Water-Rock Interactions on Mars: Production of Valuable Resources

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Introduction

Applying water to dry Martian regolith could produce viable in-situ resources to support long-term human exploration on Mars.

Previous studies have shown that hydrogen gas (H_2) is generated through the oxidation of ferrous iron (Fe^{2+}) in minerals coupled with the reduction of water (Eq. 1) [1]. H_2 can be used as a propellant, to create water, or in the production of ammonia for plant fertilization.

$$2(FeO)_{mineral} + H_2O = (Fe_2O_3)_{mineral} + H_2 \text{ (Eq. 1)}$$

Minerals on Mars tend to be more iron-rich and ferrous (Fe^{2+}) than on Earth [2]. In addition to iron, studied locations on Mars contain an abundance of other elements, including magnesium (Mg) and chlorine (Cl) that could be used in-situ [2, 3, 4].

- Iron (Fe) and magnesium (Mg) are essential nutrients that can be water leached and used in fertilizers to support a sustainable food source.

Perchlorate salts are widespread on Mars and highly soluble during the wetting process [5,6].

- Davila et al. (2013) has demonstrated that purified enzymes involved in microbial ClO_4^- metabolism can dismantle ClO_4^- into breathable oxygen.

We are using Martian simulants that are developed based on quantitative mineralogy from the Mars Science Laboratory (MSL) Curiosity rover, as our Martian analog material for anoxic water-rock experiments [7].

Experimentally quantifying the release of these products from water-rock interactions of a Mars-like soil can provide insight into potential resource reservoirs to support human life on Mars.

Methods

- Martian simulants, minerals, and respective sources used in preliminary experiments are shown in Table 2.
- Materials heated 160 °C for 2 hours for sterilization.
- 3 g of each solid material is placed in acid-washed and autoclaved 20 ml borosilicate vials. We spiked some samples with 1 weight % of $NaClO_4$.
- Vials sealed in an N_2-purged glovebox.
- 3 ml of N_2 sparged 18 MΩ water with 0.01 M KNO_3 adjusted to a pH of 4.71 with HNO_3 is injected into sealed vials (Figure 3).
- Samples are incubated for 90 days at 25°C in a shaker bath set to 100 shakes/min.
- At day 3, a ClO_4^- solution sample collected, filtered and diluted 1000x for analysis in a Dionex 2000 series ion chromatograph. The detection range for perchlorate is 4 ppb – 4 ppm.
- After ~60 days, gas samples were taken by removing 1.5 ml of headspace and injected into an SPI 8610 gas chromatograph for analysis with a detection limit of 40 ppm.

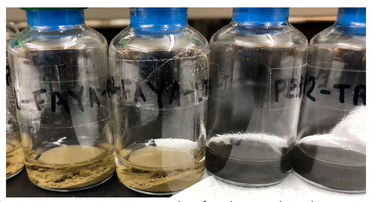

Figure 3. *Preliminary experiment samples fayalite and troilite set up and ready to be placed in the shaker bath.*

Preliminary Results

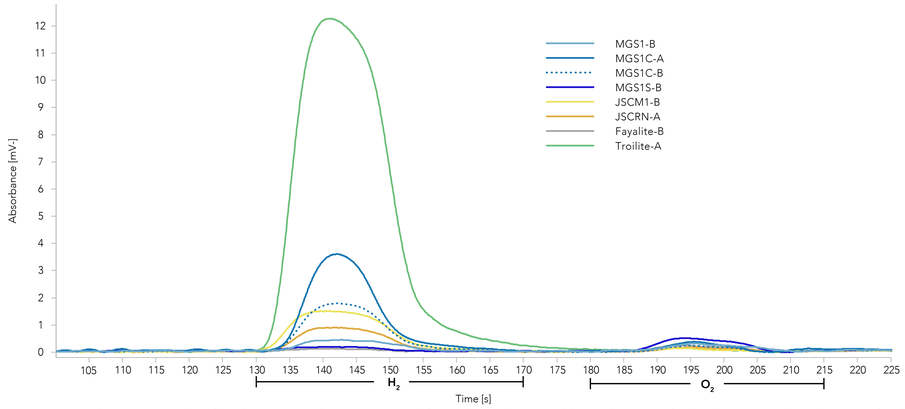

Figure 1. *Preliminary results of hydrogen production at 25 °C from the GC. Dotted lines distinguish duplicate samples that were both successfully analyzed. 130 - 170 s is the window for the H_2 peak, and 180 - 215 s is the window for the O_2 peaks. The larger the area under the curve, the higher the H_2 concentration.*

