NITROGEN ON MARS: INSIGHTS FROM CURIOUSITY. J. C. Stern1, B. Sutter2, W. A. Jackson3, Rafael Navarro-González4, Christopher P. McKay5, Douglas W. Ming6, P. Douglas Archer2, D. P. Glavin1, A. G. Fairen7,8 and Paul R. Mahaffy1. 1NASA GSFC, Code 699, Greenbelt, MD 20771, jennifer.c.stern@nasa.gov, 2 Jacobs, NASA Johnson Space Center, Houston, TX 77058, 3Texas Tech University, Lubbock, TX 79409, 4Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, 5NASA Ames Research Center, Moffett Field, CA 94035, 6NASA Johnson Space Center, Houston TX 77058, 7Centro de Astrobiología, Madrid, Spain, 8Cornell University, Ithaca, NY 14853

Introduction: Recent detection of nitrate on Mars [1] indicates that nitrogen fixation processes occurred in early martian history. Data collected by the Sample Analysis at Mars (SAM) instrument on the Curiosity Rover can be integrated with Mars analog work in order to better understand the fixation and mobility of nitrogen on Mars, and thus its availability to putative biology. In particular, the relationship between nitrate and other soluble salts may help reveal the timing of nitrogen fixation and post-depositional behavior of nitrate on Mars. In addition, in situ measurements of nitrogen abundance and isotopic composition may be used to model atmospheric conditions on early Mars.

Methods: The data presented are from analyses of solid Martian drilled and scooped samples by the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover. SAM performs evolved gas analysis (EGA), in which a sieved (<150 μm) and portioned (~76 mm3) sample is delivered into one of SAM’s quartz-glass cups and is subsequently heated from Mars ambient temperature to ~870 °C [2]. Gas evolved during pyrolysis is continuously monitored using the quadrupole mass spectrometer (QMS), and a portion of this gas can be sent to the hydrocarbon trap (Tenax®) for gas chromatograph – mass spectrometer (GC-MS) analysis. The SAM instrument and the quantification of nitrate and perchlorate has been described in detail elsewhere [3]. Briefly, nitrate and perchlorate are identified and quantified by their thermal decomposition products, NO and O2, respectively.

Results: Nitrate abundance reported by SAM in situ measurements ranges from non-detection to 681 ± 304 mg/kg [1] in the samples examined to date. Recent evolved gas measurements from Oudam (OU) and Marimba (MB) in the Murray formation represent the only samples SAM has measured so far in which no volatile perchlorate decomposition products were detected. This has fundamental implications on the geochemical history of Mars, and may be the first definitive evidence that perchlorate formation has not been pervasive at all times and places, challenging previous implications of Curiosity’s analysis [4]. Nitrate was similarly below detection limits at MB and present at low abundance at OU (85 ± 35 mg/kg). Samples from the rest of the Murray and Stimson formations were relatively low in both nitrate and perchlorate when compared to eolian materials, with the exception of Buckskin (BK) in the Murray Formation.

Discussion: The linear correlation (Figure 1) between nitrate and perchlorate reflects the consistent nitrate/perchlorate (average NO3- /ClO4- = 0.2 ± 0.1) of the sampled materials. The similarity in NO3- /ClO4- among all sedimentary rock samples measured thus far from Gale suggests one of two scenarios: 1) Constant accumulation rates for nitrate and perchlorate, where differences in measured abundances represent differences in exposure time and/or local environmental enrichment, or 2) Variable deposition of nitrate and perchlorate over the millions of years of sedimentation of Gale Crater sediments, where post-depositional processes have averaged NO3- /ClO4- and abundances are dependent upon exposure to diagenetic fluids.

Constant accumulation: The lack of variation in NO3- /ClO4- is consistent with steady state processes of production and possibly loss of both species over the time of sediment deposition represented by the formations sampled by SAM/MSL at Gale Crater. Such steady state processes have been observed in the most hyper-arid places on Earth such as University Valley in
samples, consistent with the notion that these materials are locally sourced. Although RN contains a small portion of global martian dust [9], it is otherwise thought to be locally sourced, and its ratio is consistent with the CB and JK samples from nearby Yellowknife Bay. GB1 and GB2 materials were taken from Bagnold dunes that are active today and likely locally sourced based on their larger particle size (>45-500 µm).

**Timing of nitrate deposition:** While little is known regarding the timescales over which nitrate and perchlorate deposition occurred, comparisons of NO$_3^-$/ClO$_4^-$ measured in rocks of various ages and in global martian dust could provide a better understanding of when these processes were active, and if they are still active today. Although production of NO in the ionosphere has been reported [10,11], there is no evidence for current dry deposition of nitrate. Therefore, it is possible that all nitrate on Mars is relic, with no modern contribution. This is supported by strong evidence that impact processes may account for the observed nitrate abundances [12]. Therefore, it is likely that all nitrate was formed and deposited prior to or during the emplacement of Gale Crater sediments, and what we see is a mixing of nitrate transported into Gale Crater from elsewhere with an *in situ* component.

The nitrogen isotopic composition ($\delta^{15}$N) of nitrate from an unconsolidated surface sample with a significant component of martian dust may shed light on the timing of nitrogen fixation, as this value would be skewed towards atmospheric N$_2$ ($\delta^{15}$N $\approx$ 574‰[13]) if there is a modern mechanism for nitrogen fixation. $\delta^{15}$N measured in ancient Hesperian rocks at Gale Crater should reflect the $\delta^{15}$N of atmospheric N$_2$ during nitrate deposition and formation, could also be used to constrain atmospheric loss of N$_2$ and the atmospheric pressure at the time of deposition. Therefore, these measurements will a priority for future SAM investigations.