DETECTION OF NITRIC OXIDE BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT. IMPLICATIONS FOR THE PRESENCE OF NITRATES.

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Introduction: One of the main goals of the Mars Science Laboratory is to determine whether the planet ever had environmental conditions able to support microbial life. Nitrogen is a fundamental element for life, and is present in structural (*e.g.*, proteins), catalytic (*e.g.,* enzymes and ribozymes), energy transfer (*e.g.,* ATP) and information storage (RNA and DNA) biomolecules. Planetary models suggest that molecular nitrogen was abundant in the early Martian atmosphere, but was rapidly lost to space by photochemistry, sputtering [1, 2], impact erosion [3], and oxidized and deposited to the surface as nitrate [4]. Nitrates are a fundamental source for nitrogen to terrestrial microorganisms. Therefore, the detection of nitrates in soils and rocks is important to assess the habitability of a Martian environment. SAM is capable of detecting nitrates by their thermal decomposition into nitric oxide, NO [5]. Here we analyze the release of NO from soils and rocks examined by the SAM instrument at Gale crater, and discuss its origin.

Samples and Methods: Rocknest soil of an inactive, sandy wind drift mantled with dust dune, and two drill holes: John Klein (JK) and Cumberland (CB), from mudstones in the Sheepbed member of the Yellowknife Bay formation, located in Gale Crater, were analyzed by the SAM instrument. The samples collected by Curiosity's solid sample acquisition and handling system called CHIMRA was sieved to <150 µm, portioned (<76 mm^3), and single or triple portion aliquots were delivered to individual SAM cups. Prior to sample analysis, a blank was run using an empty quartz cup to characterize the background of the SAM instrument. The quartz cup was sealed inside the pyrolysis oven and heated to ~840°C at a rate of 35°C/min under a He carrier gas flow rate of 1.5 cm^3/min and at an oven pressure of ~30 mb. A small fraction of the gas released from the cup was measured directly by electron impact quadrupole mass spectrometry (QMS) [6]. For some runs, a sample preheating was employed prior to pyrolysis to reduce the *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) and dimethylformamide (DMF) background.

Results and Discussion: Figure 1 shows the evolution of mass/charge (m/z) 30 as a function of temperature in three samples, where each m/z 30 pyrogram suggests a complex evolution of contributing volatiles in the temperature range from 150°C to 600°C. M/z 30 can be attributed to the following chemical species: nitric oxide (NO^+), ethane ($C_2H_6^+$), formaldehyde ($HCHO^+$), diazene ($N_2H_2^+$), aluminum trihydride (AlH_3^+), and silylene (SiH_2^+). NO and C_2H_6 are likely contributors to the signal m/z 30 in the samples. HCHO has not been observed by TLS experiments. Diazene is an unlikely product as is very unstable and readily decomposes into N_2 and H_2. Aluminum trihydride and silylene are very unstable in the presence moisture and decomposes.
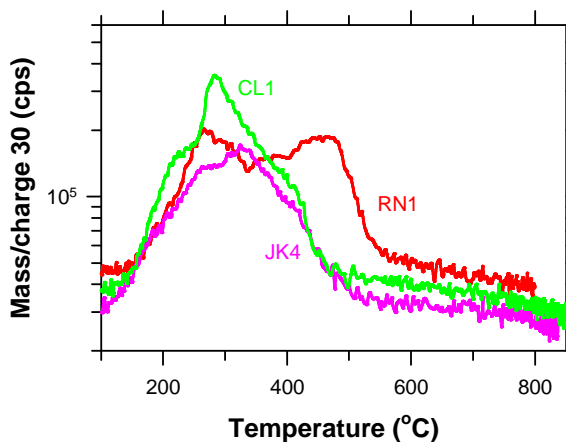
Figure 1. Release of m/z 30 versus temperature from Rocknest (RN), John Klein (JK) and Cumberland (CB) samples as measured by SAM.

