Exploring the environments of Martian impact-generated hydrothermal systems and their potential to support life

How to cite:

© 2021 Nisha K. Ramkissoon et al.

https://creativecommons.org/licenses/by/4.0/

Link(s) to article on publisher’s website:
http://dx.doi.org/doi:10.1111/maps.13697

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online’s data policy on reuse of materials please consult the policies page.

oro.open.ac.uk
Exploring the environments of Martian impact-generated hydrothermal systems and their potential to support life

Nisha K. RAMKISSOON,1,*, Stuart M. R. TURNER,1 Michael C. MACEY1, Susanne P. SCHWENZER1, Mark H. REED2, Victoria K. PEARSON1, and Karen OLSSON-FRANCIS1

1AstrobiologyOU, STEM, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK
2Earth Sciences Department, University of Oregon, Eugene, Oregon 97403–1272, USA
*Corresponding author. E-mail: nisha.ramkissoon@open.ac.uk
(Received 22 December 2020; revision accepted 13 May 2021)

Abstract—Hydrothermal systems that formed as a result of impact events possess all the key requirements for life: liquid water, a supply of bio-essential elements, and potential energy sources. Therefore, they are prime locations in the search for life on other planets. Here, we apply thermochemical modeling to determine secondary mineral formation within an impact-generated hydrothermal system, using geochemical data returned for two soils on Mars found in regions that have previously experienced alteration. The computed mineral reaction pathways provide a basis for Gibbs energy calculations that enable both the identification of available geochemical energy, obtained from Fe-based redox reactions, that could be utilized by potential microbial life within these environments, and an estimate of potential cell numbers. Our results suggest that water–rock interactions occurring within impact-generated hydrothermal systems could support a range of Fe-based redox reactions. The geochemical energy produced from these reactions would be substantial and indicates that crater environments have the potential to support microbial cell numbers similar to what has been identified in terrestrial environments.

INTRODUCTION

The presence of liquid water is central to the existence of life on Earth, and the possibility of past or present life on Mars. Today, the Martian surface is dry and cold, unconducive to sustaining liquid water unless in the form of a brine (Chevrier and Rivera-Valentin 2012). However, the presence of phyllosilicate minerals in Noachian terrains suggests that near neutral aqueous activity was widespread (Poulet et al. 2005; Ehlmann et al. 2009; Ehlmann and Edwards 2014) and there may have been habitable regions on the Martian surface (Poulet et al. 2005; Carr and Head 2010; Ehlmann and Edwards 2014; Grotzinger et al. 2014, 2015; Bishop and Rampe 2016; Hurowitz et al. 2017). At the Noachian–Hesperian boundary, a change in global climate (Carr and Head 2010) eventually led to the formation of younger Fe3+-rich deposits, such as Hematite Slope at Eagle crater (Rieder et al. 2004). These provide evidence of changing environmental conditions and a range of aqueous environments throughout Mars’ history.

In addition, hydrothermal systems generated by impacts may have provided localized sources of water, particularly during the first 500–700 Myr of Mars’ history when cratering rates were much higher. The possibility of impact-generated hydrothermal systems on Mars was first suggested by Newsom (1980); since then orbital investigations have identified a number of such systems on Mars (e.g., Marzo et al. 2010; Sun and Milliken 2014; Turner et al. 2016). Computer modeling has also shown such hydrothermal systems could have lifetimes of hundreds to thousands to millions of years (Abramov and Kring 2005). Even when the cratering rates declined and the lithosphere froze hydrothermal systems have been shown to develop in craters, particularly those with diameters of 100 km or greater (Barnhart et al. 2010; Ivanov and Pierazzo 2011). However, the permeability of the crater may have been
influenced by ground freezing, which would have restricted hydrothermal alteration to central regions where higher temperatures would be found (Barnhart et al. 2010). Nevertheless, the formation and longevity of these hydrothermal systems suggests that transient and localized aqueous activity could have extended into the Hesperian (3.7–3.0 Ga).

Exploration of impact crater environments on Earth has shown that the formation of micro-fractures and changes in target material porosity as a result of impacts would provide space for microbes to colonize (Cockell and Osinski 2007; Pontefract et al. 2014). Biosignatures, such as biofilms and fossilized microbes, have also been detected within extinct, impact-generated hydrothermal systems (Glamoclija et al. 2007; Hode et al. 2009; Ivarsson et al. 2013), which indicates such terrestrial environments were habitable. Similar environments on Mars may also have had the potential to host life or even played a critical role in the origin of life; abiogenic organic molecules may have been delivered to the Martian surface by impactors or synthesized within the hydrothermal environment (for an in-depth review, see Osinski et al. 2020).

Although initial temperatures are significantly higher than the maximum temperature at which microbial metabolic activity has been observed (122 °C; Takai et al. 2008), temperatures decline with distance from the center of the impact crater and over time, create element conditions. They also provide bio-essential elements (e.g., Gellert et al. 2004; Grotzinger et al. 2014) and energy that can be used by microbes in oxidation–reduction (redox) reactions, via water–rock interactions and the formation of secondary minerals. These interactions, in impact-generated aqueous systems, have been thermochemically modeled to identify secondary minerals, which are dependent on host rock composition and temperature (Griffith and Shock 1997; Schwenzel and Kring 2009, 2013). Previous thermochemical models have focused on Martian protolith lithologies; this article will extend these existing models to encompass lithologies, such as Hematite slope at Meridiani Planum (see Methods for more information), which have experienced alteration processes. Variations in host rock lithologies would lead to differences in secondary mineral assemblages, and the amount of energy available to support microbial metabolic activity.

On Earth, chemolithoautotrophs can obtain energy for cellular functions from environments that are in thermodynamic disequilibrium by utilizing the energy produced through redox reactions. These microbes have the ability to gain energy using only inorganic compounds and, in some instances, CO₂ as a source of carbon (Cockell 2015). It has been theorized that terrestrial microorganisms could have initially obtained metabolic energy through the anaerobic oxidation of Fe²⁺, which eventually led to the appearance of Fe³⁺-reducing microorganism and an Fe cycle during the Archean (4–2.5 Ga; Amils et al. 2004). Given the high carbon dioxide concentrations in the Martian atmosphere (Mahaffy et al. 2013), and the abundance of Fe within Martian rocks (Toulmin et al. 1977), it is possible that Fe-utilizing chemolithoautotrophic organisms were supported on Mars at some point in its history.

To assess the habitability of Martian environments, the Gibbs energy of redox reactions can be used to calculate the amount of geochemical energy available for microbial metabolism. Previous investigations have shown that microbial life could be supported by the energy produced from the disequilibrium generated by the mixing of fluids in hydrothermal systems (Varnes et al. 2003) and the weathering of Martian minerals (Jaksosy and Shock 1998; Link et al. 2005). However, the energy production from such reactions, specifically within impact-generated hydrothermal systems, has not yet been explored, despite the importance of impact cratering in the Martian geologic record.

In this article, we explore secondary mineral formation within impact-generated hydrothermal systems in Martian environments that have previously experienced alteration. We combine the findings with Gibbs energy calculations to determine whether these environments were capable of supporting microbial life. We present the results from thermochemical modeling of the pressure–temperature regimes that would be found within theoretical 100 km diameter impact craters within two host rock lithologies, the first was rich in Fe³⁺ and the second was a common Martian basaltic composition (referred to as host rocks from hereon), to determine secondary mineral assemblages. These assemblages will then be used to determine the amount of available geochemical energy, biomass, and cell number estimations from specific secondary mineral-forming reactions to assess the habitability of crater environments. These results will identify possible mineral assemblages that would be energetically favorable for microbial growth and provide estimates of biomass. This information could be used to identify suitable targets for analysis by future rover or sample return missions.

