

LABORATORY SEDIMENT COLUMN SIMULATIONS OF CHEMICAL AND REDOX GRADIENTS IN THE MARTIAN GROUNDWATER ENVIRONMENT. R. Y. Sheppard^{1*}, A. A. Fraeman¹, L. M. Barge¹, J. M. Weber¹, L. Rodriguez¹, E. Martinez¹. ¹Jet Propulsion Laboratory, California Institute of Technology. *rachel.y.sheppard@jpl.nasa.gov

Introduction: Landed missions on Mars have observed a complex history of martian subsurface diagenetic fluid flow (e.g., [1-3]). The martian subsurface shows promise as an ancient habitable environment, as it provides protection from harsh surface radiation, available groundwater at least transiently stretching into the Amazonian [1], and available CHNOPS elements necessary for life as we know it. These environments can be investigated with in situ missions, as upwelling of groundwater could have moved biosignatures or environmental indicators of habitability to the surface where they could be observed and explored today.

To understand habitability and subsurface chemical and redox gradients, as well as the connectivity between the subsurface and the easily observable surface, we conducted laboratory flow-through and batch experiments to simulate reactions of Martian groundwater with Mars surface/subsurface soils. We constructed novel sediment columns of Mars regolith simulant and exposed them to a suite of Mars groundwater simulant compositions at different flow-through rates. We seek to study the abiotic martian groundwater environment, specifically the water-rock conditions under which redox gradients can be established. Such gradients could have established redox cycles on Mars, perhaps make elements biologically available and supporting habitable environments at redox interfaces.

Background: Elements coexisting on Mars in multiple oxidation states is of great interest, as oxidation and reduction are common energy sources for microbial communities on Earth [4,5]. When there is abundant redox-sensitive material in an environment, evolutionary pressure can encourage microbial communities to evolve in a complementary way, with one community reducing and one community oxidizing the redox-sensitive material to form a cycle. This can offer an energy source for life, even in the subsurface. Additionally, redox reactions are necessary some make some elements, such as nitrogen, biologically available.

Fe is one example of an abundant redox-sensitive element on Mars that is found in different oxidation states. Fe has been found in multiple oxidation states in Gale crater, chiefly ferrous in primary mafic minerals, mixed valence in magnetite and ferric in hematite [6,7]. Oxidants on Mars include perchlorate, chlorate, peroxide, oxygen, and photooxidation (e.g. [8,9]). Nitrogen is also a redox sensitive element found on Mars [10],

but its ability to cycle through redox states on Mars has not been well studied. Earth's nitrogen cycle is centered around microbial mediation, with biological denitrification maintaining the N_2 in the atmosphere and biological nitrification forming nitrate. Complex nitrogen geochemical cycling pathways can even occur throughout early diagenesis to metamorphism. It is unclear whether a nitrogen cycle can continue in the complete absence of life or whether nitrogen would simply be oxidized from the atmosphere and stored in the subsurface, effectively breaking the cycle.

Fig. 1 shows abiotic processes that may have affected nitrogen on Mars. Atmospheric nitrogen could have been fixed to oxidized nitrogen species via volcanic lightning, thermal shock during impacts, or irradiation [11-18]. Nitrate in meteorites, bedrock, and aeolian samples may have been formed via post-depositional leaching or abiotic fixation mechanisms [10,19]. Reduced nitrogen has not been detected, leaving an open question of whether Mars experienced processes comparable to Earth's biological denitrification, which could have established a primitive nitrogen cycle on Mars and made nitrogen biologically available. If this occurred, what were the rates and mineral products of those reactions, at different sediment depths and times? This would address how coupled these different reservoirs were to each other, and where the most promising habitable environments may have existed.

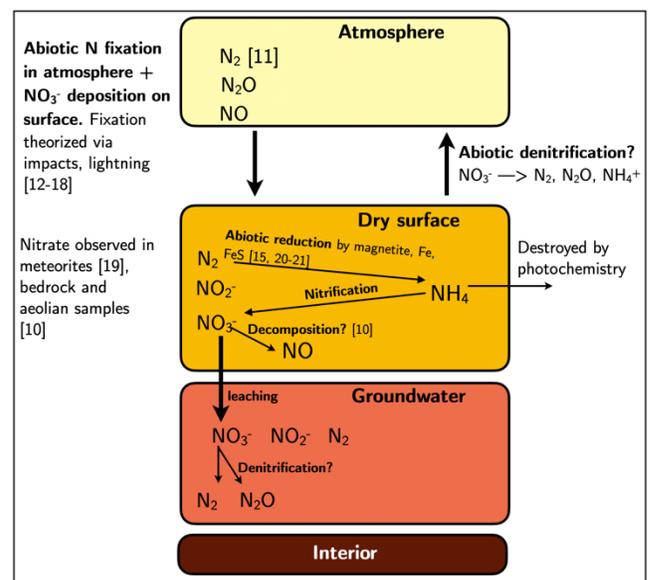


Fig. 1: Possible steps active in a martian N cycle that affect oxidation state and reservoir.

