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Niches of the pre-photosynthetic biosphere and geologic preservation of Earth's earliest ecology

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ABSTRACT

The tree of terrestrial life probably roots in non-photosynthetic microbes. Chemoautotrophs were the first primary producers, and the globally dominant niches in terms of primary productivity were determined by availability of carbon dioxide and hydrogen for methanogenesis and sulfite reduction. Methanogen niches were most abundant where CO_2-rich ocean water flowed through serpentinite. Black smoker vents from basalt supplied comparable amount of H_2. Hydrogen from arc volcanoes supported a significant methanogenic niche at the Earth's surface. SO_2 from arc volcanoes reacted with organic matter and hydrogen, providing a significant surface niche. Methane ascended to the upper atmosphere where photolysis produced C-rich haze and CO, and H escaped into space. The CO and C-rich haze supported secondary surface niches. None of these ecologies were bountiful; less than 1% of the CO_2 vented by ridge axes, arcs, and metamorphism became organic matter before it was buried in carbonate. In contrast, a photosynthetic biosphere leaves copious amounts of organic carbon, locally concentrated in sediments. Black shales are a classic geologic biosignature for photosynthesis that can survive subduction and high-grade metamorphism.

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INTRODUCTION

The ecology of modern Earth is so dominated by photosynthesis that it is difficult to envision the biosphere before this metabolic innovation. Throughout geologic time, the consequences of photosynthesis have significantly modified the composition of Earth's atmosphere and hydrosphere, and, ultimately, chemical reactions between Earth's fluid envelopes and the lithosphere (cf. Holland, 1962, 1984; Cloud, 1968, Garrels & MacKenzie, 1971; Garrels & Perry, 1974; more recently: Dismukes *et al.*, 2001; Hoehler *et al.*, 2001b; Kasting & Siefert, 2002; Berner *et al.*, 2003; Knoll, 2003; Holland, 2004; Canfield, 2005; Kopp *et al.*, 2005; Rosing *et al.*, 2006). Evidence for photosynthesis appears in even the oldest rocks (cf. Des Marais 2000; Rosing & Frei, 2004; Tice & Lowe, 2004; Olson, 2006; Westall & Southam, 2006). Although the tree of life roots in non-photosynthetic microbes (e.g. Woese *et al.*, 1990; Pace, 1991, 1997; Reysenbach & Shock, 2002; Olson & Blankenship, 2004; Nealson & Rye, 2004), geologic evidence of extant life that is not at least peripherally affected by the products of photosynthesis is rare. Thus, characterizing sources of energy for metabolic processes independent of photosynthesis is critical to understanding the ecology of early Earth (Shock 1997; Shock & Schulte, 1998), and to developing search strategies for ancient biosignatures and extant life on Earth, Mars, Venus and Europa (cf. Boston *et al.*, 1992; Jakosky & Shock, 1998; Fisk & Giovannoni, 1999; McCollom, 1999; Zolotov & Shock, 2004; Sleep *et al.*, 2004; Schulte *et al.*, 2006).

The energetics of living organisms is dependent on cycles of non-equilibrium electron transfers (Falkowski, 2006). In the pre-photosynthetic biosphere the most important redox systems providing energy for metabolic processes involve the elements Fe, S, and C together with H and O (cf. Walker, 1977), and viable niches were formed where tectonic and/or fluid movement (magma, water, air) brought together combinations of these elements with incompatible oxidation states (cf. Shock *et al.*, 1995; Nisbet & Sleep, 2001; Nisbet & Fowler, 2004; Nealson & Rye, 2004; Kharecha *et al.*, 2005; Canfield *et al.*, 2006). In this paper, we consider first-order thermodynamic and mass balance constraints on chemoautotrophic biospheres in order to identify viable bountiful niches prior to the evolution of photosynthesis. Our objective is to predict where biosignatures might be found in Earth's earliest geologic record and where one might find existing analog communities. As earliest life likely utilized metabolic strategies involving hydrogen as a reductant (Walker, 1977; Wachtershauser, 1993; Vignais *et al*, 2001; Reysenbach & Shock, 2002; House *et al.*, 2003; Battistuzzi *et al.*, 2004), we focus on processes leading to abiotic formation of H_2 and estimation of order of magnitude values for the global mass flux of H_2 within potential ecosystems of early Earth. We evaluate these processes relative to energy requirements for hydrogen-based ecosystems dominated by methanogens. In addition, we also consider potential niches related to photolysis (e.g. Ferry & House, 2006), and sulfite reduction (e.g. House *et al.*, 2003). Finally, we compare the preservation within the geologic record of pre-photosynthetic and photosynthetic biospheres. We find that organic-rich "black shale" indicates a vigorous photosynthetic ecology, one that provides a geologic biosignature capable of surviving high-grade metamorphism as low-$\delta^{13}C$ graphitic gneiss and diamond gneiss.

THERMODYNAMIC CONSIDERATIONS

Extant organisms provide a multitude of clues as possible ecological niches that are independent of photosynthesis. In our analysis, the first cellular organisms did not necessarily occupy the most bountiful niches identified below, but we recognize that there are strong selective pressures for later microbes to evolve and to occupy them. Evidence for an extensive subsurface biosphere within modern (Gold, 1992; Pedersen, 1993; Fyfe, 1996; Whitman *et al.*, 1998; Krumholz, 2000; Takai *et al.*, 2004b) and early (Canfield, 2006; Ueno *et al.*, 2006) Earth suggests that the upper crust, to depths exceeding several kilometers or more, is a potential locus for viable pre-photosynthetic niches supported by energy derived from water–rock reactions. Ecosystems where H_2 is considered to be a major electron donor for metabolic processes have been inferred in continental aquifers and geothermal systems within basaltic, granitic and metamorphic rocks (Pedersen, 1993, 1997; Stevens & McKinley, 1995; Kotelnikova & Pedersen, 1997, 1998; Chapelle *et al.*, 2002; Ward *et al.*, 2004; Spear & Pace 2004; Sherwood Lollar *et al.*, 2006), and in oceanic crust and related hydrothermal vents in basalts (Demming & Baross, 1993; Takai *et al.*, 2004a; see Baross *et al.*, 2004 for review) and in serpentinites and related ultramafic lilthologies (Kelley *et al.*, 2001, 2005; Charlou *et al.*, 2002). Biochemical and genomic evidence suggests that deeply-rooted organisms lived within ultramafic rocks, one of the bountiful niches we identify below (Nisbet & Fowler, 1996, 2004; Fraústo da Silva & Williams, 2001).

Evolutionary success of chemotrophic organisms is determined by availability of energy for metabolic processes, which, in part, defines geologic boundary conditions for viable niches and constraints on primary biomass productivity (McCollom & Shock, 1997; Hoehler, 2004; McCollom & Amend, 2005). H_2, Fe(II), H_2S and S were probably the primary electron donors of redox reactions providing energy for metabolic processes on early Earth (Canfield *et al.*, 2006). Numerous studies have predicted environmental constraints on the Gibbs energy for metabolic redox reactions involving these components for modern and early Earth, and for possible extraterrestrial ecosystems (i.e. Shock, 1990, 1992, 1997; Shock *et al.*, 1995; McCollom & Shock, 1997; Hoehler *et al.*, 1998, 2001a; Shock & Schulte, 1998; McCollom, 1999; Amend & Shock, 2001; Shock & Holland, 2004; Hoehler, 2005; McCollom & Amend, 2005). Results demonstrate the exergonic nature of these reactions, and thus the potential for viable chemolithoautotrophic niches based on geologic processes that create maximum non-equilibrium conditions among components of metabolic redox reactions.

We begin with a necessity of pre-photosynthetic life, specifically a source of energy for H_2-based metabolic processes. In the following we discuss organisms in terms of *chemically defined functional niches*. In doing so we do not imply, for example, that ancient methanogens are necessarily the ancestors of modern ones nor that they (and extraterrestrial organisms) used the same metabolic pathways. That is, extant life provides our frame of reference for characterizing energetics of pre-photosynthetic ecosystems.

With forethought, we initially consider the energy for metabolic processes with respect to methanogens and acetogens. The methanogenic reduction of CO_2 by H_2 is a dissimilative reaction

$$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O \qquad (1)$$

providing energy that methanogens couple with the energy-consuming reaction of adenosine diphosphate plus inorganic phosphate to form ATP. Acetogenic reduction of CO_2 is an assimilative reaction

$$2CO_2 + 4H_2 \Rightarrow CH_3COOH + 2H_2O \qquad (2)$$

providing complex organic matter (idealized formula CH_2O) for the cell as well as energy if the reactants CO_2 and H_2 are abundant (e.g. Hoehler *et al.*, 1998). In an opposite case, the reverse of reaction 2 can provide Gibbs energy if a methanogen locally depletes the concentration of H_2 through reaction 1 (Lee & Zinder, 1988; Kotsyurbenko *et al.*, 2001).