METHODS

CHIM-XPT

The computer code CHIM-XPT (Reed et al. 2010) was used to model water–rock interactions that would occur within an impact-generated hydrothermal system under various pressure–temperature regimes (P–T). The code requires the input of system pressures and
temperatures, together with rock and fluid compositions (Tables 1 and 2). The model applies mass balance and mass action equations to determine the equilibrium of secondary mineral assemblages and fluid composition at various water–rock ratios. These models used the Soltherm database, which is a modified version of the sloop07.dat database (available at http://geopig.asu.edu/sites/default/files/) that has been combined with heat capacity, mineral, and gas data from Holland and Powell (2011). Hydrothermal systems within a 100 km diameter crater after 4000 yr of cooling were modeled by Abramov and Kring (2005), and showed pressures and temperatures ranged from 1 to 1000 bar and 5 to 600 °C, respectively. Five $P$–$T$ regimes were selected from this model to represent regimes that would be found across the entire crater. However, models were run to a maximum temperature of 300 °C for comparison with previous thermochemical modeling research (Schwenzer and Kring 2009, 2013; Filiberto and Schwenzer 2013). It should also be noted that fluid circulation is minimized at temperatures near the brittle–ductile transition (>400 ± 100 °C; Violay et al. 2015, 2017). Temperatures suitable for microbial life are much lower (metabolic activity within cells have been reported at a temperature of 122 °C; Takai et al. 2008) and models using higher $P$–$T$s are used here solely for examining secondary mineral assemblages that may occur within such craters.

The results from thermochemical modeling are presented as a function of water–rock ratio (W/R; a mass ratio), which is representative of the amount of rock that reacts in water (referred to as W/R* from hereon), as opposed to the actual water and rock present in the system. For example, a W/R* of 1000 would be the equivalent to 1 g of host rock reacting with 1 kg of water. Therefore, the W/R* can be indicative of water–rock interactions, as explained by Bridges et al. (2015) and Palandri and Reed (2004). W/R*s of 1,000,000 are generally representative of water–rock interactions where large amounts of water react with the host rock, such as at the surface. Lower W/R*s 100–1000 can represent interactions where lower quantities of water react with host rock, such as in the bedrock. In systems where water is stagnant, W/R*s within the bedrock could be less than 10 since a large amount of rock dissolves in a small amount of water. The circulation of fluids increases the amount of water reacting with a given amount of host rock, which increases the W/R*. However, variations in W/R*s can also occur as flow rates of circulating fluids would influence the amount of water reacting with rocks. For example, regions with high flow rates are assumed to have relativity high W/R*s compared to regions with lower flow rates.

**Initial Conditions**

**Host Rock Composition**

Previous work focusing on secondary mineral assemblages has predominantly explored the aqueous alteration of possible Martian protolith compositions...
The determination of the mineralogy of the selected host rocks was vital in evaluating the energy available for microbial activity, because it is the water–rock interactions with these minerals and fluids that result in the thermodynamic disequilibrium of the environments. Mineralogical analysis of the Rocknest samples was conducted by the Curiosity rover’s Chemistry and Mineralogy (CheMin) instrument using X-ray diffraction (Bish et al. 2013; Vaniman et al. 2014), which showed 27% of the sample was amorphous (Bish et al. 2013). It also showed olivine was an Fe-forsterite, and augite was rich in Mg (Table 3). However, to account for adjusting the concentration of Fe$^{2+}$ to 90% of Fe$_{\text{tot}}$, the quantity of the Fe-endmembers within these minerals were increased, which is shown in Table 3. The only mineralogy data for Hema2 was provided by Mössbauer analysis, which showed the presence of olivine (29% of Fe$_{\text{tot}}$), pyroxene (30% of Fe$_{\text{tot}}$), magnetite (6% of Fe$_{\text{tot}}$), hematite (22% of Fe$_{\text{tot}}$), and a nanophase ferric oxide (13% of Fe$_{\text{tot}}$; Morris et al. 2006b). Owing to the relatively high primary silicates in the Hema2 samples, the same mineralogy was assumed, but proportions were changed to match APXS chemistry data (Table 3). It should be noted that the mineralogies were identified for both host rock compositions to help determine what redox reactions occurred (see Table S1 in supporting information for mineral formulae). Data from both Rocknest and Hema2 did show the presence of an amorphous phase (Morris et al. 2006a, 2006b; Bish et al. 2013; Vaniman et al. 2014). However, given the lack of thermodynamic data available for these phases, the Gibbs energy calculations were restricted to only the crystalline phases. Therefore, it was not possible to determine how much energy could be provided to support microbial life through the reduction or oxidation of Fe within these phases.

**Fluid Chemistry**

The composition of Martian groundwaters is unknown; however, experiments and thermochemical modeling have shown that the local geological environment and the pH of incoming fluids will strongly influence groundwater composition (e.g., Baker et al. 2000; Bullock et al. 2004; Hurowitz et al. 2005; Schwenzer et al. 2016). For example, experiments conducted under relatively acidic starting conditions (pH 5) reported Fe concentrations on the order of $10^{-5}$–$10^{-6}$ M at 25 °C (Bullock et al. 2004), whereas at higher pH (8.5), no Fe was detected at 23 °C (Baker et al. 2000). Therefore, initial fluid compositions for each host rock were derived, using CHIM-XPT, by titrating pure water with initial host conditions.
rock composition at 25 °C and 1 bar, which is similar to the approach taken by Varnes et al. (2003). The fluid composition identified at a W/R* of 1000 was selected for initial groundwater compositions, and 1.68 × 10^{-4} M of HCO₃⁻ was added as an estimation of the concentration of carbon-bearing species. This concentration has been used in previous work because it impedes carbonate formation and is equivalent to the concentrations found when the Martian atmosphere, at its current pressure, is reacted with fluid (Schwenzer and Kring 2009; Schwenzer et al. 2012; Bridges et al. 2015). The resultant groundwaters were dilute, with low ionic strength, in the order of 10^{-3} M, and near neutral pH. Fluids were rich in SiO₂, Ca²⁺, Na⁺, and K⁺, and depleted in Fe²⁺, Mg²⁺, and Al³⁺, which is consistent with previously modeled Martian fluids (Schwenzer et al. 2016). The depleted concentrations of Fe²⁺, Mg²⁺, and Al³⁺ found within these fluids are due to these components being partitioned into mineral phases, such as chlorite for Mg²⁺ and nontronite for Fe²⁺. These groundwater-type fluids are different from surface fluids, because the latter would incorporate soluble salts that would influence ion concentrations, such as Mg²⁺, Ca²⁺, and SO₄²⁻, which would be concentrated by surface process, such as evaporation (Hecht et al. 2009; Kounaves et al. 2010). These compounds are unlikely to have formed in the subsurface environments modeled in this study and have, therefore, not been considered in our models.

**Thermodynamic Calculations**

Gibbs energy calculations were used to determine the amount of geochemical energy that would be available for microbes to use in suitable temperature environments. These calculations focused on water–rock reactions that produced Fe-bearing secondary minerals. The Gibbs energy (ΔG) under non-standard P–Ts was calculated using Equation 1.

\[
\Delta G = \Delta G^\circ_{(T,P)} + RT \ln Q
\]

where \(\Delta G^\circ_{(T,P)}\) is the standard molar Gibbs energy of reaction at a given temperature (T) and pressure (P), \(R\) is the universal gas constant, \(T\) is the temperature in Kelvin, and \(Q\) is the reaction quotient. The latter value enables the activities of the reacting materials (aqueous species and minerals) to be incorporated into the calculation, and, therefore, incorporates the conditions within the system. An activity of one was used for minerals and H₂O, and the activity of aqueous species following water–rock interactions were calculated along with secondary mineral assemblages. The activity and concentration of aqueous species from initial groundwater fluids were determined using aqueous speciation code SOLVEQ-XPT (Reed et al. 2016), a companion code to CHIM-XPT.

