THE NITRATE/PERCHLORATE RATIO ON MARS AS AN INDICATOR FOR HABITABILITY

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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 N_2 in the form of nitrate. The ratio of nitrate to oxychlorine 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 related in arid environments such as the Atacama Desert and the Dry Valleys of Antarctica due to their similar mobilities and the fact that both accumulate via dry deposition mechanisms [1,2]. Here, low NO_3^-/ClO_4^- 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 N_2 to NO_3^-, and there is no corresponding biological source of perchlorate, resulting in much higher NO_3^-/ClO_4^- molar ratios (~50,000). Biological input of NO_3^- 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 ºC at 35ºC/min under a ~0.8 sccm He flow and a pressure of ~25 mbar in the pyrolysis oven. NO_3^- abundances are calculated from m/z 30 (NO) abundances. ClO_4^- was not directly detected but the presence of chlorinated oxidants is inferred from the evolution O_2, HCl, and chlorinated organic compounds [4] during heating of all samples, and is consistent with 0.6 wt. % ClO_4^- detected by Phoenix [5]. ClO_4^- equivalents are calculated from O_2 abundance [e.g. 6,7].

Results: NO_3^- and ClO_4^- 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 Windjana 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 NO_3^- and ClO_4^- in Gale Crater sediments is due to formation processes, or reflects similarities in mobility and reconcentration of both species after their initial deposition. SAM measurements give NO_3^-/ClO_4^- molar ratios of ~ 0.1 for Gale Crater sites (Figure 2). These very low ratios are vastly different than even the Ata-

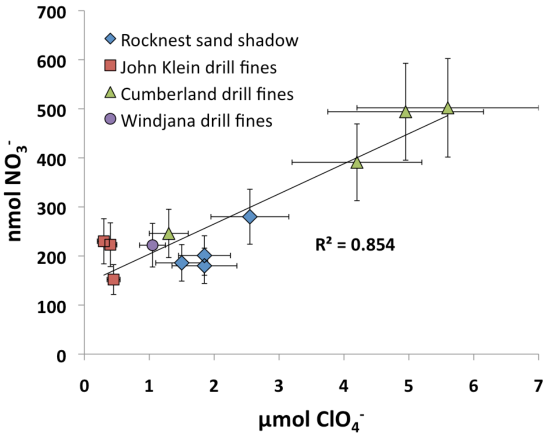

Figure 1. Linear regression of SAM measurements yield an r^2 of 0.854, indicating strong correlation between NO_3^- and ClO_4^-.

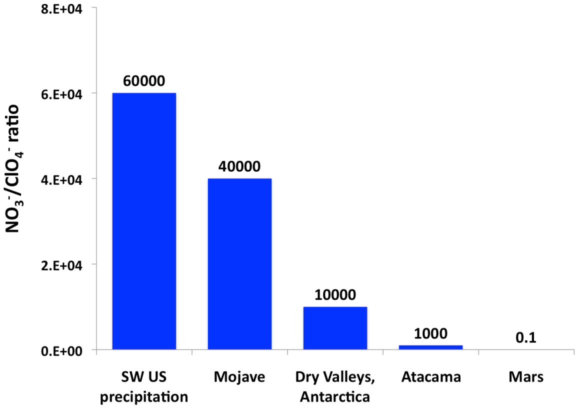

Figure 2. NO_3^-/ClO_4^- molar ratios of ~ 0.1 for Gale Crater sites are low in comparison to terrestrial Mars analogs.

cama due to not only lower NO_3^- abundances on Mars than on Earth, but primarily due to the presence of several weight percent of perchlorate as inferred from SAM data (Figure 3). The low NO_3^-/ClO_4^- ratio at all sites in Gale Crater suggests that N fixation to nitrate on Mars, whether biologically mediated or abiotic, was extremely limited compared to the potentially ongoing abiotic formation and deposition of oxychlorine species on the martian surface [e.g., 8]. It is possible that the nitrate seen in both aeolian deposits at Rocknest and in drilled sediments at John Klein, Cumberland, and Windjana represents N_2 fixation from impacts long ago [e.g., 9,10] and that NO_3^- is no longer being produced in the atmosphere.