The Gibbs energy (ΔG_1) for methanogenic reduction of CO_2 by H_2 (reaction 1) is the sum of two terms:

$$\Delta G_1 = \Delta G_1^\circ + RT \ln Q, \qquad (3)$$

where ΔG_1° is the standard Gibbs energy (at the specified temperature and pressure), R is the gas constant, T is temperature in Kelvin, and Q denotes the activity quotient for the reaction. It is important to note that the standard Gibbs energy (ΔG_1°) is a function of the standard states chosen for the components, as is the numerical value for Q (cf. Helgeson *et al.*, 1978; Amend & Shock, 2001). For example, if we chose a standard state for $CO_{2,gas}$, $H_{2,gas}$ and $CH_{4,gas}$ with unit fugacity of the pure component at any temperature and pressure then ΔG_1° is approximately -131 kJ mol^{-1} at 25 °C and 1 bar (cf. Johnson *et al.*, 1992), and if we assume unit activity of liquid H_2O and that the gaseous species can be approximated by ideal mixtures, then Q is determined from measured partial pressures by $P_{CH4}/(P_{CO2} \cdot P_{CO2}^4)$. Alternatively, if we chose the aqueous species standard state defined by Helgeson & Kirkham (1976) for $H_{2,aq}$, $CO_{2,aq}$, $CH_{4,aq}$, then ΔG_1° is approximately -194 kJ mol^{-1} at 25 °C and 1 bar (cf. Johnson *et al.*, 1992), and if we assume unity for aqueous activity coefficients, then Q is the molal quotient $m_{CH4}/(m_{CO2aq} \cdot m_{H2aq}^4)$. We adopt both conventions in our analysis below.

Irrespective of the standard states chosen, reaction 1 is endothermic so values of ΔG_1° decrease with increasing temperature, as illustrated by the solid curves in Fig. 1, denoting the two alternate standard states adopted above. The solid curves are isopleths for $\Delta G_1 = 0$, that is, equilibrium for reaction 1 numerically represented by values for the standard Gibbs energy of reaction (ΔG_1°) divided by 2.3 RT, which is the logarithm of the equilibrium constant (K) for the reaction (Krauskopf & Bird, 1995). For comparison with the equilibrium curves for reaction 1, symbols in the figures are calculated values of log Q (equation 3) for the reaction computed from analyses of fluids from present-day shallow marine sediments (Hoehler *et al.*, 2002), from a continental basaltic aquifer (Chapelle *et al.*, 2002), from continental hot springs (Yellowstone, Spear *et al.*, 2005), and from basalts (Lucky Strike and Menez Gwen, Charlou *et al.*, 2000) and ultramafic rocks and serpentinites (Logatchev, TAG, Rainbow; Charlou *et al.*, 2002) of the Mid-Atlantic Ridge, including meteoric water (MW)- and seawater (SW)-dominated geothermal systems in the central volcanic zone of Iceland (Stefánsson & Arnórsson, 2002). We note that values of Q for geologic fluids shown in Fig. 1 are commonly within five orders of magnitude (+/– 60 kJ mol^{-1}) of equilibrium for reaction 1. These variations characterize the spectrum of viable niches for extant methanogens in oceanic and hydrothermal environments.

Calculated Gibbs energies (ΔG_1) for methanogenic reduction of CO_2 by H_2 based on measured quantities for Q in equation (3) for laboratory cultures, sediments and soils, and fluid mixing at deep sea hydrothermal vents demonstrates the exergonic nature of reaction 1 (i.e. a negative value for ΔG_1; Hoehler *et al.*, 1994, 2001a; McCollom & Shock, 1997; Kral *et al.*, 1998; Conrad, 1999; Chong *et al.*, 2002). For actively growing cultures and ecosystems, values of ΔG_1 are typically of the order of –20 to –40 kJ mol^{-1} (Thauer *et al.*, 1990; Schink, 1997; Scholten & Conrad, 2000). The minimum value of ΔG_1 under which methanogens can metabolize H_2 is measured in anoxic sedimentary environments and is approximately –10 kJ mol^{-1} (Hoehler *et al.*, 1994, 2001a). Values of ΔG_1 ranging between –9 to –15 kJ mol^{-1} appear to be the minimum exergonic energy yield for reaction 1 required for synthesis of ATP from ADP and inorganic phosphate in static or starving microbial communities (Schink & Stams, 2002; Hoehler 2004). The maintenance energy of the methanogen *Methanospirillum hungatei* is relatively low for microbes. In laboratory experiments, it consumed 0.005–0.022 of its C in reaction (1) per C in its biomass per hour (Scholten & Conrad, 2000).

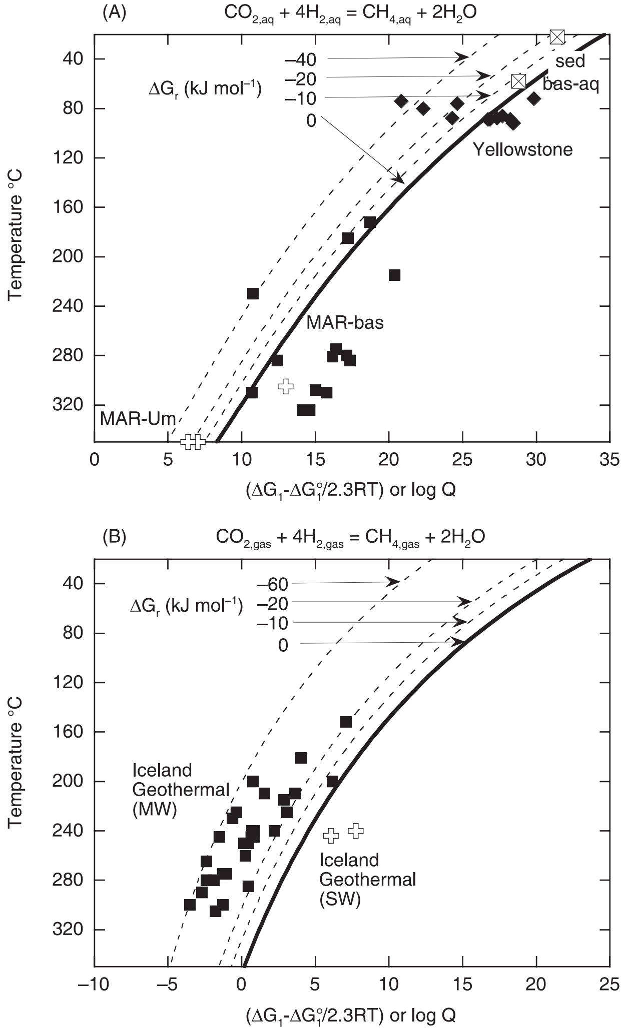

Fig. 1 Temperature dependence of the Gibbs energy for the methanogenic reaction (1) computed using the gas standard state (A) and aqueous species standard state (B) for H_2, CO_2, and CH_4. The lines represent isopleths of ΔG_1; zero representing equilibrium, and –10 and –20 kJ mol^{-1} denoting limiting conditions for starvation and growth, respectively, for methanogens (cf. Hoehler, 2004; computed using SUPCRT, Johnson *et al.*, 1992). Symbols denote values of log Q (equation 3) computed from measured concentrations or partial pressures of H_2, CO_2, and CH_4: sed = barrier island lagoonal marine sediments Cap Lookout Bight, North Carolina, USA (Hoehler *et al.*, 2002); bas-aq = continental basalt aquifer, Idaho, USA (Chapelle *et al.*, 2002); Yellowstone = hot springs in Yellowstone National Park, USA (Spear *et al.*, 2005); MAR-bas = Mid-Atlantic Ridge hydrothermal systems in basalt, including Lucky Strike (37°17′N) and Menez Gwen (37°50′N; Charlou *et al.*, 2000); MAR-um = Mid-Atlantic Ridge hydrothermal systems in ultramafic rocks and serpentinites, including Rainbow (36°14′N), Logatchev (14°45′N) and TAG (26°N; Charlou *et al.*, 2002); Iceland geothermal (MW) = meteoric water-dominated geothermal systems in Iceland, Iceland geothermal (SW) = seawater-dominated geothermal systems in Iceland (Stefánsson & Arnórsson, 2002).

