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## GEOCHEMICAL ENERGY AVAILABLE TO MICROBES IN MARTIAN IMPACT CRATERS

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Introduction Impacts are a ubiquitous process in the Solar System and have long been associated with the destruction of life on Earth. However, on Mars, hydrothermal systems generated from impacts have been proposed as possible habitable environments [1]. Impacts, even into frozen surfaces [2], can generate hydrothermal systems that have lifetimes of hundreds to millions of years [2,3]. This would result in longlived and localized occurrences of liquid water that could support microbial life. However, the presence of liquid water is not the only requirement for life; bioessential elements and energy are also required, which can be supplied within impact-generated hydrothermal systems. Water-rock interactions that would occur within these systems could provide a suitable source of geochemical energy, via reduction-oxidation (redox) reactions, which could be used by microbial life.

Chemolithoautotrophic microorganisms are thought to be some of the earliest types of organisms to have evolved on Earth [4], and could be supported on Mars [5]. This group of microorganisms is capable of gaining energy from reactions of inorganic compounds and atmospheric CO<sub>2</sub>. Previous studies have used Gibbs energy calculations to demonstrate that the weathering of martian minerals [5,6] and the mixing of hydrothermal fluids [8] is capable of supporting microbial metabolic activity. However, the energy available within martian impact crater environments has yet to be explored in this context.

We have used thermochemical modelling and Gibbs energy calculations to explore secondary mineral formation within martian impact-generated hydrothermal systems, and determined how much energy would be available to microbes [9].

**Methods:** CHIM-XPT was used to determine secondary minerals that would have occurred as a result of water-rock interactions within a hypothetical 100 km diameter crater [3] at temperatures and pressures of 5-100 °C and 1-1000 bars. Mineral reaction pathways were then determined using these secondary mineral assemblages. Given the high abundance of Fe found on Mars [9], only Fe-based reactions were considered in this study. These reaction pathways were used to calculate the Gibbs energy ( $\Delta G$ ), using the following equation:

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

Where,  $\Delta G^{\circ}$  is the Gibbs energy of the reaction under standard conditions, T is the temperature, R is the gas constant, and Q is reaction quotient. The energy

yield was then converted to ATP and biomass [6], and then cell numbers were estimated by assuming the mass of one cell was  $6.65 \times 10^{-13}$  g [10].

Initial compositions: The initial composition of the host rock was based on two regolith samples, Rocknest [11] and Hema2 [12], which have similar chemical compositions, except for iron. Mineralogical analysis of the Rocknest samples was determined by the ChemMin instrument onboard the Curiosity rover, which identified Fe-olivine ((Mg<sub>0.62</sub>Fe<sub>0.38</sub>)<sub>2</sub>SiO<sub>4</sub>), augite (Ca<sub>0.75</sub>Mg<sub>0.88</sub>Fe<sub>0.37</sub>)Si<sub>2</sub>O<sub>6</sub>), magnetite and haematite as the Fe-bearing mineral phases [11]. Given the similarity in composition between the two host rocks, a comparable mineralogy was assumed for Hema2, albeit at different abundances. Initial groundwater compositions were derived by titrating these rock compositions with pure water (similar to [13]).

**Results and Discussion:** Thermochemical modelling showed nontronite, chlorite, goethite, Feceladonite and pyrite were the dominant Fe-bearing secondary minerals formed for both Rocknest and Hema2 host rock compositions. They also showed changes in the distribution of Fe-species within selected crater environments (Fig. 1), which indicated that redox reactions would occur.