Methods: To identify if there are abiotic pathways by which nitrogen cycling can occur in the martian subsurface, and more broadly to study the chemical and redox gradients that might exist in the Martian subsurface, we constructed sediment columns (Fig. 2) where we can closely monitor simulated Martian soil and groundwater conditions through time. We monitor the chemical and redox gradients that developed within the column during aqueous exposure, and characterize the secondary mineral products. We also expose the column to varying surficial conditions, including an anoxic martian gas analog atmosphere, different geothermal gradients, and photo-oxidation at the surface. This creates an abiotic environment to explore redox cycling that is possible in the martian subsurface. We vary the volume, pH, refresh rate and residence time, and solute concentration of the groundwater simulant in a series of experiments to test the links between environmental conditions, chemical gradients, and changes in nitrate reservoir sizes through time. We measure the solid and liquid through time at different positions in the column through the side ports.

Results and discussion: In these experiments we observe changes in mineralogy in the solid sample and Fe and N oxidation state in the liquid sample through both time (from 0-20 days) and space (depth in the column) as the Mars regolith simulant reacts with the groundwater simulant.

Highly soluble Ca and Mg sulfates are more abun-

dant lower in the column, mobilized from the solid phase by the gravity-driven groundwater (Fig. 2a). The ratio of nitrate:nitrite is time and position dependent (Fig. 2b). Fe oxidation state in the groundwater is time and position dependent, and may be driven by transient changes in fluid pH related to Fe oxidation and reduction (Fig. 2c). Future work will vary the ratios of redox sensitive reactive phases and the geometries of where in the column they are distributed.

Implications and Conclusions: There is growing interest in redox pairs of elements in the martian near-surface environment that could have been an energy source for life and made CHNOPS elements biologically available. Nitrate is highly soluble and easily leached into the groundwater, meaning that the subsurface tends to store more nitrate than the uppermost surface. Additional work will experimentally constrain the active chemical pathways responsible for changing the oxidation state and position of N and Fe in the sediment columns. This work will advance our understanding of how to search for martian habitable environments, both in samples that might be returned from Mars and for future in situ Mars missions. This is relevant as active and upcoming missions are conducting increasingly detailed examinations of the martian subsurface.

References: [1] Martin 2017, *JGR: Plan.*, [2] Sun 2019, *Icarus*, [3] Kronyak 2019, *Earth & Space Sci.*, [4] Hays 2017, *Astrobio.*, [5] Onstott 2019, *Astrobio.*, [6] Rampe 2017, *EPSL*, [7] Hurowitz 2017,

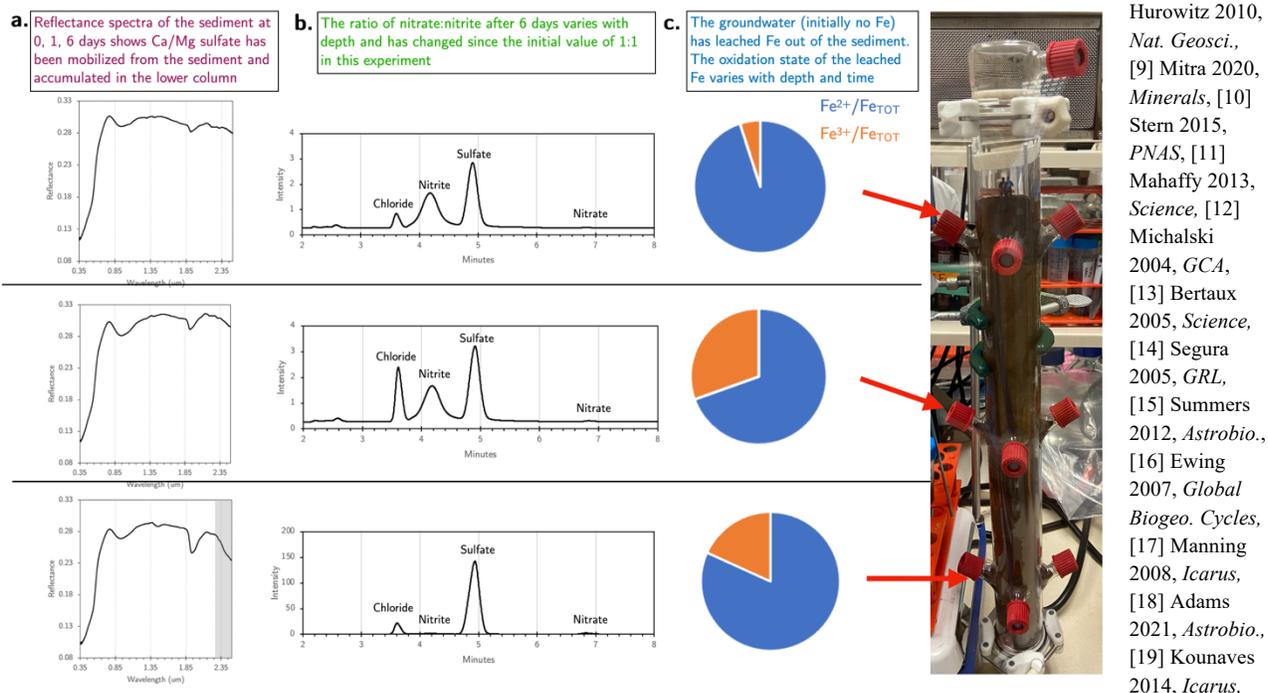


Fig. 2: Example results from one of the column experiments showing (a) mineral spectra, (b) groundwater dissolved phases, and (c) groundwater Fe oxidation state for samples from the upper, middle, and lower position in the column (shown at far right).

[20] Summers 1993, *Nature*, [21] Smirnov 2008, *Geochem Trans.*