**ATMOSPHERIC ENERGY LIMITS ON SUBSURFACE LIFE ON MARS.** B. P. WEISS<sup>1</sup>, Y. L. YUNG<sup>1</sup> and K. H. NEALSON<sup>1,2</sup>, <sup>1</sup>Division of Geological and Planetary Sciences, 150-21, California Institute of Technology, Pasadena, California 91125, <sup>2</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

It has been suggested that the terrestrial biomass of subterranean organisms may equal or exceed that at the surface [1]. Taken as a group, these organisms can live in heavily saline conditions at temperatures from 115 °C to as low as -20 °C [2,3]. Such conditions might exist on Mars beneath the surface oxidant in an aquifer or hydrothermal system, where the surrounding rock would also protect against the solar ultraviolet radiation. The way that such systems could obtain energy and carbon is not completely clear, although it is believed that on Earth, energy flows from the interaction of highly reduced basalt with groundwater produce H<sub>2</sub>, while carbon is derived from CO<sub>2</sub> dissolved in the groundwater [4,5]. Another potential source is the Martian atmosphere, acting as a photochemical conduit of solar insolation [6,7].

The most stable molecules containing carbon and hydrogen in the atmosphere of Mars are  $CO_2$  and H<sub>2</sub>O, respectively. Absorption of solar ultraviolet radiation by the atmosphere leads to the production of disequilibrium products such as CO, O<sub>2</sub> and H<sub>2</sub>, as outlined in a comprehensive set of photochemical reactions by Nair et al. [8]:

$$\operatorname{CO}_2 + h\boldsymbol{n} \to \operatorname{CO} + \frac{1}{2}\operatorname{O}_2$$
 (R1)

$$H_2O + h\boldsymbol{n} \rightarrow H_2 + \frac{1}{2}O_2$$
 (R2)

In the current photochemical models of Mars, the surface is assumed to be biologically inactive. The ultimate fate of the disequilibrium products produced in R1 and R2 is conversion back to the thermodynamically most stable molecules,  $CO_2$  and  $H_2O$ , in a timescale of 5 and 260 years, respectively. However, if the subsurface of Mars contains an active biosphere, a small fraction of the photochemically produced CO and  $H_2$  may diffuse downward into the soil to be oxidized by a subterranean biosphere. These are by far the most abundant reactive gases and could therefore provide significantly more energy than other species [8].

We estimated the maximum energy flux (energy per second per unit area of the Martian surface) available to a putative layer of organisms living at a depth of 10 m which catalyse the reactions:

$$CO + \frac{1}{2}O_2 \to CO_2 \tag{R3}$$

$$H_2 + \frac{1}{2}O_2 \to H_2O \tag{R4}$$

Many different species of terrestrial microorganisms derive their energy from  $H_2$  and CO [2]. We assumed that the only source of these reactants is from photochemistry in the atmosphere.

The energy flux is determined by the rate at which the reactants diffuse down to the biotic layer from the surface. Since the mean free paths of CO and H<sub>2</sub> through the background atmosphere are greater than the typical  $D \cong (4\varepsilon r_0 / 3\tau) \sqrt{2kT / \pi m}$ size pore (~1 μm), molecular collisions with the walls of the pores dominate the transport of these molecules. This is known as Knudsen diffusion, for which we can take the diffusion coefficient to be , where  $r_0$  is the pore size,  $\boldsymbol{e}$  is the porosity, t is the tortuosity, and m is the molecular mass of the diffusing component [9]. Diffusion models of Mars typically use  $r_0 \approx 3 \times 10^{-4} \,\mathrm{cm}$ ,  $e \approx 0.5$ , and  $t \approx 5$  at the depths considered here, although these numbers are not well constrained [9, 10, 11].

We assumed that there is a thin biotic layer at depth z which consumes all the CO and H<sub>2</sub> it receives. Using a globally averaged surface temperature of T = 220 K and H<sub>2</sub> and CO surface densities from [8] we find the diffusive fluxes of CO and H<sub>2</sub> to be  $F_{CO} = 8.8 \times 10^9 \text{ cm}^{-2}\text{s}^{-1}$  and  $F_{\text{H}_2} = 1.1 \times 10^{10} \text{ cm}^{-2}\text{s}^{-1}$ , respectively. This H<sub>2</sub> flux derived this way is actually not reasonable since it exceeds the photochemical production rate of H<sub>2</sub> in the atmosphere. This is because the H<sub>2</sub> flux was calculated using a surface abundance from a photochemical model with no H<sub>2</sub> surface sink. Thus, the above flux is clearly not sustainable. The maximum flux into the surface can only be equal to the production rate, and so we take  $F_{\rm H_2} = 8.6 \times 10^8 \,{\rm cm}^{-2} {\rm s}^{-1}.$ 

