

POTENTIAL CHEMOSYNTHETIC ENERGY YIELDS FROM MARTIAN HYDROTHERMAL SYSTEMS. E.S. Varnes and B.M. Jakosky, Laboratory for Atmospheric and Space Physics and Department of Geological Sciences, University of Colorado, Boulder, CO 80309, email varnes@lasp.colorado.edu.

Introduction: A source of energy to power metabolism is crucial to life, and may be a limiting factor in the occurrence of past or extant life on Mars [1]. On Earth, the vast majority of all life draws its energy either directly or indirectly from photosynthesis. However, a small but significant fraction of organisms utilize chemosynthesis, energy from chemical disequilibrium, to power metabolism. It has been suggested that chemosynthesis may be the most plausible energy source for putative martian life (e.g. [1], [2], and [3]). Although a global average of energy available from chemosynthesis on Mars has been estimated [1], issues of how the energy is distributed and which particular environments have the greatest potential to support life remain unresolved. We are currently addressing these questions by developing geochemical models using the speciation/solubility and reaction path software EQ3/6. Given the likely occurrence and biological significance of hydrothermal systems, they are the subject of our models.

Model Overview: Numerical geochemical modeling is an efficient method of investigating complex geochemical systems. EQ3/6 has been used previously in the development of models of hydrothermal sequestration of carbonates and hydrous silicates in the martian crust [4] and [5], and in assessing the biological productivity of terrestrial submarine hydrothermal vents [6] and [7], as well as putative hydrothermal systems on Europa [8].

Certain assumptions must be made about the geochemistry and geology of the near-surface environment of Mars in order to employ the aforementioned software. The elemental composition of the groundwater and the initial host rock with which it interacts must be defined for input to EQ3/6. Given the limited information on these input parameters, it cannot be expected that the results of the modeling will be unique, but they will be consistent with our current understanding of Mars. By using appropriate ranges of parameters, we can bracket the expected response.

Host rock compositions may be constrained by lander and SNC meteorite measurements. In geochemical models of terrestrial hydrothermal systems, the compositions of the fluids involved are known from sampling. Without direct sampling, the compositions of groundwaters on Mars are unknown; however, they may be constrained by our knowledge of the composition of the martian crust and

atmosphere. Our approach to defining groundwater compositions is to simulate the interaction of pure H₂O with the martian atmosphere and also with soil compositions described by lander measurements. This technique produces a spectrum of possible groundwater compositions.

Model Inputs: As mentioned above, the host rock and groundwater composition must be defined for input to the model. The rock is reacted with the groundwater at high temperature (350°C) to produce a hydrothermal fluid. This hydrothermal fluid is then reacted with increments of the original, cool groundwater to simulate the mixing that occurs in hydrothermal systems.

Host rock composition. For the models described here, we have constrained the host rock composition with the meteorite LEW 88516, using the analysis given by Driebus et al. [9]. LEW 88516 is an ultramafic rock similar to the martian mantle [9]. It was chosen to be representative of rocks that may be found at depth within the crust.

Groundwater compositions. To explore the dependence of energy yield on water composition, we have defined three different groundwaters (see Table 1). The first of these, labeled Water 1, is pure H₂O in equilibrium with the present day composition of the martian atmosphere. Water 2 is defined by the equilibrium between Water 1 and an average Pathfinder composition soil as reported by Bell et al. [10]. This soil composition has been reported in a highly oxidized state, where, for example, all of the iron present is reported as Fe³⁺. We have therefore produced a soil composition modified from the Bell et al. soil that is in a less oxidized state, where, for example, half of the iron is present as Fe³⁺ and half as Fe²⁺. Equilibrium between this less oxidized soil and Water 1 yields Water 3.

Table 1 – Abbreviated list of groundwater species

	Water 1	Water 2	Water 3
Chemical species	concentration (mmolal)	concentration (mmolal)	concentration (mmolal)
log fO ₂	-5.0	1.3653	-74.04
pH	4.96	8.96	9.00
ΣCO _{2,aq}	0.44	0.02	0.02
O _{2,aq}	~10 ⁻²⁰	44.98	~10 ⁻⁷⁴
H _{2,aq}	~10 ⁻²⁰	~10 ⁻⁴⁷	1.7×10 ⁻⁹
CH ₄	0	0	3.8×10 ⁻¹⁵
ΣSO ₄	~10 ⁻²⁰	31.5	31.41
ΣH ₂ S	1.9×10 ⁻⁶	0	1.9×10 ⁻⁶
other species	negligible	substantial & various	substantial & various

Energy Calculations: Water drawn into the vicinity of hot volcanic rocks reacts chemically with the rock and rises buoyantly upwards where it may encounter groundwater. The hot, metal-rich fluids are out of equilibrium with the cooler groundwater with which they mix, and it is this disequilibrium that terrestrial organisms exploit for metabolism. In modeling such systems, it is generally assumed that a state of partial equilibrium prevails. That is, oxidation/reduction reactions (utilized for metabolism) are kinetically inhibited, while equilibrium may be achieved among other reactions.