The amount of available energy was constrained by changes in Fe-species distribution in secondary minerals when compared to the distribution in the initial host rock compositions. It should be noted that this approach was

<table>
<thead>
<tr>
<th>Initial minerals</th>
<th>wt%</th>
<th>wt%</th>
<th>Mineral wt%</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase (An57)</td>
<td>29.8</td>
<td>40.8</td>
<td>Anorthite</td>
<td>23.26</td>
</tr>
<tr>
<td>Fe-Forsterite</td>
<td>16.4</td>
<td>22.4</td>
<td>Albite</td>
<td>17.54</td>
</tr>
<tr>
<td>Augite</td>
<td>10.7</td>
<td>14.6</td>
<td>Forsterite</td>
<td>11.00</td>
</tr>
<tr>
<td>Pigeonite</td>
<td>10.1</td>
<td>13.8</td>
<td>Fayalite</td>
<td>11.00</td>
</tr>
<tr>
<td>Magnetite</td>
<td>1.5</td>
<td>2.1</td>
<td>Hedenbergite</td>
<td>11.00</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>1.1</td>
<td>1.5</td>
<td>Diopside</td>
<td>17.80</td>
</tr>
<tr>
<td>Quartz</td>
<td>1</td>
<td>1.4</td>
<td>Magnetite</td>
<td>2.10</td>
</tr>
<tr>
<td>Sanidine</td>
<td>0.9</td>
<td>1.3</td>
<td>Anhydrite</td>
<td>1.50</td>
</tr>
<tr>
<td>Hämaité</td>
<td>0.8</td>
<td>1.1</td>
<td>Quartz</td>
<td>1.40</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.7</td>
<td>0.9</td>
<td>Sanidine</td>
<td>1.30</td>
</tr>
<tr>
<td>Amorphous</td>
<td>27</td>
<td>–</td>
<td>Hämaité</td>
<td>1.10</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>99.9</td>
<td>Ilmenite</td>
<td>0.90</td>
</tr>
</tbody>
</table>

### Table 3. Mineralogies determined for Rocknest and Hema2 host rocks.

<table>
<thead>
<tr>
<th>Rocknest target mineralogy</th>
<th>Recalculated mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rocknest Fe²⁺ 90%</td>
<td>Hema 2 Fe²⁺ 50%</td>
</tr>
<tr>
<td>Fe₂⁺</td>
<td>90%</td>
</tr>
<tr>
<td>Initial minerals</td>
<td>wt%</td>
</tr>
<tr>
<td>Plagioclase (An57)</td>
<td>29.8</td>
</tr>
<tr>
<td>Fe-Forsterite</td>
<td>16.4</td>
</tr>
<tr>
<td>Augite</td>
<td>10.7</td>
</tr>
<tr>
<td>Pigeonite</td>
<td>10.1</td>
</tr>
<tr>
<td>Magnetite</td>
<td>1.5</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>1.1</td>
</tr>
<tr>
<td>Quartz</td>
<td>1</td>
</tr>
<tr>
<td>Sanidine</td>
<td>0.9</td>
</tr>
<tr>
<td>Hämaité</td>
<td>0.8</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.7</td>
</tr>
<tr>
<td>Amorphous</td>
<td>27</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

*aMineral formulae for all minerals can be found in Table S1.
*bMineralogy of Rocknest soil determined from X-ray diffraction analysis (Bish et al. 2013; Vaniman et al. 2014).
*cNormalized mineralogy of the crystalline component of Rocknest soils.
*dMinerals reported in a solid solution are separated into endmember minerals.*
taken for simplicity in constraining the amount of energy that could be produced, based solely on either the oxidation or reduction of Fe within the system.

$\Delta G^\circ_{\Delta H,\Delta G}$ was calculated using Supercp92 (Palandri 2020), which is a modified version of Supercp92 (Johnson et al. 1992) using the Sporns92 database (Palandri 2020). The endmembers of minerals that occur in solid solutions, for example, augite, olivine, and plagioclase, were used to determine mineral reaction pathways and to calculate $\Delta G^\circ_{\Delta H,\Delta G}$. Calculated energy values were used to estimate the biomass and potential cell numbers by determining the quantity of adenosine triphosphate (ATP) that could be generated (Jakosky and Shock 1998). It was assumed that only 10% of available energy would be used to generate new cells (Jakosky and Shock 1998; McCollom and Amend 2005); 41.8 kJ is required to produce 1 mol of ATP and 0.02 mol of ATP is required to generate 1 g of cells, which can then be used to determine cell numbers by assuming one cell has a mass of $6.65 \times 10^{-13}$ g (Ilic et al. 2001).

RESULTS AND DISCUSSION

Characteristics of Varied Chemical Environments

Thermochemical modeling was used to determine mineral reaction pathways for a 100 km in diameter hypothetical complex impact crater. The results from these models are presented in Fig. 1.

Rocknest Environment

At 5°C, 1 bar, high W/R* (>10,000) produced mineral assemblages that were dominated by quartz. Chlorite minerals were the second most abundant, ranging from 23 wt% at a W/R* of 10,000 to 5% at a W/R* of 100,000. As the W/R* decreased to intermediate ratios (between W/R*s of 100 to 10,000), there was a shift in the mineral assemblage, which became dominated instead by chlorite minerals and nontronite. An increase in stilbite abundance occurred at intermediate W/R*s, and Fe-celadonite also became stable. At a W/R* of 140, there was a decrease in the abundance of nontronite and chlorite when goethite began to form. At low W/R*s (<100), a stilbite–chlorite-dominated mineral assemblage formed. Goethite, Fe-celadonite, and antigorite formed in abundances of 10–12 wt% each.

At 50°C, 500 bar, and high W/R*s, quartz was the most abundant mineral, and chlorite minerals the second most abundant. At intermediate W/R*, this changed to chlorite minerals being the most abundant, and at W/R* 2000 nontronite became stable, which resulted in a chlorite–nontronite–stilbite assemblage at W/R*s of 500 and lower. At low W/R*, mineral...
assemblages were still dominated by chlorite and nontronite, unlike at a $P$–$T$ of 5°C, 1 bar Fe-oxides were not stable. The latter may have resulted from the precipitation of greater amounts of chlorite minerals (a 22 wt% difference when comparing maximum abundances between the two $P$–$T$ regimes).

Mineral assemblages observed at 100 °C, 1000 bar were similar to those identified at 50 °C, 500 bar. However, nontronite became stable at lower W/R* (500) when compared to the results from 50 °C, 500 bar models. This was presumably due to changes in the solubility of Ca at lower W/R*, which enabled the stability of both nontronite and stilbite.

Chlorite minerals continued to dominate mineral assemblages at 150 °C, 700 bar, and high W/R*s. However, at an intermediate W/R* of 1110, low-grade metamorphic minerals became stable. At low W/R*, riebeckite and prehnite became the most abundant minerals, and chlorite minerals were the third most abundant.

At the highest $P$–$T$ regime considered in this study (300 °C, 1000 bar), epidote formed in abundances of greater than 30 wt% and was the most dominant mineral across all W/R*s. At high W/R*, hematite was also stable, which created an epidote–hematite–antigorite mineral assemblage. At intermediate W/R*s, magnetite became stable and hematite abundances began to decrease at a W/R* of 5000. Unlike previous $P$–$T$ regimes, chlorite minerals only became stable at a W/R* of 2000. At low W/R*s, an epidote–chlorite–riebeckite mineral assemblage formed, and microcline became stable at W/R* of 50.

Hema2 Environment

The most significant difference between the Hema2 and Rocknest host rock compositions was the proportion of Fe and the distribution of Fe species. This variation was reflected in the mineral abundances determined for each $P$–$T$ regime.

At 5 °C, 1 bar, quartz was found to be the dominant mineral precipitated at high W/R*s. At intermediate W/R*s, nontronite and chlorite minerals became the most abundant minerals from a W/R* of 500. These mineral types had abundances of 22–42 wt% for nontronites and 22–39 wt% for chlorite at intermediate W/R*s, which is greater than the abundances observed for Rocknest (3–30 wt% for nontronite and 18–33 wt% for chlorite). Antigorite and stilbite became stable at a W/R* of 1430. Fe-celadonite did not have an abundance above 5 wt%, which was dissimilar to the results for the Rocknest model. This was presumably due to the Rocknest composition possessing a greater initial quantity of Fe$^{2+}$. At low W/R*s, nontronite minerals decreased in abundance to a minimum of 12 wt% at a W/R* of 10. At the same time, goethite and stilbite abundances increased, which would have utilized Fe, Ca, and Si previously used by nontronite.

At 50 °C, 500 bar, quartz was the dominant mineral formed at high W/R*s, which was similar to the results for Rocknest models. However, unlike the results for Rocknest, both chlorite and nontronite minerals were the most abundant minerals (between 30 and 36 wt% for nontronite and 33–45 wt% for chlorite) at intermediate and low W/R*s. Tobermorite became stable from W/R* of 500 and increased in amounts to 12 wt% at low W/R*, which was slightly lower than the abundances identified for the Rocknest host rock composition.

