THE SEARCH FOR AMMONIA IN MARTIAN SOILS WITH CURIOSITY'S SAM INSTRUMENT. James J. Wray[1], P. D. Archer, Jr.[2], W. B. Brinckerhoff[3], J. L. Eigenbrode[3], H. B. Franz[3], C. Freissinet[3], D. P. Glavin[3], P. R. Mahaffy[3], C. P. McKay[4], R. Navarro-González[5], A. Steele[6], J. C. Stern[3], C. R. Webster[7], and the MSL Science Team, [1]Georgia Institute of Technology, Atlanta, GA (jwray@gatech.edu), [2]NASA Johnson Space Center, Houston, TX, [3]NASA Goddard Space Flight Center, Greenbelt, MD, [4]NASA Ames Research Center, Moffett Field, CA, [5]Universidad Nacional Autónoma de México, Mexico City, Mexico, [6]Carnegie Institute of Washington, Washington, DC, [7]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

Introduction: Nitrogen is the second or third most abundant constituent of the Martian atmosphere [1,2]. It is a bioessential element, a component of all amino acids and nucleic acids that make up proteins, DNA and RNA, so assessing its availability is a key part of Curiosity's mission to characterize Martian habitability. In oxidizing desert environments it is found in nitrate salts that co-occur with perchlorates [e.g., 3], inferred to be widespread in Mars soils [4-6]. A Mars nitrogen cycle has been proposed [7], yet prior missions have not constrained the state of surface N.

Here we explore Curiosity's ability to detect N compounds using data from the rover's first solid sample. Companion abstracts describe evidence for nitrates [8] and for nitriles (C≡N) [9]; we focus here on non-nitrile, reduced-N compounds as inferred from bonded N-H. The simplest such compound is ammonia (NH_3), found in many carbonaceous chondrite meteorites in NH_4^+ salts and organic compounds [e.g., 10].

Data and Methods: Curiosity's Sample Analysis at Mars (SAM) instrument suite [11] identifies gases (from the atmosphere or evolved from heated samples) primarily based on their masses. Its quadrupole mass spectrometer (QMS) has at least unit mass resolution across the 2–535 amu range, and gases can be passed through gas chromatograph columns to allow further discrimination based on elution times. Here we focus on direct-to-QMS evolved gas analyses (EGA) during sample heating from ambient temperatures to ~835°C.

In November 2012, Curiosity scooped ~20–30 cm^3 of soil from the Rocknest sand drift, an accumulation of fine sand with primarily basaltic composition [12]. Four portions of the <150 µm fraction (<76 mm^3 each) were delivered to SAM for pyrolysis experiments.

Ionized NH_3 has a mass to charge ratio (m/z) of 17 (hereafter m17), and in the QMS produces m16,15,14 fragments of progressively lower abundance. But the m17,16 data primarily reflect contributions from OH and O, which evolved with H_2O and O_2 from the Rocknest sediment [13]. We therefore turn to m15 (NH) as a potential proxy for NH_3, with the caveat that CH_3 can also contribute to this mass (discussed below).

Results: The Rocknest m15 data show a distinct peak at ~260°C (Fig. 1). This feature is unique to the Rocknest sample, as it was not observed in a previous SAM "blank" run (pyrolysis of an empty cup). The blank did evolve m15 (likely from the MTBSTFA derivatizing agent in other SAM cups) [14], but lacks the sharp peak at 260°C seen in Rocknest data (Fig. 1). In the first SAM analysis of Rocknest sediment, the m15 peak corresponds closely in time with a peak in m14, with proportional count rates of m15/m14 ≈ 3.5 (Fig. 1). A second weaker m15 peak near ~800°C may be related to different N-bearing compounds [9].

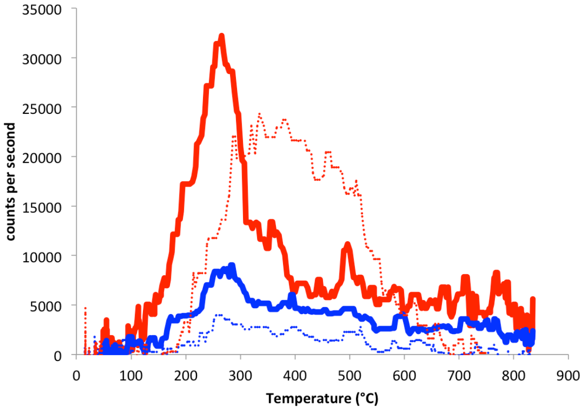

Figure 1. SAM EGA data from the first Rocknest soil analysis (solid) vs. a "blank" (dashed) run; red is m15 and blue is m14. Beyond ~300°C, "blank" m15 is likely terrestrial CH_3, which is oxidized in the Rocknest EGA by evolved O_2 [13].

