POSSIBLE DETECTION OF NITRATES ON MARS BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT.

R. Navarro-González[1], J. Stern[2], B. Sutter[3], D. Archer[3], A. McAdam[2], H.B. Franz[2], C.P. McKay[4], P. Coll[5], M. Cabane[6], D.W. Ming[3], A.E. Brunner[2], D. Glavin[2], J.L. Eigenbrode[2], J.H. Jones[3], C. Freissinet[2], L. Leshin[7], M. Wong[8], S. Atreya[8], J.J. Wray[9], A. Steele[10], A. Buch[10], B.D. Prats[2], C. Szopa[6], D. Coscia[6], S. Teinturier[6], P. Conrad[2], P. Mahaffy[2], and the SAM Team, [1]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, navarro@nucleares.unam.mx, [2]NASA Goddard Space Flight Center, Greenbelt, MD 20771, [3]NASA Johnson Space Center, Houston TX 77058, [4]NASA Ames Research Center, Moffett Field, CA 94035, [5]LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, [6]LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, [7]Rensselaer Polytechnic Institute, Troy, NY 12180, [8]University of Michigan, Ann Arbor, MI 48109, [9]Georgia Institute of Technology, Atlanta, GA 30332, [10]Geophysical Laboratory, Washington, DC 20015, [10]Ecole Centrale Paris, LGPM, 92295 Châtenay-Malabry, France.

Introduction: Planetary models suggest that nitrogen was abundant in the early Martian atmosphere as dinitrogen (N_2). However, it has been lost by sputtering and photochemical loss to space [1, 2], impact erosion [3], and chemical oxidation to nitrates [4]. Nitrates, produced early in Mars' history, are later decomposed back into N_2 by the current impact flux [5], making possible a nitrogen cycle on Mars. It is estimated that a layer of about 3 m of pure $NaNO_3$ should be distributed globally on Mars [5]. Nitrates are a fundamental source for nitrogen to terrestrial microorganisms. Therefore, the detection of soil nitrates is important to assess habitability in the Martian environment. The only previous mission that was designed to search for soil nitrates was the Phoenix mission but was unable to detect evolved N-containing species by TEGA and the MECA WCL [6]. Nitrates have been tentatively identified in the Nakhla meteorite [7]. The purpose of this work is to determine if nitrates were detected in first solid sample (Rocknest) in Gale Crater examined by the SAM instrument.

Materials and Methods: Samples collected from Rocknest, located in Gale Crater, which consists of an inactive, sandy wind drift mantled with dust, were analyzed by the SAM instrument. 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 He carrier gas flow. A small fraction of the gas released from the cup was measured directly by electron impact quadrupole mass spectrometry (QMS mass range 2-535 Da, resolution 0.1 Da). Then four samples of rocknest bedform materials < 150 µm diameter size fraction (~20 mg), which consisted mostly of uconsolidated sand and dusty material, were examined by SAM. A thermal analyzer (Netzsch STA 449 F1 Jupiter Simultaneous TG/DSC) coupled to a mass spectrometer (Netzsch QMS 403 C Aeolos) has been configured in the laboratory to operate similar to the SAM oven/QMS system. Several mixtures of perchlorates, nitrates, and ammonium salts were analyzed and results utilized to assist in SAM data interpretation.

Results and Discussion: Nitrates generally decompose into nitric oxide (NO) and O_2 at temperatures above 560°C and up to 900°C [8]. Figure 1 shows the evolution of mass/charge (m/z) 30 as a function of temperature in a blank and the four portions of a scooped sample (Scoop#5) collected at the Rocknest site. There appear to be at least three peaks associated with the release of m/z 30: the first centered at 280°C, the second at 380°C, and the third at 460°C. M/z 30 was identified as NO using the NIST database, which reports the ratio of (m/z 14)/(m/z 30) in NO as 0.075. Other plausible contributions to m/z 30 include an isotopologue of CO, $^{12}C^{18}O$. Surprinsingly the evolution of m/z 30 in the Rocknest samples is well below the expected thermal decomposition of nitrates. However, the lowest temperature peaks (~200° - 300°C) have the best spectral match for NO based on (m/z 14)/(m/z 30) ratios, and diverge from the CO_2 trace (as represented by m/z 45). The higher temperature peaks (>300° C) track with m/z 45 and may represent some contribution of $^{12}C^{18}O$ to m/z 30.

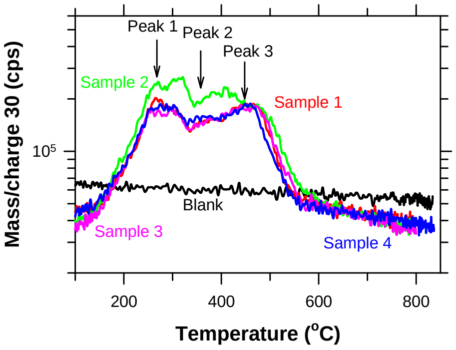

Figure 1. Release of m/z 30 versus temperature from the blank and Rocknest samples as measured by SAM.