At 100 °C, 1000 bar, high W/R*s showed quartz and chlorite minerals were dominant, and minor quantities of hematite were also stable at these W/R*s; this differs from the Rocknest results and could be attributed to the higher amounts of Fe$^{3+}$ found in the initial Hema2 host rock composition. Nontronite became stable at a W/R* of 10,000 and became the second most abundant mineral at a W/R* of 5000. This led to a chlorite–nontronite mineral assemblage for all W/R*s below 5000. The amount of nontronite formed in this model was much greater than those observed for Rocknest, which again could have been contributed to by the variations in Fe-species distribution of the initial host rock compositions.

Chlorite minerals were the dominant phases stable at W/R*s greater than 100 at 150 °C, 700 bar, which was similar to Rocknest. However, unlike Rocknest, hematite was the second most abundant mineral at high W/R*s. Riebeckite became the second most abundant mineral at a W/R* of 3330, which may have resulted from hematite becoming unstable. Prehnite became stable at W/R* 1000 and nontronite was stable at a W/R* of 500. This again differed from the Rocknest model, which resulted in the stability of prehnite and nontronite at W/R*s of 10,000 and 100, respectively.

An epidote–hematite-antigorite mineral assemblage was dominant at high W/R*s and at 300 °C, 1000 bar, which was similar to Rocknest. However, magnetite became stable at W/R* of 14,300, which occurred at a lower W/R* of 5000 for Rocknest. At intermediate W/R*s, epidote remained the most abundant mineral but declined as the W/R* decreased, from 47 wt% at a W/R* of 10,000 to 27 wt% at a W/R* of 100. Chlorite minerals were stable at a W/R* of 5000 and hematite did not form below a W/R* of 300. Magnetite maintained an abundance of over 10 wt% for intermediate W/R*s, which was not observed for Rocknest where quantities peaked at 12 wt% at a W/R* of 330. At low W/R*s, both chlorite minerals and
epidote were the most abundant, antigorite was the third dominant mineral, and riebeckite abundances increased as W/R* decreased, which generated a similar assemblage to Rocknest.

Comparison to Previous Investigations

The secondary alteration minerals reported for these models differed from the results of previous studies (Schwenzer and Kring 2009, 2013; Filiberto and Schwenzer 2013; Bridges et al. 2015).

Schwenzer and Kring (2013) examined the alteration of various protolith lithologies at 300, 150, and 90 °C, and showed that at 300 °C, mineral assemblages were dominated by hematite (70–80 wt% at a W/R*s of 100 and 100,000). A similar high abundance of hematite (90–85 wt%) was also formed at 150 °C at a W/R* of 100,000 but decreased to 30–65 wt% at a W/R* 1000, it also showed 40–50 wt% of nontronite forming under these conditions. Investigations into the formation of Home Plate and Columbia Hills, conducted by Filiberto and Schwenzer (2013), also showed a high proportion of Fe-oxide (90 wt%), in this case magnetite, at 300 °C and W/R* of 10,000, which decreased to 20 wt% at a W/R* of 1000. Epidote was not stable in these systems until W/R*s of 60 and below and occurred in abundances of <10 wt%. The higher concentrations of Fe-oxides seen in previous work could be reflective of the initial fluid composition used, which was more oxidizing and possessed a greater concentration of Fe (approximately six orders of magnitude greater than that used in the Rocknest and Hema2 host rock compositions).

Filiberto and Schwenzer (2013) also examined mineral alterations at 13 °C, which showed nontronite–chlorite–goethite and chlorite–amphibole mineral assemblages at W/R*s of 10,000–1000 and 100–10, respectively. These mineral assemblages differed from both Rocknest and Hema2 compositions, which also showed quartz was a dominant mineral at a W/R* of 1000. They also showed amphibole and goethite were not stable until W/R*s of ~100 and below for both Rocknest and Hema2 compositions at comparable P–Ts.

Low temperature investigations were also conducted by Bridges et al. (2015) at 10 °C using a Portage soil composition (a sediment sample taken by Curiosity at Gale crater) as the host rock. These models resulted in similar minerals forming but with different abundances at comparable W/R*s for both Rocknest and Hema2 models. For example, the Portage soil host composition resulted in mineral assemblages dominated by chlorite minerals that ranged in abundances of 38–58 wt% across equivalent W/R*s, which is 5–25 wt% greater than what was found for Rocknest in this study. It was also reported that Portage soil led to less stilbite (Bridges et al. 2015), which could have contributed to the higher proportions of chlorite, since more Si was available. Portage soil compositions also showed less quartz forming and it was restricted to low W/R*s, whereas Rocknest and Hema2 compositions result in a secondary mineralogy dominated by quartz at high W/R*s at: 5 °C, 1 bar; 50 °C, 500 bar, and 100 °C, 1000 bar. This variation in quartz between models in this paper and previous studies in low P–T environments and at high W/R*s (Filiberto and Schwenzer 2013; Bridges et al. 2015) presumably results from the differences in Si concentrations in initial groundwater chemistries. Groundwaters for both Rocknest and Hema2 environments had Si concentrations of $10^{-3}$ mol kg$_{\text{water}}^{-1}$, which is two orders of magnitude higher in the groundwater for Portage models (Bridges et al. 2015) and three orders of magnitude greater than the model conducted by Filiberto and Schwenzer (2013), which had no Si in groundwaters. This higher concentration of Si would have resulted in fluids oversaturated in Si, leading to the stability of quartz at much higher W/R*s for both Rocknest and Hema2 models.

Impact Crater Environment

In order to apply these models to the environments that could be found within a Martian crater (100 km in diameter), W/R*s were selected to represent the different water–rock interactions that could occur within either bedrock or a fracture (Fig. 2 and Tables S2 and S3 in supporting information). The selection of W/R*s was based on the type of interaction and the relative amount of water in the location within the crater subsurface environment, which was presented in Abramov and Kring (2005). The method section discusses how W/R*s for these models can be influenced by flow of water interacting with a specific amount of rock.

The contextualized results showed changes in mineralogy as $P$–$T$ increased with depth (Fig. 2 and Tables S2 and S3). In a bedrock setting at 5 °C, 1 bar, stilbite–chlorites–Fe–celadonite–goethite and chlorite–nontronite–stilbite–antigorite mineral assemblages are formed in Rocknest and Hema2 environments, respectively, whereas at higher $P$–$T$s (150 °C, 700 bar), more low-grade metamorphic minerals were formed, leading to mineral assemblages of chlorite–prehnite–riebeckite–quartz and chlorite–riebeckite for Rocknest and Hema2, respectively. At 300 °C 1000 bar, both low- and moderate-grade metamorphic minerals were stable, which resulted in mineral assemblages that were dominated by epidote in bedrock settings (epidote–antigorite and epidote–chlorite–antigorite–magnetite for Rocknest and Hema2, respectively).

Mineral assemblages within a fracture also showed a change in mineralogy as $P$–$T$s increased. This resulted in
mineral assemblages dominated by nontronite and chlorite at low $P$–$T$s, to epidote and hematite at high $P$–$T$s for both Rocknest and Hema2 environments. However, low-grade metamorphic minerals were not found at 150 °C, 700 bar within a fracture (W/R* of 10,000); the models showed these minerals formed at intermediate to low W/R*s for both host rock chemistries.

