SOLAR-DRIVEN CHEMICAL ENERGY SOURCE FOR A MARTIAN BIOTA

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Abstract. Microorganisms deep in the Martian soil could derive energy indirectly from the sun via chemical reactions involving atmospheric photolysis products of the solar ultraviolet flux. The Viking discovery of a chemically uniform regolith which, though poor in organics, is rich in sulfur-containing compounds suggests reaction sequences in which sulfur is recycled through reduced and oxidized states by biologically catalyzed reactions with photochemically-produced atmospheric constituents. One candidate reaction, reduction of soil sulfate minerals by molecular hydrogen, is already exploited on earth by bacteria of the ubiquitous and tenacious *Desulfovibrio* genus.

1. Introduction

Any theory of life on another planet must include a mechanism by which organisms obtain free energy for growth and replication. Even the resting state cannot persist without expenditure of maintenance energy for repair of damage and degradation by natural influences such as heat, chemical reactants, ionizing solar and cosmic radiation, etc.

Major advances in our knowledge of the Martian surfaces have recently been possible by the landings of the Viking automated spacecraft. Experiments seeking evidence of metabolic activity in the soil have demonstrated conversion of organic substrates to carbon-containing gases (Levin and Straat, 1976) and, conversely, the apparent fixation of $CO + CO_2$ mixtures into stable compounds (Horowitz *et al.*, 1976). Although these carbon-cycling processes could readily be interpreted as the biochemical functions of catabolism and anabolism, analyses of the details of these experiments, coupled with the negative results of the third life-detection experiment (Oyama *et al.*, 1977), and the finding that organic compounds are exceedingly low or absent (Biemann *et al.*, 1977), have led to proposals that the reactions are due to unexpected inorganic compounds in the soil (Klein, 1977; Ponnamperuma *et al.*, 1977).

On Earth the biosphere is dominated by (a) photosynthetic organisms, which derive energy from the photolytic splitting of water, and (b) respiratory organisms, which derive energy from the oxidation of the organic compounds within organisms or present as excretion and decomposition products of other organisms. All organisms of group (b) owe their existence to the primary production of organics by group (a) organisms, which depend in turn upon the availability of sunlight. Other sources of metabolic energy, of lesser importance from a quantitative standpoint but of considerable interest because of the versatility they represent, include the fermentative reactions for deriving energy from organic compounds in the absence of molecular oxygen and the capacity of certain photoautotrophic microorganisms to split compounds other than the water molecule, e.g. H_2S and H_2R (where R denotes any of a large number of suitable organic radicals) by

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members of the *Thiorhodaceae* and *Athiorhodaceae* families of bacteria. Again, these reactions are directly or indirectly dependent upon solar energy. However, an additional class of organism, the chemoautotroph, derives energy required for life functions directly from the reaction of naturally occurring inorganic compounds without the coparticipation of light photons. It is the purpose of this paper to examine the likelihood that organisms of this class comprise an important part, perhaps all, of any microbiota which may exist on Mars, and to demonstrate the manner in which their source of energy may in fact be ultimately derived from the solar flux.

2. The Role of Sulfur

The most discordant finding by the Viking X-ray fluorescence analysis experiment is that the Martian soil at both landing sites contains about 3% sulfur by weight (most probably in the form of sulfate; Clark *et al.*, 1976), some 10 to 100 times the amount in common terrestrial and lunar soils and rocks. Likewise, the greatest surprise in the gas chromatograph–mass spectrometer experiment is the lack of detection of indigenous organic compounds at levels in the parts per billion range (Biemann *et al.*, 1977), a depletion by several orders of magnitude compared even to most 'ahumic' terrestrial soils. This latter finding imparts a lower probability for a biota of the type in class (b) above, or for heterotrophic organisms of any type. However, the finding of an omnipresent sulfur compound recommends fuller consideration of the possible role of S in Martian biological energetics.

