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DETECTION AND QUANTIFICATION OF NITROGEN COMPOUNDS IN THE FIRST DRILLED MARTIAN SOLID SAMPLES BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE ON THE MARS SCIENCE LABORATORY (MSL). J. C. Stern1,†, R. Navarro-González2, C. Freissinet1, C. P. McKay1, D. P. Archer, Jr.3, A. Buch4, A. E. Brunner2, P. Coll1, J. L. Eigenbrode1, H. B. Franz1, D. P. Glavin1, A. C. McAdam1, D. W. Ming3, A. Steele4, B. Sutter5, C. Szopa10, J. J. Wray11, P. G. Conrad1, P. R. Mahaffy1, and the MSL Science Team. 1NASA Goddard Space Flight Center, Greenbelt, MD, 20771 jennifer.c.stern@nasa.gov, 2Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, 3NASA Postdoctoral Program, NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, 4NASA Ames Research Center, Moffett Field, CA 94035, 5JETS/Jacobs Technology, Inc. at NASA Johnson Space Center, Houston, TX 77258, 6Ecole Centrale Paris, 92295 Chatenay-Malabry, France, 7LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS 94010 Créteil, France, 8NASA Johnson Space Center, Houston TX 77058, 9Carnegie Institution of Washington, Washington, DC 20015, 10LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, 11Georgia Institute of Technology, Atlanta, GA 30332.

Introduction: The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover detected both reduced and oxidized nitrogen-bearing compounds during the pyrolysis of surface materials at Yellowknife Bay in Gale Crater. Preliminary detections of nitrogen species include NO, HCN, CICN, CH3CN, and TFMA (trifluoro-N-methyl-acetamide). Confirmation of indigenous Martian N-bearing compounds requires quantifying N contribution from the terrestrial derivatization reagents (e.g. N-methyl-N-tert-butylidimethylsilyltrifluoroacetamide, MTBSTFA and dimethylformamide, DMF) carried for SAM’s wet chemistry experiment that contribute to the Sam background [1]. Nitrogen species detected in the SAM solid sample analyses can also be produced during laboratory pyrolysis experiments where these reagents are heated in the presence of perchlorate, a compound that has also been identified by SAM in Mars solid samples [1].

Methods: Curiosity’s first drill hole was at John Klein (JK), a mudstone in the Sheepbed member of the Yellowknife Bay formation in Gale Crater. The JK Evolved Gas Analysis (EGA) experiments consisted of one blank, three single-portion (45 ± 18 mg) samples [2], and one triple portion sample. A second hole was drilled at Cumberland (CB), ~3 meters from JK. Cumberland EGA experiments included two blanks, four single portions (CB1, 2, 3, 5), two triple portions CB6, CB7), and a run where CB6 residue was pyrolyzed after being re-exposed to the Sample Manipulation System (SMS) on SAM, where it would have come into contact with MTBSTFA/DMF. EGA experiments CB1-5 involved pre-heating the sample at <70°C for 25 minutes, then ramping the oven to ~835°C (sample temperature) in a stream of 30 mb He at ~0.8 scm at a ramp rate of 35°C/min. In experiments CB6, CB7, sample was delivered to a hot cup (~285°C) and heated for 25 minutes prior to the ramp to 835°C. All gas was analyzed by EGA-MS. In each experiment, gases evolved over selected temperature ranges were analyzed by GCMS, which was used to positively identify N-bearing species by comparison to the NIST standard database.

Preliminary Results: The most abundant N-bearing species in all runs was m/z 30, NO, present up to ~390 nmol in CB3. The second most abundant compounds are m/z 27, HCN, and m/z 41, CNCH3, both present at ~40 nmol. CNCH3 is consistently present as a broad peak in blank runs. Also present in trace amounts are CICN and TFMA, the latter being a decomposition product of MTBSTFA.

John Klein Experiments: Fig. 1 shows the distribution of N compounds for each run. NO comprises the largest fraction of N species, and is present at 160 nmol in single portions JK1 and JK2 and at 390 nmol in triple portion JK3. JK1-3 employed a temperature hold at ~325°C for 25 minutes, during which a significant portion of volatile species were removed. Most NO is removed during this “boil off,” suggesting that it comes from a volatile source, while a smaller amount (30-100 nmol) is evolved around 400°C. Evolution of NO at these temperatures has been attributed to thermal decomposition of nitrate [3,4,5].

Cumberland Experiments: Midway through the Cumberland campaign, the EGA experimental procedure was optimized in order to remove MTBSTFA and products of its decomposition, including N-species.

Figure 1. Nitrogen bearing compounds evolved during pyrolysis of John Klein drilled samples.
produced by breakdown of MTBSTFA. Prior to run CB6, samples were heated to $<70^\circ$ C (sample temperature) and held for 25 minutes. Because of the persistence of MSW, BSW, and TBDMS-F, products of MTBSTFA decomposition, samples in experiment CB6 and CB7 were delivered to a hot cup ($\sim 285^\circ$ C) to avoid transfer of MTBSTFA, then held at this temperature to “boil off” these and other possible decomposition products of MTBSTFA.

This method was successful in reducing MTBSTFA contributions to EGA. Fig. 2 shows total and individual abundance of N species for each run. All N compounds decrease in abundance when the hot cup delivery is employed, suggesting loss of volatile N compounds, including those associated with MTBSTFA. However, it is difficult to determine whether some species, such as HCN, are no longer present in experiments CB6 and CB7 because they are products of MTBSTFA decomposition, or because they are indigenous but removed due to their volatility.

**Discussion:** Confirmation of indigenous martian nitrogen in solid samples is complicated by the fact that pyrolysis of MTBSTFA in the presence of perchlorate evolves all of the N-bearing compounds detected. However, we can put constraints on the total abundance of MTBSTFA, and thus, the terrestrial N contribution, to an experiment. Total MTBSTFA present in a sample can be estimated from quantifying the three major decomposition products of MTBSTFA: monosilylated water (m/z 127), bisilylated water (m/z 147), and TBDMS-F. MTBSTFA and DMF molecules each contain one N atom. The MTBSTFA:DMF ratio is 4:1, which is used to calculate DMF derived nitrogen. Fig. 3 shows the estimated nanomoles of N contributed by MTBSTFA/DMF compared to the total nanomoles N as measured by SAM. The total nanomolar concentration of all nitrogen species is orders of magnitude greater than estimated N contribution from MTBSTFA/DMF. Fig. 4 shows the estimated nanomoles of N contributed by MTBSTFA/DMF compared to N from TFMA, a fluorinated compound formed by decomposition of MTBSTFA. Based on this quantification, it is reasonable to assume that the majority of the N contributed by MTBSTFA can be accounted for by the formation of TFMA. This data suggests the presence of indigenous martian N-bearing compounds, detected as NO in SAM. The presence of indigenous volatile N compounds such as HCN cannot be ruled out, as they will not be seen in any analysis optimized to remove MTBSTFA.

**References:**

Figure 2. Nitrogen compounds evolved during pyrolysis of Cumberland drilled samples. Higher temperature boil-off reduces abundance of MTBSTFA-derived compounds as well as any other volatile martian N-bearing compounds that may be present.

Figure 3. Nanomole N calculated from the sum of all detected nitrogen-bearing compounds in non-blank samples is orders of magnitude greater than the nanomole nitrogen estimated to be contributed by MTBSTFA/DMF.

Figure 4. The molar abundance of nitrogen from MTBSTFA/DMF in non-blank samples is similar to the molar abundance of nitrogen in TFMA.