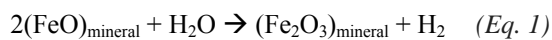


IN SITU Resources from water-rock interactions for human exploration of Mars. C. T. Adcock¹, E. M. Hausrath¹, E. B. Rampe², R. D. Panduro-Allanson¹ and S. M. Steinberg³, ¹University of Nevada Las Vegas, Department of Geoscience, 4505 S. Maryland Pkwy, Las Vegas, NV, 89154, ²NASA Johnson Space Center, Houston, TX 77058, University of Nevada Las Vegas, Department of Chemistry and Biochemistry, 4505 S. Maryland Pkwy, Las Vegas, NV, 89154. Correspondence: Christopher.Adcock@unlv.edu

Introduction: Modern space exploration has entered a phase where we seek to expand further into our solar system and establish a sustainable presence on bodies such as the Moon and Mars [1]. Among the challenges of these new endeavors is the requirement for *In Situ* Resource Utilization (ISRU) to supplement or replace materials transported from Earth. The energy required to escape a planetary gravity well is immense. Deliverable payloads from rockets to the Moon or Mars make up <3% of the launch vehicle mass [2, 3], and propellant (oxidizer + fuel) is generally 85 to 95% of the launch vehicle mass [3-5]. Potential ascent vehicles from Mars would also need to be approximately 80% propellant by mass to return to Earth [4, 6]. This return propellant would usually be delivered as payload. However, ISRU of fuel reactants could exchange delivered fuel mass directly for payload mass on the order of several metric tons.

Devices like MOXIE [7] are being designed to address the oxidizer component. However, up to 40% of the propellant mass in an ascent vehicle is the fuel reactant, and ISRU of this component has not been sufficiently addressed for Mars or the Moon. Toward addressing this need, we are investigating methods to recover components, including H₂, from lunar and martian relevant materials as potential *in situ* resources for future extended human missions. Hydrogen is an ideal resource to target. Not only can H₂ be used directly as part of a propellant, but it can also be combined to produce other fuels such as methane [8]. It is also useful agriculturally for fixing nitrogen [9] and can be oxidized to produce heat and water.

Background: Previous work on Earth has shown that interactions of liquid water with Fe-rich mineral surfaces produce hydrogen through the oxidation reaction:



where (FeO)_{mineral} indicates the ferrous constituent of a primary mineral such as olivine, and (Fe₂O₃)_{mineral} indicates the ferric constituent of a secondary alteration mineral such as hematite [10, 11]. This reaction occurs in nature, has been demonstrated in experiments under multiple laboratory conditions with multiple minerals, and unlike methods such as electrolysis, requires relatively little energy input [11, 12]. Minerals on Mars tend to be more iron-rich than on Earth [13, 14], and

on the Moon, iron is generally more reduced than on Earth [15]. This suggests that hydrogen released in this manner could be a valuable resource on both bodies. However, development of methods for generating H₂ by this means with martian or lunar relevant materials or under martian or lunar deployable conditions has received little attention.

Methods: Thirty-eight water-rock interaction experiments were conducted at 25°C and 4°C using four martian regolith simulants and four Mars-relevant minerals as solids (Table 1). Regolith simulants and select minerals were sourced from Exolith, Johnson Space Center, Alfa Aesar, Ward's Scientific or synthesized. martian regolith simulants were doped with approximately 1 wt% Na-perchlorate to better simulate martian conditions. JSC-RN contains approximately 1 wt% Na-perchlorate as received so none was added. Minerals were not perchlorate doped. For each experiment, 3 grams of regolith or 1 gram of mineral was transferred into a 20ml acid washed, autoclaved borosilicate serum vial under a laminar flow hood. Vials were capped with aluminum foil then dry sterilized with the regolith or mineral material at 160°C for >2 hours before being transferred into an N₂ purged glove box. In the glove box, vial headspaces were purged with N₂ and then capped and crimped after removing aluminum foil with acid washed, autoclaved butyl rubber stoppers previously boiled in 0.1N NaOH for 1 hour [16]. Vials were then removed from the box.

Table 1. Minerals and simulants used in experiments.

Source	Material
Exolith	MGS-1
Exolith	MGS-1C
Johnson Space Center	JSC Mars-1
Johnson Space Center	JSC Rocknest
Ward's Scientific	Pyrite
Alfa Aesar	Troilite
Alfa Aesar	Magnetite
In-house synthesis	Fayalite

Reaction solutions for experiments were made with sterilized equipment using UV and filter sterilized 18 MΩ water with 0.01M KNO₃, pH adjusted with high purity HNO₃, and N₂ sparged for 1 hr per 100ml. Final pH was 4.85. Solution was transferred in an N₂ purged glove box into sterile serum bottles which were capped and crimped. Experiments were initiated by injecting 3

ml of solution into each vial using a sterile needle and 0.2 μ m syringe filter for further solution sterilization. An equivalent volume of N₂ gas was removed from each vial by syringe and sterile needle to relieve overpressure. Experiments were shaken for ~1 minute by hand to ensure mixing of water and solids before incubating at 25°C in a shaker bath set to 100 shakes per minute or on a shaker table in a 4°C cold room. Hand agitation was repeated weekly.