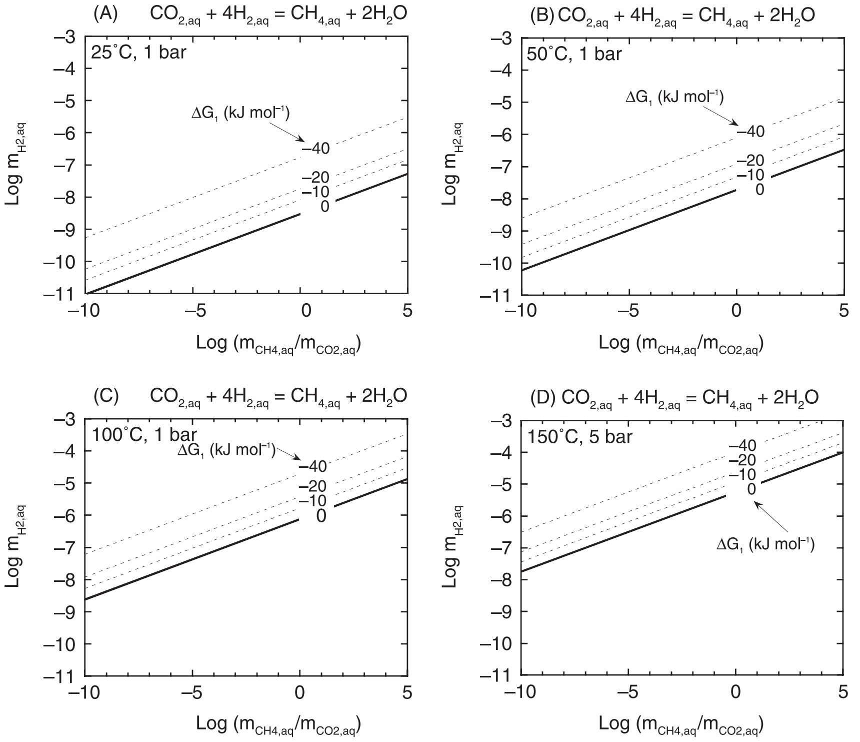

Fig. 2 Dependence of the concentration of aqueous H_2 on the molal ratio of CH_4 to CO_2 and the Gibbs energy for the methanogenic reaction 1 at 25, 50 100 and 150 °C and low pressures. Solid line denotes equilibrium conditions and the dashed lines labeled –10 and –20 kJ mol^{-1} denote limiting conditions for starvation and growth, respectively, for methanogens (cf. Hoehler, 2004; computed using SUPCRT, Johnson *et al.*, 1992).

Isopleths of ΔG_1 of –10 kJ mol^{-1} and –20 kJ mol^{-1}, representing approximate limiting conditions for starvation and growth for methanogens, are shown in Fig. 1, where they can be compared to values of Q computed from measured concentrations of H_2, CO_2, and CH_4 in present-day environments within marine sediments, basaltic aquifers, and continental and marine hydrothermal environments. Thermodynamic constraints imposed by these values of ΔG_1 and equation 3 on the concentration of $H_{2,aq}$ are shown in Fig. 2 as a function of the molal ratio of $CH_{4,aq}$ to $CO_{2,aq}$ over a temperature range of 25 to 150 °C at low pressures. The diagrams illustrate that minimum values of $H_{2,aq}$ required to support basic metabolic processes of methanogenesis encompasses some four or more orders of magnitude at constant temperature, and that at constant concentrations of $CH_{4,aq}$ and $CO_{2,aq}$, minimum values of $H_{2,aq}$ increase two or more orders of magnitude with increasing temperature.

Stoichiometry coupling of exergonic methanogenesis (reaction 1) with endergonic synthesis of ATP from ADP and inorganic phosphate is not constant; the chemo-osmotic reaction of ATP synthesis is dependent on the available energy on a cellular basis, and thus directly on environmental constraints on values of Q in equation 3 (Thauer, 1998; Schink & Stams, 2002). Qualitative estimates presented by Thauer *et al.* (1993) and Muller *et al.* (1993) suggest that less than 1 mol of ATP can be synthesized per mol of CH_4 produced from reaction 1 (based on methanogenic ecosystems with P_{H2} of 10^{-4} to 10^{-5} bar, ΔG_1 of –20 to –40 kJ mol^{-1}, and cellular synthesis of ATP of about 50 kJ mol^{-1}; Thauer *et al.*, 1977, Thauer & Morris, 1984). Similar stoichiometry was predicted by Kral *et al.* (1998) using measurements for cultured methanogens and a value for ATP synthesis of –36 kJ mol^{-1}. A number of studies suggest a stoichiometry of 1/3 mol ATP produced per mol CH_4 produced via reaction 1 (cf. Conrad, 1999; Scholten & Conrad, 2000; Chong *et al.*, 2002). In general, based on the stoichiometry of reaction 1, it appears that more than 4 mol of H_2 provided from geologic processes is required to form 1 mol of ATP under environmental conditions where ΔG_1 is of the order of –20 to –40 kJ mol^{-1}. To place limiting constraints on the amount of H_2 required to produce ATP, we adopt a minimum Gibbs energy where methanogens can metabolize H_2 of –9 to –15 kJ mol^{-1} (Hoehler *et al.*, 2001a; Schink & Stams, 2002) and a Gibbs energy for cellular synthesis of ATP of 50 kJ mol^{-1} (Thauer *et al.*, 1977), to which an additional 20 kJ mol^{-1} is added to account for irreversible heat loss during reaction (Schink, 1997), thus requiring the production of approximately 20 mol of H_2 by abiotic processes to produce 1 mol of ATP.

For mass balance purposes, the mole yield ratio of organic carbon per CO_2 production is relevant. Laboratory methanogens utilizing reactions (1) and (2) obtain 0.2 mol of CH_2O and produce 0.8 mol of CH_4 for 1 mol of CO_2 (Scholten & Conrad, 2000). The yield ratio is variable for methanogens, for example Heijnen & van Dijken (1992) report values of 0.015–0.056.

These thermodynamic constraints only modestly limit methanogens where there is an adequate supply of the reactants. Both CO_2 and H_2 need not have been major constituents of the atmosphere once methanogens evolved. However, hydrogen not consumed by methanogens may have become a significant trace gas in the atmosphere. For example, hot spring methanogens investigated by Chapelle *et al.* (2002) deplete hydrogen to values of ~13 nM. Air at habitable temperature in equilibrium with this water contains ~20 ppm by volume of H_2.

GEOLOGIC MASS BALANCES OF NICHES

We now consider geologic constraints that characterize niches for pre-photosynthetic life with globally significant productivity. We consider global mass balances on the fluxes of hydrogen, carbon dioxide, and sulfur, all of which are important reactants in providing chemical energy for pre-photosynthetic life. By assumption, photosynthetically derived organic matter and oxygen were absent. In order to identify the more productive niches, we first focus on geologically active regions, the mid-oceanic ridges and arc volcanoes. We consider H_2 as a substrate for methanogens and SO_2 as a substrate that may react with H_2, CH_4, or organic matter to form sulfide. We strive for factor-of-two accuracy but retain several significant figures for illustrative purposes. We evaluate chemical fluxes for modern Earth (Table 1) and qualitatively discuss differences between the present and the Hadean, and address how the fluxes and their estimates arise with uncertainties.

Mathematically, our estimated fluxes are products of the global rate of seafloor spreading A and a term B that is a weak function of the conditions on the Earth's surface and its interior, formally,

$$F_i = B_i A, \tag{4}$$

where the subscript i denotes a chemical component. The B_i coefficients depend, for example, on the concentration of a component in the rocks hosting the hydrothermal systems, the flux of water through the systems, or the partition of the element between water and rock. The latter is a function of the hydrothermal fluid temperature, its initial composition as seawater, and the mineralogy of the host rock. We use data from modern systems to calibrate the coefficients and assume for simplicity that they have not changed over time. To provide numerical examples, we adopt an approximate modern global spreading rate of $A = 3\ \text{km}^2\ \text{year}^{-1}$ (White *et al.* 1992). The results of our calculations as the products B_iA are presented in Table 1.

Table 1 Flux estimates before photosynthesis*

Process	Product	Flux, Tmol year^{-1}	Comment
A. Hot basaltic vents	H_2	0.06	
B. Serpentine vents	H_2	0.19	
C. Arc volcanoes	H_2	0.17	
D. Total	H_2	0.42	A + B + C
E. Primary methanogenesis	CH_4	0.105	0.25D
F. Photolysis and surface methanogenesis	CH_4	0.105	~E
G. Total methane	CH_4	0.21	E + F
H. Arc volcanoes	SO_2	0.08	
I. Ridge + arc volcanic + metamorphic	CO_2	8	

*Using current crustal production rate 3 km^2 year^{-1} assumed; fluxes scale to this rate (Tmol = 10^{12} mol).