Other masses evolving near 260°C include m26,27 in a narrower peak centered ~15°C higher; these may be attributed to CN and HCN [9]. But these cyanides would yield negligible m15 and could only account for ~25% of the observed m14, based on fragmentation patterns in the NIST database. NO evolved from nitrates might explain a similarly timed m30 peak and could account for much of the m14 observed [8], but should produce negligible m15—only ~10% of that observed—in the form of doubly ionized NO^{++}. $^{15}N/^{14}N$ would have to be enriched by a factor of ~400 in nitrates relative to the Martian atmosphere [15] for ^{15}N from NO to explain the observed counts at m15.

Discussion: The implausible enrichments required to explain the m15 release as ^{15}N from CN or NO imply that this mass is a distinct species, most probably CH_3 and/or NH. We now explore each of these in turn.

CH_3 would be an intriguing Martian soil component in its own right, but could it be terrestrial contamination? The tert-butyl fragment from MTBSTFA has three CH_3 groups, but the full fragment (m57) should be more abundant than m15, whereas in the Rocknest data m57/m15 < 0.2. This fragment may react with Martian perchlorate to produce the chloromethylpropene observed in Rocknest data [16], but this can account for <0.2% of the m15. Similarly, dimethylformamide ($HCON(CH_3)_2$), also present in MTBSTFA cups, should have m73/m15 and m42/m15 >> 1, but both are < 1 in Rocknest data. SAM's other wet chemistry cups contain two CH_3 sources, TMAH and methanol [11], but respectively they should have peaks > m15 at m74 and m31, neither of which we observe.

CH_3Cl was observed during the Rocknest analyses [17], and should yield significant CH_3: m15/m50 ≈ 0.72, according to NIST. But at Rocknest we have m15/m50 ≈ 1.7, and additionally m15 peaks at least slightly before m50, so chloromethane seems capable of explaining at most about half the m15 signal. Larger organic molecules—whether Martian or terrestrial in origin—are an alternative source of CH_3, but in most cases at least one larger mass fragment should identify the source. For example, carboxylic acids have been proposed as metastable products of organics oxidized on the Martian surface [18], but (e.g.) acetic acid (CH_3COOH) should have m43/m15 and m60/m15 >> 1, whereas both are << 1 for Rocknest soils at ~260°C.

According to the NIST NH_3 fragmentation pattern, NH should yield m15/m14 ≈ 3.4, nearly equal to our Rocknest soil result of ~3.5. If at least some observed m15 is NH, then what is its source? We must again consider MTBSTFA, which could react with the water from Rocknest to produce a N-H bond in its methyltrifluoroacetamide fragment (which also contains CH_3). The mass spectrum of this fragment includes m15, but m58 and m69 should be more abundant, whereas both are orders of magnitude lower in the Rocknest data. Also m127 should co-evolve abundantly, but instead peaks clearly earlier than m15, at low abundance [9].

Curiosity landed in Gale crater with retrorockets propelled by hydrazine (N_2H_4). Its NIST mass spectrum has m31/m15 ≈ 6, clearly inconsistent with Rocknest data, but N_2H_4 would have reacted with CO_2 after landing to form carbazic acid ($NH_2NHCOOH$). Its mass spectrum would include m15, but m60 and m76 should be at least as abundant, and neither is observed at ~260°C. NH_3 formed in the descent engines and perhaps later through photochemical degradation of carbazic acid, but minimal contamination of Rocknest is expected based on its ~400 meter distance from the landing site and the fortuitous local wind patterns.

NH_3 itself is highly volatile, so if present naturally it would likely have to be bound in a mineral or organic compound. Organics with NH_2 groups include amino acids, but again these are generally ruled out by the paucity (in Rocknest data) of specific heavier masses, e.g. m30,75 for glycine or m42 for alanine. The data are also inconsistent with simple amides; e.g., formamide predicts too much m29 and acetamide too much m59 (NIST). Amines can be thermal degradation products of amino acids [19], and the simplest amines evolve most of the N-related masses we seek to explain in Rocknest data; e.g., methylamine (CH_3NH_2) evolves m14,15,26,27,28,30,31. But the proportions do not match our data; e.g., the predicted m31/m15 is too high. More detailed modeling of the mass spectra using amines and other components will be conducted.

A simpler hypothesis is that NH_3 occurs as ammonium adsorbed on or within mineral phases. For example, H_3O-bearing jarosite releases H_2O at low temperatures [20], and the strong H_2O release from Rocknest soils peaks at a similar temperature to m15; perhaps some NH_4^+ substitutes for H_3O^+ in hydronium jarosite. Or NH_4^+ could substitute for alkalis in feldspars, the most abundant mineral class in Rocknest soils [12]. Other candidate NH_4^+ salts are discussed by [8].

Conclusions and Future Work: SAM EGA data on Rocknest soils provide possible evidence for reduced-N species on Mars, but further laboratory work of the kind described by [9] is needed to determine how SAM conditions and Martian chemistry (e.g., perchlorate) may alter fragmentation patterns to produce more CH_3 from terrestrial contaminants. SAM's Tunable Laser Spectrometer (TLS) covers lines of trace gases that include NH_3 [21]. TLS data may therefore provide an independent upper limit on evolved NH_3, to be checked against the QMS data for consistency.

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