Both the NO_3^- abundances and the NO_3^-/ClO_4^- ratios <1 measured by SAM in Gale Crater sediments are consistent with predictions for impact generated nitrates and the notion that nitrates have not been recycled back into atmospheric N_2. Manning et al. [10] calculated an impact generated nitrate reservoir of ~5 x 10^{15} moles on Mars that is unlikely to have experienced significant decomposition. This translates into ~0.11 wt. % NO_3, using a 950 m impact veneer depth [e.g., 10] and a soil density of 2 g/cm^3, and is consistent with the upper limit of our detection of ~0.11 wt % NO_3 in Cumberland drill fines.

Little data for nitrate and perchlorate in Mars meteorites has been published, but recent $\delta^{15}N$ for Elephant Moraine 79001 (EETA 79001) NO_3^- was reported as $\delta^{15}N \approx -10.5‰$[11], lighter than present day Martian atmospheric N_2 at $\delta^{15}N \approx 572‰$ [12], suggesting nitrate in the meteorite is older than the meteorite itself (~173 Mya) and formed prior to atmospheric loss.

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 NH_3 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 N_2 back into the atmosphere. Instead, NO_3^-/ClO_4^- molar ratios <1 suggest that nitrate formation may have been limited to an earlier period in Mars history, prior to atmospheric loss, while ClO_4^- continues to be produced by current atmospheric processes [eg., 8]. This is in contrast to terrestrial Mars analogs, where accumulation of NO_3^- even in areas thought to be mostly devoid of biology, such as the Atacama Desert, outstrips production and accumulation of ClO_4^-, resulting in NO_3^-/ClO_4^- ratios >1000.

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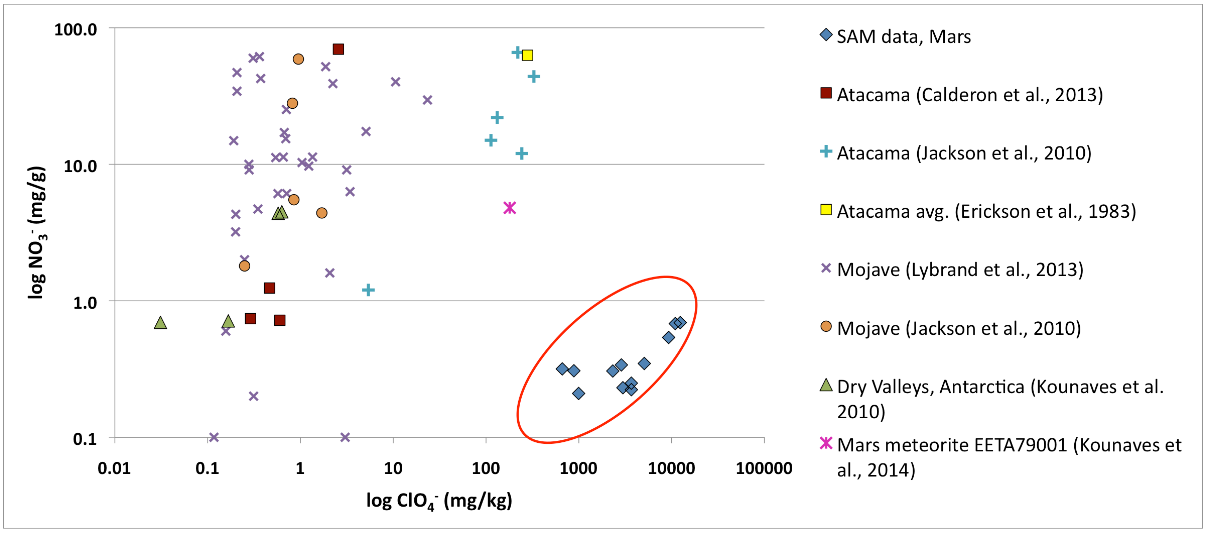

Figure 3. Mars *in situ* measurements reveal deviations from nitrate/perchlorate concentrations in terrestrial analogs due to large wt. % of perchlorate in Mars surface materials.