We discuss hydrogen fluxes from hydrothermal circulation through basalt and serpentinite, and from arc type volcanoes. Chemically, the FeO component of silicates (i.e. olivine, pyroxene, and serpentine) reacts with water to form magnetite and $H_{2(aq)}$,

$$3FeO_{(\text{in silicate})} + H_2O \Rightarrow Fe_3O_{4(\text{magnetite})} + H_{2(aq)} \tag{5}$$

A reaction of this form also releases H_2 from arc magmas. FeO can also react to form ferrous iron in silicates, such as epidote,

$$2FeO_{(\text{in silicate})} + H_2O \Rightarrow Fe_2O_{3(\text{in epidote})} + H_{2(aq)} \tag{6}$$

These reactions couple with sulfur reactions, for example, the formation of pyrite (FeS_2) by H_2S oxidation of Fe(II) monosulfide (FeS)

$$FeS + H_2S \Rightarrow FeS_{2(\text{pyrite})} + H_{2(aq)} \tag{7}$$

(Wachtershauser, 1988; Drobner *et al.*, 1990; Rickard, 1997; Rickard & Luther, 1997; Hoehler, 2005). As a consequence of varying degrees of alteration and hydration there is a continuous range of composition and oxidation state between basalt and serpentinized peridotite of oceanic crust. For bookkeeping purposes, we discuss basaltic and serpentinite systems separately. We do not explicitly consider seamounts, which are clearly sites of hydrothermal circulation (e.g. Eddy *et al.*, 1998) because we regard their effect to be within the uncertainty of our basaltic system estimates.

Our estimates do not apply to very early Earth. An amount of hydrogen comparable to that in the modern ocean may have escaped to space following the Moon-forming impact (Kuramoto & Matsui, 1996; Sleep *et al.*, 2004). Below we do not consider this epoch when high surface temperatures precluded life (Sleep *et al.* 2001). Neither do we consider a time when the Earth's interior was so hot that rocks of mantle composition erupted directly on the surface. If surface temperatures were clement then, the atmosphere was in dynamic equilibrium with serpentinite. In this case, the atmosphere of very early Earth likely contained significant H_2 and trace CO_2.

Finally, we do not attempt to resolve effects of differences between Hadean and modern tectonics on the ratio of oceanic serpentinite crust to basaltic crust. Qualitatively, Earth scientists typically assume that the Hadean sublithospheric mantle was hotter than the present mantle even though there is little direct evidence in the rock record. Oceanic crust was thicker because the fraction of partial melting increases with temperature (Klein 2003), which made it more difficult for tectonics to exhume peridotite. However, Hadean basalts were more magnesian, giving rise to abundant dunite cumulates. Large asteroid impacts in the Hadean exhumed significant masses of reactive rock, including mantle peridotite. Today, serpentinite covers ~10% of the global seafloor (Dick *et al.*, 2003) and hence constitutes a similar percentage of the global oceanic crust production. This ultramafic rock is most common at very slowly spreading ridges, and at fracture zones where tectonics exhumes the mantle (Dick *et al.*, 2003). We use the approximation of 0.1 to represent the fraction of serpentinite in our calculations for oceanic crust.

Basalt-hosted systems

We consider two approaches for predicting the global flux of H_2 from basaltic oceanic crust based on empirical geologic observations. One is to compare unaltered 'fresh' basalt with altered oceanic crust in drill holes and outcrop. Mathematically, this flux estimate of hydrogen is

$$F_{HB} = A_B Z_B M_{HB} \Delta\xi_{HB}, \quad (8)$$

where the subscript HB indicates hydrogen from the basaltic oceanic crust, A_B is the rate that basalt oceanic crust forms (now 2.7 km^2 $year^{-1}$ = 3 km^2 $year^{-1}$ $*$ 0.9, assuming 90% of the crust formed is basalt, 10% ultramafic rocks), Z_B is the equivalent thickness of basalt available for reaction, M is the amount of reactant available per volume, and $-1 \le \Delta\xi \le 1$ is reaction progress (cf. Helgeson, 1979). A second approach is to obtain the concentration difference between incoming fluid (ambient seawater) and the vented hydrothermal fluid, mathematically represented by

$$F_{HB} = A_B \xi_B \Psi_{HB}, \quad (9)$$

where ξ_B is the volume of fluid per area of seafloor and Ψ_{HB} is the concentration of H_2 in a vent fluid as the concentration in ambient seawater is negligible.

The former approach yields a useful estimate for the maximum limit of hydrogen generated from basaltic crust. For an example calculation, we assume that an equivalent reaction thickness of 1 km is readily accessible to interaction with circulating seawater. Realistically, the reaction progress decreases with depth. For example, $\Delta\xi = 1/2$ in the uppermost kilometer, $\Delta\xi = 1/4$ in the second kilometer, $\Delta\xi = 1/8$ in the third kilometer, and so on would have the same effect (eqn 8). The depth of alteration depends on the depth distribution of porosity and permeability, which are complex functions of lithostatic and hydrostatic pressures, and the volumetric and thermal properties of metasomatic reactions (cf. Manning & Ingebritsen, 1999). Reaction progress is thus weakly dependent on the thickness of oceanic crust and its composition. To obtain numerical results, we assign a rock density of ~3000 kg m^{-3} and assume that the principle reductant is FeO, which comprises about 10% of the rock mass in both basalt and peridotite that forms serpentinite. The absolute maximum global flux of FeO in the 2.7 km^3 $year^{-1}$ of reactive basaltic crust is 11.3 Tmol $year^{-1}$ (1 Tmol = 10^{12} mol). This would release 3.75 Tmol $year^{-1}$ of H_2 if reaction (5) went to completion in a kilometer of equivalent section (i.e. $\Delta\xi$ equals 1 for reaction 5). Bach & Edwards (2003) use drilled samples of the oceanic crust to obtain a flux of 0.45 ± 0.30 Tmol $year^{-1}$ of H_2, a range that is equivalent to $\Delta\xi$ between 0.04 and 0.20 for reaction 5. The flux that we obtain below from vent fluids is much less than the upper limit and somewhat less than Bach & Edwards' (2003) range.

With regard to the latter approach (eqn 9), Alt (2003) and German & Von Damm (2003) have reviewed the flux of various chemical components from basaltic hydrothermal systems. Hot axial systems carry the bulk of the H_2 flux from basaltic crust. We begin by discussing mineralogic controls of H_{2aq} in present day vent fluids before evaluating the methodology and data to put the estimates in context. Traditionally, geologists represent the redox state of geologic systems dominated by mafic and ultramafic rocks with quartz, fayalite and magnetite (QFM) equilibrium represented by (Basaltic Volcanism Study Project, 1981, p. 382).

$$3Fe_2SiO_4 + 2H_2O \leftrightarrow 3SiO_2 + 2Fe_3O_4 + 2H_{2(aq)}; \quad (10)$$

fayalite + water ↔ quartz + magnetite + aqueous hydrogen

which closely approximates redox conditions of ultramafic rocks under igneous conditions [which are mostly olivine $(Mg,Fe)_2SiO_4$ and pyroxene $(Mg,Fe)SiO_3$, with atomic Mg:Fe ratios of ~9:1], and the more silicic mafic rocks, like basalt (Morse *et al.*, 1980), even to temperatures of hydrothermal processes (Bird *et al.*, 1986; Stefánsson & Arnórsson, 2002). We use equilibrium for reaction (10) as a comparative reference to evaluate the temperature dependence of H_2 concentrations, which are often sub-parallel to the trend of this buffer.

There is considerable variability of the hydrogen concentration among individual analyses of vent fluids from the mid-ocean ridge hydrothermal systems, which illustrates processes affecting the fluids. A suite of vent fluids from the East Pacific Rise illustrating quenching by conductive heat loss, where H_2, CH_4, and CO_2 behave to the first order as conservative components (is shown in Fig. 3A). The abiogenic methane concentration is small compared to the H_2 concentration. Geothermal solutions from Iceland show effects of partial equilibration with the basaltic host rock and the alteration assemblages (Fig. 3D; Stefánsson & Arnórsson, 2002). Note, in comparison with Fig. 3A, that the aqueous H_2 concentrations in Iceland geothermal systems increase with increasing temperature. In Fig. 3B it is apparent that fluids from vents in basalts of the Mid-Atlantic Ridge have methane concentrations that behave

