
Introduction: Planetary models suggest that nitrogen was abundant in the early Martian atmosphere as dinitrogen (N2). 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 N2 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 NaN3 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 unconsolidated 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 O2 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, 13C18O. Surprisingly 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 CO2 trace (as represented by m/z 45). The higher temperature peaks (>300° C) track with m/z 45 and may represent some contribution of 13C18O 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 decomp-
osition of metal (M) perchlorates follows two reaction paths: Reaction 1 for alkali metals (M\(^1\)) or group 1 (Na, K, etc): \(\text{M}^1\text{ClO}_4 \rightarrow \text{M}^1\text{Cl} + 2\text{O}_2\); and, reaction 2 for alkaline earth metals (M\(^2\)) or group 2 (Be → Ba except for Ca and Mg): \(2\text{M}^2\text{(ClO}_4\text{)}_2 \rightarrow 2\text{M}^2\text{O} + 2\text{Cl}_2 + 7\text{O}_2\); 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) \(\text{M}^1\text{NO}_3 + \text{HCl} \rightarrow \text{M}^1\text{Cl} + \text{HNO}_3\); and (2) \(2\text{M}^2\text{(NO}_3\text{)}_2 + 2\text{HCl} \rightarrow 2\text{M}^2\text{Cl}_2 + 2\text{HNO}_3\). HCl arises by the reaction of Cl\(_2\) with water vapor, and HNO\(_3\) thermally decomposes into NO, water, and O\(_2\).

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. Ammonium 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 presence of (90%) magnesium perchlorate in laboratory experiments.

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