CURIOSITY'S SAMPLE ANALYSIS AT MARS (SAM) INVESTIGATION: OVERVIEW OF RESULTS FROM THE FIRST 120 SOLS ON MARS.

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Introduction: During the first 120 sols of Curiosity's landed mission on Mars (8/6/2012 to 12/7/2012) SAM sampled the atmosphere 9 times and an eolian bedform named Rocknest 4 times. The atmospheric experiments utilized SAM's quadrupole mass spectrometer (QMS) and tunable laser spectrometer (TLS) while the solid sample experiments also utilized the gas chromatograph (GC). Although a number of core experiments were pre-programmed and stored in EEProm, a high level SAM scripting language enabled the team to optimize experiments based on prior runs.

SAM and its Initial Experiment Sequences: The SAM instruments, its gas processing system (GPS) and its sample manipulation system (SMS) have been described [1]. During the first few weeks of the landed mission SAM carried out instrument health checks and then began a series of experiments to measure atmospheric composition and isotope ratios. SAM was operated 39 times in the first 120 sols for commissioning and science activities. From sol 56 to 102 Curiosity lingered at Rocknest to clean out the surfaces of the sample processing system by scooping several times into this fine grained material, vibrating to abrade possible contaminants from surfaces, and then discarding before finally delivering sample to SAM.

Atmospheric Mixing Ratios of CO_2, Ar, N_2, O_2, and CO: The mixing ratios of the 5 most abundant gases as measured by the QMS are shown in Figure 1. Significant differences discussed in this meeting [2] are present from the Viking results for Ar and N_2, while results for the other gases are consistent with Viking. Calibration and data reduction methods are summarized by Trainer et al. [3]. In the first 120 sols on Mars the atmosphere has only been sampled at night but to search for diurnal variations day time measurements are also planned.

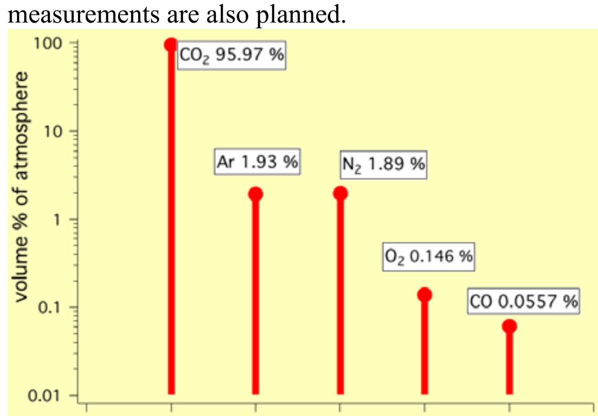

Figure 1. Volume mixing ratios for major atmospheric species. In contrast, Viking reported 2.7% and 1.6% for N_2 and Ar mixing ratios respectively.

Atmospheric Methane: After the two sequences that combined QMS and TLS experiments, dedicated scripts were developed for each instrument to increase integration time and secure improved S/N for the trace methane detection. The six runs that exercised the SAM TLS IC laser have produced, to date, a 2 sigma upper limit of 3.5 ppb volume mixing ratio [4] from direct atmospheric sampling into the TLS. The methane enrichment experiment has not yet been run.

Atmospheric Isotope Ratios: $^{40}Ar/^{36}Ar$ determined by introducing gas from the GPS manifold in dynamic mode through a small capillary leak into the

QMS is ~1.9x10^3 [5]. The CO_2 $\delta^{13}C$ of ~45 per mil given by the QMS [6] is consistent with that derived from the TLS [6]. $\delta^{18}O$ measured by the TLS [7] shows that the O in CO_2 is also substantially heavier than the terrestrial average. Future SAM atmospheric experiments are planned to include gas enrichment sequences to measure the abundance and isotopic composition of Kr and Xe, to refine the $^{38}Ar/^{36}Ar$ and $^{15}N/^{14}N$ ratios.

