DETECTION OF REDUCED NITROGEN COMPOUNDS AT ROCKNEST USING THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT ON THE MARS SCIENCE LABORATORY (MSL). J. C. Stern[1], A. Steele[2], A. Brunner[1], P. Coll[3], J. Eigenbrode[1], H. B. Franz[1], C. Freissinet[1], D. Glavin[1], J. H. Jones[4], R. Navarro-Gonzalez[5], P. R. Mahaffy[1], A. C. McAdam[1], C. McKay[6], J. Wray[7], and the MSL Science Team, [1]NASA Goddard Space Flight Center, Greenbelt, MD, jennifer.c.stern@nasa.gov, [2]Carnegie Institution of Washington, Washington, DC 20015, [3]LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, [4]NASA Johnson Space Center, Houston TX 77058, [5]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [6]NASA Ames Research Center, Moffett Field, CA 94035, [7]Georgia Institute of Technology, Atlanta, GA 30332.

Introduction: The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover detected nitrogen-bearing compounds during the pyrolysis of Rocknest material at Gale Crater. Hydrogen cyanide and acetonitrile were identified by the quadrupole mass spectrometer (QMS) both in direct evolved gas analysis (EGA) (SS-EGA sequence, see [1]) and after gas chromatograph (GC) separation (SS-GCMS, see [1]). SAM carried out four separate analyses from Rocknest Scoop #5. A significant low temperature release was present in Rocknest runs 1-4, while a smaller high temperature release was also seen in Rocknest runs 1-3. Here we evaluate whether these compounds are indigenous to Mars or a pyrolysis product resulting from known terrestrial materials that are part of the SAM derivatization experiment [2].

Methods: SAM received a portion [3] of Rocknest material (< 150 μm size fraction) for analysis. EGA experiments involved pre-heating the sample at 35° C for 5 minutes, then ramping the oven to ~835° C (sample temperature) in a stream of 30 mb He at 1.5 sccm at a ramp rate of 35° C/min. All gas was analyzed by EGA. Rocknest runs 1-3 also analyzed gases evolved over selected temperature ranges by GCMS [2].

Preliminary Results: Several masses associated with nitrogen-bearing compounds were preliminarily or definitively identified. Figure 1 shows a representative analysis from Rocknest runs 1 - 3 (in this case 2). Due to the possible presence of one or more molecular species at any particular m/z, the correlation of several related masses becomes a useful and important tool in deconvolving the molecular species present at a particular temperature range. One example is that CO likely accounts for a significant amount of m/z 28 in Fig 1; however, the peak at ~275° C does not track with m/z 45 (an isotopologue of CO_2) and co-exists with several other possible N-bearing compounds, including m/z 14 (N), and m/z 28 (N_2) suggesting possible N_2 contribution. NO has also been proposed for mass 30 [4], although other possible compounds cannot be excluded. However, m/z 15, which could correspond to CH_3 or NH [5], is present as a broad peak that may correlate to the m/z 14 peak at ~275°C.

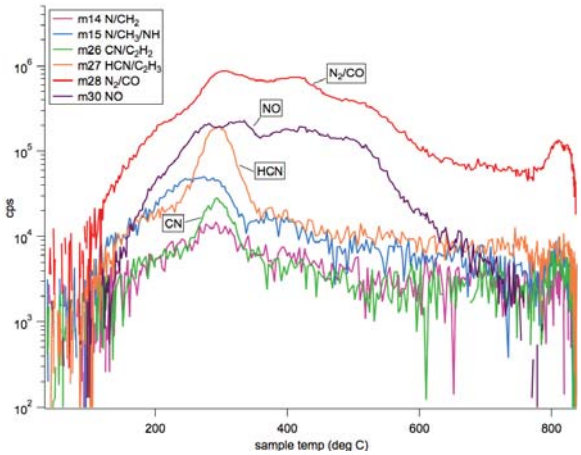

Figure 1. *EGA Pyrogram showing evolved N-bearing compounds versus temperature from the second Rocknest analysis by SAM*

Peaks associated with m/z 14, 26, 27, and 28 all have a maximum release at ~275° C. The m/z 27 peak was identified as hydrogen cyanide (HCN) by matching m/z ratios of 26/27 from the NIST database for HCN. Masses consistent with HCN are not present in EGA results for the blank (an empty cup analysis run prior to Rocknest analyses). Preliminary calculations give nanomolar concentrations of HCN in all four Rocknest samples. HCN was positively identified during GCMS analytical sequence in multiple temperature cuts sent to the GC. Rocknest 1 and 2 both had GC temperature cuts bracketing the HCN evolution temperature of 300° C in direct EGA; however, analysis of GCMS data reveal that Rocknest 1 had 2.2 times more HCN than the blank, while Rocknest 2 had 9.8 times more HCN than the blank. Interestingly, direct EGA data for both of these runs give roughly equivalent concentrations of HCN for Rocknest runs 1 and 2. Rocknest 3, which sampled temperatures above 535° C, had 1.5 times more HCN than the blank run.

Acetonitrile, CH_3CN (base peak at mass 41), was also identified by GCMS using the NIST spectral library, and is present in the EGA as a broad release from ~130° to 300° C (Figure 2). However, acetoni-

trile is also present in both EGA and GCMS sequences in the blank run. In GCMS, acetonitrile is 1.4 times more abundant in Rocknest 2 than in the blank. This difference could be explained by a contribution of m/z 41 from another species, or by differing temperature cuts between the solid sample, starting at 98º C, and the blank, starting at 146º C. Thus we cannot confirm the presence of acetonitrile in the solid sample.