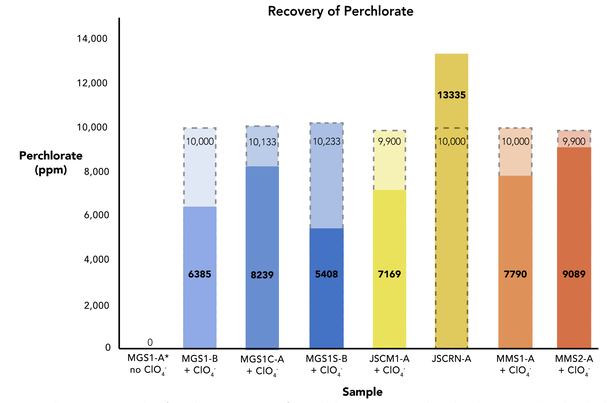

Figure 2. *Preliminary results for the amount of perchlorate (ppm) leached at 25 °C. The lighter filled, dashed bordered bars are the amount of ClO_4^- added. The solid bordered and filled bars are the amount of ClO_4^- recovered and overlay the added ClO_4^- bars. *JSCRN is reported to be 1 wt. %, so 10000 ppm is assumed for calculations [8].*

Preliminary Concentrations of H_2 Production

Sample	Duration (Days)		H_2 Conc. (ppm)
MGS1-A*	64		nd
MGS1-A	64		nd
MGS1-B	66	+ClO_4^-	320
MGS1C-A	69	+ClO_4^-	2370
MGS1C-B	69		1346
MGS1S-B	66	+ClO_4^-	155
JSCM1-B	69		1351
JSCRN-A	69	+ClO_4^-	779
MMS1-A	69		nd
MMS1-B	72	+ClO_4^-	nd
MMS2-A	72	+ClO_4^-	nd
Troilite-A	69		7568
Fayalite-B	69		92
Glove Box Ambient	64		nd
Glove Box Ambient	69		nd

Table 1. *The preliminary quantification of H_2 at 25 °C from Figure 1 in ppm. "n.d." = not detected. "+ClO_4^-" means we added 1 wt.% of $NaClO_4$ to the sample. MGS1-A* has 18 g of material and 18 ml of sample. Approximate uncertainity is 10%.*

Sample Material

Source	Material
Exolith	MGS1
Exolith	MGS1C
Exolith	MGS1S
JSC	JSC Mars 1
JSC	JSC Rocknest
The Martian Garden	MMS-1
The Martian Garden	MMS-2
Alfa Aesar	Troilite
Alfa Aesar	Magnetite
In-house synthesis	Fayalite

Table 2. *Martian simulants and minerals used in preliminary experiments. Troilite = FeS. Magnetite = $FeFe_2O_4$. Fayalite = Fe_2SiO_4.*

The preliminary results indicate that substantial amounts of H_2 can be produced by some of the Martian simulants and ferrous bearing minerals at 25 °C.

- MGS1C-A, MGS1C-B, JSCM1-B, and troilite all produced over 1000 ppm of H_2 within ~60 days, while other samples did not produce as much, or any at all. Some of the samples might need extended incubation periods to reach larger quantities of H_2.

$NaClO_4$ was added to some of the samples to gauge ClO_4^- recoverability. All of the samples with added ClO_4^- recovered 50% or more (Figure 2).

- MGS1-A* is a sample containing no added ClO_4^- and no ClO_4^- was detected. Rates of perchlorate dissolution are important for estimating oxygen retrieval and will be investigated in future experiments.

Discussion

H_2 generation may be controlled by particle size and/or secondary mineral formation.

- Sample MGS1C has the smallest overall particle size and substantial H_2 production. As particle size decreases, the surface area tends to increase. Smaller particles could provide more available surface area for reactions to take place and possibly be favored to generate more H_2.
- Although no analyses of secondary mineral phases have been conducted for this experiment, it has been discussed that secondary mineral formation, such as magnetite or other iron-(hydr)oxides, could potentially lock up Fe^{2+} from reacting with water and suppressing H_2 generation [9].

Future experiments will be optimized to understand the effects of particle size and secondary mineral formation on H_2 production; the release of Fe and Mg ions; and check for the reproducibility of results.

Conclusion

Although these are preliminary experiments and further optimizations can be done, H_2 generation from water-rock interactions may be a viable pathway for supplementing propellant production on Mars.

Further investigations into the controls of H_2 production from water-rock interactions and the dissolution rates from these materials will provide insight into potential in-situ resources that can bring long-term human exploration of Mars closer to reality.

Acknowledgments

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