as count rates or S/BG ratios. To reduce uncertainty in this factor, high-precision measurements must be conducted on gases with known nitrogen isotopic composition. Only a limited number of calibration experiments were done with the SAM flight model before launch, and all of these experimental results are included in the determination of the splitting pattern [*Wong et al.* 2013]. However, additional experiments can be conducted on the SAM testbed, currently operating at NASA GSFC. With the flight instrument, an improvement could be achieved by measuring on-board calibration gas cell samples on Mars (after enrichment, to eliminate CO^+ signal at m/z 28).

5. δ^{15}N VS. EXPERIMENTAL SIGNAL/BG RATIO

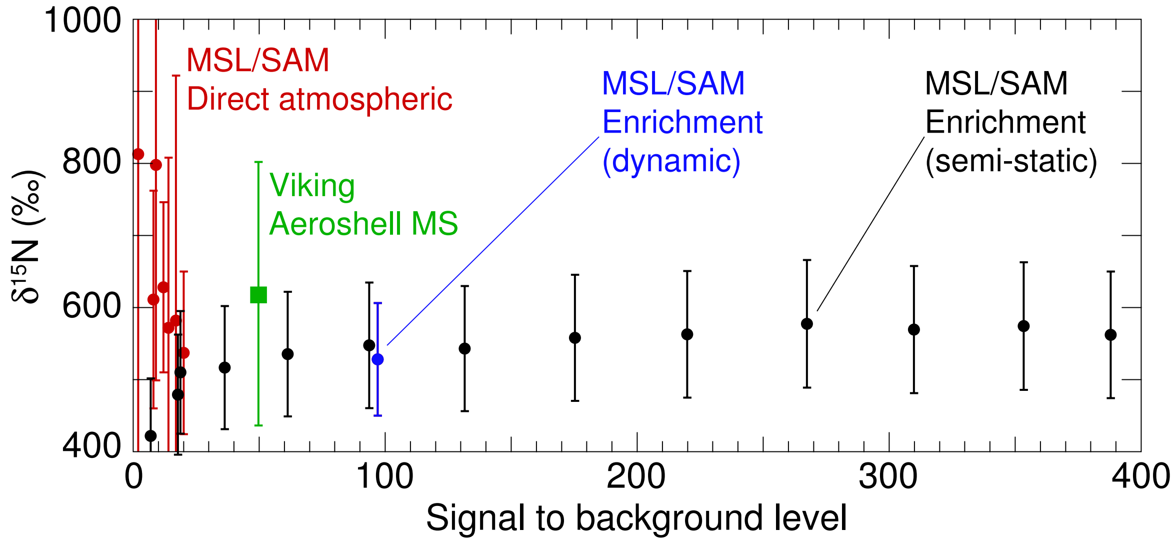

FIGURE S2. Stable δ^{15}N at different S/BG levels indicates that the background correction is not significant in the enrichment experiments. The largest single source of uncertainty at high S/BG is the uncertainty in splitting fraction β. Experiment sol numbers are given in Table 1.

6. SUPPLEMENTAL REFERENCES

Bevington, P.R., and D.K. Robinson (1992), *Data Reduction and Error Analysis for the Physical Sciences*, WCB/McGrawHill, Dubuque, IA.