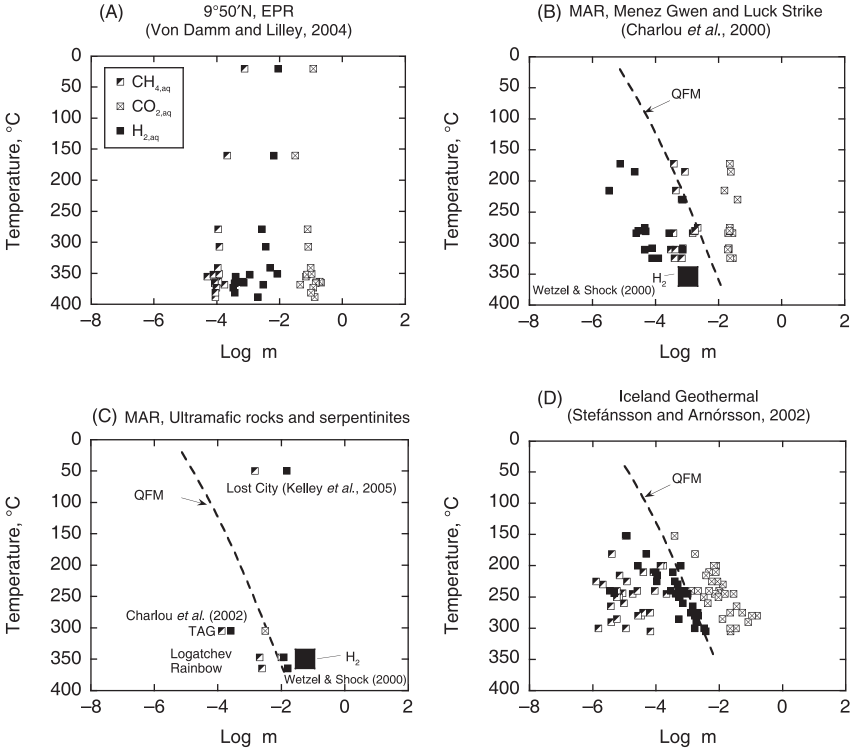

Fig. 3 Molal concentrations of aqueous CH_4, CO_2 and H_2 from (A) basalt-hosted vents and diffuse flow from 9°50′N East Pacific Rise (Von Damm & Lilley, 2004), (B) basalt-hosted vents from the Mid-Atlantic Ridge (Menex Gwen and Lucky Strike; Charlou *et al*., 2000), (C) vents from ultramafic rocks and serpentinites of the Mid-Atlantic Ridge (TAG, Logatchev, Rainbow; Charlou *et al*., 2002) and Lost City (Kelley *et al*., 2005), and (D) geothermal drill holes in active geothermal systems in Iceland (Stefánsson & Arnórsson, 2002). Theoretical calculations of $H_{2,aq}$ concentrations of hydrothermal fluids in basalt-hosted and ultramafic submarine hydrothermal systems are shown by the large solid square in diagrams B and C, respectively (Wetzel & Shock, 2000).

conservatively during quenching, but that hydrogen appears buffered by reaction with the basalts (Fig. 3B).

Overall, the hydrogen concentrations presented in Fig. 3 indicate that a few millimoles of H_2 are present at ~350 °C in the mid-ocean ridge vent systems. Wetzel & Shock (2000) predicted this amount from irreversible mass transfer calculations. We use 2 mM for a numerical example. Alt (2003) reports a high-temperature axial hydrothermal flux of $0.4–1.8 \times 10^{13}$ kg year^{-1}, and German and Von Damm use 5.6×10^{13} kg year^{-1}. Nielsen *et al.* (2006) obtain $0.17–2.93 \times 10^{13}$ kg year^{-1} with a best estimate of 0.72×10^{13} kg year^{-1} for the flux that vents at high temperatures using thallium as a tracer. Here we follow Sleep & Zahnle (2001) who report a value of 3×10^{13} kg year^{-1}, in the middle of this range. This yields an H_2 flux from basalt of 0.06 Tmol year^{-1} (Table 1), a value that is a factor of two to eight times greater than the range reported by Canfield *et al.* (2006) for H_2 flux for mid-ocean ridge systems. They use the water flux estimate of Alt *et al.* (2003). An overall reaction progress value of $\Delta\xi$ of ~0.02 for reaction 5 is required to predict our flux using our first approach for estimating H_2 fluxes (eqn 8).

Note that Kump & Seyfried (2005) suggest that early Archean black-smoker fluids likely contained significant Fe(II), 80 mM at 400 bars and 400 °C. This would yield 0.80 Tmol year^{-1} of H_2 if reaction (5) went to completion. However, such fluids are quenched when mixed with seawater; a modest fraction of the Fe(II) is precipitated as FeS (Kump & Seyfried, 2005) and much of the rest is precipitated as $FeCO_3$ before oxidants were available or iron-based photosynthesis evolved. We do not include this process as a separate H_2 source in Table 1.

Serpentinite systems

The hydration and oxidation of ultramafic rocks to form serpentinites is a more productive source of H_2 than basalt (Berndt *et al*, 1996; Wetzel & Shock, 2000; McCollom & Seewald, 2001; Charlou *et al.*, 2002; Seyfried *et al.*, 2004; Sleep *et al.*, 2004; Kelley *et al.*, 2005). Unaltered ultramafic rock of oceanic crust have mantle composition that is modified to varying degrees by reaction with seawater (cf. Alt & Shanks, 2003; Fruh-Green *et al.*, 2004; Bach *et al.*, 2006; Schulte *et al.*, 2006). Continuing to assume that 10% of oceanic crust is serpentinite (3 km^3 year^{-1} $*$ 0.1 = 0.3 km^3 year^{-1}), the maximum possible annual production of H_2 via reaction (5) is 0.38 Tmol year^{-1} if the reaction goes to completion (i.e. $\Delta\xi = 1$) within an equivalent depth of 1 km (again reaction progress $\Delta\xi$ decreases with depth, as discussed above).

As with basaltic systems, idealized reactions help to constrain the actual H_2 flux from ultramafic rocks and their metamorphic equivalents. The redox conditions defined by reaction (10) are inappropriate at temperatures below ~350 °C for these rocks, as the stable phases are serpentine $(Mg,Fe)_6Si_4O_{10}(OH)_8$, brucite $(Mg,Fe)(OH)_2$, and magnetite (Coleman, 1971; O'Hanley, 1996). The redox reaction is (Sleep *et al.*, 2004),

$$Fe_6Si_4O_{10}(OH)_8 + 6Mg(OH)_2 \leftrightarrow Mg_6Si_4O_{10}(OH)_8 + 2Fe_3O_4 + 2H_{2(aq)} + 4H_2O, \qquad (11)$$

greenalite + Mg-brucite ↔
chrysotile + magnetite + hydrogen + water

where stoichiometry corresponding to greenalite ($Fe_6Si_4O_{10}(OH)_8$) and chrysotile ($Mg_6Si_4O_{10}(OH)_8$), and to Mg-brucite ($Mg(OH)_2$) denotes components of Mg-Fe^{2+} substitution in the serpentine mineral chrysotile and in brucite, respectively. Sleep *et al.* (2004) give the hydrogen concentration in equilibrium with this reaction in terms of serpentine composition and temperature.

The volume of hydrothermal fluid circulation through serpentinite systems is not well constrained. Allen & Seyfried (2004) discuss the heat balance of submarine vents in serpentinites, and note that off-axis fluid circulation is likely controlled by tectonic processes near slow spreading ridges and not by the exothermic heat production during olivine hydrolysis. Slow seafloor spreading occurs over a broad zone of extension where there is no axial magma lens (Dick *et al.*, 2003). The specific heat of the upwelling mantle fuels circulation, but the latent heat of freezing basalt does not contribute. As a first-order approximation, we adopt a value of 1/10 of the fluid flux through basalts (see above), 0.3×10^{13} kg year^{-1}, for our example. This yields an annual H_2 production of 0.09 Tmol year^{-1}, a value that is within the range of values reported by Canfield *et al.* (2006; 0.08 to 0.13 Tmol year^{-1}).

There is also significant hydrogen in warm hydrothermal vents. The H_2 concentration of end-member Lost City vent fluid is 15 mM (Kelley *et al.*, 2005). Warm basalt vents discharge 6×10^{14} kg year^{-1} globally (Sleep & Zahnle, 2001). Using 1/10 of this number for warm serpentinite vents as a first-order approximation yields a flux of 0.9 Tmol year^{-1}, which would consume more than the available reactant in a kilometer of section of upper crust from reaction (5).

In practice, the concentration of magnetite in serpentinite provides a monitor of the progress of reaction (11) that is easily measured in thin section because there is little if any magnetite in the unaltered ultramafic rock. There is in fact significant magnetite in exposed serpentinite (Schulte *et al.*, 2006), indicating that reaction (11) has progressed. That is, following Bach *et al.* (2006) we use magnetite as a proxy for $\Delta\xi$ in reaction 8 (cf. Ferry, 1986). For example, 50% completion of the reaction in a kilometer equivalent section implies a global flux of H_2 of 0.19 Tmol year^{-1}. We use this as our preferred estimate (Table 1), which is approximately a factor of 2 larger than estimated H_2 fluxes from ocean crust serpentinization reported by Canfield *et al.* (2006). They assume that 5% of the seafloor is serpentinite. Other estimates of equivalent thickness are in approximate agreement with ours. Skelton *et al.* (2005) and Bullock & Minshull (2005) give ~2 km for crust associated with the break-up margin of Iberia. Rüpke *et al.* (2004) state that an additional equivalent thickness of 0.5 km forms at the expense of the uppermost mantle, near the Moho ~6-km beneath the seafloor. However, this process is inapplicable to the Archean as the oceanic crust was >6 km thick on early Earth (e.g. Klein, 2003), and it is unlikely that much serpentinite formed beneath it. Data from marine serpentinites now exposed on land do not provide sufficient information to do more than to confirm that significant oxidation and hydration did occur.

