

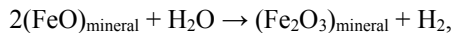
HYDROGEN PRODUCTION FROM SULFIDE MINERALS AS A POTENTIAL RESOURCE ON MARS.

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Introduction: Space exploration has entered a new era where we seek to establish a sustainable human presence on bodies such as the Moon and Mars [1]. This is one of the most ambitious efforts undertaken by humankind and brings with it new challenges. Among these challenges is providing the resources required for habitation of other solar system bodies. The Earth's gravity is immense, and thus, propellant loads make up approximately 90% of a launch vehicle mass, with deliverable payloads from Earth to other bodies of <5% of a launch vehicle mass [2-4]. In addition, human missions require a return vehicle. For a target such as Mars, propellant requirements for the return vehicle are estimated at 80% of the vehicle mass [3, 5], further restricting other resource payloads.

In Situ Resource Utilization (ISRU) could be used to supplement or replace resources otherwise transported from Earth to a target such as Mars [6, 7]. In previous work we studied hydrogen (H₂) as a potential Martian ISRU target [8]. H₂ is a versatile resource that can be used directly, or converted to methane, for use as fuel in a return vehicle [9, 10]. H₂ can also be used as a heat or power source, or to fix nitrogen for agricultural purposes [11]. Low energy methods for generating H₂ *in situ* on Mars could greatly enhance long-term human mission resources and free up payload mass.

H₂ evolves during water/rock interactions with Fe-rich mineral surfaces through the oxidation reaction:



where (FeO)_{mineral} indicates the ferrous constituent of a mineral, and (Fe₂O₃)_{mineral} indicates the ferric constituent of a secondary alteration mineral [12-14]. This reaction occurs regularly on Earth during serpentinization (i.e. hydrous alteration of mafic minerals like olivine to serpentine and other alteration products) [12] and is therefore commonly called the serpentinization reaction. However, H₂ generation during water/rock interactions, presumably following the same overall reaction, has been demonstrated in experiments under multiple laboratory conditions and with multiple rocks and minerals [14-16] including non-mafic materials and oxides [13, 17].

In previous work using water/rock interaction experiments with multiple Mars-relevant minerals and regolith simulants to generate H₂, we noted relatively high H₂ production from the Mars-relevant pyrite and troilite sulfide minerals [8]. Here we present extended results from those experiments with a focus on H₂

production from the Mars-relevant sulfide minerals. We also include data from fayalite experiments for comparison as well.

Methods: Water/rock interaction experiments, including blanks and duplicates, were conducted at 25°C and 4°C on Martian regolith simulants and Mars-relevant minerals [8]. Here we focus on pyrite, troilite, and fayalite mineral experiments. For each of these experiments, 1 gram of mineral was transferred into a 20ml acid washed, autoclaved borosilicate serum vial under a laminar flow hood sterilized with 70% ethanol and UV light. Vials (with solids) were dry sterilized at 160°C for 2 hours and transferred to an N₂ glove box to purge the headspaces with N₂. Vials were capped with butyl rubber gas septa that had been boiled in 0.1N NaOH for 1 hour [13], soaked in 18 MΩ DI water for 4 hours, rinsed, dried, acid washed and autoclaved. 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 (Aristar Plus) to 4.85, and N₂ sparged for 1 hour. To start experiments, 3ml of solution was injected into each vial with a sterile needle and 0.2 μm syringe filter. Gas headspaces of vials were sampled twice over a 259-day period and analyzed for H₂ by Gas Chromatography (GC). Reference standards for H₂ were created by spiking aliquots of high purity N₂ with certified H₂/N₂ gas mixtures (Airgas inc.). The 4°C experiments were first sampled and analyzed (sample event 1) at 83 days and then at 224 or 231 days (sample event 2). The 25°C experiments were first sampled between 69 and 76 days and then sampled and analyzed a second time at 259 days.