The hydrothermal mineral assemblages identified for Rocknest and Hema2 crater environments compare favorably to a range of terrestrial impact-generated hydrothermal systems. One of the most well-preserved impact craters on Earth is the 180 km Chicxulub impact structure in Mexico, which is believed to have possessed an impact-generated hydrothermal system (Zürcher and Kring 2004). The Chicxulub impact occurred in a marine setting and into a stratified target. Core samples revealed that the target rocks were granitoid and mafic clasts have also been observed in the target material (Kring et al. 2004; Simpson et al. 2020). These mafic clasts are believed to have been from diabase, pyroxenite, or amphibolite source rock (Kring et al. 2004), which would be mineralogically similar to Mars. It is assumed impact-generated hydrothermal alteration initially occurred at temperatures of greater than 300 °C.
and as the crater cooled overprinting of initial alteration minerals occurred at temperature of <200 °C (Kring et al. 2020; Simpson et al. 2020). Studies examining the hydrothermal alteration of minerals within the structure have reported the detection of minerals that include zeolites, clays, chlorite, pyrite, silica, and epidote (Zürcher and Kring 2004; Kring et al. 2020). In particular, chlorite, clay, and epidote would have been formed through the alteration of clinopyroxenes at temperatures of <300 °C (Zürcher and Kring 2004). Impact-generated hydrothermal systems have also been observed in subaerial impact structures, such as the 100 km Popigai and the 80 km Puchezh-Katunki structures in Russia (Naumov 2002, 2005; Osinski et al. 2013). Target rocks for both impact structures are believed to have been a mixture of crystalline and sedimentary rock, which were altered at temperatures below 300–350 °C (Naumov 2002). Examination of hydrothermal alteration of minerals within the structure has shown the presence of chlorite, sulfide, quartz, smectite, stilbite, and prehnite (Naumov 2002). In addition, a review of terrestrial impact-generated hydrothermal systems, conducted by Osinski et al. (2013), found that phyllosilicates (predominantly smectites, chloride, celadonite, and mica), zeolite, amphiboles, and epidote were common minerals formed from the alteration of silicates. The favorable comparison of terrestrial hydrothermal mineralogies to those anticipated for the Martian environments modeled here indicate such systems could have existed on Mars.

Studies that explored Hesperian–Amazonian aged craters on Mars found evidence for chlorite, phyllosilicates, kaolinite, Fe/Mg smectites (nontronite and montmorillonite), hydrated silica, and prehnite (Marzo et al. 2010; Sun and Milliken 2014; Turner et al. 2016; Pan et al. 2018). Although some of these craters are smaller than the crater size examined here, such as Stokes crater (62.5 km in diameter; Turner et al. 2016) or Ritchey crater (78 km in diameter; Sun and Milliken 2014), models at low $P-T$ regimes would still be applicable because it has been shown that host rock composition and temperature are the dominant controls on secondary mineralogy (Griffith and Shock 1997; Schwenzer and Kring 2009, 2013). This would suggest that such Hesperian–Amazonian impact craters could have possessed impact-generated hydrothermal systems and could have formed in Rocknest or Hema2 type host rock chemistries.

**Energy for Microbes**

**Redox of Fe**

Fe-based redox reactions were observed within thermochemical models resulting in a net change in the distribution of Fe-species in secondary mineral assemblages compared to the initial host rock distribution. In both the Rocknest and Hema2 alteration products, Fe was found in nontronite, chlorite, Fe-celadonite, and Fe-oxides for temperatures of 100 °C and less. At higher temperatures, Fe-rich minerals also included riebeckite and epidote. It should be noted that <5 wt% of pyrite was formed in all models and $P-T$ regimes (for both host rock chemistries). Therefore, the net change in Fe-species was calculated for the contextualized crater environment for both Rocknest and Hema2 (Fig. 3 and Tables S4 and S5 in supporting information). These values were used as the limiting factor to constrain Gibbs energy calculations, because reactions that led to changes in Fe oxidation state would be the source of energy utilized by microbes.

Redox reactions occurred across the crater and overall the $P-T$ regimes did not control the redox state of the environment. Alteration products of Hema2 host rock showed a net increase in total $\text{Fe}^{2+}$ in all but three environments ($5^\circ\text{C}, 1\text{ bar W/R}^\ast 1000$, and $300^\circ\text{C} 1000\text{ bar at both W/R}^\ast$s) when compared to initial host rock...
rock abundances. Initial fluid chemistries between Rocknest and Hema2 models were also similar (Table 2): no gases were saturated that could have contributed to the redox of the system, and the pH did not differ between the two host rock chemistries. Therefore, the Fe-species distribution of the initial host rock has played a role in whether the overall environments led to net changes in Fe species. For example, Rocknest started with 90% of Fe as Fe$^{2+}$ and showed a net increase in Fe$^{3+}$ in all but three environments.

These results also showed that variation in the distribution of Fe-species was greatest for Rocknest alteration minerals formed at 300 °C, 1000 bar, and 300 °C, 1000 bar produced some of the greatest variation for overall Fe-species distribution, these temperatures were too high to support microbial life. The change in the distribution of Fe-species in secondary minerals indicates that redox reactions would be feasible within Martian impact crater environments.

**Available Energy**

The secondary minerals identified from thermochemical models were used to determine the redox reaction that would be feasible within the crater environment (Table 4). However, based on our current understanding, the maximum temperature for cell metabolic activity is 122 °C (Takai et al. 2008), which limited the regions within the crater where microbial life could exist. Therefore, energy calculations were limited to regions of 5, 50, and 100 °C. On Earth, microorganisms have been shown to contribute to the formation of the secondary minerals in a variety of aquatic environments and temperature regimes. For