Island arcs and hydrogen

Island arcs are a source of both H_2 and SO_2. The latter provides a potential niche for sulfite reducers considered in the next section. Fluxes of H_2 from arc environments in the Archean are difficult to constrain using modern analogs because subducted products of photosynthesis enter modern magmas, in particular, sulfide in the oceanic crust from seawater sulfate in ridge-axis hydrothermal systems. However, the mantle source regions of modern arc volcanoes have oxygen fugacities similar to MORB (Lee *et al.*, 2005), and Archean source regions for arc magmas were similar to modern ones (Canil, 2002).

Crustal level processes are responsible for the oxidized state of modern arc magmas (Lee *et al.*, 2005). Auto-oxidation with hydrogen escape at depth (homologous to reaction 5) is a likely abiotic process applicable to the Archean (Holloway, 2004). The H_2 escapes into hot hydrothermal systems where it reacts with ferric iron in the rock. The oxygen liberated by hydrogen escape also oxidizes sulfide within the magma, which we represent simply as (e.g. Aiuppa *et al.*, 2005),

$$H_2S + 2H_2O \rightarrow SO_2 + 3H_2. \qquad (12)$$

Convection through magma conduits from upper crustal chambers effectively liberates SO_2 into the air (e.g. Witter *et al.*, 2005). The composition of an average shallow magma chamber is misleading, since more reduced magmas supply the bulk of the H_2 to the air and the more oxidized ones the SO_2.

Holland (2002) proposes a global volcanic plus hydrothermal flux of 5 Tmol year^{-1} for H_2, a value which Canfield *et al.* (2006) and Hayes & Waldbauer (2006) consider excessive. The mass of Fe in the magma provides an upper limit. For example, a flux of 2 km^3 year^{-1} for arc magmas with 10% FeO could only supply 3 Tmol year^{-1} of H_2 if reaction (5) went to completion (that is $\Delta\xi = 1$ for reaction 5). Mass balance constraints for water in island arcs provide the basis for Hayes & Waldbauer's (2006) more reasonable estimate. Water in arc magmas comes primarily from subducted hydrothermally altered oceanic crust. We assume that a balance between subducted water and volcanic water grossly constrains the flux. Hydrothermally altered basalt typically contains ~3% by weight, or 10% by volume, of H_2O (Staudigel, 2003) structurally bound in minerals like clays, chlorite, epidote, and amphiboles. Assuming an equivalent hydrated thickness of

1 km implies that 0.3 km^3 of water is subducted each year, equal to 17 Tmol $year^{-1}$ of H_2O. We consider this number to be uncertain by a factor of ~2. For example, Rüpke *et al.* (2004) report a value that is ~1.8 times our estimated flux of subducted water using 2.7% by weight H_2O and a 2-km equivalent thickness of altered crust. However, our estimated flux of water is equal to that proposed by Wallace (2005) and used by Hayes & Waldbauer (2006) based on magmatic products of arcs (that is, 2.5 km^3 $year^{-1}$ of arc magma with 4% by weight water; also see Oppenheimer, 2003). We bias our estimate to oceanic crust produced at fast-spreading ridges with shallow hot hydrothermal systems and depths of hydration on the inference that the global renewal rate of early Earth was faster than that of present. We have already ignored serpentinization of the uppermost mantle beneath typical crust on the grounds that the oceanic crust on early Earth was too thick for it to be significant. The water flux within sediments is modest (Rüpke *et al.*, 2004), and we ignore it also.

We now have sufficient information to estimate the volcanic H_2 flux. QFM conditions (reaction 8) are a reasonable approximation at volcanic temperatures for the more reduced arc magmas that are significant hydrogen sources (e.g. Lee *et al.*, 2005). The H_2/H_2O ratio at QFM and conditions suitable for a volcanic orifice (1200 °C and 5 bars) is ~0.01 (Giggenbach, 1996; also see Krauskopf & Bird, 1995, Table 18–1). This ratio and a water flux of 17 Tmol $year^{-1}$ imply a global flux of 0.17 Tmol $year^{-1}$ of H_2, comparable to the estimated flux from serpentinite (Table 1). As shown in Table 1 the total basalt (0.06 Tmol $year^{-1}$) plus serpentinite (0.19 Tmol $year^{-1}$) plus arc flux (0.17 Tmol $year^{-1}$) is 0.42 Tmol $year^{-1}$, a value that is an order of magnitude less than that reported by Holland (2002) and near the upper limit predicted by Canfield *et al.* (2006; 0.18 to 0.5 Tmol $year^{-1}$)

Some uncertainty results as only extrusive magmas are a source of hydrogen. Water in intrusive magmas that cool slowly equilibrates near QFM at hydrothermal temperatures where the concentration of H_2 is small. The fraction of the initial (slab-derived) magmatic water that makes it to arc eruptions in reduced magmas is unknown, as is the amount of water assimilated from crustal rocks by these magmas. It is obvious that magmatic water is entrapped at depth and crustal water is added to magmas as they migrate upward. Sulfur systematics provides a crude constraint on the mobility and flux of water, as only ~0.5 of the S in the primary magma reaches the surface (Wallace, 2005).

Island arcs and sulfite

SO_2 is a major component in arc volcanic gas (Gerlach, 1993; Wallace, 2005). We use estimates of modern fluxes to constrain the SO_2 flux on early Earth. Wallace (2005) reports a global SO_2 flux to the air of 0.30 Tmol $year^{-1}$ from modern arc volcanoes. Aiuppa *et al.* (2005) compile a range of 0.15 to 0.30 Tmol $year^{-1}$. Hayes & Waldbauer (2006) report 0.16–0.28 Tmol $year^{-1}$, a range in values similar to that adopted by Canfield *et al.* (2006).

The pre-photosynthetic flux is likely to be lower. Some of the sulfur in arc magmas is derived from subducted sulfate, a product of photosynthesis in the marine environment (Kump & Seyfried, 2005). Alt (1995) notes that $\delta^{34}S$ of arc volcanics is ~6‰. A mixture of 30% seawater sulfate from the slab with $\delta^{34}S$ of ~20‰ and magmatic sulfur with $\delta^{34}S$ of ~0‰ would yield this ratio.

The high oxidation state of some modern arc magmas may result from assimilation of photosynthetically derived ferric iron in the crust rather than auto-oxidation (Lee *et al.*, 2005). Some of the SO_2 in modern fumaroles maybe derived from seawater in the volcanic edifice and ultimately from photosynthetic processes (e.g. Aiuppa *et al.*, 2005). Note that sulfite may disproportionate into sulfide and sulfate, see reaction (21). We use SO_2 and sulfite for brevity in this section.

We are in agreement with the reasoning presented by Hayes & Waldbauer (2006) in that the pre-photosynthetic SO_2 flux was significant, but that it was less than the present value. For an example calculation, we reduce Hayes and Waldbauer's lower limit of 0.16 Tmol $year^{-1}$ by a factor of 2 (0.08 Tmol $year^{-1}$) to account for this difference (Table 1). This flux is less than the 0.17 Tmol $year^{-1}$ that could consume our H_2 flux of 0.42 Tmol $year^{-1}$ via reaction (12) (Table 1). In accord with this significant flux of SO_2, the last Archaeal common ancestor may have reduced sulfur species as suggested by House *et al.* (2003). There is geological evidence for metabolic sulfate reduction before 3.4 Ga (Shen & Buick, 2004). The biochemical ability to reduce sulfur compounds from volcanoes pre-adapted organisms to the bounty that followed the advent of sulfate-producing photosynthesis.

The geologic and structural details of volcanic vents and related hydrothermal systems affect the surface flux of SO_2 in arc environments. It reacts abiotically (with water if no O_2 is present) to form sulfite in hydrothermal systems (e.g. Symonds *et al.*, 2001). Once sulfite is in a habitable environment, microbes utilize it as a source of energy through reaction with hydrogen, methane or organic matter (Hoehler *et al.*, 2001a, 2001b). The net effect is,

$$SO_3^{-2} + 3H_2 \rightarrow S^{-2} + 3H_2O. \qquad (13)$$

As hydrogen in reaction (13) may be derived from reaction of water with ferrous iron (reaction 5), the net effect of magmatic degassing, abiotic oxidation of Fe(II) (reaction 5) and chemoautotrophic metabolism (reaction 13) is,

$$H_2SO_3 + 9FeO \rightarrow H_2S + 3Fe_3O_4. \qquad (14)$$

This reaction also occurs abiotically in hydrothermal systems, reducing the sulfite flux available to biota (Symonds *et al.*, 2001) and the amount of methane in the atmosphere (reaction 1), as well as the global rate of hydrogen escape. The 3:1 mass balance between hydrogen and sulfur in reaction (13) indicates that a volcanic SO_2 flux of 0.08 Tmol year^{-1} would consume a flux of H_2 of 0.24 Tmol year^{-1}, a significant fraction of the 0.42 Tmol year^{-1} that we obtained from hot basalt vents, serpentinite systems, and arc volcanoes (Table 1).