Since perchlorates have been detected on Mars [6], we have investigated their interaction effect on the thermal decomposition of nitrates. Thermal decomposition of metal (M) perchlorates follows two reaction paths: Reaction 1 for alkali metals (M^1) or group 1 (Na, K, etc): $M^1ClO_4 \rightarrow M^1Cl + 2O_2$; and, reaction 2 for alkaline earth metals (M^2) or group 2 (Be → Ba except for Ca and Mg): $2M^2(ClO_4)_2 \rightarrow 2M^2O + 2Cl_2 + 7O_2$; however, for Ca- and Mg-perchlorates reactions 1 and 2 are equally important. Therefore, we conducted experiments on the effect of Na-perchlorate on the decomposition of Mg-, Ca-, Na-, and K-nitrates and found no effect. The decomposition of nitrates with Mg-perchlorate is enhanced as more perchlorate is added to the mixture (Figure 2). This effect is probably due to the reaction of HCl with nitrates derived from hydrated Mg-perchlorate decomposition [e.g., 9] according to the following reactions: (1) $M^1NO_3 + HCl \rightarrow M^1Cl + HNO_3$; and (2) $M^2(NO_3)_2 + 2HCl \rightarrow M^2Cl_2 + 2HNO_3$. HCl arises by the reaction of Cl_2 with water vapor, and HNO_3 thermally decomposes into NO, water, and O_2.

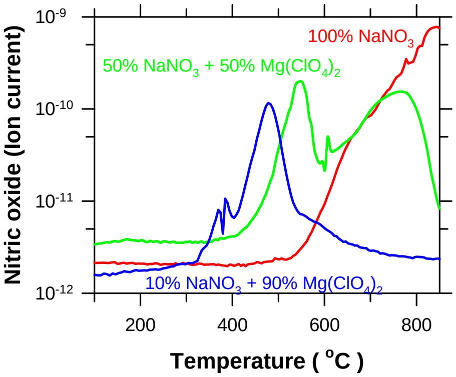

Figure 2. Effect of magnesium perchlorate on the thermal stability of Na-nitrate in laboratory experiments.

We investigated the thermal stability of Mg-, Ca-, Na-, and K-nitrates by monitoring NO released during thermal analysis which spans from 330°C to 600°C (Figure 3), and from 360°C to 650°C (data not shown), in the presence of Mg- and Ca-perchlorate, respectively. These values may be consistent with the second and third evolved NO peaks but cannot explain the evolution of NO at 280°C in Rocknest materials. A possible explanation that we are exploring is the presence of chlorate and chlorite species in the soil. To date we have conducted experiments with Na-chlorate and chlorite. While the release of O_2 as a function of temperature is decreased, the temperature of NO evolution is significantly increased, probably because HCl is not produced. It is possible that Mg- or Ca-chlorates or chlorites can explain the observed temperature of evolution of NO in the martian soil. Experiments are currenlty underway to examine Ca- and Mg-chlorate/chlorite interactions with nitrates.

Another possibility to explain the evolution of the first peak is the presence of NH_4^+ in the soil [10], which undergoes combustion in the presence of perchlorates leading to the formation of NO. Figure 4 shows the evolution of NO by different ammonium salts. Ammoniun nitrate would probably explain the behavior observed for the first peak. However, we are exploring the possibility that the first peak could also arise from terrestrial contamination from MTBSTFA known to be present in the system [11, 12].

Further work is underway to fully understand the release of NO in the Rocknest samples.

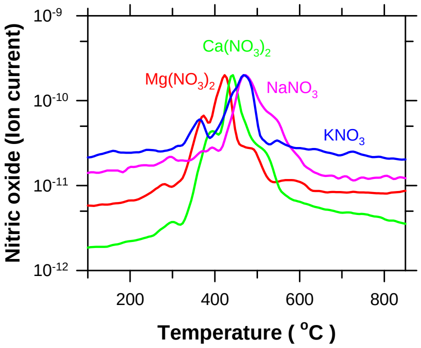

Figure 3. Thermal stability of different (10%) nitrates in the precence of (90%) magnesium perchlorate in laboratory experiments.

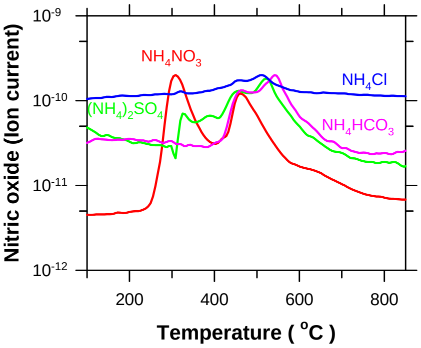

Figure 4. Combustion of (10%) ammonium salts in the presence of (90%) magnesium perchlorate in laboratory experiments.

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