THE NITRATE/PERCHLORATE RATIO ON MARS AS AN INDICATOR FOR HABITABILITY
J. C. Stern1, B. Sutter2, C. P. McKay3, R. Navarro-González4, C. Freissinet5, P. G. Conrad6, P. R. Mahaffy1, P. D. Archer, Jr.7, D. W. Ming8, P. B. Niles9, M. -P. Zorzano2, F. J. Martin-Torres4 and the MSL Science Team. 1NASA Goddard Space Flight Center, Greenbelt, MD, 20771, jennifer.c.stern@nasa.gov, 2Jacobs, NASA Johnson Space Center, Houston, TX 77058, 3NASA Ames Research Center, Moffett Field, CA 94035, 4Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, 5NASA Postdoctoral Program, NASA Goddard Space Flight Center, Greenbelt, MD 20771, 6NASA Johnson Space Center, Houston TX 77058, 7Centro de Astrobiología, Torrejón de Ardoz, Madrid, Spain, 8Instituto Andaluz de Ciencias de la Tierra, Granada, Spain & Division of Space Technology, Luleå University of Technology, Kiruna, Sweden

Introduction: Discovery of indigenous martian nitrogen in Mars surface materials has important implications for habitability and the potential development of a nitrogen cycle at some point in martian history. The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover detected evolved nitric oxide (NO) gas during pyrolysis of scooped aeolian sediments and drilled mudstone acquired in Gale Crater. The detection of NO suggests an indigenous source of fixed N, and may indicate a mineralogical sink for atmospheric N2 in the form of nitrate. The ratio of nitrate to oxchlorine species (e.g. perchlorate) may provide insight into the extent of development of a nitrogen cycle on Mars.

Background: Nitrate and perchlorate on Earth are geochemically similar in arid environments such as the Atacama Desert and the Dry Valleys of Antarcctica due to their similar mobilities and the fact that both accumulate via dry deposition mechanisms [1,2]. Here, low NO3/ClO4 molar ratios (~1000 in the Atacama, ~10,000 in the Dry Valleys) dominate, in comparison to other places on Earth, where the main nitrate source is biological fixation of N2 to NO3, and there is no corresponding biological source of perchlorate, resulting in much higher NO3/ClO4 molar ratios (~50,000). Biological input of NO3 also results in a less significant correlation between the two species, such as in the Mojave Desert [3].

In situ Mars measurements: During SAM’s nominal solid sample analysis mode, evolved gas analysis (EGA) is performed, in which the quadrupole mass spectrometer (QMS) directly analyzes the gases released from samples heated to ~870 °C at 35°C/min under a ~0.8 sccm He flow and a pressure of ~25 mbar in the pyrolysis oven. NO3 abundances are calculated from m/z 30 (NO) abundances. ClO4 was not directly detected but the presence of chlorinated oxidants is inferred from the evolution of O2, HCl, and chlorinated organic compounds [4] during heating of all samples, and is consistent with 0.6 wt. % ClO4 detected by Phoenix [5]. ClO4 equivalents are calculated from O2 abundance [e.g. 6,7].

Results: NO3 and ClO4 are strongly correlated (Figure 1) in results from solid sample EGA performed by SAM at four sample sites in Gale Crater (Rocknest aeolian deposits, John Klein, Cumberland, and Wind-

Figure 1. Linear regression of SAM measurements yield an r² of 0.854, indicating strong correlation between NO3 and ClO4.

jana drill fines), similar to the Atacama and the Dry Valleys of Antarctica, hyperarid environments dominated by dry deposition of photochemically produced nitrates. It is unclear as to whether the correlation of NO3 and ClO4 in Gale Crater sediments is due to formation processes, or reflects similarities in mobility and recondensation of both species after their initial deposition. SAM measurements give NO3/ClO4 molar ratios of ~0.1 for Gale Crater sites (Figure 2). These very low ratios are vastly different than even the Ata-

Figure 2. NO3/ClO4 molar ratios of ~0.1 for Gale Crater sites are low in comparison to terrestrial Mars analogs.

The presence of reduced nitrogen species, which have not been definitively detected, would lend evidence to development of more complex N chemistry than is evident from the presence of nitrates alone. However, reduced N species such as HCN and NH3 are highly volatile and can be difficult to detect by mass spectrometry due to mass interferences with other species. Detection of reduced N could provide evidence for development of either an abiotic or a biological mechanism to both fix N and recycle N back into the atmosphere.

Summary: Nitrates detected on Mars are proposed to represent the establishment of the first half of an abiotic N cycle to fix atmospheric N to a biologically available substrate [9,10]. Currently there is no data to support any abiotic or biological means of recycling N2 back into the atmosphere. Instead, NO3/ClO4 molar ratios <1 suggest that nitrate formation may have been limited to an earlier period in Mars history, prior to atmospheric loss, while ClO4 continues to be produced by current atmospheric processes [eg., 8]. This is in contrast to terrestrial Mars analogs, where accumulation of NO3 even in areas thought to be mostly devoid of biology, such as the Atacama Desert, overturns production and accumulation of ClO4, resulting in NO3/ClO4 ratios >1000.


Figure 3. Mars in situ measurements reveal deviations from nitrate/perchlorate concentrations in terrestrial analogs due to large wt. % of perchlorate in Mars surface materials.