Experiments were sampled and analyzed between 77 and 83 days by removing 1.5 ml of headspace gas from the vials with a gas syringe and injecting it into an SRI 8610C gas chromatograph (GC) with a Hayesep D nickel 7m \times 3.2mm \times 2.1mm heated column. Pressure was equalized in each vial with an equal volume of high purity N₂ after sampling using a sterile needle and gas syringe. Mineral free blanks, both with and without solution, were used to ensure no contribution of H₂ from the septa or glove box.

Results and Discussion: Preliminary results of GC analysis indicate that nearly all of the material types produced at least trace H₂, although not every experiment for each material generated detectable H₂ (Figure 1). A potential exception is magnetite in which H₂ was only detected at the detection limit in one experiment. Of the minerals tested, pyrite and troilite both produced the highest amounts of H₂, with pyrite being the largest producer of the tested materials. There was relatively high variance between duplicates for pyrite, however, even the lowest measured concentrations were higher than other materials for a given temperature (Figure 1). Magnetite and fayalite produced the least H₂. Fayalite only produced H₂ in one 25°C experiment with no detection in the 25°C duplicate. It is interesting that the Fe-sulfides are among the largest H₂ producers while the silicate and oxide minerals produced almost no H₂. Anoxic dissolution of Fe-sulfide phases would release S²⁻ which could then be available to interact with H⁺. Follow-up measurements of pH and possibly resulting mineral phases at the conclusion of the experiments may yield further insights into this.

The martian simulant experiments also showed broad variability. The MGS1C experiments produced H₂ at both 4°C and 25°C. These experiments were second only to pyrite in terms of gas evolved at 4°C and 25°C. MGS-1 experiments also produced significant H₂ at both temperatures, but at lower concentrations. The material difference between MGS-1 and MGS-1C is the addition of 40 wt% smectite clay to MGS-1 [17, 18]. Thus, the clay must play a critical role in H₂ production.

Differences in temperature between 4°C and 25°C experiments greatly impacted H₂ production. Based on averages of duplicate experiments (Figure 1), MGS-1C, MGS-1, and troilite all produced approximately

85% less H₂ at 4°C. In the pyrite experiment, the reduction was only about 25%. For simulants JSC-RN and JSCM-1, as well as minerals magnetite and fayalite, no H₂ was detected in the 4°C experiments.

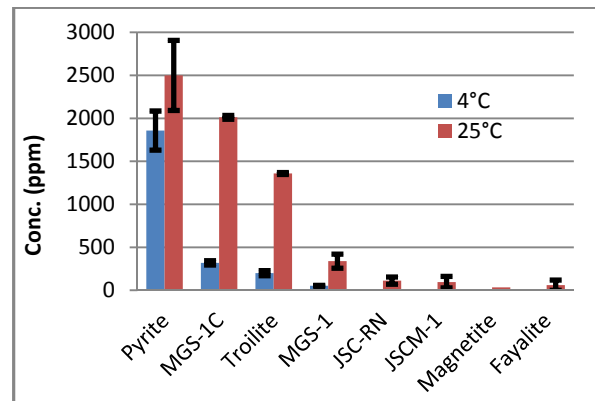


Figure 1. H₂ concentrations produced at 4°C (blue) and 25°C (red). Black brackets show the difference between duplicate analyses.

Conclusions: Every kilogram of propellant supplemented by H₂ on Mars or the Moon equates to a kilogram that does not have to be delivered from Earth as payload. Results from these experiments on Mars-relevant materials indicate that oxidation of materials from Mars or the Moon may be viable for supplementing propellant resources, thus, effectively increasing deliverable mission payload capacity.

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References: [1] NASA, *NASA 2018 Strategic Plan*, 2018, NASA. [2] Orloff, R.W., *Apollo by the numbers: a statistical reference*. Vol. 4029. 2000: NASA. [3] Kyle, E., *Space Launch Report: SpaceX Falcon 9 v1.2 Data Sheet*, 2020. www.spacelaunchreport.com [4] Holt, J. and T. Monk. *AIAA SPACE 2009 Conference & Exposition*. 2009. [5] SpaceX, *Falcon Users Guide*, 2020, www.spacex.com. [6] Drake, B.G. and D. Watts Kevin, *Human exploration of Mars design reference architecture 5.0* 2014. [7] Hartvigsen, J., et al., *ECS Trans.*, 2017. 78(1). [8] Bassano, C., et al., *Fuel*, 2019. 253. [9] Ramachandran, R. and R.K. Menon, *Int. J. Hydrogen Energy*, 1998. 23(7). [10] Telling, J., et al., *Nat. Geos.*, 2015. 8(11). [11] Miller, H.M., et al., *GCA*, 2017. 209. [12] Mayhew, L.E., et al., *Nat. Geos.*, 2013. 6(6). [13] Best, M.G., *Igneous and metamorphic petrology*. 2013. Wiley & Sons. [14] McSween, H.Y., et al., *Science*, 2004. 305(5685). [15] French, B.M., G. Heiken, and D. Vaniman, *Lunar sourcebook: A user's guide to the Moon*. 1991. [16] Oremland, R.S., L.G. Miller, and M.J. Whiticar, *GCA*, 1987. 51(11). [17] Exolith, *MGS-1C Clay ISRU | Fact Sheet*, 2019. sciences.ucf.edu/class/exolithlab [18] Cannon, K.M., et al., *Icarus*, 2019. 317.