On Earth, many organisms are known which can oxidize native sulfur. Indeed, it was Winogradsky's studies of *Beggiatoa*, at the turn of the century, that defined the chemoautotrophic mode of life. This organism, as well as bacteria of the *Thiobacillus* genus and many other organisms, obtain energy via the reaction (Silverman and Ehrlich, 1964)

$$S + \tfrac{3}{2}O_2 + H_2O \rightarrow H_2SO_4 + 118 \text{ kcal} \quad (1)$$

followed by reaction with cations to produce sulfates; in the case of *T. denitrificans* free oxygen is not required (Delwiche, 1967):

$$5\,S + 6\,KNO_3 + 2\,CaCO_3 \rightarrow 3\,K_2SO_4 + 2\,CaSO_4 + 2\,CO_2 + 3\,N_2 + 5(132) \text{ kcal} \quad (2)$$

(Note: The yields specified are the free energies of reaction under standard conditions of 25°C and 1 atmosphere total pressure; somewhat different energy yields would occur under Martian environmental conditions). The importance of the energy yield is that it most likely must be in excess of a certain value to provide the energy for coupled reactions for energy storage; e.g., terrestrial organisms require ≈15 kcal/mole to efficiently drive the ADP → ATP energy-storage reaction (Delwiche, 1967). Other forms of reduced S are also readily oxidized: H_2S by some of the organisms cited above; metallic sulfides by *T. ferroxidans*.

Ample terrestrial precedent has thus been set for microbial exploitation of the relatively large energy release available from oxidation of S. This is germane to the

Martian setting since the initial appearance of S at the surface of the planet was quite likely in a reduced form, whether the source was endogenous, as pyrite (FeS_2) in igneous rocks or H_2S from volcanic exhalations, or exogenous, as troilite (FeS) from infall of meteorites. If, prior to quantitative completion of natural oxidative processes, there originated a biota capable of catalyzing the reaction of reduced sulfur with atmospheric oxygen, this large reservoir of chemical potential energy could be tapped to sustain biological activity. This scheme results in a 'dead-end' biology, since once all reduced S has been transformed to the oxidation state in thermodynamic equilibrium with the prevailing atmosphere (presumably SO_4^{2-} under present conditions), the source of Gibbs free energy is exhausted. Nonetheless, because of the vast size of the regolith, considerable latitude for population development and evolution could have existed. For example, assuming a 7% efficiency for production of biomass (per unit substrate) by chemoautotrophic metabolism (Lees, 1955), and a bioavailable regolith 10 meters in depth, a cumulative biomass of 0.8×10^{18} g could have been created. With a dry mass per cell equivalent to typical terrestrial microorganisms ($\approx 10^{-13}$ g), about 10^{31} organisms and the same number of genomes would have resulted. The implied large magnitude of replication would surely lead to considerable speciation, particularly in view of the high level of mutation-inducing ultraviolet and cosmic rays at the Martian surface.

3. The Desulfovibrio Archetype

As the abundance of reduced S decreased, and that of SO_4^{2-} increased, selection pressures would favor emergence of a symbiotic form capable of utilizing the latter. Once again, we have in the terrestrial biosphere a very pertinent example in the case of the dissimilatory sulfate-reducing bacteria, capable of catalyzing energy-yielding reactions such as

$$MSO_4 + 4H_2 \rightarrow MS + 4H_2O + \Delta G, \tag{3}$$

where M is an appropriate metal ion. The classic organism of this type is *Desulfovibrio desulfuricans*. Considering that this bacterium requires sulfate and a suitable hydrogen donor (either H_2 gas or certain organic compounds) and is an obligate anaerobe, its ubiquitous distribution in the soils of the world (Davis, 1967; Ogata and Bower, 1965; Barghoorn and Nichols, 1961; Postgate, 1965) is surprising. Relative to the *prevailing* environment on Earth, it is strongly non-adapted. Occurrences in small, isolated kettle-hole ponds in Antarctica (Barghoorn and Nichols, 1961) demonstrate the extreme environmental tolerance of such organisms. Halophilic forms (Davis, 1967), and a comparable genus (*Desulfotomaculum*) capable of transforming to resistant endospores (Postgate, 1965) as a result of nutrient deprivation, are known. The organism is notorious for its ability to rapidly and destructively corrode metallic Fe under anaerobic conditions (e.g., underground pipes) by formation of FeS (Davis, 1967). Biochemical versatility is further demonstrated in that some strains fix atmospheric N_2 and others can oxidize CO (Postgate, 1965).

These organisms, as presently known, are not strict chemoautotrophs, being instead

mixotrophs; atmospheric CO_2 can be fixed into certain organic molecules, but this source of carbon atoms is not sufficient in and of itself for the synthesis of all organic materials required by the cell. If it were not for the requirement for liquid water, and this apparent need for trace organics, these remarkable microbes would seem more suited to the Martian environment than to the nominal Earth one.