The amount of energy an organism can obtain from a chemical reaction is limited by the Gibbs free energy of that reaction. The Gibbs free energy for a reaction i is given by

$$\Delta G_i = \Delta G_i^\circ + 2.3 RT \log Q \quad (1)$$

where ΔG_i° is the Gibbs free energy of the standard state, R the universal gas constant, T the temperature in Kelvin, and Q the reaction quotient, which depends upon the chemical activities of the reactants.

For each of our mixing models, we have calculated the energy yield of reactions that are important for terrestrial chemosynthetic organisms and likely representative for putative martian organisms. These include methanogenesis, sulfate reduction, and in certain cases, sulfide oxidation. For each of the three mixing models presented here, we have developed two endmember cases in order to determine an upper and lower limit on energy yield. In the first case, we suppress the precipitation of all minerals during the mixing simulation. In the second case, we allow all of the supersaturated species to precipitate to equilibrium. In a natural mixing system, precipitation does occur, but because of kinetic inhibitions, not every species precipitates to equilibrium.

Results: We present the results for three mixing models. Each of the waters listed in Table 1 was mixed with hydrothermal fluid produced by the reaction of that same water with the LEW 88516 composition rock. A summary of the energy yields for each of these models is given in Table 2.

Discussion: Groundwater composition plays a defining role in determining which reactions yield substantial energy. In Model 1, energy is available only from methanogenesis because CO_2 species are essentially the only constituents of Water 1. Model 2 is the only model for which sulfate oxidation was calculated, because Water 2 is the only water to contain a substantial concentration of dissolved

Table 2 – Energy yield

Model	Methanogenesis		Sulfate reduction		Sulfate oxidation	
	no ppt	ppt	no ppt	ppt	no ppt	ppt
1	high	negligible	negligible	negligible	n/a	n/a
2	negligible	negligible	negligible	negligible	moderate	negligible
3	low	negligible	high	high	n/a	n/a

oxygen. This reflects the highly oxidized state of the soil composition used to define that water. If any Fe^{2+} were present in that soil, it would scavenge the available oxygen, leaving aqueous ferrous iron oxides and hydroxides. Sulfate reduction yields a high amount of energy in Model 3, in part because Water 3 contains both sulfate and sulfide species in abundance, and also because Water 3 contains a small but non-negligible concentration of H_2 , which is the limiting reactant for sulfate reduction at moderate to low temperatures.

For each of our mixing models, a significant energy yield is possible from at least one of the calculated reactions when mineral precipitation is suppressed. When minerals are allowed to precipitate to equilibrium, energy yields drop to negligible values in all but one case—sulfate reduction in Model 3. Model 3 is therefore the most robust of our mixing models, and we conclude that if martian groundwaters are similar to Water 3, it is likely that a substantial amount of energy is available to putative organisms.

Future Work: We plan on studying the effect of varying host rock composition on energy yield using other SNC meteorites as constraints. Groundwaters on Mars may have been concentrated into brines, so we will also explore the effect of brine-like groundwater compositions on energy.

References: [1] Jakosky B.M. and Shock E.L. (1998) *JGR*, 103, 19359-19364. [2] Shock E.L. (1997) *JGR*, 102, 23687-23694. [3] Fisk M.R. and S.J. Giovannoni (1999) *JGR*, 104, 11805-11815. [4] Griffith L.L. and E.L. Shock (1995) *Nature*, 377, 406-408. [5] Griffith L.L. and E.L. Shock (1997) *JGR*, 102, 9135-9143. [6] McCollom T.M. and E.L. Shock (1997) *Geochim.*, 61, 4375-4391. [7] McCollom T.M. (2000) *DSRI*, 47, 85-101. [8] McCollom T.M. (1999) *JGR*, 104, 30729-30742. [9] Driehus G. et al. (1992) *Meteoritics*, 27, 216-217. [10] Bell J.F. et al. (2000) *JGR*, 105, 1721-1755.