Using the above fluxes and assuming that the biological oxidation process is 10% efficient, we find that the energy flux to a biotic layer situated at depth z < 1 km (over which the soil constants listed above are approximately constant) is

$$\Phi_3(z) = \frac{F_{CO}}{z} \frac{\Delta H_3}{N_A} 10\% = 10^{-10} \left(\frac{\text{lcm}}{z}\right) \text{Kcal cm}^{-2} \text{s}^{-1}$$

$$\Phi_4(z) = \frac{r_{H_2}}{z} \frac{\Delta H_4}{N_A} 10\% = 10^{-11} \left(\frac{1\text{cm}}{z}\right) \text{Kcal cm}^{-2} \text{s}^{-1}$$
where  $N_{-1}$  is  $\Delta$  vogedro's number and  $\Delta H_{-1}$ 

where  $N_A$  is Avogadro's number, and  $\Delta H_3$  and  $\Delta H_4$ are the enthalpies of R3 and R4. Since the timescale for diffusion to a depth *l* is approximately  $l^2/D$ , CO and H<sub>2</sub> should be able to penetrate to 30 and 300 m, respectively, without significant loss due to photochemical reconversion back to CO<sub>2</sub> and H<sub>2</sub>O. Below these depths, the energy sources postulated here are available at a fraction of what would be estimated from the above linear scaling.

Is this energy being utilized? To first order, the photochemical model, which included no surface sink, predicts a H<sub>2</sub> and CO surface mixing ratio of 37 ppm and 490 ppm [8], in good agreement with the measured values of  $40 \pm 10$  ppm and  $600 \pm 150$  ppm, respectively. This immediately suggests that biological oxidation of the atmosphere is not widespread. In particular, any H<sub>2</sub> or CO sink in the subsurface is restricted from perturbing the H<sub>2</sub> and CO surface abundances below ~30 ppm and ~400 ppm, or by more than  $\sim 10\%$  and  $\sim 25\%$ , respectively. We sequentially added surface sinks of increasing magnitude to the photochemical model to roughly estimate the maximum sink permissible by the observations. The maximum H<sub>2</sub> and CO fluxes into the subsurface were about  $-2 \times 10^7 \text{ cm}^{-2} \text{s}^{-1}$ be found to and  $-6 \times 10^7$  cm<sup>-2</sup>s<sup>-1</sup>, respectively. These fluxes are respectively only 2% and 1% of the potential H<sub>2</sub> and CO fluxes to biota at 10 m calculated above, and 2% and 0.03% of their photochemical production rates. This means that the atmospheric energy is going almost completely unused on Mars, and that both biological and non-biological oxidation (e.g., by the regolith oxidant) of atmospheric H<sub>2</sub> and CO appears to be extremely limited. Since a biotic layer at even 300 m depth could oxidize H<sub>2</sub> at up to 30% of the production rate, this suggests that aerobic biological activity may be extremely limited in the top ~300 m of the Martian subsurface. Thus, extant biota of any kind, especially O<sub>2</sub> reducers, may be inaccessible to the current generation of surface landers and rovers designed for the 2005 sample return mission.

Jakosky and Shock [5] estimated the geochemical energy available from two other sources on the Earth and Mars: hydrothermal systems and chemical weathering. They found that on Mars, a total of  $\sim 20 \text{ g cm}^{-2}$  of biota over the last four billion years

could be produced from these two inventories. Scaled for today's lower rate of volcanism, the present-day energy flux from these sources is about 60000, 6000 and 2000 times lower than that which could be provided today by the atmosphere to 1, 10, and 30 m depth, respectively. The average of these geochemical fluxes (over 4 Ga) is about a factor of 2 closer to the present atmospheric flux. Even more interestingly, the total flux that they calculated for the early Earth  $-500-800 \text{ g cm}^{-2}$  - is 800-1300, 80-130, and 20-40 times lower. Nevertheless, on Mars the geochemical flux should dominate in the vicinity of hydrothermal systems where that energy is highly concentrated (~0.01 Kcal/kg of vent fluid [5]), as well as at greater than km depth where the atmospheric flux is small. On the cold outskirts of hydrothermal systems, the atmospheric energy could be more impor-Although it appears that on a globally avertant. aged scale, biological oxidation of the Martian atmosphere is extremely limited, very active oxidation could still be occurring locally. The presence of such pockets of subsurface life could be detected by observing how the mixing ratios of atmospheric CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and other species deviate on a local scale from the equilibrium values predicted by the photochemical model [8]. Detection of formaldehyde, methane, or the other products short-lived gases would also provide significant evidence for biology. One might even speculate that spatially resolved measurements of these or other species at the Martian surface by landers, penetrators, or orbiting spacecraft might some day be precise enough so that spatial variations could be used to locate biologically active zones in the Martian interior.

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