Gases Evolved from Rocknest Samples: The major volatiles (Figure 2) released from Rocknest samples heated to ~835°C are H_2O, CO_2, SO_2, and O_2. Molar ratios of these gases are given by Archer et al. [8]. The high temperature component of the evolved CO_2 can be interpreted [9] as decomposition of an Fe or Mg carbonate. Likewise, the evolved SO_2 may be derived from a sulfate or sulfide [10]. Support for the suggestion that the evolved O_2 is produced from the decomposition of a perchlorate [11] such as $Ca(ClO_4)_2$ comes from the evolution of simple chlorinated compounds [12,13] coincident with the O_2. Water at several weight percent was the most abundant gas released from these samples with possible or likely minor species H_2S, HCN, C_2H_3N, and NO also detected [14,15,16].

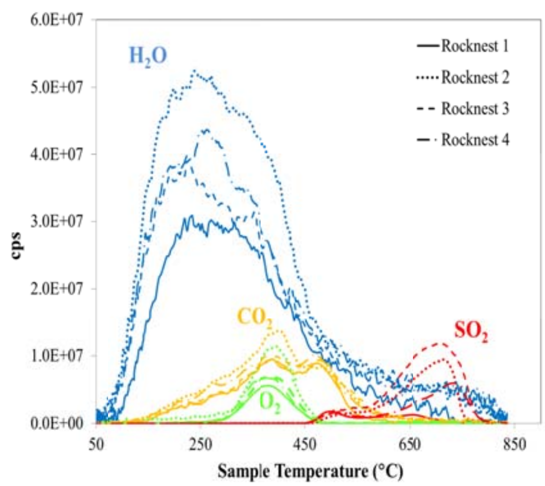

Figure 2. Major gases from Rocknest samples.

Isotope Results from Evolved Rocknest Gases: Isotope ratios that can be derived, to date, from Rocknest EGA gases are $\delta^{13}C$ and $\delta^{18}O$ in CO_2, D/H in H_2O, $\delta^{18}O$ in O_2, and $\delta^{34}S$ in SO_2. While refined analysis of these data is in progress, prelimary results have been reported [4,6,7,16,17]. The $\delta^{34}S$ is consistent with martian meteorites and the D/H of ~5 times terrestrial is consistent with spectroscopic measurements [18].

Rocknest GCMS Results: All elements of the GCMS system including thermal conductivity detectors of the GC system performed as designed [19]. Four chlorinated compounds [12,13] (as well as H_2O, SO_2, & HCN) were detected by the SAM GCMS analysis of the first three Rocknest samples. In addition, several products of residual MTBSTFA (N-Methyl-N-tert-butyldimethylsilyltrifluoroacetamide) were found to be present in the SMS and detected both in the direct and the GCMS parts of the sequence. Derivitized water and a silylated chlorine compound [20,21] were among the compounds derived from this residual vapor.

Discussion: The SAM results, to date, represent a significant step toward realizing some of the core mission objectives. Both the revised-from-Viking Ar/N ratio and preliminary $^{15}N/^{14}N$ ratios show consistency with the atmospheric composition derived from meteoritic data and comparison of the isotopic composition of the current atmosphere with the same elements in ALH 84001 [22] may allow us to take further steps in understanding changes in the atmosphere over billions of years. The Rocknest EGA-TLS-GCMS data set is consistent with perchlorate detection by Phoenix and chloromethane and dichloromethane by Viking. Steps will be taken before analysis of the next set of solid samples to minimize the effects of the MTBSTFA since this may be the source of carbon in the simple chlorinated compounds detected by SAM. It is significant that while derivatized water is detected, no complex derivatized organics, chlorinated organic compounds that might have been produced from a perchlorate, or other organic compounds were detected by the GCMS experiment. UV radiation, high energy cosmic particles, degradation by H_2O_2 or other oxidants are among the processes that may have conspired to remove organic componds from surface exposed materials such as the fines of Rocknest.

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