

RESOURCES FROM WATER-ROCK INTERACTIONS FOR FUTURE HUMAN EXPLORATION OF

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Introduction: One of the most exciting endeavors in modern space exploration is extended human exploration of the Moon and Mars. We have entered a new phase in the human venture where we seek to expand our "...presence deeper into space and to the Moon for sustainable long-term exploration and utilization" [1]. With this endeavor come new challenges. Among them is the requirement for *In Situ* Resource Utilization (ISRU) methods to supplement or replace materials transported from Earth. The energy required to leave Earth's gravity well is immense, as is well illustrated by the nearly 3000 metric ton Saturn V required to deliver a payload of less than 50 metric tons to the Moon during the Apollo era [2]. Much of this mass is propellant. Launch vehicles from Earth into space are generally 85 to 95% propellant (oxidizer + fuel) by mass [3].

Potential ascent vehicles from Mars would also need to be approximately 80% propellant by mass to return to Earth [3, 4]. ISRU of fuel reactants could exchange delivered fuel mass directly for payload mass on the order of several metric tons. Devices like MOXIE [5] are being designed to address the oxidizer component. However, 40% of the propellant mass in an ascent vehicle is the fuel reactant, and ISRU of this component has not been addressed for Mars or the Moon.

Toward addressing this need, we have begun to develop and optimize methods to generate and recover fuel 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, it can also be used as a component in other fuels, such as methane. It is useful agriculturally for fixing nitrogen and can be oxidized to produce heat and water.

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



where (FeO)_{mineral} indicates the ferrous constituent of a primary silicate mineral such as olivine, and (Fe₂O₃)_{mineral} indicates the ferric constituent of a secondary alteration mineral [6]. This reaction occurs naturally under terrestrial conditions and has been

demonstrated in experiments under multiple laboratory conditions and with multiple minerals [6-8]. Minerals on Mars tend to be more iron-rich than on Earth [9, 10], and on the Moon, iron is generally more reduced than on Earth [11]. Furthermore, Lunar maria can contain as much as 15 wt.% Fe [12]. This suggests that hydrogen released in this manner could be a valuable resource for ISRU on both bodies. However, no technical development or optimization of methods for generating H₂ by this means with martian or Lunar regolith analogs or under martian or Lunar deployable conditions has been previously investigated.

Methods: Two sets of water-rock interaction experiments (10 and 15 individual experiments each, respectively) were started, separated by approximately 60 days to allow for method testing. Both sets used the following methods. Martian soil/regolith simulants and select minerals were sourced from Exolith, The Martian Garden, Johnson Space Center, Alfa Aesar, or by synthesis to be used as solids in the water-rock interaction experiments (Table 1). For each experiment, 3 grams of <2mm material was transferred into 20 ml acid washed and autoclaved borosilicate serum vials before being transferred into an N₂ purged glove box. In the glove box, vial headspaces were purged with high purity N₂ and then capped with autoclaved butyl rubber stoppers and crimp sealed. Vials were then removed from the glove box.

Table 1. Minerals and simulants used in experiments.

Source	Material
Exolith	MGS-1
Exolith	MGS-1C
Exolith	MGS-1S
The Martian Garden	MMS-1
The Martian Garden	MMS-2
JSC	JSC Mars-1
JSC	JSC Rocknest
Alfa Aesar	Troilite
Alfa Aesar	Magnetite
In-house synthesis	Fayalite

To start the experiments, 3 ml of reaction solution was injected into the vials. Then an equivalent volume of gas from the vial headspace was removed with a syringe. Reaction solutions were either N₂ sparged (>2 hr) anoxic 18 MΩ water with 0.01 molar KNO₃ adjusted to a pH of 4.8 - 4.9 with HNO₃, or N₂ sparged (>2 hr) anoxic seawater which had been 0.20 μm

filtered and acidified to the same pH. Samples were shaken for approximately 1 minute by hand to ensure mixing of water and solids, and then were incubated for 60 days at 25°C in a shaker bath set to 100 shakes per minute. Additional hand agitation was done weekly.

After 60 days of incubation, the first experiment set was analyzed by removing 1 ml of headspace gas from the vials with a syringe and injecting it into an SRI 8610C TCD equipped gas chromatograph with a Hayesep D nickel 7 m × 3.2 mm × 2.1 mm heated column. TCD cell temperature was set to 80°C, column temperature was 30°C with N₂ as the carrier gas at a 30 cc/min flow rate. To prevent any effects from underpressure and ensure outside air did not contaminate the vial headspaces, the pressure was equalized in each vial with an equal volume of high purity N₂ after sampling. The second set of experiments is still ongoing and scheduled for future sampling.

Results and Discussion: Preliminary results from the first set of experiments indicate a significant amount of H₂ can be evolved from some martian simulants. Concentration estimates evolved from experiments with Exolith simulants (MGS-1) exceeded 2% H₂ (Figure 1). The experiment run with seawater and MGS-1 simulant produced the highest concentration of H₂.

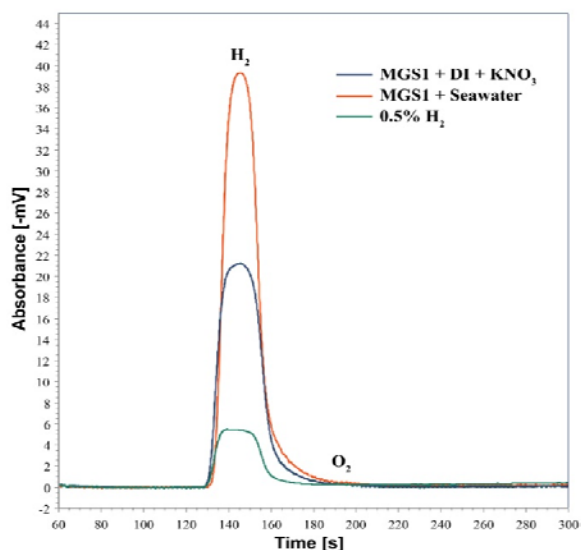


Figure 1. Hydrogen concentrations produced from the MGS-1 in DI (red) and filter-sterilized seawater (blue), which produced significantly more hydrogen than the 0.5% reference (green).

The Martian Garden MMS-2 and Exolith MGS-1S simulants did not produce quantifiable (>40 ppm) H₂. These simulants are similar to the Exolith MGS-1 simulant, but have been sulfate enhanced. It is possible

the added sulfate is interacting with the H₂ produced. However, experiments with magnetite as the solid also did not produce GC quantifiable hydrogen despite no added sulfate. Other simulants which are not sulfate enhanced (including MMS-1, MGS-1C, JSC Mars-1, and JSC Rocknest) are part of the second experimental run which has yet to be sampled. Results from these may shed more light on potential sulfate interactions.

These experimental methods will also be further optimized. Factors such as particle size reduction may significantly increase the H₂ production rates and concentrations. We are also in the process of testing different temperatures, a wider range of simulants (including Lunar), and checking for scalability and reproducibility. Longer term monitoring and future experiments are also planned. These optimizations and ongoing experiments will help to address why some materials seem to evolve H₂ and others do not while also yielding light on exactly how much H₂ can be expected per gram of material.

Conclusions: Although these experiments have yet to be optimized, the H₂ concentrations evolved from MGS-1 experiments indicate this approach may be viable for supplementing propellant resources on Mars or the Moon. 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 on a return vehicle. Thus, the effective delivered payload capacity (e.g. to Mars) of a return vehicle would be increased.

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