Carbon dioxide flux

In addition to hydrogen, methanogens require CO_2 for their basic metabolic processes (reactions 1 and 2). The flux of CO_2 from degassing of basalts at ridge axes is most likely greater than H_2 fluxes discussed above. The CO_2/H_2 ratio in hot basaltic hydrothermal fluids, where H_2 is more abundant than CH_4, is ~25:1 (Fig. 3A,D). Sleep & Zahnle (2001) compile estimates of current global flux of 1 to 3 Tmol year^{-1}, and the lower end of the range is most probable (Saal *et al.*, 2002; Hayes & Waldbauer, 2006). There are comparable estimates of fluxes from arcs of 1.7 mol year^{-1} (Wallace 2005), and from global metamorphism of 6 Tmol year^{-1} (Brantley & Koepenick, 1995). We use 8 Tmol year^{-1} for combined mid-ocean ridge, volcanic arc, and continental metamorphic CO_2 fluxes (Table 1).

The internal temperature of early Earth was hotter than that in modern times, which increased the thickness of mantle that melted at ridge axes (Klein, 2003). The direct effect was that more CO_2 vented from the mantle per area of new seafloor. Mass balance considerations suggest, relative to modern volcanic arcs, that more CO_2 was subducted and that higher temperatures increased the fraction of CO_2 that was returned to arc-type environments of early Earth. The net effect is that we underestimate CO_2 fluxes by extrapolating from present conditions.

There is no geologic record that bears on Hadean atmospheric CO_2. We use observations of exposed 3.46-Ga oceanic crust (Kitijima *et al.*, 2001; Nakamura & Kato, 2004) to provide a belated constraint. The concentration of CO_2 per volume in the 3.46-Ga oceanic crust is about nine times that in Cretaceous crust based on studies reviewed by Staudigel (2003). Sleep & Zahnle (2001) contend that this concentration depends linearly on the concentration of CO_2 in the ocean, and hence we use the estimate of ~900 ppm by volume in the Cretaceous atmosphere to obtain ~4500 ppm at 3.46 Ga. Even if this estimate is too large by a factor of a few, CO_2 was a significant atmospheric component. For example, Kharecha *et al.* (2005) use 1500 ppm in their calculations.

Radiolytic dissociation of water

For completeness, we note that alpha, beta, and gamma particles from U, Th, and K decay dissociate water into H_2, H_2O_2, and O_2 (Lin *et al.*, 2005). The flux of H_2 per surface area is 8×10^{-6} mol m^{-2} year^{-1} in the Witwatersrand Basin of South Africa (Lin *et al.*, 2005). Extrapolation over the 2×10^{14} m^2 area of continental crust gives 0.00016 Tmol year^{-1} globally. This is three orders of magnitude less than our estimated flux for serpentinite. This relative insignificance applies to the Hadean when the radioactive particle production rate was a few times the present level and the area of continental crust was less (cf. Rino *et al.*, 2004), and thus we ignore radiolysis as a significant contribution to the global H_2 flux. We note that the production of O_2 and H_2O_2 provided local niches and pre-adaptation for organisms that reacted these components with H_2, ferrous iron, sulfide, and organic carbon before the advent of photosynthesis.

SUBSURFACE AND SEAFLOOR NICHES

Globally, hydrogen was the limiting ingredient for methanogens. Our total H_2 flux of 0.42 Tmol year^{-1} is much less than the total CO_2 flux of 8 Tmol year^{-1}. Only a small fraction of the vented carbon in CO_2 was ever reduced to methane before it was buried. An even smaller fraction entered organic matter. Still, subsurface H_2 production was localized within young serpentinite-hosted hydrothermal systems and hot basaltic vents. CO_2 may have been locally limiting in determining negative values of ΔG for reaction 1 required for viable methanogenic niches (see eqn 3 and Fig. 1).

We begin with a serpentinite system where water does not become hot enough to preclude life. Downwelling seawater contains significant CO_2. Serpentinization supplies H_2 to the fluid. (It has not escaped us that life might obtain chemical energy from the serpentinization reaction 11). A microbe would gain additional chemical energy by using olivine or volcanic glass as a substrate. Notably, microbes may have formed micron-scale tubes into volcanic glass as old as ~3.5 Ga (Furnes *et al.*, 2004). Methanogens would have consumed H_2 as it was produced by irreversible reactions between these substrates and hydrothermal solutions. Formation of carbonate minerals ($(Ca,Mg,Fe)CO_3$) would have depleted the circulating fluids in CO_2. The fluid eventually became grossly depleted in CO_2 while H_2 accumulated.

CO_2-depleted vents from serpentinite and hot vents from basalt discharged H_2 into clement seawater. It was to the advantage of methanogens to be near these vents. They consumed the H_2, reacting it with the abundant CO_2 in the water. In contrast, subsurface organisms and their dead remains were dispersed in the rock, making identification difficult without a planned search even in modern systems (cf. Schulte *et al.*, 2006). Hydrothermal vents, like those of the Lost City field (Kelley *et al.*, 2005), are relatively easy to identify both on the modern Earth and as deposits in ancient rocks.

PHOTOLYSIS AND SURFACE NICHES

Photolysis inefficiently accomplishes the same net effect as photosynthesis by producing potential reactants, such as, CO and methane haze. We consider that the pre-photosynthetic atmosphere contained CO_2, methane, as well as nitrogen, and some water vapor. The formation of carbonates by weathering of silicates on land and by hydrothermal reactions on the seafloor buffered CO_2. Kasting & Catling (2003) review the general aspects of habitable atmospheres.

The methane produced by methanogens built up in the ocean and came into dynamic equilibrium with the air. The escape of hydrogen to space buffered these methane concentrations. The tropopause did not act as a methane cold trap, so total hydrogen was well mixed to ~100 km elevation. Photolysis produced gaseous and solid species from methane. As we are interested in net effects, we represent gases with the idealized reaction,

$$CH_4 + CO_2 \Rightarrow 2CO_{(gas)} + 2H_2\uparrow. \qquad (15)$$

We represent the complex organic solids in methane haze with

$$CH_4 \Rightarrow C_{(haze)} + 2H_2\uparrow. \qquad (16)$$

Haze forms when methane is abundant relative to CO_2 (Pavlov *et al.*, 2001).

We presume that hydrogen readily escapes from the atmosphere (Kharecha *et al.*, 2005). That is, a negligible fraction of the hydrogen produced by photolysis in the upper atmosphere ever returns to surface environments. Recently, Tian *et al.* (2005) contended that hydrogen does not escape efficiently after photolysis, an approach criticized by Catling (2006). We do not attempt to resolve this dispute and consider the consequences where hydrogen escapes. That is, our calculations are inapplicable if photolytic hydrogen recycled to the surface.

The CO and C-rich haze (reaction 16) were gravitationally bound, and eventually returned to surface environments, making widely dispersed niches. Dissimulative reactions provide mass balance constraints. For example, the global flux of CO to surface environments reacts biologically with water,

$$2CO + H_2O \Rightarrow 0.75CO_2 + 0.5CH_4, \qquad (17)$$

where we retain the product stoichiometry of 2CO from reaction (15) to make the mass-balance calculations easier to follow. In addition, various extant organisms consume CO in alternative ways, where H_2 is a dissimilative product (Rother & Metcalf, 2004; Sokolova *et al.*, 2004), and acetate is an assimilative product (Rother & Metcalf, 2004; Ferry & House, 2006). The latter pathway may have predated methanogenesis (Ferry & House, 2006).

In analogy with meteor smoke (Gabrielli *et al.*, 2004), C-rich haze (reaction 16) descends to Earth near the poles, where it can biologically react with water

$$C\text{ (haze)} + H_2O \Rightarrow 0.5CO_2 + 0.5CH_4. \qquad (18)$$

Decomposition of organic matter yields the same products

$$CH_2O \Rightarrow 0.5CO_2 + 0.5CH_4. \qquad (19)$$

(e.g. Scholten & Conrad, 2000). The net effect of reactions (15) and (17) produces 0.5 of a methane molecule from the original methane molecule that was photolyzed. Reactions (16) and (18) also have this effect. The total amount of methane photolyzed is (for simplicity) 1 unit from the initial reaction, plus 1/2 unit from reactions (17) and (18), 1/4 unit when that methane photolyzes, and so on. As the geometric series 1, 1/2, 1/4, 1/8, . . . sums to 2, total methane photolyzed is the primary flux times 2. The productivity of surface niches dependent on photolysis is thus comparable to the productivity of the niches dependent on hydrogen from rocks.

Organisms near the surfaces of the ocean and land had the first opportunity to utilize the H_2 from arc volcanoes. Rain droplets were habitable, but were nutrient and ultraviolet (UV) light limited. Overall, viable ecologies were dispersed over Earth's surface. The remains of dead organisms of marine biota sank to the bottom, where they were subject to decomposition (reaction 19). C-rich haze preferentially settled near the poles, and again organisms near the surface had the first opportunity to use this energy source (reaction 18). Any unused haze (soot when in water or on the ground) or dead organisms of a marine haze-based ecology sunk to the bottom, where further decomposition occurred.