On Mars, hydrogen gas and the free radical H are predicted to occur in the atmosphere as products of UV photolysis of H_2O vapor (Hunten and McElroy, 1970). Model calculations (Liu and Donahue, 1976; Yung *et al.*, 1977) indicate an H_2 concentration of roughly 10 ppm, or a partial pressure of 0.07 μbar. The H_2 partial pressure in the Earth's atmosphere is only about 7 times higher than this, and, in comparison, our O_2 partial pressure is greater by a factor of 23,000. Mars, therefore, is currently highly anaerobic by terrestrial standards. However, certain strongly oxidizing agents are also formed on Mars by short wavelength photolytic and subsequent reactions, including O_3, H_2O_2 and the O, OH, and HO_2 free radicals (Hunten, 1974). In addition, the O_2 release measured by Oyama *et al.* (1977) during exposure of Martian soil to saturated water vapor at 9°C has been interpreted to indicate superoxide and/or peroxide compounds to the extent of $\approx$30 ppm in the soil. Some relief from ambient oxidative pressures should be available at depth in the soil because free radicals should react quickly with soil minerals and H_2O_2 may adsorb and/or freeze out on particle surfaces, whereas H_2 at the temperatures in question is inert with respect to these inorganic materials. The surface soil porosity of 45 to 75% (Clark *et al.*, 1976) thus permits diffusion of H_2 to depths greater than that penetrated by strong oxidants.

Although the partial pressure is low, the flux of H_2 impinging upon a one micrometer diameter cell is nonetheless equivalent to one cell mass in less than one Martian day. The rate of useful supply of energy ultimately depends upon the efficiency at which the cell could capture this H_2 and effect the required reaction. Bell *et al.* (1974) in providing evidence that in *Desulfovibrio gigas* the hydrogenase resides outside the cytoplasmic membrane, suggest that the enzyme not only catalyzes the H_2-sulfate reaction but also serves as a hydrogen-binding protein for the efficient trapping of low levels of environmental H_2.

It is important to note that H_2 would be virtually absent from the Martian atmosphere, because of exospheric escape, were it not for resupply from photolysis of water molecules by solar ultraviolet photons of wavelength less than 195 nm. This effectively couples the solar energy source to the microorganism at depth, via molecular hydrogen, without direct photon exposure and the required concommitant selective-shielding against the deleterious UV component. Sagan and Pollack (1974) have demonstrated the possibility of a euphotic zone at approximately 1 cm depth in Martian soil, where visible light penetrates but the ultraviolet is sufficiently attenuated to prevent lethal exposures. Existence at even greater depths has additional advantages for the Martian microorganism: it is the presumed reservoir of the missing water inventory (Fanale, 1976; Owen *et al.*, 1977) with large amounts possibly present as water of hydration of salts and clay (Clark, 1978) as well as permafrost ice; temperature fluctuations are much lower

compared to the diurnal transient of as much as 80°C at the surface; organisms are protected from eolian transport and abrasion; and shielding against the more penetrating cosmic rays and solar flare radiation is provided.

Reconversion of reduced-sulfur compounds to sulfate could occur from reaction with O_2 or other oxidizing agents, either via autoxidation, or mediated biologically by the hypothesized organism discussed above. In either case, the valence state of sulfur would be continuously recycled.

4. Reconstitution Reactions

Besides sulfur reactions, a number of other energy-yielding pathways are possible – some of which are heterogeneous reactions (atmospheric gases with soil solids) – while others occur between components found in the gas phase. The latter include the class of 'reconstituting the atmosphere' reactions, defined as all back reactions tending to return the atmosphere to the state in which it would be were it not for photolysis by the ultraviolet component of sunlight, viz. a mixture of CO_2, N_2, O_2, and H_2O vapor with trivial amounts of other compounds in thermodynamic equilibrium with them. The simplest example of a reconstitution reaction is:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 + 62 \text{ kcal.} \tag{4}$$

