National Aeronautics and Space Administration

Experimental Constraints on Groundwater-Driver Redox Gradients on Mars

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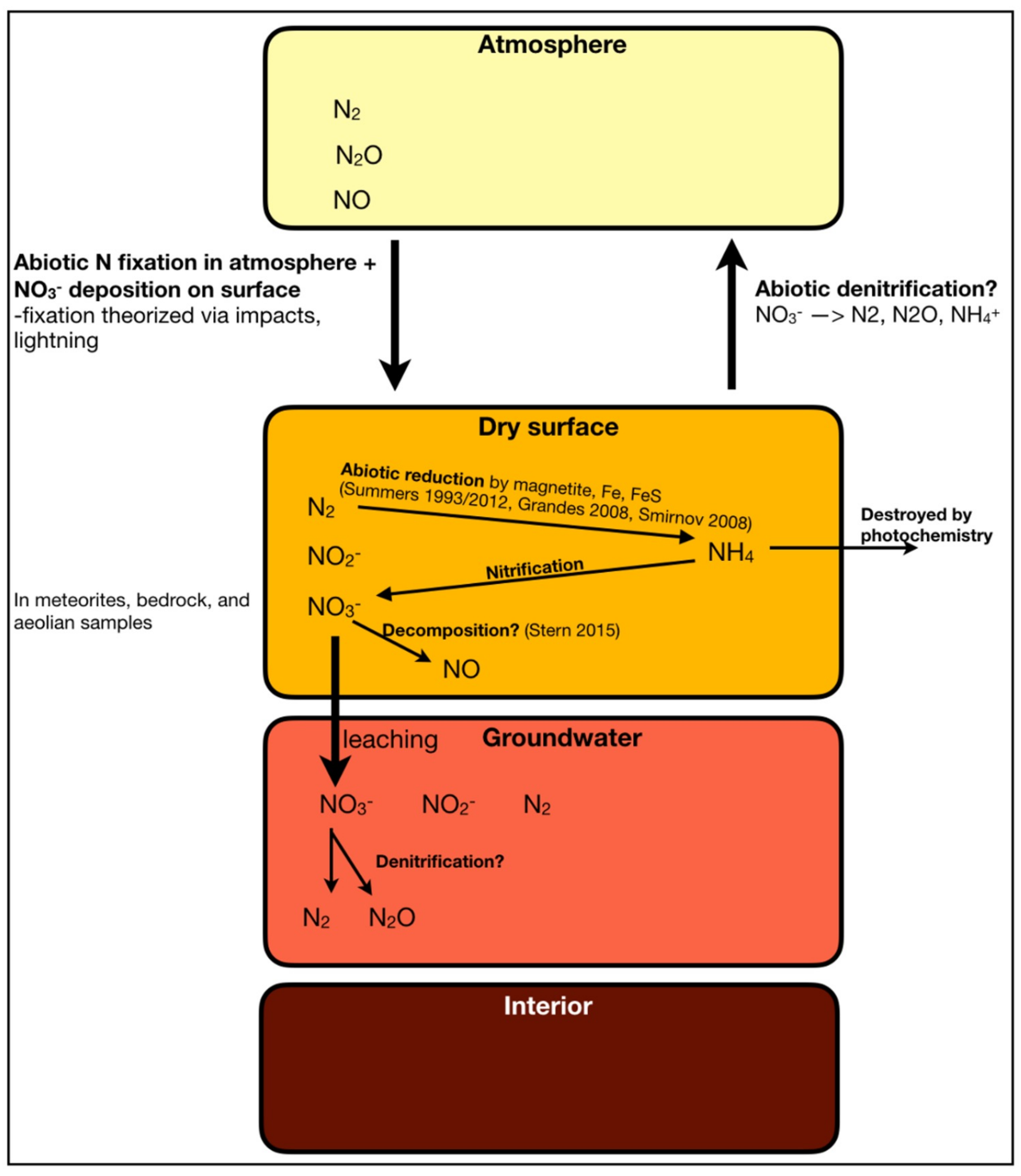
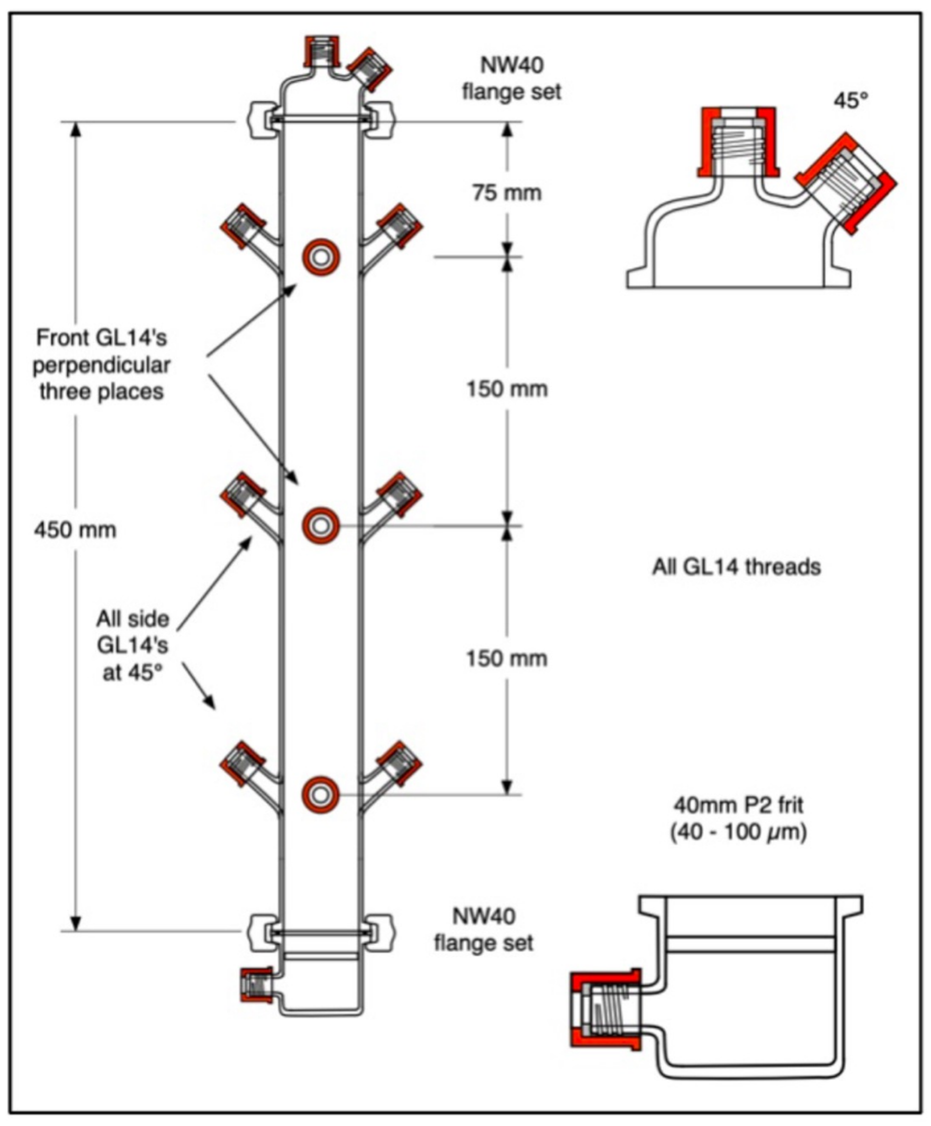
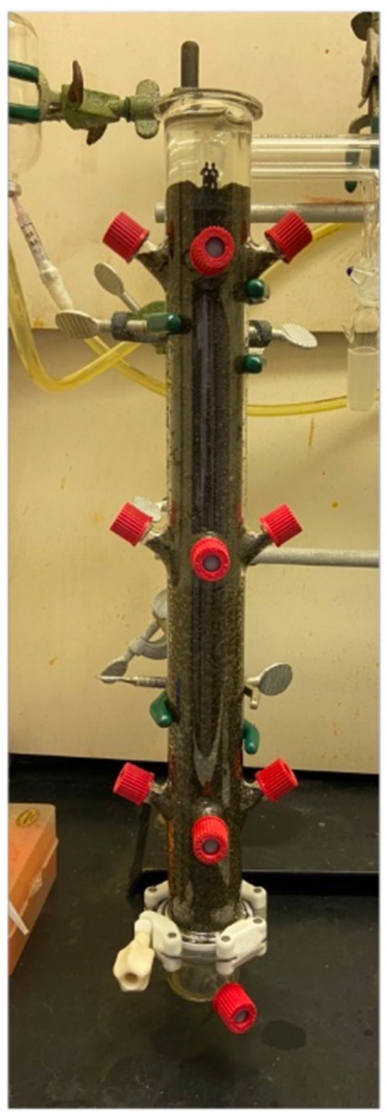
Objectives: Oxidation and reduction are common energy sources for microbial communities on Earth. The martian interior hosts unmixed reservoirs of differing redox states and lacustrine sediments at Gale crater host plausible redox couples. The spatial coexistence of redox pairs could provide energy-yielding processes that life could harness. Furthermore, any upwelling of groundwater could have moved biosignatures or environmental indicators of habitability to the surface where they could be observed and explored today. Detailed laboratory studies of environments analogous to those that may host redox cycling are necessary to understand the conditions it can act under and the chemical record it leaves behind. Our column experiments have applied state-of-the-art terrestrial soil/subsurface characterization techniques to the Mars subsurface environments for the first time to study the conditions under which abiotic nitrate cycling may have occurred in the martian subsurface.