Rocknest samples 1 – 3 show a high temperature m/z 28 peak at ~800° C. This could be ascribed to CO; however, a small m/z 26 peak and a less distinct m/z 27 peak also evolve at this temperature.

Discussion: The presence of *cyanide / nitrile* in gases evolved from the Rocknest samples is intriguing, although more work is required to verify whether these compounds are indigenous to Mars. HCN can play a crucial role in several abiotic reactions, including the formation of amino acids and other N-heterocycles, and during pyrolysis it could be a decomposition product of these molecules. However, CN itself is technically an inorganic compound and maybe present as cyanides such as FeCN.

The thermal evolution of m/z 26 and 27 (suspected to be from HCN), m/z 127 and 147 (known to reflect two MTBSTFA-water reaction products [2]), and m/z 32 (diagnostic for O_2), may shed some light on reaction chemistry (Fig. 2). The onset of O_2 evolution correlates with the sharp drop in m/z 147, presumably due to oxidation of MTBSTFA. m/z 41, acetonitrile, also peaks at about the same temperature as m/z 127 (~200° C). m/z 26 and 27 begin to evolve at about this temperature and peak around ~275° C.

Confirmation of Martian HCN will require ruling out its presence as contamination, particularly its formation during pyrolysis of the derivatization reagents carried for SAM's wet chemistry experiment, i.e., MTBSTFA and DMF. MTBSTFA has been detected in GC and EGA blanks and in all Rocknest runs [6,2]. In addition, the HCN is present at similar abundances to the chlorohydrocarbons [7] detected in the same samples by SAM. Preliminary laboratory work using commerical EGA-MS instrumentation to pyrolyze MTBSTFA and DMF shows evolution of m/z 41, 26, and 27 at low temperatures. Addition of Mg-perchlorate to these experiments results in oxidation and chlorination of these species, as well as changes in the temperature at which they are evolved. Laboratory work will continue in order to determine the possible contribution of MTBSTFA/DMF to N-bearing species identified during SAM analysis of Rocknest materials.

High temperature releases: The second release of masses 26, 27 and 28 at ~800°C without an increase in masses related to CO_2 may indicate the release at these masses is related to CN, HCN, and N_2, respectively.

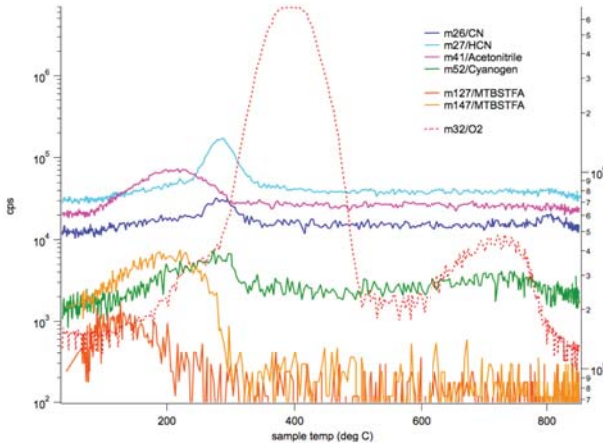

Figure 2. Relationship of HCN to MTBSTFA/DMF fragments, acetonitrile, and oxygen release.

Alternatively, some or all of this m/z 28 peak may come from the partial oxidation of native carbon to CO. There is no known means by which MTBSTFA or DMF may source the m/z 27 and 28 signature observed at 800° C, thus these terrestrial reagents seem to be an unlikely source for organics produced at high temperatures. Stepped combustion experiments on SNC meteorites and most recently the Tissint meteorite show a release of heavy nitrogen ($\delta^{15}N$ ~ +100) in the temperature range 600 – 800°C [8]. However, a mystery remains as to the provenance of the N-containing phases in these meteorites. Indeed the original identification of the SNCs meteorites as Martian relied on the Viking missions measurement of the isotopic composition of noble gases and nitrogen [9]. Becker and Pepin [10] invoke a two-component mixing model of a possible terrestrial atmospheric or indigenous (to Mars) light $\delta^{15}N$ isotope component to explain the isotope trends in the SNC meteorites relative to Viking atmospheric measurements. The nature of this phase has not been identified but the discovery of CN in inclusions within the Tissint meteorite [11] give intriguing relevance to the measurements made at Rocknest. Initial analysis of Tissint has yielded the presence of several CN-containing molecules with identification of HCN, acetonitrile and benzonitrile in GCMS in a temperature cut from 600-1000º C. Work is continuing on the Tissint meteorite samples run in a similar fashion to SAM on Curiosity.

References: [1] Mahaffy et al. (2012) *Space Sci. Rev.* [2] Buch (2013) LPS XLIV [3] Archer et al. (2013) LPS XLIV [4] Navarro-Gonzalez et al. (2013) LPS XLIV [5] Wray et al. (2013) LPS XLIV [6] Freissinet et al. (2013) LPS XLIV [7] Glavin et al. (2013) LPS XLIV [8] Aoudjehane et al., (2012) *Science* 338(6108) [9] Bogard & Johnson, *Science* **221**, 651(1983). [10] Becker & Pepin *EPSL, 69 (1984)* [11] Steele et al. (2013) LPS XLIV