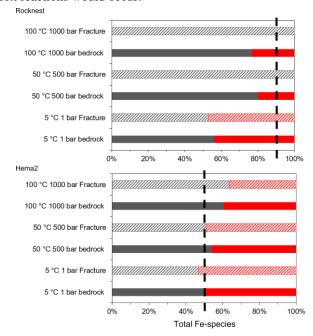


Fig. 1. Distribution of  $Fe^{2+}$  (grey) and  $Fe^{3+}$  (red) in secondary mineral assemblages. Initial  $Fe^{2+}$  abundance in host rock composition is indicated by black dashed lines

Energies determined from ΔG (normalized to react 1 kg of rock) showed water-rock interactions would be capable of supporting 10<sup>10</sup>-10<sup>13</sup> and 10<sup>9</sup>-10<sup>12</sup> cells kg<sub>(dissolved rock)</sub>-1 for Rocknest and Hema2 compositions, respectively. Extreme environments on Earth, such as the continental deep subsurface and aphotic ocean have cell numbers that range between 10<sup>5</sup>-10<sup>10</sup> cells L<sup>-1</sup> [15,16], whereas 10<sup>13</sup> cells kg<sub>(dry soil)</sub>-1 is found in terrestrial soil [16]. The cell numbers suggests that systems formed within Rocknest and Hema2 host rock compositions would not be considered low biomass environments.

Overall, Hema2 host rock environments could be capable of supporting one to two orders of magnitude fewer cells than Rocknest (Table 1). This is owing to higher energy yielding Fe-oxidizing reactions occurring for Rocknest, which was highlighted by the net increase in Fe<sup>3+</sup> for these environments (Fig. 1). The opposite was true for Hema2 environments, in which Fe-reduction was the dominant reaction. This suggests that the composition of the host rock will influence the energy yield, and subsequently the cell numbers that could be supported.

Conclusions: Although it is unclear whether life could have existed on Mars, the results from this study support previous work that suggests impact craters, particularly ones large enough to possess long-term hydrothermal systems, could support life. The results from  $\Delta G$  calculations showed that there would be suf-

ficient energy to support cell numbers similar to those found in terrestrial soils. It also showed that host rock compositions would lead to some variation in energy yields.

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Table 1. Available energy (in kJ) and cell numbers (in brackets) that is supplied when 1 kg of host rock is dissolved within the bedrock and fractures.

	5 °C 1bar				50 °C 500 bar				100 °C 1000 bar			
	Bedrock		Fracture		Bedrock		Fracture		Bedrock		Fracture	
Rocknest												
Fe-olivine to nontronite	40.45	(7.27E+12)	55.81	(1.00E+13)	13.67	(2.46E+12)		-	14.78	(2.66E+12)		-
Fe-pyroxene to nontronite		-	2.33	(4.19E+11)	0.42	(7.50E+10)		-		-		-
Fe-olivine to goethite	8.82	(1.58E+12)		-		-		-		-		-
Fe-pyroxene to goethite		-		-		-		-		-		-
Magnetite to pyrite		-		-		-	10.19	(1.83E+12)		-		-
Haematite to pyrite		-		-		-	9.76	(1.75E+12)		-		-
Magnetite to daphnite		-		-			2.26	(4.07E+11)		-	1.08	(1.95E+11)
Haematite to daphnite		-		-		-	1.83	(3.30E+11)		-	0.72	(1.30E+11)
Hema2												
Fe-olivine to nontronite		-	5.99	(1.08E+12)		-		-		-		-
Fe-pyroxene to nontronite		-	0.34	(6.15E+10)		-		-		-		-
Fe-olivine to goethite		-		-		-		-		-		-
Fe-pyroxene to goethite		-		-		-		-		-		-
Magnetite to pyrite		-		-	1.99	(3.57E+11)	1.62	(2.92E+11)		-	4.03	(7.24E+11)
Haematite to pyrite		-		-	1.78	(3.20E+11)	1.57	(2.82E+11)		-	3.46	(6.21E+11)
Magnetite to daphnite	0.08	(1.45E+10)		-	0.78	(1.40E+11)	0.30	(5.45E+10)	0.94	(1.70E+11)	2.01	(3.62E+11)
Haematite to daphnite	0.04	(6.55E+09)		-	0.58	(1.03E+11)	0.25	(4.46E+10)	0.50	(8.95E+10)	1.44	(2.59E+11)