### Table 4. List of reactions considered.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-oxidation reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fayalite to nontronite</td>
<td>$2 \text{Fe}_2\text{SiO}_4 + 2.67\text{CaAl}_2\text{Si}_2\text{O}_8 + 4 \text{H}_2\text{O}$</td>
<td>$2 \text{Ca}_0.165 \text{Fe}<em>2\text{Al}</em>{0.33}\text{Si}_3.67\text{O}_12\text{H}_2 + 4.68 \text{AlO}_2^- + 2.34 \text{Ca}^{2+} + 2 \text{H}_2(\text{aq})$</td>
</tr>
<tr>
<td>Hedenbergite to nontronite</td>
<td>$2 \text{CaFeSi}_2\text{O}_6 + 0.33 \text{CaAl}_2\text{Si}_2\text{O}_8 + 4 \text{H}_2\text{O}$</td>
<td>$2 \text{Ca}_0.165 \text{Fe}<em>2\text{Al}</em>{0.33}\text{Si}_3.67\text{O}_12\text{H}_2 + 0.33 \text{AlO}_2^- + 2.165 \text{Ca}^{2+} + 0.99 \text{HSiO}_3^- + 3.01 \text{OH}^- + \text{H}_2(\text{aq})$</td>
</tr>
<tr>
<td>Magnetite to nontronite</td>
<td>$2 \text{Fe}_3\text{O}_4 + 2 \text{SiO}_2 + 2.67 \text{Ca(Al}_2\text{Si}_2\text{O}_8 + 4 \text{H}_2\text{O}$</td>
<td>$2 \text{Ca}_0.165 \text{Fe}<em>2\text{Al}</em>{0.33}\text{Si}_3.67\text{O}_12\text{H}_2 + 4.68 \text{AlO}_2^- + 2.34 \text{Ca}^{2+} + \text{H}_2(\text{aq}) + 2 \text{HFeO}_2(\text{aq})$</td>
</tr>
<tr>
<td>Ilmenite to nontronite</td>
<td>$4 \text{FeTiO}_3 + 2 \text{SiO}_2 + 2.67 \text{Ca(Al}_2\text{Si}_2\text{O}_8 + 4 \text{H}_2\text{O}$</td>
<td>$2 \text{Ca}_0.165 \text{Fe}<em>2\text{Al}</em>{0.33}\text{Si}_3.67\text{O}_12\text{H}_2 + 4.68 \text{AlO}_2^- + 2.34 \text{Ca}^{2+} + 2 \text{H}_2(\text{aq}) + 4 \text{Ti(OH)}_4$</td>
</tr>
<tr>
<td>Fayalite to goethite</td>
<td>$\text{Fe}_2\text{SiO}_4(\text{s}) + 4 \text{H}_2\text{O}$</td>
<td>$2 \text{FeO(OH)}(\text{s}) + \text{H}_2\text{SiO}_4(\text{aq}) + \text{H}_2(\text{aq})$</td>
</tr>
<tr>
<td>Hedenbergite to goethite</td>
<td>$2 \text{CaFeSi}_2\text{O}_6(\text{s}) + 12 \text{H}_2\text{O}$</td>
<td>$2 \text{FeO(OH)}(\text{s}) + 2 \text{Ca}^{2+} + 4 \text{H}_2\text{SiO}_4(\text{aq}) + 4 \text{OH}^- + \text{H}_2(\text{aq})$</td>
</tr>
<tr>
<td>Magnetite to goethite</td>
<td>$2 \text{Fe}_3\text{O}_4 + 4 \text{H}_2\text{O}$</td>
<td>$6 \text{FeO(OH)} + \text{H}_2(\text{aq})$</td>
</tr>
<tr>
<td>Ilmenite to goethite</td>
<td>$2 \text{FeTiO}_3 + 6 \text{H}_2\text{O}$</td>
<td>$2 \text{FeO(OH)} + \text{H}_2(\text{aq}) + 2\text{Ti(OH)}_4$</td>
</tr>
<tr>
<td>Fe-reduction reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite to pyrite</td>
<td>$\text{Fe}_3\text{O}_4(\text{s}) + 6 \text{CaSO}_4(\text{s}) + 22 \text{H}_2(\text{aq})$</td>
<td>$3 \text{Fe}_2\text{S}_2(\text{s}) + 6 \text{Ca}^{2+} + 12 \text{OH}^- + 16 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Hematite to pyrite</td>
<td>$\text{Fe}_2\text{O}_3(\text{s}) + 4 \text{CaSO}_4(\text{s}) + 15 \text{H}_2(\text{aq})$</td>
<td>$2 \text{Fe}_2\text{S}_2(\text{s}) + 4 \text{Ca}^{2+} + 8 \text{OH}^- + 11 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Magnetite to celadonite</td>
<td>$\text{Fe}_2\text{O}_3(\text{s}) + 2\text{KAISi}_2\text{O}_8(\text{s}) + \text{SiO}_2(\text{s}) + \text{H}_2(\text{aq})$</td>
<td>$\text{KFeAlSi}_4\text{O}_10(\text{OH})_2(\text{s}) + 2 \text{FeO}(\text{aq})$</td>
</tr>
<tr>
<td>Hematite to celadonite</td>
<td>$\text{Fe}_2\text{O}_3(\text{s}) + 2\text{KAISi}_2\text{O}_8(\text{s}) + \text{SiO}_2(\text{s}) + \text{H}_2(\text{aq})$</td>
<td>$\text{KFeAlSi}_4\text{O}_10(\text{OH})_2(\text{s}) + \text{FeO}(\text{aq})$</td>
</tr>
<tr>
<td>Magnetite to daphnite</td>
<td>$2 \text{Fe}_3\text{O}_4(\text{s}) + 2\text{CAI}_2\text{Si}_2\text{O}_8(\text{s}) + \text{SiO}_2(\text{s}) + 3 \text{H}_2\text{O} + 2 \text{H}_2(\text{aq})$</td>
<td>$\text{Fe}_3\text{Si}_2\text{O}_8(\text{OH})_2(\text{s}) + \text{FeO}(\text{aq}) + \text{Ca}^{2+} + 2 \text{OH}^- + 12 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Hematite to daphnite</td>
<td>$3 \text{Fe}_2\text{O}_3(\text{s}) + 3\text{CAI}_2\text{Si}_2\text{O}_8(\text{s}) + 2\text{SiO}_2(\text{s}) + 2 \text{H}_2\text{O} + 3 \text{H}_2(\text{aq})$</td>
<td>$\text{Fe}_3\text{Si}_2\text{O}_8(\text{OH})_2(\text{s}) + \text{FeO}(\text{aq}) + \text{Ca}^{2+} + 2 \text{OH}^- + 12 \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
Table 5. ΔG values (kJ mol\(^{-1}\)) calculated at standard molar concentrations.

<table>
<thead>
<tr>
<th>Reaction (see Table 4)</th>
<th>5 °C 1 bar W/R*100</th>
<th>1 bar W/R*1000</th>
<th>50 °C 500 bar W/R*1000</th>
<th>50 °C 500 bar W/R*1000</th>
<th>100 °C 1000 bar W/R*100</th>
<th>100 °C 1000 bar W/R*1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rocknest</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fayalite to nontronite</td>
<td>−179.61</td>
<td>−202.44</td>
<td>−188.97 N/A</td>
<td>N/A</td>
<td>−151.58 N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hedenbergite to nontronite</td>
<td>26.39</td>
<td>−4.23</td>
<td>−2.88 N/A</td>
<td>N/A</td>
<td>19.95 N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to nontronite</td>
<td>−151.71</td>
<td>−133.61</td>
<td>−156.64 N/A</td>
<td>N/A</td>
<td>−126.27 N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Ilmenite to nontronite</td>
<td>−32.47</td>
<td>−70.20</td>
<td>−35.08 N/A</td>
<td>N/A</td>
<td>36.55 N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fayalite to goethite</td>
<td>−19.57</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hedenbergite to goethite</td>
<td>43.48</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to goethite</td>
<td>−24.94</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Ilmenite to goethite</td>
<td>28.90</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to pyrite</td>
<td>60.73</td>
<td>−22.56</td>
<td>−18.36 −103.02</td>
<td>48.40</td>
<td>2.62</td>
<td></td>
</tr>
<tr>
<td>Hematite to pyrite</td>
<td>43.82</td>
<td>−11.70</td>
<td>−9.36 −65.80</td>
<td>34.69</td>
<td>4.17</td>
<td></td>
</tr>
<tr>
<td>Magnetite to celadonite</td>
<td>60.81</td>
<td>55.44</td>
<td>N/A</td>
<td>N/A</td>
<td>61.41</td>
<td>N/A</td>
</tr>
<tr>
<td>Hematite to celadonite</td>
<td>6.87</td>
<td>4.19</td>
<td>N/A</td>
<td>N/A</td>
<td>8.03</td>
<td>N/A</td>
</tr>
<tr>
<td>Hematite to daphnite</td>
<td>−15.83</td>
<td>−32.39</td>
<td>−29.08 −45.74</td>
<td>−13.16</td>
<td>−21.86</td>
<td></td>
</tr>
<tr>
<td>Hematite to daphnite</td>
<td>−5.81</td>
<td>−22.38</td>
<td>−20.43 −37.10</td>
<td>−5.88</td>
<td>−14.58</td>
<td></td>
</tr>
<tr>
<td>Hema2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fayalite to nontronite</td>
<td>−180.10</td>
<td>−204.88</td>
<td>−206.40 −234.51</td>
<td>−152.75</td>
<td>−180.37</td>
<td></td>
</tr>
<tr>
<td>Hedenbergite to nontronite</td>
<td>24.98</td>
<td>−5.86</td>
<td>−6.80 −38.43</td>
<td>20.17</td>
<td>−2.24</td>
<td></td>
</tr>
<tr>
<td>Magnetite to nontronite</td>
<td>−151.96</td>
<td>−178.63</td>
<td>−172.75 −203.79</td>
<td>−127.66</td>
<td>−152.43</td>
<td></td>
</tr>
<tr>
<td>Ilmenite to nontronite</td>
<td>−37.09</td>
<td>−77.65</td>
<td>−57.82 −98.21</td>
<td>28.66</td>
<td>−20.13</td>
<td></td>
</tr>
<tr>
<td>Fayalite to goethite</td>
<td>−19.82</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hedenbergite to goethite</td>
<td>42.07</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to goethite</td>
<td>−8.48</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Ilmenite to goethite</td>
<td>53.25</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to pyrite</td>
<td>47.27</td>
<td>−40.20</td>
<td>−39.20 −119.39</td>
<td>35.14</td>
<td>−23.53</td>
<td></td>
</tr>
<tr>
<td>Hematite to pyrite</td>
<td>34.70</td>
<td>−23.61</td>
<td>−23.42 −76.88</td>
<td>25.65</td>
<td>−13.46</td>
<td></td>
</tr>
<tr>
<td>Magnetite to celadonite</td>
<td>3.97</td>
<td>−0.84</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hematite to celadonite</td>
<td>6.30</td>
<td>3.89</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to daphnite</td>
<td>−17.44</td>
<td>−34.42</td>
<td>−30.82 −44.66</td>
<td>−14.13</td>
<td>−23.53</td>
<td></td>
</tr>
<tr>
<td>Hematite to daphnite</td>
<td>−7.88</td>
<td>−24.86</td>
<td>−22.71 −36.54</td>
<td>−7.45</td>
<td>−16.86</td>
<td></td>
</tr>
</tbody>
</table>

N.B. Reactions that were not possible due to the secondary mineral not being stable in the environment have N/A.

example, microbially induced nontronite and goethite formation by the iron-oxidizing microorganisms *Mariprofundus ferrooxydans* and *Leptothrix ochracea*, respectively, have been identified in low temperature (8–90 °C) seafloor hydrothermal systems (Kennedy et al. 2003; Ta et al. 2017); and biomineralization of goethite has been observed in river reservoir sediments (Che et al. 2006).