Indeed, the effective rate of this reaction in the Martian atmosphere is known to be faster than what one would predict *a priori* (Hunten, 1974). It has been explained by catalysis by odd hydrogen, coupled with an hypothesized very rapid downward mixing rate (McElroy and Donahue, 1972; Hunten, 1974). Huguenin *et al.* (1977) attribute this reaction, however, to the formation of an intermediate, ferrous carbonate, by CO reactions with Fe^{2+} sites on pristine mineral surfaces, followed by photoactivated desorption of CO_2. Either or both explanations may suffice, but biological activity provides a third alternative, as originally pointed out by Wolfgang (1970). The biological reconversion of CO to CO_2 was also earlier proposed by Lederberg (1970) and later by Postgate (1970) and Mitz (1974) as an alternative to photosynthesis for Martian microorganisms. Terrestrial soils contain microorganisms which can metabolize CO, including some such as *Methanobacterium formicicum* which perform reduction (to CH_4) when H_2 is present, or oxidation (to CO_2) otherwise (Inman *et al.*, 1971) and *M. thermoautotrophicum*, which derives energy from the reaction (Daniels *et al.*, 1977).

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2 + 50.5 \text{ kcal.} \tag{5}$$

In the Viking carbon assimilation experiment, soil samples were incubated with 28,000 picomoles of radioactively-labelled CO and twelve times that amount of labelled CO_2. About 10 picomoles of CO-equivalent of carbon atoms were observed to be fixed (Horowitz *et al.*, 1977). Since O_2 is 0.13% of the Martian atmosphere (Owen *et al.*, 1977), there was 2,000 picomoles of O_2 available in the 4 cm^3 trapped volume of the incubation cell. If the reaction proceeded as in (4), and gave a 7% yield for formation of

biomass, the result would be 140 picomoles of carbon fixed. This calculation indicates that an energy source as in Equation (4) could possibly account for the results obtained, and if this were the case, the supply of energy was not exhausted during the incubation. Horowitz *et al.* (1977) believe, however, that their observed fixation reaction is abiotic on the grounds of its resistance to thermal inactivation.

5. Vigor of the Biosphere

Table I is a compilation of illustrative exergonic reactions for which the required reactants are known or predicted to be on Mars. Some examples of terrestrial organisms which benefit from such reactions are included. These reactions all occur spontaneously. Biological competition for the reactants is permitted only by the normally slow rates of reaction, one reason for which is the cold ambient temperature (mean daily subsurface temperatures are estimated to range from annual highs of $-50°C$ at both lander sites, to a low of $-70°C$ at the first site, and a low of $-100°$ at the second site; Kieffer, 1977). The development of catalytic capabilities analogous to the enzyme systems of terrestrial life, is a fundamental requirement in this scheme and the vigor of the biota is thus

TABLE I
Some candidate energy-source reactions for Mars*

Reaction	$-\Delta G_{298}$	$-\Delta G_{220}$	Terrestrial example
Reconstitution reactions			
a. $CO + \frac{1}{2}O_2 \rightarrow CO_2$	61.5	63.1	*Methanobacterium formicicum*
b. $CO + H_2O_2 \rightarrow CO_2 + H_2O$	96.4	94.8	
c. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	54.6	55.5	*Hydrogenomonas facilis*
d. $\frac{1}{2}H_2 + HNO_3 \rightarrow H_2O + NO_2$	23.1	19.3	
e. $NO + \frac{1}{2}O_2 \rightarrow NO_2$	8.3	9.7	
f. $2HNO_3 \rightarrow H_2O + N_2 + 5/2O_2$	16.4	5.6	
Heterogeneous reactions			
g. $MgSO_4 + 4H_2 \rightarrow MgS + 4H_2O$	22.5	18.9	(*Desulfovibrio*)
h. $MgSO_4 + 4CO \rightarrow MgS + 4CO_2$	49.8	49.3	
i. $MgS + 2O_2 \rightarrow MgSO_4$	196.1	203.0	(*Thiobacillus*)
j. $Ca(NO_2)_2 + CO_2 \rightarrow CaCO_3 + N_2 + 3/2O_2$	43.0	–	
k. $Ca(NO_2)_2 + O_2 \rightarrow Ca(NO_3)_2$	44.9	–	*Nitrobacter*
l. $4FeCO_3 + O_2 + 6H_2O \rightarrow 4Fe(OH)_3 + 4CO_2$	69.2	77.9	*Gallionella*
m. $CaSiO_3 + 2NO + 3/2O_2 \rightarrow Ca(NO_3)_2 + SiO_2$	53.0	63.7	
n. $CaSiO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + SiO_2 + H_2O$	28.0	27.4	