Approach: We designed custom sediment columns to simulate the martian subsurface environment. These can be filled with Mars regolith analog. Ports on the side and top of the column allowed for placement of microsensors which could monitor pore water composition through time (1 second intervals), including N2O concentration and redox potential. Solid samples from the top and bottom of the column were collected to monitor formation of secondary minerals and the effect of these processes on sample spectra.

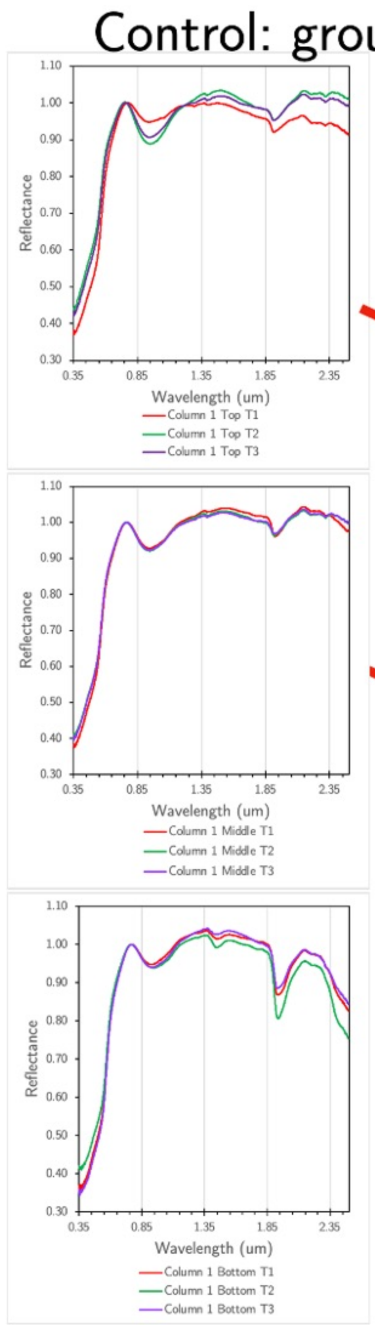






VNIR spectra of dried sediment samples

Control: groundwater mixture only



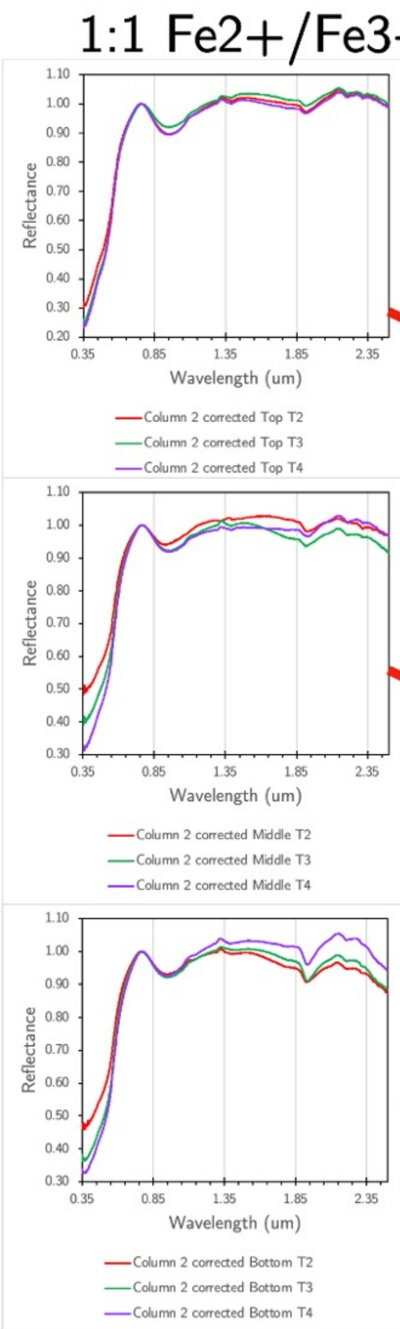
Added redox reactive phases:

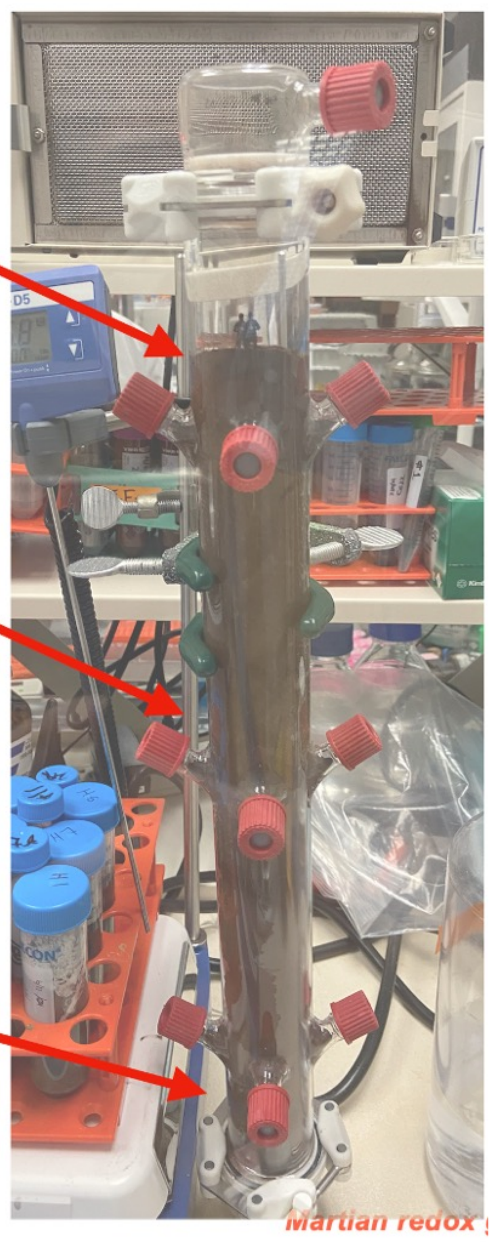
	No Fe	Fe2+	1:1	Fe3+
No N	Left			
Nitrite				
1:1			Right	
Nitrate				

Highly soluble Ca and Mg sulfates are more abundant lower in the column

Mineralogical variability based on redox reactive phases added

1:1 Fe2+/Fe3+ and 1:1 nitrate/nitrite





Results: Visible-near infrared reflectance spectra of sediment from different positions in the column demonstrated that the final mineralogy is affected by the Fe and N redox-reactive phases present. We also observed that sulfates are more abundant in the sediment from lower in the column, mobilized by groundwater after as little as an hour. Measurements of sediment particle size, bulk chemistry from ICP, mineralogy from XRD, and sample spectra of the entire parameter space of redox-reactive additives are currently being finalized which will allow us to model which pipelines for N oxidation and reduction that function on Earth may have applied to Mars. Oxidized nitrogen has been detected at the martian surface as nitrate in meteorites, bedrock, and aeolian samples; possible formation mechanisms for this bedrock nitrate include post-depositional leaching or a/biotic fixation mechanisms. But reduced nitrogen has not been detected, raising the question of whether Mars had a way to close this redox loop, comparable to Earth's biological denitrification. Our final calculations will be to focus on this question and address the rates and mineral products of any Fe and N redox processes occurring in our Mars subsurface simulations.

Significance/Benefits to JPL and NASA: This work explores the source and fate of nitrogen reservoirs in Mars-relevant conditions. Understanding the specifics of the martian near-surface groundwater environment will help constrain the geochemical environment (and habitability) of Jezero and Gale craters being explored by in situ missions. There are also applications to future missions to icy worlds such as Europa, where the connectivity of the subsurface and surface ice will be critical to constraining habitability.

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Publications:

R. Y. Sheppard, M. T. Thorpe, A. A. Fraeman, V. K. Fox, R. E. Milliken. "Merging perspectives on secondary minerals on Mars: A review of ancient water-rock interactions in Gale crater inferred from orbital and in situ observations." 2021. Minerals, 11(986).
2022 R. Y. Sheppard, A. A. Fraeman, L. M. Barge, J. M. Weber, L. Rodriguez, E. Martinez. Laboratory sediment columns to explore habitability of the martian subsurface under different groundwater conditions. AbSciCon, Atlanta, GA.
2022 R. Y. Sheppard*, A. A. Fraeman, L. M. Barge, J. M. Weber, L. Rodriguez, E. Martinez. Laboratory sediment column simulations of chemical and redox gradients in the martian groundwater environment. Lunar and Planetary Science Conference, The Woodlands, TX.
2021 R. Y. Sheppard*, L. Barge, A. A. Fraeman, J. M. Weber, L. Rodriguez, E. Flores, E. Martinez. Laboratory sediment column simulations of chemical and redox gradients in the martian groundwater environment. American Geophysical Union Fall Meeting, New Orleans, LA.

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