The results from ΔG calculations (that represent standard molar concentrations) showed that not all the selected reactions were feasible (i.e., resulted in a negative ΔG; Table 5). For example, the reduction of Fe\(^{3+}\) in hematite and magnetite to form Fe\(^{2+}\) in celadonite was not a feasible reaction for Rocknest chemistries even though it was stable at temperatures of 5 and 100 °C. However, the reduction of Fe\(^{3+}\) in magnetite to form daphnite (chlorite endmember) was a feasible reaction and produced 13.16–45.74 kJ mol\(^{-1}\) or greater in all physicochemical environments. These results demonstrate that the oxidation of fayalite to form nontronite is the most favorable reaction and yields equal to or greater than 25 kJ mol\(^{-1}\) more than the second most favorable reaction (magnetite to nontronite) for all Rocknest and Hema2 environments. The quantity of the redox-active mineral present within the host rock would influence the amount of energy available to microbes. For example, magnetite to nontronite was the second most favorable reaction but magnetite comprised 2.1 wt% of the composition for Rocknest whereas fayalite represented 11.0 wt% (Table 3). Therefore overall, more energy would have been contributed through fayalite reactions per kilogram of material reacted than magnetite.
Energies from $\Delta G$ calculations (at standard molar concentrations) were then constrained to the net change in the distribution of Fe-species between the host rock and the secondary minerals to determine the amount of energy available. It is important to remember that the amount of energy presented here is reflective of the total energy, as the products and total Fe-species distribution were determined from systems that have reached equilibrium. It should also be noted that both oxidation and reduction reactions would have occurred simultaneously within the crater environments, and reactions would be constrained to the abundance of available reactants. For example, reduction reactions would most likely be limited by the availability of $H_2$, and availability of mineral components limits oxidation reactions. However, all selected oxidation reactions would generate $H_2$, which could then be used in reduction reactions and lead to the development of a hydrogen cycle.

The alteration of host rocks with a Rocknest composition produced greater energy yields than Hema2 alteration, $10^{-1} - 10^{-4}$ and $10^{-3} - 10^{-5}$ kJ, respectively (Table 6), because oxidation reactions were prevalent within the Rocknest crater environment, whereas reduction reactions dominated Hema2 crater environments. However, in crater environments where either reduction or oxidation was prevalent for both host rocks, energy yields were similar (within one order of magnitude), and variations in energy yields resulted from the net increase in Fe$^{3+}$ abundance. For example, at 5 °C 1 bar and a $W/R^*$ 1000, Rocknest alteration resulted in an increase in Fe$^{3+}$ abundance of 37%, and Hema2 alteration increased Fe$^{3+}$ abundance by 3%. This resulted in greater energy yields for Fe-oxidation with the Rocknest composition.

The available energy yields (Table 6) were then used to estimate the total amount of biomass and cell numbers that could be supported by these initial reactions (Table 7). In order to compare estimations of biomass and cell numbers to previous work, results were converted to a normalized reaction of 1 kg of rock. These calculations showed the synthesis of biomass would range between 0.050–4.834 and 0.004–0.715 g kg$^{-1}$ (or cell numbers of $10^{10}$–$10^{13}$ and $10^9$–$10^{12}$ cells kg$^{-1}$) for Rocknest and Hema2 environments, respectively, which is

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Reaction</th>
<th>Rocknest</th>
<th>Hema2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 °C 1 bar</td>
<td>$W/R^*$ 100</td>
<td>Fayalite to nontronite 4.04E-01</td>
<td>5.58E-02</td>
<td>1.37E-02</td>
</tr>
<tr>
<td>5 °C 1 bar</td>
<td>$W/R^*$ 1000</td>
<td>Fayalite to nontronite 2.28E-01</td>
<td>2.46E-02</td>
<td>7.55E-03</td>
</tr>
<tr>
<td>50 °C 500 bar</td>
<td>$W/R^*$ 1000</td>
<td>Fayalite to goethite 8.82E-02</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>50 °C 500 bar</td>
<td>$W/R^*$ 1000</td>
<td>Fayalite to goethite 3.74E-02</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>50 °C 500 bar</td>
<td>$W/R^*$ 10,000</td>
<td>Hematite to pyrite 1.02E-03</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>100 °C 1000 bar</td>
<td>$W/R^*$ 1000</td>
<td>Hematite to pyrite 9.76E-04</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>100 °C 1000 bar</td>
<td>$W/R^*$ 10,000</td>
<td>Hematite to pyrite 2.26E-04</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>100 °C 1000 bar</td>
<td>$W/R^*$ 10,000</td>
<td>Hematite to pyrite 1.83E-04</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* N/A, Reactions that were not possible due to secondary mineral not being stable in the environment. Dash indicates reactions that were either not feasible under the environment or did not correspond to the net change in Fe-species distribution.
Table 7. Estimation of the number of cells and grams of biomass (in parentheses) that can be supported when 1 kg of rock is dissolved.*

<table>
<thead>
<tr>
<th>Rocknest</th>
<th>5 °C 1 bar W/R*100</th>
<th>5 °C 1 bar W/R*1000</th>
<th>50 °C 500 bar W/R*1000</th>
<th>50 °C 500 bar W/R*1000</th>
<th>100 °C 1000 bar W/R*1000</th>
<th>100 °C 1000 bar W/R*1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bedrock Fracture</td>
<td>Bedrock Fracture</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fayalite to nontronite</td>
<td>7.27E+12 (4.834)</td>
<td>1.00E+13 (6.669)</td>
<td>2.46E+12 (1.634)</td>
<td>N/A</td>
<td>N/A</td>
<td>2.66E+12 (1.767)</td>
</tr>
<tr>
<td>Hedenbergite to nontronite</td>
<td>–</td>
<td>–</td>
<td>4.19E+11 (0.279)</td>
<td>7.50E+10 (0.050)</td>
<td>N/A</td>
<td>–</td>
</tr>
<tr>
<td>Magnetite to nontronite</td>
<td>4.09E+12 (2.722)</td>
<td>4.41E+12 (2.934)</td>
<td>1.36E+12 (0.903)</td>
<td>N/A</td>
<td>N/A</td>
<td>1.48E+12 (0.981)</td>
</tr>
<tr>
<td>Ilmenite to nontronite</td>
<td>1.31E+12 (0.874)</td>
<td>3.48E+12 (2.313)</td>
<td>4.56E+11 (0.303)</td>
<td>N/A</td>
<td>N/A</td>
<td>–</td>
</tr>
<tr>
<td>Fayalite to goethite</td>
<td>1.58E+12 (1.054)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to goethite</td>
<td>6.73E+11 (0.447)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to pyrite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hematite to pyrite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnetite to daphnite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hematite to daphnite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fayalite to nontronite</td>
<td>–</td>
<td>1.08E+12 (0.715)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hedenbergite to nontronite</td>
<td>–</td>
<td>6.15E+10 (0.041)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Magnetite to nontronite</td>
<td>–</td>
<td>6.25E+11 (0.416)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ilmenite to nontronite</td>
<td>–</td>
<td>4.08E+11 (0.271)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Magnetite to pyrite</td>
<td>–</td>
<td>–</td>
<td>3.57E+11 (0.237)</td>
<td>2.92E+11 (0.194)</td>
<td>–</td>
<td>7.24E+11 (0.481)</td>
</tr>
<tr>
<td>Hematite to pyrite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.20E+11 (0.213)</td>
<td>2.82E+11 (0.187)</td>
<td>–</td>
</tr>
<tr>
<td>Magnetite to daphnite</td>
<td>1.45E+10 (0.010)</td>
<td>–</td>
<td>1.40E+11 (0.093)</td>
<td>5.45E+10 (0.036)</td>
<td>1.70E+11 (0.113)</td>
<td>3.62E+11 (0.241)</td>
</tr>
<tr>
<td>Hematite to daphnite</td>
<td>6.55E+09 (0.004)</td>
<td>–</td>
<td>1.03E+11 (0.069)</td>
<td>4.46E+10 (0.030)</td>
<td>8.95E+10 (0.060)</td>
<td>2.59E+11 (0.172)</td>
</tr>
</tbody>
</table>

* N/A, Reactions that were not possible to secondary mineral not being stable in the environment. Dash indicates reactions that were either not feasible under the environment or did not correspond to the net change in Fe-species distribution.
The distribution of Fe-species within these various physicochemical environments showed changes in their distribution in the alteration assemblages produced compared to the initial host rock. This indicates that both Fe oxidation and reduction reactions could occur within these Martian environments, leading to Fe geochemical, and potentially biogeochemical, cycling.