Other plausible contributions to m/z 30 include an isotopologue of CO, $^{12}C^{18}O$ arising from the electron

impact ionization of CO and CO_2 and isotopologues of HCN, $H^{13}C^{15}N$ or $D^{13}C^{14}N$. In addition other molecules have ionization fragments at m/z 30 such as N_2O, NO_2, N_2H_4, CH_3OH and HCO_2H. N_2O, NO_2, if formed, cannot be directly examined by SAM as they are masked by CO_2 and $^{12}C^{18}O^{16}O$, respectively.
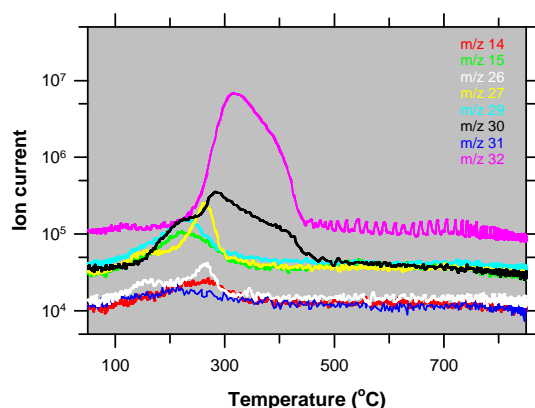
Figure 2. Selected signals versus temperature from CB1 as measured by SAM.

Figure 2 shows the signals arising from the following m/z values 14, 15, 26, 27, 29, 31 and 32 in comparison to m/z 30 during pyrolysis of a Cumberland drilled sample (CB1) with no boiloff used to remove the contribution MTBSTFA and DMF. The signals m/z 14, 15, 26, 27, 29 and 31 attributable to various carbon and nitrogen components (N^+, CH_2^+, NH^+, CH_3^+, CN^+, $C_2H_2^+$, CN^{15+}, HCN, $C^{13}N^+$, $C_2H_3^+$, $C_2H_5^+$, $C^{13}O$, $^{13}C^{12}CH_6^+$, $^{13}C^{18}O^+$, and CF^{3+} a known fragment of MTBSTFA) correlate to the initial shoulder of the m/z 30 signal prior to the evolution of molecular oxygen (m/z 32). It is assumed that any simple carbon and nitrogen volatiles evolving with O_2 are oxidized in the oven resulting in net effect to m/z 30.
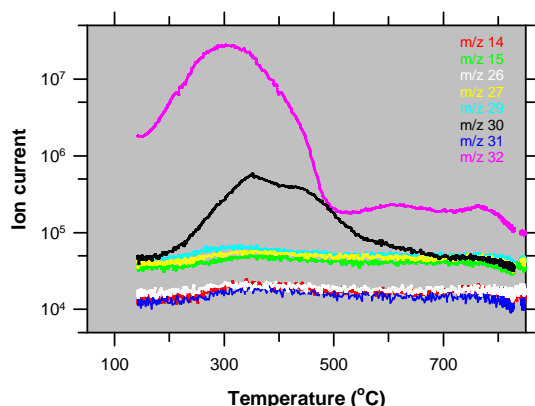
Figure 3. Selected signals versus temperature from CB6 as measured by SAM.

Figure 3 shows same signals as in Figure 2 from the pyrolysis of another Cumberland drilled sample (CB6), in which an MTBSTFA-reduction protocol was implemented that involved sample delivery to a hot cup and extra helium flushing as the cup was put in the oven. Surprisingly, the initial shoulder in the m/z 30 signal of CB disappears suggesting it may be related to MTBSTFA, DMF or thermally desorbed sample components. Interestingly, most of the m/z 30 signal evolves after the O_2 evolution in CB6, suggesting that it is not entirely dependent on the oxidation of a sample component. Assuming most volatile components contributing to the remaining CB m/z 30 signal are negligable, NO and possibly ethane are the most significant contributors.

We have previously discussed that the release of NO at temperatures ≥ 200°C could be attributed to the thermal decomposition of nitrates in the presence of perchlorates [6]. The thermal decomposition of iron nitrates is also feasible. The contribution of NO from terrestrial contamination (MTBSTFA) has been estimated to be small [7]. C2 hydrocarbon contributions might be expected if organic components are degrading at <600°C temperatures (e.g., 8) Therefore, these results are consistent with the existence of nitrates and possible organic matter in the Sheepbed mudstone at Gale Crater [9].

References: [1] Luhmann, J.G. et al. (1992), *GRL*, 19, 2151-2154. [2] Jakosky, B.M. et al. (1994), *Icarus,* 111, 271–288. [3] Melosh, H.J. & Vickery, A.M. (1989), *Nature*, 338, 487–489. [4] Mancinelli, R.L. & McKay, C.P. (1988), *Origins Life* 18, 311–325. [5] Navarro-González, R. et al. (2013), 44th LPSC, 2648. [6] Mahaffy, P. *et al.* (2012) *Space Sci Rev, 170,* 401-478. [7] Stern, J.C. et al., this meeting. [8] Eigenbrode, J. et al., this meeting. [9] Support from the following grants is acknowledged: IN106013 and CONACYT 98466.