*Effective overall reactions; many intermediate steps, not shown, may exist.
$-\Delta G_{298}$ is the free energy (kcal) released at 298 K, 1 atmosphere pressure.
$-\Delta G_{220}$ is the estimated free energy change at 220 K, 1 atm., assuming all enthalpies are constant with temperature.
Values for the thermochemical constants were taken from Garrels & Christ (1965) and Weast (1975).
Reactions g. through i. use Mg as the example cation for S; for terrestrial organisms, the analogous reactions have been demonstrated for a number of cations other than Mg (e.g., Fe, Cu, Zn, Pb, H_2, etc.) (Silverman and Ehrlich, 1964).

potentially limited by three factors: (a) supply of the reactants, (b) capture probability, and (c) the catalysis rate. Even with very high efficiency for (b) and (c), the overall metabolism rate will necessarily be extraordinarily small if contrasted with the vigor of the terrestrial biosphere. This follows from the rate at which the solar photolysis products can be formed and transported to the planetary surface. Calculations by McElroy *et al.* (1976) indicate that the maximum rate of supply of O_2 to an irreversible sink in the soil (e.g., reactions a, c, e, i, k, or l of Table I) cannot exceed 10^{-15} g cm^{-2} sec. For comparison, this is about 10 orders of magnitude lower than the rate of uptake of O_2 by respiratory organisms, averaged over the earth's land surface. At the 7% conversion efficiency, the net biomass production rate per unit area would be less than 10^{-13} of the average primary productivity typical for desert and arctic tundra regions on Earth (Bowen, 1966). A biosphere which, like the terrestrial one, continuously recycles O_2 by complementary reactions for uptake and release would not be so stringently limited.

Constant cycling may indeed be necessary to maintain the biota above some critical population threshold. For example, for the 'dead-end' biology scheme (oxidation of primary forms of reduced sulfur) above, the average population would reach only the order of 700 organisms cm^{-2}, if mean lifetimes were 0.1 year per organism and 10^9 years were allowed for exhaustion of the supply of reduced sulfur. Much greater activity could be expected in a tightly-connected symbiosis, particularly if accompanied by higher temperature conditions and greater abundances of free water, H_2, and O_2. Today's extant biota could then be relic survivors of a more clement Martian environment (Sagan and Mullen, 1972), much as *Desulfovibrio* apparently is today on earth.

A similar calculation (Yung *et al.*, 1977) for soil fixation of nitrogen via reactions with photoproduced HNO_3 (e.g., see reaction *n*) sets that maximum rate also at about 10^{-15} g cm^{-2} sec. The abiotic photosynthesis of simple organic compounds under Martian conditions, as reported by Hubbard *et al.* (1973), is approximately 10^{-12} gram organics per second per gram of substrate irradiated, rigidly limiting organic oxidation energy sources (heterotrophic metabolism). In the geocentric reference frame, the above rates are trivial; such soils are 'sterile'.

6. The Detection of Life Indigenous to Mars

Discovery of some of these reactions would not have been possible by the Viking biology experiments, primarily because soil samples were sealed into incubation cells, necessarily restricting the amounts of available gaseous nutrients. In particular, metabolic activity based upon consumption of H_2, O_3, NO, HNO_3, or other trace constituents present in the Martian atmosphere at the tens of parts per million level or less (Yung *et al.*, 1977), would have been constrained to levels below the one picomole sensitivity limit of the carbon assimilation experiment. Therefore, hydrogen-mediated sulfate reduction could not have been observed even if it did occur under the conditions of the experiment. Furthermore, all samples analyzed by the Viking biology experiments were from shallow depths, i.e., surface to a few centimeters. One sample from beneath a loose rock gave somewhat different results (Klein, 1977).

On future missions, detection of a Martian biota which consumes atmospheric photolysis products might be best accomplished by incubations under artificial atmospheres containing higher than normal abundances of selected constituents. If the putative organisms are adapted only for the environment at depth, it may also be of critical importance to (a) obtain the sample from depth, (b) prevent the sample from rising far above the annual temperature maximum at that depth, and (c) incubate at a water activity somewhat below the vapor pressure of H_2O in equilibrium with ice at that temperature.

Postscript. Since beginning this paper, the discovery of hot water vents which support a vigorous biota some 3 km below the ocean's surface was made by the submersible *Alvin* near the Galapagos Rift. Both conventional and exotic life forms were observed; the food chain base is presumably sulfur-oxidizing bacteria whose energy source is supplied by continual release of H_2S from the vent. This provides an interesting contemporary example on earth of the first branch of the biological cycle postulated for Mars.

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