Estimations of cell numbers showed that both host rock compositions would be able to support potential total cell numbers in the range of $10^9$–$10^{13}$ cells kg$_{(\text{dissolved rock})}^{-1}$. Potential cell numbers suggest that if life did exist within these hydrothermal environments, it would be detectable if suitable biosignatures were left behind.

Exposure to ionizing radiation at the Martian surface would lead to the degradation of organic biomarkers (Dartnell et al. 2007; Pavlov et al. 2012); therefore, geochemical or mineralogical biosignatures would be more likely to be found in near surface environments (Banfield et al. 2001). This might include biofilms (e.g., Chan et al. 2016) or microbial structures formed by biomineralization (e.g., Kennedy et al. 2003) or encrustation (e.g., Ta et al. 2017).

In this investigation, we have focused on the availability of energy from either the oxidation or reduction of Fe, but it is more than likely that microbial communities would develop in these systems and that they would exploit a range of energy sources. For example, the oxidation of Fe to produce nontronite or goethite would also produce H$_2$, which hydrogenotrophic microorganisms including methanogens are able to use as a source of energy (Lackner et al. 2018). Abiotic and biotic (produced by chemoautotrophic microorganisms) organic material could also be utilized by chemoorganotrophic and fermentative microorganisms (Westall et al. 2015), leading to the formation of a diverse microbial community within the impact crater environment.

While it is still unclear whether microbial life has ever existed on Mars, there is increasing evidence that Mars hosted habitable conditions throughout the Noachian (e.g., Poulet et al. 2005; Schulze-Makuch et al. 2008; Carr and Head 2010; Ehlmann and Edwards 2014). The results from this study suggest that life could have continued to be supported within an impact-generated hydrothermal system as the Martian surface began to lose its water during the Noachian–Hesperian climate transition. These results have also suggested possible mineral assemblages that may be associated with substantial quantities of biomass and could be used by future missions to identify sampling sites. In relatively young craters that have experienced little erosion, and especially in the areas with increased postimpact hydrothermal flow, nontronite would be the favorable mineral in which to search for signs of life. In craters that have experienced extensive erosion, chlorite would be more the favorable mineral to examine, particularly in reducing environments. The results from this work indicate that impact crater environments have the potential to supply substantial quantities of energy for microbial life. This, along with the identification of bio-essential elements and evidence of liquid water on early Mars (e.g., Gellert et al. 2004; Marzo et al. 2010; Turner et al. 2016), suggests that they are ideal targets for searching for evidence of life on Mars.

Acknowledgments—We would like to thank Dr. Tom McCollom for his helpful comments on earlier drafts of this manuscript. We also wish to thank Dr. Gordon Osinski, an anonymous reviewer, and associate editor Dr. Daniel Glavin for their constructive comments, which greatly improved this manuscript.

FUNDING

This work was supported by Leverhulme (grant code RPG-2016-200), UKSA (grant code ST/S001522/...
l), and Research England. Expanding Excellence in England (E3) fund (grant code 124.18).

Data Availability Statement—The data that support the findings of this study are available in the supplementary material of this article.

Editorial Handling—Dr. Daniel Glavin

REFERENCES


with the Chicxulub impact crater upper peak-ring breccias.  

Soderblom L. A., Anderson R. C., Arvidson R. E., Bell J. F.,  
Cabrol N. A., Calvin W., Christensen P. R., Clark B. C.,  
Economou T., Ehlmann B. L., Farrand W. H., Fike D.,  
Gellert R., Glotch T. D., Golombek M. P., Greeley R.,  
Grotzinger J. P., Herkenhoff K. E., Jerolmack D. J.,  
Johnson J. R., Jolliff B. L., Kleinbohmer C., Knoll A. H.,  
Learner Z. A., Li R., Malin M. C., McLennan S. M.,  
McSween H. Y., Ming D. W., Morris R. V., Rice J. W.,  
Richter L., Rieder R., Rodionov D., Schröder C., Seelos F.  
P. IV, Soderblom J. M., Squyres S. W., Sullivan R., Watters  
2004. Soils of Eagle crater and Meridiani Planum at the  

Sun V. Z. and Milliken R. E. 2014. The geology and  
mineralogy of Ritchey crater, Mars: Evidence for post-  
Noachian clay formation. Journal of Geophysical Research:  

Ta K., Peng X., Chen S., Xu H., Li J., Du M., Hao J., and Lin Y.  
2017. Hydrothermal nontronite formation associated with  
microbes from low-temperature diffuse hydrothermal vents  
at the South Mid-Atlantic Ridge. Journal of Geophysical  

Takai K., Nakamura K., Toki T., Tsunogai U., Miyazaki M.,  
Miyazaki J., Hirayama H., Nakagawa S., Nunoura T.,  
and Horikoshi K. 2008. Cell proliferation at 122°C and  
iso-topically heavy CH4 production by a hyperthermophilic  
methanogen under high-pressure cultivation.  

Toulmin P. III, Baird A. K., Clark B. C., Keil K., Rose H. J.,  
Geochemical and Mineralogical Interpretation of the  
Viking Inorganic Chemical Results. Journal of Geophysical  
Research 82:4625–4634.

Turner S. M. R., Bridges J. C., Grebby S., and Ehlmann B. L.  
2016. Hydrothermal activity recorded in post Noachian-  
aged impact craters on Mars. Journal of Geophysical  


Biological potential of Martian hydrothermal systems.  

Brittle versus ductile deformation as the main control of  
the deep fluid circulation in oceanic crust. Geophysical  

Porosity evolution at the brittle-ductile transition in the  
continental crust: Implications for deep hydro-geothermal  

Westall F., Foucher F., Bost N., Bertrand M., Loizeau D.,  
Vago J. L., Kminek G., Gaboyer F., Campbell K. A.,  
Biosignatures on Mars: What, where, and how?  
Implications for the search for Martian life. Astrobiology  
15:998–1029.

Yen A. S., Gellert R., Schröder C., Morris R. V., Bell J. F.,  
Knudson A. T., Clark B. C., Ming D. W., Crisp J. A.,  
Arvidson R. E., Blaney D., Brückner J., Christensen P. R.,  
DesMarais D. J., De Souza P. A., Economou T. E.,  
Ghosh A., Hahn B. C., Herkenhoff K. E., Haskin L. A.,  
Hurwitz J. A., Jolliff B. L., Johnson J. R., Klingelhöfer  
G., Madsen M. B., McLennan S. M., McSween H. Y.,  
Richter L., Rieder R., Rodionov D., Soderblom L.,  
Squyres S. W., Tosca N. J., Wang A., Wyatt M., and  
Zipfel J. 2005. An integrated view of the chemistry and  

in the core of the Yaxcopoil-1 borehole, Chicxulub impact  
structure, Mexico. Meteoritics & Planetary Science  
39:1199–1221.

**SUPPORTING INFORMATION**

Additional supporting information may be found in  
the online version of this article.

Table S1. Mineral formulae and Fe speciation for  
Fe-bearing mineral.

Table S2. Minerals for selected environments for  
Rocknest host rock chemistry.

Table S3. Minerals for selected environments for  
Hema2 host rock chemistry.

Table S4. Change in the total Fe-species distribution  
Rocknest host rock chemistry.

Table S5. Change in the total Fe-species distribution  
Hema2 host rock chemistry.