SULFITE-BASED NICHES

We have inferred that the SO_2 flux from arc volcanoes was significant on the pre-photosynthetic Earth (Table 1), but insufficient to consume the available hydrogen and methane. That is, it was the stoichiometric-limiting quantity in the open ocean. Idealized reactions are

$$SO_3^{-2} + CH_4 \rightarrow S^{-2} + CO_2 + 2H_2O \qquad (20)$$

and (13). Some sulfite probably disproportionated into sulfide and sulfate

$$4SO_3^{-2} \rightarrow S^{-2} + 3SO_4^{-2} \qquad (21)$$

These reactions affect the mobility of sulfur and the location of viable niches based on these reactions, but not the overall mass balance. (This can be seen by noting that there are 12 available oxygen molecules on each side of reaction 21.) Venting of SO_2 occurred directly into the air and into shallow oceans. This atmospheric SO_2, along with sulfate (reaction 21), provided for dispersed ecosystems that depended on rain and air–sea gas exchange. Surface biota and perhaps cloud biota had the first opportunity to utilize these energy sources.

Submarine hydrothermal systems and volcanic vents supplied SO_2 and sulfate to shallow marine environments. Concentrated ecosystems around the vents reacted the oxidized sulfur species with methane, organic matter, and hydrogen. The sulfur flux from vigorous vents most likely exhausted the local supply of reductants. A dispersed ecology dependent on these reactions existed distally from the vents where reductants were present.

CONCLUSIONS: CARBON BURIAL AND BIOSIGNATURES

As a consequence of geologic history we are forced to search for evidence of early life in ancient highly metamorphosed rocks. Thermochemical and mass balance considerations presented here point to several durable biosignatures.

First as already noted, most of the CO_2 that vented to the surface on the pre-photosynthetic Earth never entered organic carbon before it was buried in carbonates. Still, the primary productivity gives an upper limit on the total rate of carbon burial. Reaction with sulfite and decomposition decrease the amount. Our combined oceanic vents (serpentinite and basalt) and volcanic fluxes of H_2 are 0.42 Tmol year^{-1} (Table 1). Stoichiometrically this corresponds to a maximum yield of 0.14 Tmol methane per year ($\Delta\xi = 1$ for reaction 1). Photolysis reactions could yield a comparable amount.

We apply the result that laboratory methanogens produce 0.8 mol of methane and 0.2 mol of organic carbon per mol of CO_2 (Scholten & Conrad, 2000) to obtain the primary productivity and hence an upper limit on carbon burial. Decomposition (reaction 19), the maintenance energy requirements of microbes, and reaction of organic matter with sulfite from volcanoes would have reduced this amount. That is, less than 0.056 Tmol year^{-1} was buried as organic carbon. Our CO_2 flux is 8 Tmol year^{-1}. About one C atom out of 143 derived from ridge axes, volcanoes, or metamorphism entered organic matter at some time before it was buried as carbonate. A factor of a few errors in this ratio would not effect our conclusion that organic carbon burial was rare before photosynthesis.

The actual burial rate of organic carbon was likely to have been much less than the upper limit based on primary productivity. Actual ecologies tend to a Malthusian state where the biota are near the carrying capacity and much of the available energy goes to maintenance rather than growth (T. Hoehler, personal communication, 2006). For example, carbon burial is analogous to exportive harvest from an ecosystem, like a fishery. The maximum sustained yield is unstable and the standing stock reaches a maximum at the carrying capacity (Roughgarden & Smith, 1996).

Still, organic carbon burial had some aspects similar to the present cycle. Entombment within impervious rocks and a molecular structure unpalatable to microbes aided burial. The nature of reactions for remobilization was different than at present. Today, organic carbon accumulates where it is so abundant that it uses up the oxidants O_2 and sulfate. For organic carbon to be buried then, it only had to escape decomposition reactions of the form of reactions (18) or (19). There was no obvious limiting reactant (like O_2) that could be locally depleted.

Hydrogen-based niches involve common rock types, like basalt and serpentinite. They should have existed on Mars, and on Venus, if it was once clement too. One would like to know if they were inhabited, but like on the Earth, the putative ecologies leave behind only a sparse and dispersed record.

We now apply our inferences of pre-photosynthetic Earth to evaluate observable differences with an Earth that has since been dominated by photosynthesis. In particular, we do not expect to see the remains of a teeming biota like organic mats or black shales within pre- (or post)-photosynthetic deposits.

Near-surface niches provide an essential pre-adaptation for photosynthesis, that is, exposure to sunlight. Hydrogen-based lifestyles provide a pre-adaptation for hydrogen-consuming photosynthesis. This ability could have begun as photocatalysis as both methanogenesis (reaction 1) and acetogenesis (reaction 2) provided chemical energy on the early Earth. In contrast to pre-photosynthetic times, the current organic carbon burial rate is 10 Tmol year^{-1} and the carbonate burial rate is 40 Tmol year^{-1} (Holser *et al.*, 1988; Sleep, 2005). The primary productivity is a factor of ~1000 greater than the organic burial rate. Each carbon atom, once eroded from outcrops, goes through photosynthesis ~200 times before it is buried again.

Between the advent of photosynthesis and the notable increase in atmospheric O_2, there was no obvious upper limit to the production of biological methane. The net cycle had C in CH_4 act as a carrier of hydrogen from water at the surface to the top of the atmosphere. The net reaction for FeO-based photosynthesis and decay to methane is,

$$CO_2 + 4FeO + 2H_2O + h\nu \Rightarrow 2Fe_2O_3 + CH_4. \qquad (22)$$

The reverse reaction of methane with ferric iron potentially provides energy to microbes. Some of the methane ascends into the upper atmosphere where it dissociates via reactions (15) and (16). Hydrogen escapes to space. The carbon returns to the surface where it reacts with water in reactions (17) and (18), making additional methane. The net effect of the cycle is reaction (5) or (6) (depending on the final oxidation state of iron), implying that the availability of iron limits this hydrogen escape mechanism.

The hydrogen escape rate could have been large if tectonic processes copiously exposed Fe(II)-rich minerals to weathering and hydrothermal processes. Catling *et al.* (2001) give 20 Tmol of H_2 as the upper limit for escape to space before the advent of atmospheric oxygen. This is enough H_2 to oxidize the Earth's crust to its present state in 240 Myr (Sleep, 2005). Note that free oxygen- or sulfate-producing photosynthesis can have the same net effect. The organic matter decays to produce methane (reaction 16), and O_2 and sulfate from photosynthesis oxidize Fe(II) in rocks at hydrothermal conditions. Thus, voluminous red and magnetite series granites are a durable indication of photosynthesis. The oldest known oxidized granites intruded the Kaapvaal Craton at 3230 Ma (Ishihara *et al.*, 2006).

Observations of modern Earth demonstrate that high productivity makes carbon very mobile. A carbon atom can be transported in air or water until it either ends up in carbonate or as organic carbon in sediments. The latter locations are geographically limited. Black shales accumulate several percent of organic carbon. Importantly, the clays in shale have already reacted chemically with their environment. That is, they provide no disequilibrium mineral energy source for chemoautotrophs. Before photosynthesis, shales contained only small concentrations of the dead remains from widely dispersed, low-productivity ecologies.

Black shales are thus an attractive biosignature for photosynthesis. This is true for both modern oxygen-producing photosynthesis and earlier sulfate- or ferric iron-producing photosynthesis. Exploration is practical in ancient rocks, as much of the carbon in black shale is immobile during metamorphism (e.g. Westall & Southam, 2006). Black shale is the protolith of graphite- and diamond-bearing gneiss (Searle *et al*., 2001). Even diamonds from kimberlites may represent deeply subducted organic material (Tappert *et al*., 2005. cf., Cartigny, 2005; Horita, 2005). Recognition in areas of descent geologic exposure where the sedimentary protolithology is evident is not a problem. The same is true of black chert. Carbonate is less useful because the siderite ($FeCO_3$) component can decompose to magnetite and graphite at high metamorphic temperatures. In other cases, the protolith is not obvious. These include inclusions within zircons and diamonds from kimberlites. Trace element and isotopic geochemistry is then essential. For example, Tappert *et al*. (2005) used carbon isotopes and europium anomalies in diamond inclusions. The robustness of these biosignatures gives some hope for deducing the biotic history of Venus, which may have once been clement. For example, impervious graphitic gneiss out of direct contact with the air might persist. Such rocks and kimberlites are not easy targets for drop-and-die probes.

Note added in proof. See Larowe & Helgeson (2007) for methods of quantifying Gibbs energy for cellular reactions involving ADP and ATP.

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