

NITROGEN AS A BIOSIGNATURE: INSIGHTS FROM CURIOSITY. J. C. Stern¹, B. Sutter², W. A. Jackson³, R. Navarro-González⁴, C. P. McKay⁵, and A. G. Fairen^{6,7}. ¹NASA GSFC, Code 699, Greenbelt, MD 20771, jenifer.c.stern@nasa.gov, ²Jacobs, 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. ⁶Centro de Astrobiología, Madrid, Spain, ⁷Cornell University, Ithaca, NY 14853

Introduction: “Follow the nitrogen” has been proposed as a strategy in the search for both extant and extinct life on Mars [e.g., 1]. Nitrogen is so crucial to life on Earth that life developed metabolic pathways to break the triple bond of N₂ and “fix” atmospheric nitrogen to more biologically available molecules for use in proteins and informational polymers. The origin of biological N fixation was probably triggered by a drop in the available N during the origin of life on Earth [2] or later in biological evolution due to changes in the abiotic N fixation rate [3]. Therefore, the detection of “fixed” N on Mars in the form of nitrate [4] has major implications for martian habitability.

Was there a nitrogen cycle on Mars?: Sequestration of nitrate in regolith has long been predicted to contribute to the removal of N from the martian atmosphere [e.g., 5]. But was this fixed N transformed once deposited, and if so, by what mechanism? An indicator of more complex chemistry would be reduced N, which has, as yet, not been definitively detected on Mars [6]. For example, reduced N in the form of NH₃ or NH₄⁺ would suggest reduction of nitrate by Fe(II) [7], or even biological fixation or ammonification of atmospheric N.

Mars data in context of Earth The goal of this work is to compare terrestrial and martian nitrate and co-occurring species (e.g., perchlorate) to determine if an N cycle has ever occurred on Mars. Extremely arid, low productivity environments on Earth, such as parts of the Atacama Desert and the McMurdo Dry Valleys (MDV) of Antarctica, may represent the best analogs for N cycling Mars. In these environments, microorganisms capable of fixing N instead utilize the available fixed N [8]. Therefore, these environments where abiotic processes dominate, yet the overprinting of life usually persists, may well represent what life on Mars would look like in terms of N chemistry.

On Earth, arid conditions allow accumulation of nitrate and co-occurring perchlorate, similar to what we have reported for Gale Crater materials [9]. Recent work [e.g. 10] has shown that the nitrate/perchlorate ratio (NO₃⁻/ClO₄⁻) on Earth is strongly affected by biological activity, and can help assess biological cycling in a terrestrial environment. A comprehensive study presented a global survey of NO₃⁻/ClO₄⁻ in arid and semi-arid environments and identified three general sets of environments with NO₃⁻/ClO₄⁻ between ~10³ and ~10⁵ [10]. The first set had ratios of 10⁵ and had both contributions of

atmospheric nitrate and biogenic nitrate. The second set had ratios of 10⁴ due to active biological cycling of nitrate that no longer retained atmospheric nitrate isotopic composition. The third set corresponded to hyper-arid sites, including the MDV and Atacama Desert, which had the lowest ratios at 10³ and the largest component of unaltered atmospheric nitrate.

On Mars, NO₃⁻/ClO₄⁻ is <1, massively offset by the greater abundance of perchlorate. Presumably, significant deviation from this ratio could indicate either input or consumption of N, as we see on Earth. In other words, future detections of martian NO₃⁻/ClO₄⁻ that differ from current ratios could reflect nitrification or denitrification, through abiotic or biological processes. Defining the magnitude of deviation suggesting these processes would come from a close examination of the magnitude and causes of the variation of NO₃⁻/ClO₄⁻ in terrestrial Mars analog environments. Variation in samples analyzed by Curiosity thus far (Fig. 1) is within an order of magnitude, similar to the MDV. We hypothesize that we would need to see a deviation of 10²-10³ to suggest either biological or abiotic processing of N on Mars.

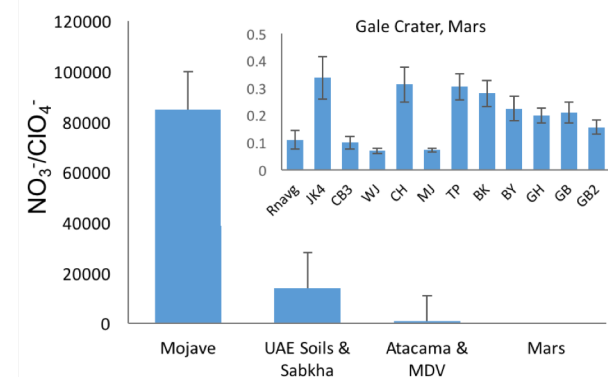


Figure 1. NO₃⁻/ClO₄⁻ on Earth vs. Mars

References:[1] Capone et al. (2006) *Science*, 312(5774), 708-709. [2] Kasting & Siefert, 2001 *Nature*, 412, 26-27. [3] Navarro-Gonzalez et al. (2001) *Nature*, 412, 61-64. [4] Stern et al. (2015) *PNAS*, 112(14), 4245-4250. [5] Mancinelli & Banin (2003) *Int. J. Ast.* 2(3), 217-225. [6] Wray et al. (2013) *LPSC XLIV* Abstract #1719. [7] Summers et al. (2012) *Astrobiology* 12(2), 107-115. [8] Friedmann & Kibler (1980) *Microbial ecology*, 6, 95-108. [9] Stern et al. (2015) *LPSC XLVII* Abstract #1832. [10] Jackson et al. (2015) *GCA* 164, 502-522.