Results: Preliminary results from the two sampling events for the minerals at 4°C indicate only the sulfides produced measurable H₂ while the fayalite did not produce H₂ (Figure 1). Results from the mineral experiments at 25°C show H₂ production from the sulfide minerals and fayalite measured after 259 days (Figure 2). Unfortunately, data from Fayalite Exp. B second sampling event were not collected due to an equipment malfunction. With one exception, all blank analyses (12 analyses total) had H₂ results below the GC detection limit. The exception was a blank from the 25°C experiments during the second sampling event and plotted in Figure 2.

Discussion: The substantially higher H₂ produced from sulfide minerals compared to fayalite was initially surprising. The serpentinization reaction is based on mafic mineral water/rock interactions and numerous

low temperature (<120°C) studies have produced H₂ from olivine or olivine-bearing materials [e.g. 14, 15, 18]. However, although it is difficult to cross-compare results from these types of studies [14], scaling H₂ results from a shorter time duration study of fayalite at 30°C [18] generated values in the same order of magnitude as our result for fayalite at 25°C and 259 days. Therefore, our interpretation is that production of H₂ from fayalite is not low in these experiments, but rather, very high H₂ was produced from the pyrite and troilite sulfide minerals.

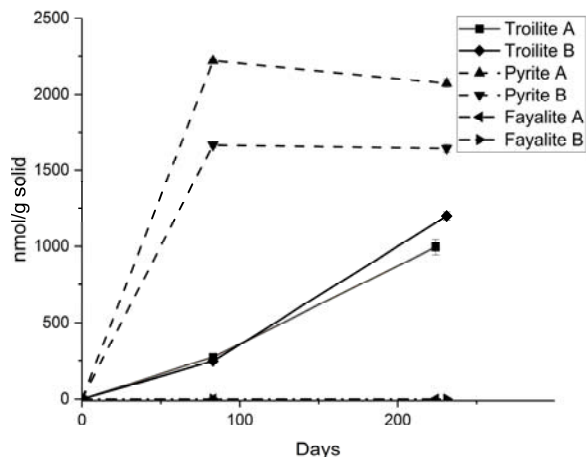


Figure 1. Results of 4°C experiments.

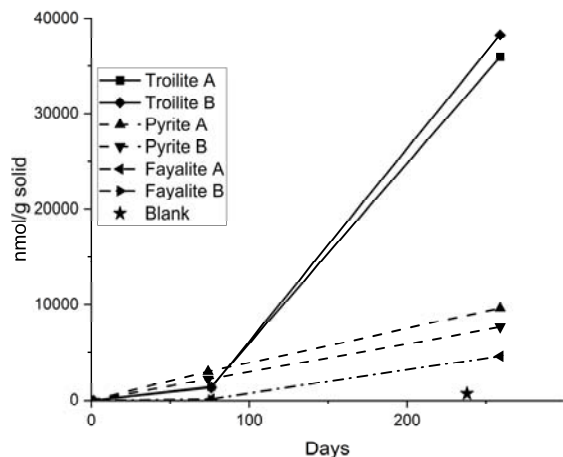


Figure 2. Results of 25°C experiments. Note: Data for the second sampling event for Fayalite B could not be collected.

The exact mechanism of H₂ production is unclear. Recent studies have used metal-sulfides (including pyrite) as electro-catalysts to split either water or an H-bearing component in solution to evolve H₂ gas [e.g. 19, 20]. Although these studies use electrical potentials, complex solutions, and/or metal-sulfide pretreatments [21, 22], it may be catalysis with the metal-sulfides is generating the H₂ in this study. Ongoing work will yield

further insights into the how these Mars-relevant sulfides produce such substantial amounts of H₂.

The results in this work have important implications for Mars. While olivine is probably more common on Mars, a deposit of pyrite or troilite, or a regolith that is rich in metal-sulfides could be an important H₂ producer and resource for Mars. Further, these experiments were not optimized for H₂ production from sulfides, and sulfide oxidation is sensitive to conditions such as pH and impurities [23]. Thus, substantially more H₂ generation may be possible from these Mars-relevant sulfides.

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